CRANFIELD UNIVERSITY

FEDERICO LUPPI

INERT AND NITRATED CROSS-LINKED β-CYCLODEXTRIN
BINDERS FOR ENERGETIC APPLICATIONS

CRANFIELD DEFENCE AND SECURITY
PhD in Defence and Security

PhD
Academic Year: 2015 - 2019

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This thesis is submitted in partial fulfilment of the requirements for the degree of PhD
(NB. This section can be removed if the award of the degree is based solely on examination of the thesis)

Abstract

This PhD project focuses on the synthesis of new inert and nitrated cross-linked cyclodextrin systems as binders for energetic formulations. Three diglycidyl ethers with polyethylene glycol segments differing in length were used to cross-link β-cyclodextrin. The physicochemical properties of the compounds were investigated by proton nuclear magnetic resonance spectroscopy, differential scanning calorimetry, thermogravimetric analysis and dynamic mechanical analysis. The polyethylene glycol chains linked to the rigid β-cyclodextrin conferred low glass transition temperatures (≥ –20 °C) on the inert binders and also on their nitrated derivatives (≥ –14 °C). This is the first time that nitrated β-cyclodextrin derivatives have shown viscoelastic behaviour at temperatures below 0 °C. The viscoelasticity of both the inert and nitrated compounds increased with the amount of polyethylene glycol chains in the system. Inert binders with higher polyethylene glycol:β-cyclodextrin units ratios were softer and exhibited self-healing behaviour. The thermo-mechanical characterisation of these binders revealed that the system was exposed to mechanical stress below the glass transition temperature, and the stress was directly related to the proportion of the soft polyethylene glycol segments. The nitrated cross-linked derivatives were characterised by decomposition temperatures of ~200 °C and thermal degradation energies of 1400–2100 J g^{-1} strictly dependent on the degree of cross-linking and nitration. Self-healing properties were confirmed in nitrated products with a high polyethylene glycol segments content. Nitrated samples with polyethylene glycol segments:β-cyclodextrin units ratios >3.8:1 were safer to handle in the laboratory as determined by small-scale hazard and compatibility tests with various energetic fillers. Additionally, preliminary Energetic Materials Testing Assessment Policy (EMTAP) tests confirmed the samples were not sensitive to electrostatic discharge up to 4.5 J but were sensitive to impact, with a figure of insensitiveness of 29. The nitrated samples were unstable at temperatures >80 °C. The materials developed during this PhD project could facilitate the manufacturing and storage of new binders and may offer a suitable replacement for nitrocellulose and other binders in

energetic formulations. The stabilisation of the nitrated cross-linked binders should be prioritised in future work.

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2,4-NDPA	2,4-Dinitrodiphenylamine
AP	Ammonium perchlorate
CD	Cyclodextrin
CEF	Trichloroethyl phosphate
CL-20	Hexanitrohexaazaisowurtzitane
CTPB	Carboxyl-terminated polybutadiene
D_2O	Deuterated water
DMA	Dynamic mechanical analysis
DMSO-d_6	Deuterated dimethylsulfoxide
DNAN	2,4-Dinitroanisole
DPA	Diphenylamine
DS	Degree of substitution
DSC	Differential scanning calorimetry
E′	Storage modulus
EMTAP	Energetic Materials Testing Assessment Policy
ESD	Electrostatic discharge
FoI	Figure of insensitiveness
FTIR	Fourier transformed infrared
GPC	Gel permeation chromatography
HEG	Hexaethylene glycol unit
HEGDGE	Hexaethylene glycol diglycidyl ether
HFC	Heat flow calorimetry
HTPB	Hydroxyl-terminated polybutadiene
IH	Inert cross-linked βCD containing HEG units
IM	Insensitive munition
IP	Inert cross-linked βCD containing PEG units
IR	Infrared
IT	Inert cross-linked βCD containing TEG units
Kel-F 800	Poly(chlorotrifluoroethylene-*co*-vinylidene fluoride)
MIL-STD	Military standard
MWCO	Molecular weight cut-off

NC	Nitrocellulose
NCD	Nitrated cyclodextrin
NH	Nitrated cross-linked βCD containing HEG units
NMR	Nuclear magnetic resonance
NP	Nitrated cross-linked βCD containing PEG segments
NT	Nitrated cross-linked βCD containing TEG segments
PBAA	Polybutadiene-acrylic acid copolymer
PBAN	Polybutadiene-*co*-acrylonitrile
PEG	Polyethylene glycol unit
PEGDGE	Polyethylene glycol diglycidyl ether (500 Da)
PTFE	Polytetrafluoroethylene
RT	Room temperature
SEM	Scanning electron microscopy
STANAG	Standardisation agreement
tanδ	Damping factor
TBAB	Tetrabutyl ammonium bromide
TEG	Triethylene glycol unit
TEGDGE	Triethylene glycol diglycidyl ether
T_g	Glass transition temperature
TGA	Thermal gravimetric analysis
THF	Tetrahydrofuran
TIVS	Thermal initiated venting system
TMETN	Trimethylolethane trinitrate
TNAZ	1,3,3-Trinitroazetidine
TNT	Trinitrotoluene
TPE	Thermoplastic elastomer
XEG	Generic polyethylene glycol unit, used as a collective term for TEG, HEG and PEG units
βCD	β-Cyclodextrin
βCHCD	Cross-linked βCD containing HEG units
βCPCD	Cross-linked βCD containing PEG units
βCTCD	Cross-linked βCD containing TEG units
βCXCD	Generic cross-linked βCD system containing X segments, where

	X=TEG, HEG or PEG
βNCD	Nitrated βCD
βNCHCD	Nitrated cross-linked βCD containing HEG units
βNCPCD	Nitrated cross-linked βCD containing PEG units
βNCTCD	Nitrated cross-linked βCD containing TEG units
βNCXCD	Generic nitrated cross-linked βCD system containing X units, where X=TEG, HEG or PEG
Ω	Oxygen balance

1 Overview

The development of new binders is fundamental to the design of more advanced insensitive munitions (IMs). The function of the binder is to support the constituents of a formulation and create a cohesive mass. Binders also improve the properties of formulations, increasing their mechanical strength and/or the processability of the formulated energetics.

Binders used in the defence industry must enable the production of safe formulations with low vulnerability to stimuli such as impact, heat and electrostatic discharge (ESD) without compromising the energetic performance of the formulations.

Most traditional binders are unsustainably derived from crude oil and do not make an energetic contribution to the formulation. One exception is nitrocellulose (NC), which is sustainably derived from cotton cellulose and has been used extensively through history as a filler and energetic binder. However, NC has inconsistent batch-to-batch physicochemical properties due to structural differences caused by the origin of the cotton and the conditions of cultivation, harvesting and storage. These differences affect the properties of the biomass (lignocellulose) and ultimately those of the nitrated derivatives and the resulting energetic formulations. The selection and certification of cotton batches suitable for NC production is therefore a long and expensive process.

This PhD project focused on the development of reliable, sustainable binders that contribute to the energetic content of a formulation. With insight from the pharmaceutical industry, β-cyclodextrin (βCD) was considered as one of the most promising building blocks for future binders. This compound can be synthesised inexpensively from a renewable resource (starch) using a robust, enzymatic process. Natural βCD can be used entrap small molecules such as drugs in pharmaceutical formulations.

The functionalisation of the hydroxyl groups in βCD is a simple and convenient method to produce new oligomeric and polymeric derivatives. The multiple hydroxyl groups in βCD macrocycles allow the creation of three-dimensional

(3D) macrostructures with enhanced inclusion ability. The main constituents of energetic formulations such as explosives, oxidisers and pyrotechnic fillers would be less susceptible to external stimuli when embedded in a βCD-based binder, making the formulation safer and easier to handle.

1.1 **Objectives**

The overall aim of this PhD project was to synthesise a series of energetic cross-linked βCD derivatives and characterise them to determine their suitability as novel binders. Pure βCD and its nitrated derivatives are unsuitable for the processing of energetics due to the high crystallinity of these molecules. Flexible polyethylene glycol segments of various lengths (XEG) were therefore chosen to cross-link βCD and improve its processability.

The synthesis route selected for the production of energetic cross-linked βCDs (βNCXCDs) comprises two steps, as summarised in Scheme 1.1:

1. Cross-linking of βCD using polyethylene glycol diglycidyl ethers of various lengths to form βCXCDs.
2. Nitration of the βCXCDs.

The solubility of βCXCDs in common polar solvents such as water, methanol or ethanol would facilitate formulation development. Therefore the studies focused on finding optimal reaction parameters to obtain water-soluble compounds for easy purification and processability. The properties of the prepared compounds were investigated using the following analytical techniques:

1. Nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) spectroscopy for the chemical characterisation of the cross-linked and nitrated products.
2. Iron sulfate titration to measure the nitrogen content of the nitrated cross-linked products
3. Differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA) and dynamic mechanical analysis (DMA) for the thermo-mechanical characterisation of the cross-linked and nitrated cross-linked products to determine their compatibility with energetic fillers.

4. Hazard tests to assess the vulnerability of the compounds.
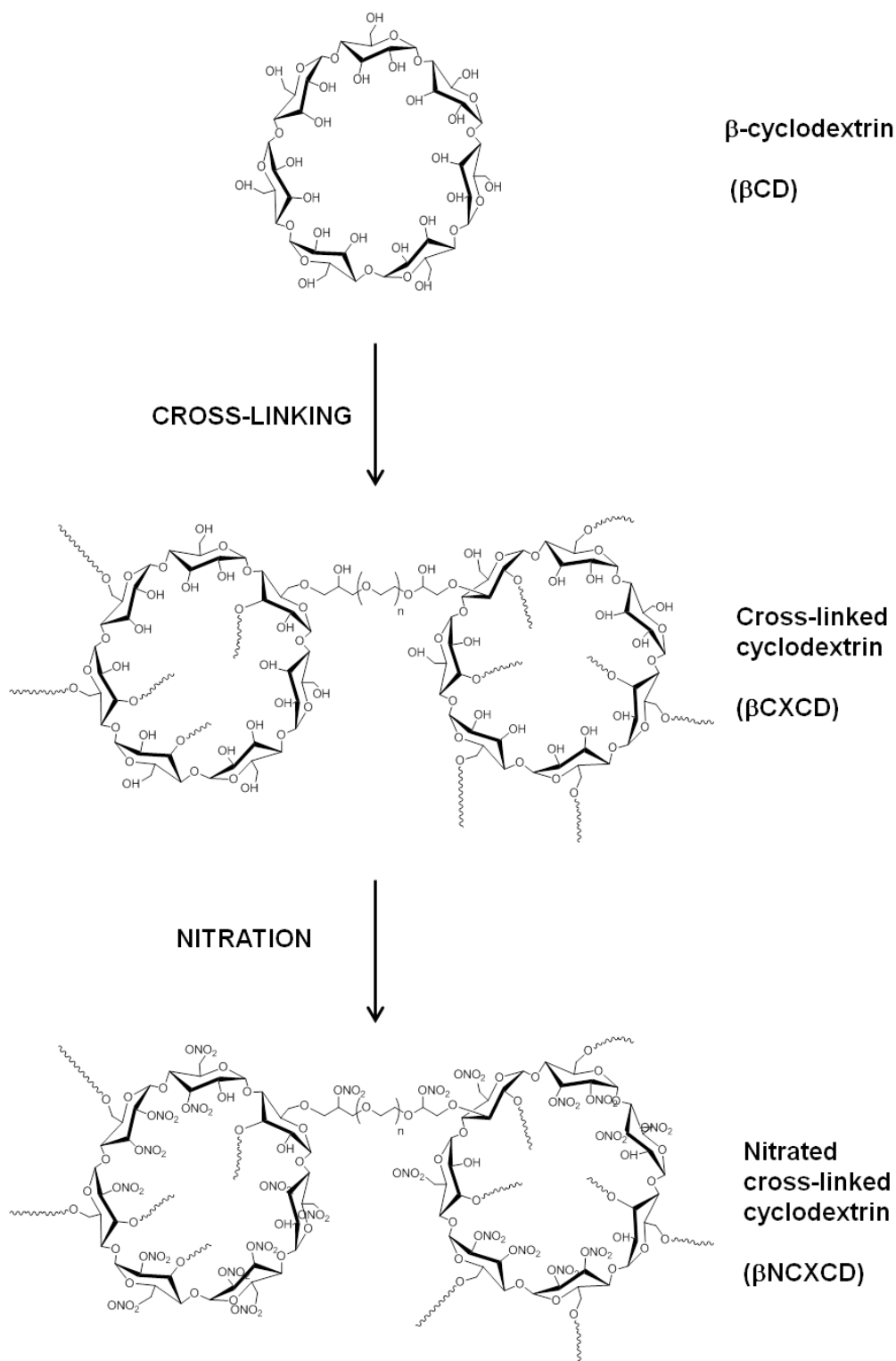
Scheme 1.1 Schematic representation of the synthesis of βCXCD and βNCXCD binders.

1.2 Academic contributions

The work described in this thesis has thus far resulted in two peer-reviewed publications (one in *Propellants, Explosives, and Pyrotechnics*, and another in *Polymer Testing*) as well as two posters presented at one domestic conference (Defence and Security Doctoral Symposium 2015–2016, Cranfield University, UK) and one international conference (Macro 2018, 47th IUPAC World Polymer Congress, Cairns, Australia). The work also contributed to the Cranfield WSTC0037 Progress Internal Reports for the "Binders by Design Project" and was presented in progress meetings with the PhD sponsor.

1.3 Thesis structure

Following this overview, Chapter 2 (*Introduction*) guides the reader through the concept of binders and their use in energetic formulations, followed by a summary of current knowledge about the chemical properties of cyclodextrins, particularly their use in the energetics industry. Chapter 3 (*Experimental*) describes the materials, reactions and methods used to synthesise and characterise the compounds, as well as test conditions for hazard assessment.

Chapter 4 (*Synthesis and characterisation of inert βCXCDs*) explains the rationale behind the optimisation of the first synthesis reaction, and also describes the physicochemical and thermomechanical characterisation of the inert compounds. Chapter 5 (*Synthesis and chemical characterisation of energetic cross-linked βNCXCDs*) mirrors the structure of Chapter 4 but describes the production and characterisation of the energetic cross-linked systems. Chapter 6 (*Compatibility, hazard and stability studies*) provides the data needed for the reader to understand the contribution and limitations of the novel inert βCXCDs and energetic βNCXCDs in the development of new energetic formulations.

Finally, Chapter 7 (*Conclusions and recommendations*) provides a summary of the findings reported in the thesis and suggests additional work required to develop this cross-linked system into a successful binder for energetic applications.

The appendices contain additional experimental details that will help the reader to understand the research, as well as the published articles based on the work described in the thesis:

- Luppi F, Cavaye H, Dossi E (2018) Nitrated cross-linked β-cyclodextrin binders exhibiting low glass transition temperatures. Prop Expl Pyrotech 43 (10) 1023–1031.
- Luppi F, Kister G, Carpenter M, Dossi E (2019) Thermomechanical characterisation of cross-linked β-cyclodextrin polyether binders. Polym Test 73, 338–345.

2 Introduction

2.1 Insensitive munitions

Energetic formulations used in the defence industry must withstand unintended stimuli to prevent unwanted violent events, and manufacturing is therefore moving towards improved safety during phases of life. The development of insensitive munitions (IMs) is a direct response to the several accidents that caused the involuntary initiation of explosives [1]. A definition developed in the American Navy stands [1]:

"Insensitive munitions are those that reliably fulfil their performance, readiness, and operational requirements on demand, but are designed to minimize the violence of a reaction and subsequent collateral damage when subjected to unplanned heat, shock, fragment or bullet impact, electromagnetic pulse (EMP), or other unplanned stimuli."

The development of IMs is guided by the handbooks STANAG 4439 and the American standard MIL-STD-2105 "Hazard Assessment Tests for Non-Nuclear Munitions", which can be summarised in the following three strategies [2–4]:

1. The development of external packaging that improves the protection of the munitions.
2. The development of mitigation devices for uncontrolled events in the munitions.
3. The development of energetic materials with an intrinsic low vulnerability.

The first strategy relies on the design of new transport tools such as containers better insulated from thermal and kinetic shock, or coated with intumescent paint.

The second strategy is the development of passive or active devices to mitigate the effects of uncontrolled events. Passive devices do not provoke a response in the energetic materials, and examples include vent plugs, thread adaptors, mitigation sleeves and intumescent paint [5–7]. Not as widely used, active devices such as the thermal initiated venting system (TIVS) cause a controlled

thermal response to external stimuli in the IM, and thus reduce the severity of unplanned events [8].

Energetic materials with low vulnerability intrinsically prevent undesired consequences. The two global conflicts in the first half of the twentieth century increased the development of novel energetic materials. Polymers were introduced in energetic formulations as a medium to bind the explosive ingredients, thus increasing the compactness of the munitions and reducing their vulnerability [9]. In this role, polymers were used and defined as binders.

Polymers have a wide range of physicochemical properties that define their efficiency in energetic applications [10].

2.2 **Polymers and their properties**

Polymers are macromolecules comprising repeat units of one or more monomers, and they offer unique benefits when used as binders, including [11]:

- Wide variety of molecular architectures, e.g. linear, branched, homopolymer, copolymer, random, alternating, star, block copolymer, cross-linked;
- Dimensional stability (linear dimensional change in response to temperature changes);
- Durability (lifetime, ageing, degradation, stabilisation);
- Easy processing (flow, forming, solidification by moulding, extrusion).

The chemical identity of a polymer defines its morphology and the physical properties of the system. The synthesis route determines the molecular structure and is designed to avoid side-reactions, thus favouring the recovery of pure products. By controlling the reaction mechanism, the system can be defined in terms of the regularity of the backbone (stereochemistry, sequencing in copolymers), the molecular weight and polydispersity, and the polymer architecture. Most of these molecular structures offer numerous opportunities for functionalisation, process control and thus new applications.

Polymer morphology describes the arrangement and macroscale ordering of polymer chains in space, which affects properties such as strength, toughness and flexibility [12]. Crystallinity is often used to describe the morphology of a polymer compound. Crystalline polymers are rigid and melt at higher temperatures than amorphous polymers. Crystallinity increases mechanical strength at the cost of low impact resistance. Amorphous polymers are softer, with lower melting points than crystalline polymers, and there is a transition point at which the polymer reversibly changes from glassy to rubbery behaviour [13]. This is known as the glass transition temperature (T_g) [12]. The glassy state is hard, rigid and brittle like a crystalline solid, but retains the molecular disorder of a liquid. When the material is heated the polymer will reach a temperature at which segments of the entangled chains can move and the behaviour will change to rubbery [11].

There are two general classes of polymers based on their behaviour when exposed to heat: thermoplastics and thermosets [14]. Thermoplastic polymers have relatively weak forces of attraction between the macrochains (electrostatic forces, few cross-links), which are overcome when the material is heated [14]. Thermoplastics are permanently fusible and can always be softened, melted down and recycled. When frozen, a thermoplastic becomes glassy and more sensitive to fracture [14]. Thermoplastics have a distinctive stress–strain curve (elongation to break). Thermosets comprise molecules that are cross-linked by strong bonds during curing due to chemical reactions or the effects of heat or radiation [14]. Effectively, the thermoset is one large molecule, with no crystalline structure. Cured thermoset polymers do not soften and will char and break down at high temperatures. Thermosets are generally harder than the thermoplastics, more rigid and more brittle, and their mechanical properties are not heat sensitive. They are also less soluble in organic solvents [15].

Thermoplastic elastomer (TPE) materials combine the functional performance and properties of thermoset rubbers with the processability of thermoplastics. TPEs are generally low-modulus, flexible materials that can be stretched repeatedly to at least twice their original length at room temperature with an

ability to return to their approximate original length when stress is released [16]. TPEs are widely used to modify the properties of rigid thermoplastics, improving impact strength. This is quite common for sheet goods and general moulding TPEs [16]. Their soft texture, ease of manufacture and ability to absorb shocks are preferred for energetic applications. Several classes of polymers can be cross-linked in the defence industry to produce TPEs, including copolyesters, styrenes, polyurethanes, polyamides and polyolefin blends [17]

2.3 Polymers as binders in energetic formulations

The binder is an important component of munition fillings because it holds the explosive crystals together, allows the formulation to be safely casted or machined into complex shapes, and reduces its vulnerability to accidental stimuli during storage. Table 2.1 lists some examples of energetic formulations.

The properties of the binder strongly influence the physical properties of the formulation and its applications. The plastic behaviour of certain polymers allows the formulation of plastic explosives, which are malleable and can be hand-moulded [18]. In contrast, viscoelastic behaviour reduces vulnerability to mechanical stress by facilitating energy dissipation in large-calibre munitions and nuclear warheads [19].

The chemical properties of the binder influence the stability of the formulations. For example, the low chemical reactivity of fluoropolymers can protect the formulations from harsh chemicals. For this reason, fluoropolymers are compatible with many energetic ingredients and reduce the likelihood of unpredicted chemical reactions [20]. The nitro-ester groups of NC undergo autocatalytic decomposition, so stabilisers are required to ensure a sufficient shelf-life [21]. Furthermore, epoxy-amines are incompatible with nitramines such as 1,3,5-trinitro-1,3,5-triazinane (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX) [22].

Table 2.1 List of binders in energetic formulations [23].

Binder[1]		Energetic		Application	Energetic formulation
Name	%	Name	%		
Polyisobutene	2.1	RDX	91	Plastic explosives	C4
Wax	1	RDX TNT	63 36	Gun shells	Comp. B
Nitrocellulose elastomer	8 29	PETN	63	Engineer charges	Detasheet C
Hydroxyl-terminated polybutadiene (HTPB)	5	HMX	29	Nuclear warheads	EDC-29
2,4-Dinitroanisole (DNAN)	43.5	NTO NQ	19.7 36.8	Gun shells	IMX-101
DNAN	31.7	NTO RDX	53 15.3	Mortars	IMX-104
Viton-A	10	HMX	90	Nuclear warheads	LX-07-2
Polyurethane rubber	< 4.5	HMX	95.5	Nuclear warheads	LX-14-0
Kel-F 800	7.5	TATB	92.5	Nuclear warheads	LX-17-0
Nitrocellulose chloroethylphosphate (CEF)	3 3	HMX	94	Nuclear warheads	PBX 9404
Kel-F 800[3]	5	TATB	95	Nuclear warheads	PBX 9502
Nylon	n.a.	RDX	85	Missiles Warheads	PBXN-3
Fluoro-elastomer	5	HMX	95	Gun shells	PBXN-5
HYTEMP 4454[2]	2	HMX	92	Various	PBXN-9
HTPB	11	RDX	88	Plastic explosives	PE7
NC	n.a.	NC,NQ, NG	/	Solid rocket propellant	Single, Double or Triple base
HTPB	n.a.	AP	/	Solid rocket propellant	AP/HTPB propellant
Styrene butadiene rubber	9	PETN RDX	40.9 41.2	Plastic explosives	Semtex H

1 The percentage of binder varies according to the application.

2 Trade name of polyacrylate binder.

The constituents of energetic formulations must be compatible to avoid side reactions. The introduction of polymers used for other applications in the development of new energetic formulations can be slow, hence the rather small number of polymers used successfully in energetic applications (Table 2.2).

NC was the first compound to be used in energetic formulations following the invention of black powder. It was first synthesised in the nineteenth century, as recorded by Christian Friedrich Schonbein in Basel and Rudolf Christian Bottger in Frankfurt-am-Main [20]. A significant milestone in the defence applications of NC was the production of the smokeless propellant Poudre B, by Paul Vieille in 1884 [24], where it was used as binder. A thick jelly was produced by kneading NC in a mixture of ether and alcohol to produce thin films. The NC gave solidity to the processed propellant and improved the control of its burning velocity. However the compound shows limited elongation below room temperature [25].
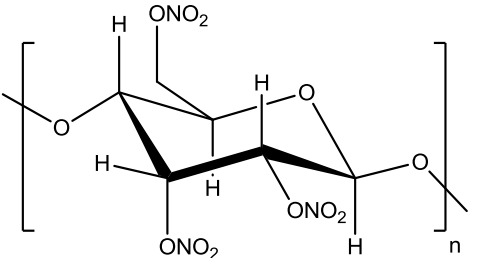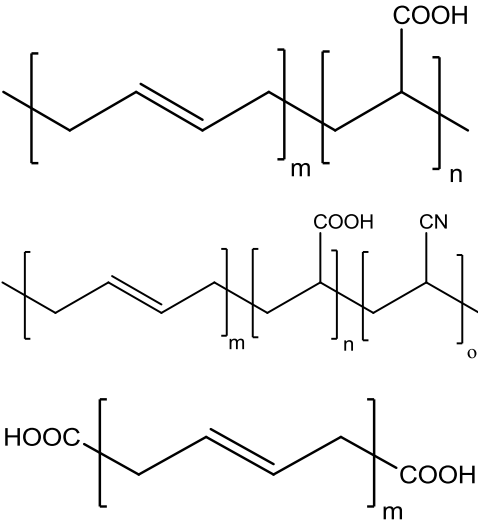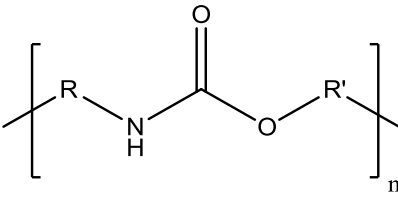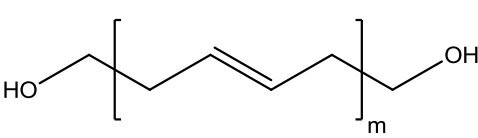
The moderate cost of NC makes it difficult to replace in defence applications even though the geographic and seasonal variations of raw cellulose mean that expensive selection processes are needed every few years to comply with military standards such as MIL-DTL-244 [26]. Special considerations are required to ensure batch-to-batch consistency in the polymer architecture [27]. In addition, it is difficult to prevent the degradation of this compound [28].
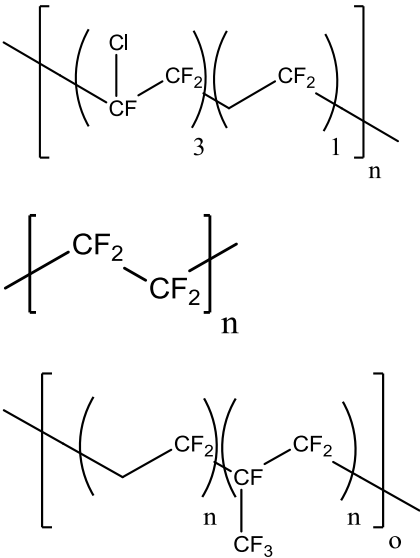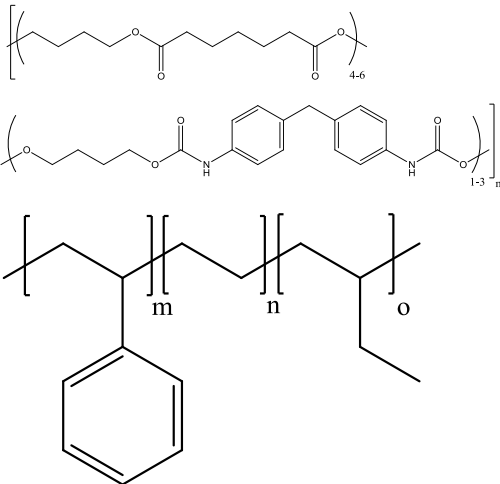
The escalation of European conflicts in the second half of the twentieth century stimulated the development of new binders. Polysulfides (PS) were the first synthetic polymers used as binders for propellants by the Thiokol Chemical Company in 1942 [29], although they are incompatible with the strong oxidisers used in many propellants and pyrotechnics [30].

Polybutadienes were developed in the 1950s to replace PS, and are more compatible with oxidisers in propellants. However, polybutadiene-acrylic acid copolymer (PBAA) showed low reproducibility during propellant manufacturing due to the synthetic nature of the radical polymerisation used to produce the binder [30]. Polybutadiene was copolymerised with acrylonitrile and acrylic acid

(PBAN) to achieve better pulse from the rockets, but a high curing temperature was needed for these binders [31].

Table 2.2 Example of polymers used in energetic applications [20].

Polymeric binder	Chemical structure	Applications
Nitrocellulose		Propellants, high explosives, 1888
Polysulfide		Propellants, 1945
Polybutadienes Poly butadiene-acrylic acid copolymer (PBAA) Poly butadiene-*co*-acrylonitrile (PBAN) Carboxyl-terminated polybutadiene (CTPB)		Propellants 1954 1954 Late 1950s
Polyurethane		Propellants, mid 1950s
Hydroxyl-terminated polybutadiene (HTPB)		Propellants and high explosives, 1972
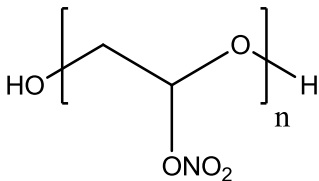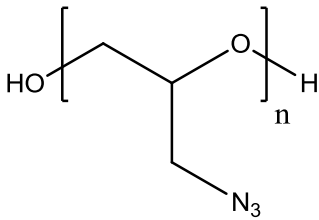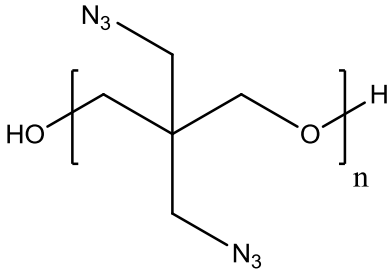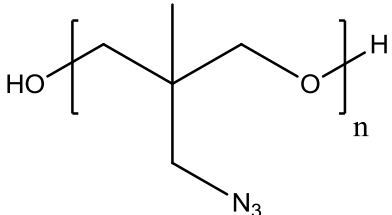
Fluoropolymers		High explosives, pyrotechnics, propellants
Kel-F 3700		Early 1960s
Teflon		Early 1960s
Viton		Early 1960s
Thermoplastic elastomers (TPEs)		Propellants
Estane 5703 [32]		Early 1980s
Kraton		Early 1980s
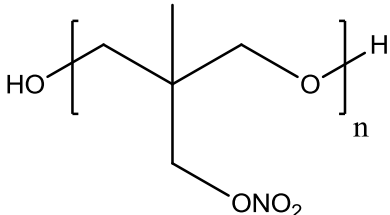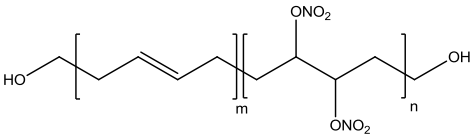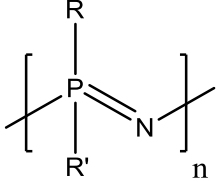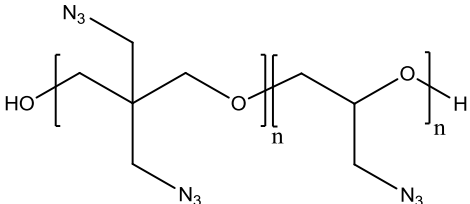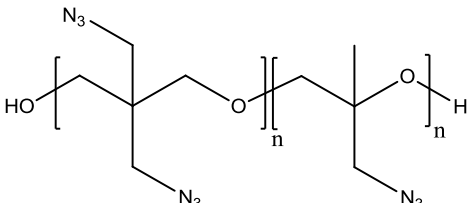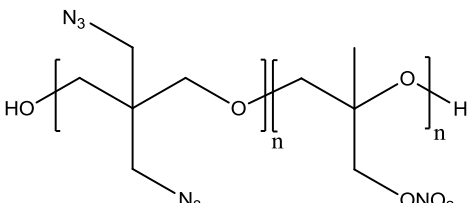
The development of new binders has been slow but continuous, although many end up in non-defence applications.
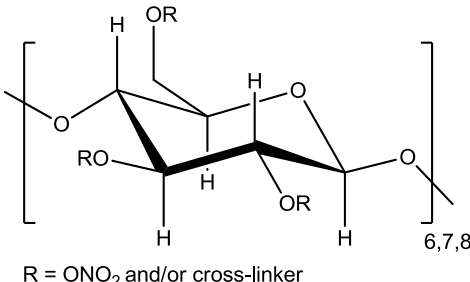
Cross-linked binders are manufactured by reacting bifunctional or multifunctional molecules such as isocyanates or polyols with these polymers to create a toughened three-dimensional (3D) network, a process defined as curing.

Hydroxyl-terminated polybutadiene (HTPB) is currently the most widely-used polymer for the preparation of polyurethane elastomer binders with unique properties such as low-temperature flexibility, hydrophobicity and resistance to hydrolysis [20,33,34]. However, with the exception of NC, the polymers listed in Table 2.2 do not contribute any energy to the formulation and negatively affect its energetic output. Energetic polymers, in which the binder contributes to the energy of the formulation, were developed to mitigate this major drawback (Table 2.3). The energetic contribution is provided by functional groups that decompose exothermically such as nitro, azido or nitro esters [35]

Table 2.3 Examples of energetic polymers used as binders [20].

Polymeric binder	Chemical structure	Applications
Polyglycidyl nitrate (PGN)		Propellants, 1953
Glycidyl azide polymer (GAP)		Propellants, 1976
Polyoxetanes		Propellants, high explosives, 1984
3,3-Bis(azidomethyl) oxetane polymer Poly(BAMO)		
3-Azidomethyl-3-methyloxetane polymer Poly(AMMO)		

Polymeric binder	Chemical structure	Applications
Poly(3-nitratomethyl-3-methyloxetane) Poly(NIMMO)		
Nitrated hydroxyl-terminated polybutadiene (NHTPB)		Propellants, 1980
Polyphosphazenes (PPZ)		Propellants, 2005
Energetic thermoplastic elastomers (ETPEs)		
BAMO-GAP		Propellants, 1984
BAMO-AMMO		
BAMO-NIMMO		

Polymeric binder	Chemical structure	Applications
Nitrated cyclodextrin polymers	$R = ONO_2$ and/or cross-linker	High explosives, propellants, early 1990s

Most recent studies have focused on polyphosphazenes and energetic cyclodextrin (CD) derivatives, both of which produce feasible energetic binders. Polyphosphazenes are non-isocyanate curable energetic polymers which are less toxic than current binders [36,37]. A successful synthetic curing process for HTPB and polyphosphazenes using a non-toxic cross-linker was developed at Cranfield University, based on the in-house diepoxide triethylene glycol diglycidyl ether (TEGDGE), as shown in Figure 2.1 [12,18,28].
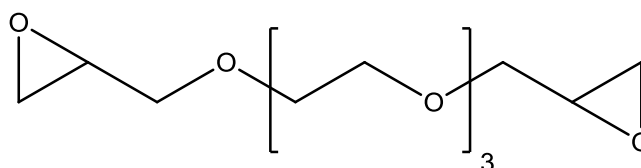
Figure 2.1 Chemical structure of triethylene glycol diglycidyl ether

The potential of CDs and their derivatives for energetic formulations is discussed in the next section. The physicochemical properties and the ability of CDs to envelop molecules is highlighted as means to reduce the vulnerability of energetic formulations.

2.4 **Cyclodextrins**

CDs are cyclic organic molecules characterised by the ability to envelop smaller molecules in their inner cavity. The three best-known CDs are α-cyclodextrin (αCD), β-cyclodextrin (βCD), and γ-cyclodextrin (γCD), which are toroidal macrocycles of six, seven and eight glucopyranose units, respectively (Figure

2.2) [38]. CDs with larger rings have been isolated but they are not used in the defence industry [39] .
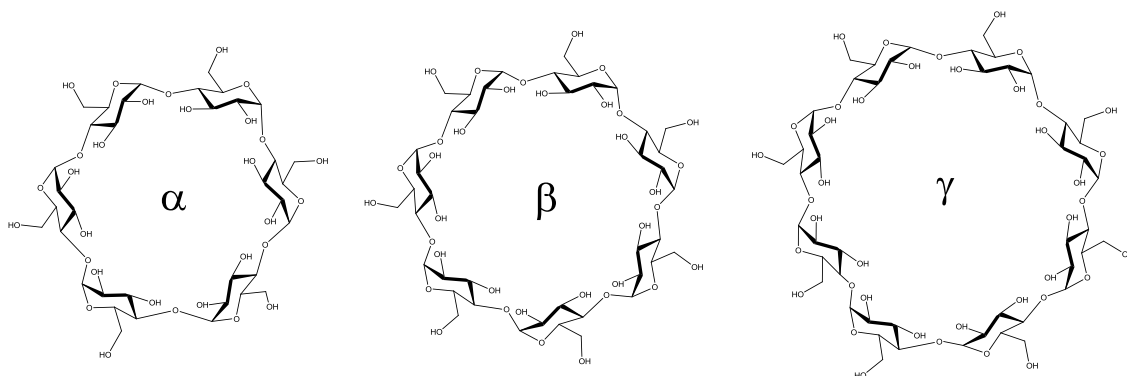
Figure 2.2 Chemical structure of α, β and γ CDs [40].

CDs were first synthesised in 1891 by Villiers and Schardinger. The work was then picked up by Pringsheim and colleagues, who discovered that CDs had the tendency to envelop organic molecules, leading to a burgeoning body of research literature during the 1970s [38].

This early research showed that α, β and γ CDs were suitable for pharmaceutical applications due to their enveloping properties [40]. However misleading information about their toxicity was publicised, reducing interest in these macrocycles. Modern toxicological tests show that CDs lack oral toxicity because they are not absorbed in the intestine [41]. Most publications concerning CDs focus on pharmaceutical applications and different functionalised variants are commercially available, including randomly methylated βCD (RAMEB), hydroxyalkylated derivatives (hydroxypropyl-βCD and hydroxypropyl-γCD), acetylated-γCD, reactive derivatives such as chlorotriazinyl-βCD, and branched versions such as glucosyl-βCD and maltosyl-βCD [38,40,42,43]. Figure 2.3 shows in the distribution of CD publications by application field over the last 20 years.
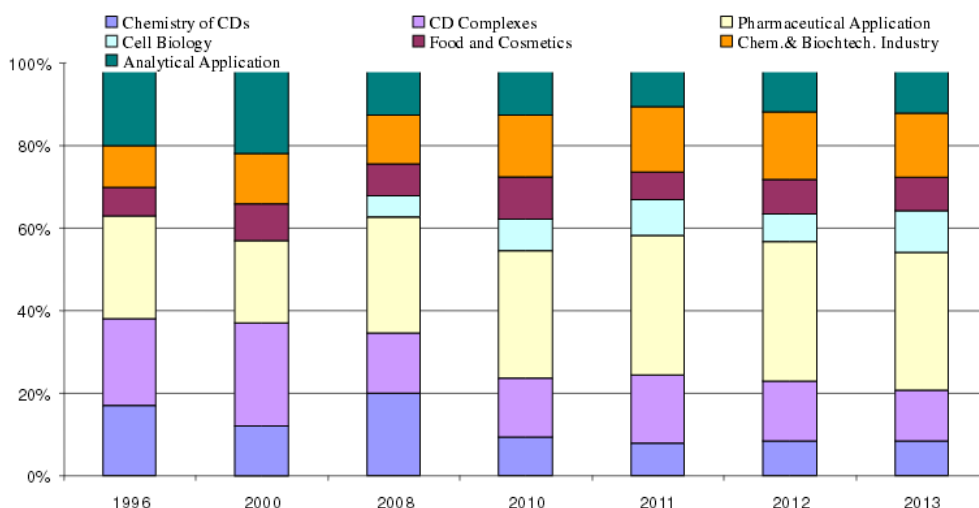
Figure 2.3 Distribution of the CD publications by application (1996–2013) according to *CD News* [38].

Most publications have considered pharmaceutical applications, where modified or unmodified CDs are used for drug delivery. The pharmaceuticals sector consumes several tons of medical-grade CD per year, with high purity and high development costs. There are smaller numbers of publications concerning applications in the food, cosmetics and detergent industries, which require a greater quantity of CDs but with less-stringent purity requirements and minimum prices of 6–7 US$ per kg in the US and European markets [38], and 2–3 US$ in the Chinese market. In Europe, Merck holds the bigger share of the CD market.

2.4.1 Properties of CDs

In the 1940s, the structures of CDs were defined by X-ray crystallography, revealing their ability to trap small molecules and to form inclusion complexes. The structural data obtained in these early studies showed how the primary hydroxyl groups cluster at one end of the toroidal molecules, whereas the secondary hydroxyl groups lie at the other end, as shown in Figure 2.4 (coloured in blue). The non-polar hydrogen atoms attached to C2 and C3 fill the inner side of the cavity along with the ether group. This leads to hydrophilic behaviour outside the toroid lipophilic cavity [40]. The physical properties of CDs are summarised in Table 2.4.

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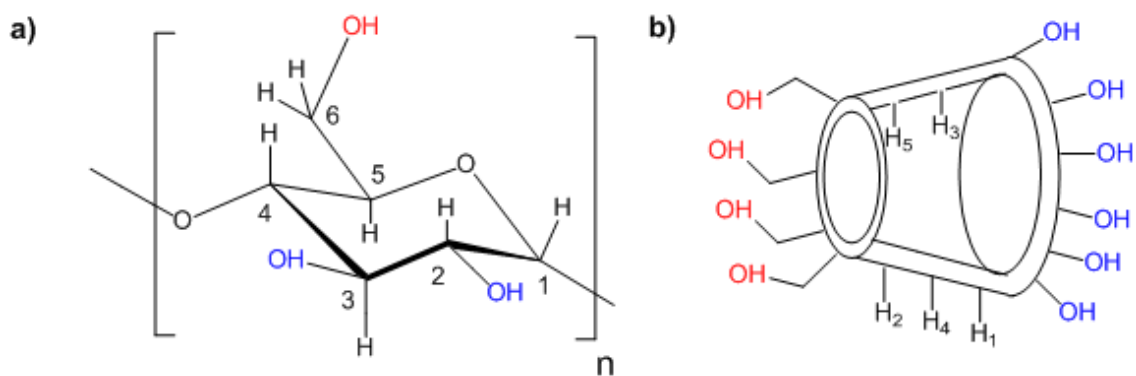
Figure 2.4 Structures of (a) α-D-glucopyranoside, the repeating unit of CD, and (b) the toroid representation of CDs, with primary and secondary hydroxyl groups in red and blue, respectively. H1, H2 and H4 are external to the toroid, whereas H3 and H5 are internal

Table 2.4 The physical properties of α, β and γ CDs [38].

CD	α	β	γ
Number of glucose units	6	7	8
Molecular weight	972	1135	1297
Solubility in water, g 100 mL^{-1} at room temperature	14.5	1.85	23.2
Cavity diameter, Å	4.7–5.3	6–6.5	7.5–8.3
[α]$_D$ 25 °C	150 ± 5	162 ± 0.5	177.4 ± 5
Height of torus, Å	7.9 ± 0.1	7.9 ± 0.1	7.9 ± 0.1
Diameter of outer periphery, Å	14.6 ± 0.4	15.4 ± 0.4	17.5 ± 0.4
Approx. volume of cavity, Å^3	174	262	427
Approx. cavity volume in 1 mol CD (ml)	104	157	256
Crystal forms (from water)	Hexagonal plates	Monoclinic parallelograms	Quadratic prisms
Crystal water (% w/w)	10.2	13.2–14.5	8.13–17.7
Diffusion constant at 40 °C	3.443	3.224	3.000
pK (by potentiometry) at 25 °C	12.332	12.202	12.081

The thermal properties of CDs, such as phase transitions or mass changes during chemical reactions, have been studied by thermal analysis using techniques such as differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). The literature reports slightly different thermal behaviours among the three cyclodextrins [44]. The main phase transitions and thermal events for the three CDs are summarised in Table 2.5.

Table 2.5 Thermal properties of α, β and γ CDs.

Cyclodextrin	Water loss (°C)	Phase transition (°C)	Degradation (°C)
αCD	74–121	224	319–304
βCD	87–110	221	328–330
γCD	63–81	-	321–324

CDs are generally stable up to 300 °C, and degradation occurs at higher temperatures. CDs are hygroscopic and can entrap water molecules in their cavity, which is described as crystal water in Table 2.4. The high temperatures cause phase transitions in the structures of α and β CDs at 224 and 221 °C, respectively. The first part of the CD thermal profile is dominated by the loss of hydration water and phase transitions in the crystal structure due to this loss [45]. Among the three CDs, the water of hydration has the highest mobility in γCD and is released earlier compared to the others [44], even though γCD is the most soluble (Table 2.4).

The solubility of all CDs in water increases at higher temperatures, although βCD is less soluble than the others [42]. The differences in solubility reflect the different hydrogen bond interactions that occur between the hydroxyl groups of each glucopyranose unit and the flexibility of the corresponding CD rings [46]. The inner cavity of αCDs cannot accommodate very large molecules due to its small size (Table 2.4), but this is not the case for β and γ CDs, which are large enough to incorporate various chemical compounds, including linear polymers and aromatic rings [41]. In the less common and non-commercialised CDs (10,

14, 26, 32 repeat units) the spatial distortion causes cavity collapse, reducing the inner volume to less than the value observed for γCDs, making them less suitable for encapsulation [47].

The enveloping structures formed by CDs in solution are influenced by the presence of solutes that could act as guest molecules. There is great interest in these compounds, reflecting their ability to form different supramolecular threads, allowing CDs to be used like polyrotaxanes (Figure 2.5) [48,49]. The interest in developing these supramolecular structures has led to more specific studies focusing on forces that control guest–host molecule interactions.
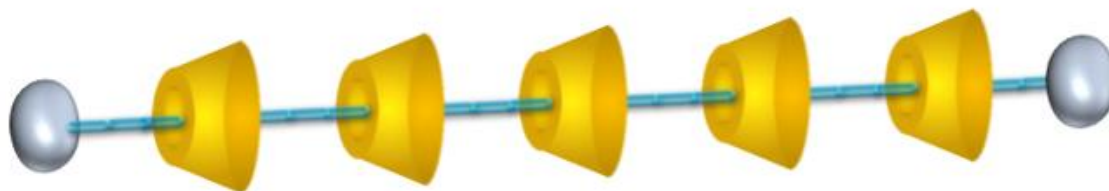
Figure 2.5 Schematic representation of a polyrotaxane formed by several CDs threaded on a polymer chain with ending caps.

2.4.1.1 Cyclodextrin inclusion complexes

CD inclusion complexes are affected by two main parameters:

- Steric hindrance;
- Replacement of solvent molecules with guest molecules.

Steric hindrance depends on the relative sizes of the guest molecule and the cavity, whereas the likelihood of replacement is based on thermodynamics. The inclusion of guest molecules by CDs involves an enthalpy-dependent driving force, i.e. water molecules inside the cavity have fewer interactions with the hydroxyl groups than water molecules in the bulk solution [50]. The replacement of water molecules with an organic molecule can therefore increase the stability, resulting in the dissolution of a sparingly soluble or insoluble organic molecule

in water. The organic molecule/CD complex is often less soluble than the CD alone [38].

Encapsulation tends to reduces the volatility, diffusion and reactivity of guest molecules [38,42,51,52]. The thermal properties of guest compounds are also affected, leading to increases in the glass transition and/or melting temperatures when embedded in CD [53]. The encapsulation ability of CDs has also been used to study their interactions with energetic molecules, as discussed later in this section.

Complexes may form in the solid state or in solution, following processes such as kneading, co-precipitation, dry mixing, sealing, slurry complexation, neutralisation, spray drying, freeze-drying, and solvent evaporation This usually leads to an inclusion ratio of 1:1 for host and guest molecules [42,54,55]. The temperature affects the solubility of the complex as well as the stability of the interaction [52]. The solubility of the complex is often inferior to the pure CD, causing a fraction of the complex to precipitate when formed [56–60].

Most of these processes have only been tested at the laboratory scale, and they have been claimed in various patents covering the manufacture of CD polymers or derivatives. Many of the patents covering the manufacture of natural CDs and modified variants such as hydroxypropyl-βCD have now expired, although existing and novel CD polymer derivatives are still manufactured [41,61,62].

2.4.1.2 Chemical stability and characterisation of CDs

CDs are chemically stable compounds, hence their use as drug carriers. They are relatively resistant to oxidation, with only strong oxidising environments leading to ring-breaking reactions. CDs are more acid resistant than linear or branched polysaccharides, but treatment with strong acids causes ring opening and the formation of oligosaccharides. The magnitude of the ring opening rate is influenced by the size of the CD molecule, so the process is slower for αCDs than γCDs [40].

In alkaline environments, the CD ether bond is stable towards nucleophilic or acid-base reactions and requires very strong conditions to react [40,42,59]. This low reactivity is also conferred to guest molecules within the CD ring.

Nuclear magnetic resonance (NMR) spectroscopy is widely used to characterise CDs because it determines their chemical structure in a complex. Figure 2.6 shows the proton assignments typical in deuterated water (D_2O) and the assignment in deuterated dimethylsulfoxide (DMSO-d_6).

Table 2.6 and Table 2.7 summarise the chemical shifts at 400 MHz reported for ^{1}H and ^{13}C NMR, respectively [63]. The signals attributed to the protons are split into two main regions. The region from 3.8 to 3.2 ppm includes most of the signals due to the chemical shifts of the aliphatic protons of the CD H-2 to H-$6_{a,b}$, whereas the region from 5.8 to 4.4 ppm includes the chemical shifts of the anomeric proton H-1 (Figure 2.6a). When DMSO-d_6 is used, the chemical shifts of the hydroxyl groups of the CD are also visible (Figure 2.6b). This region can be integrated and compared with the integration of H-1 to determine the degree of substitution (DS) that has occurred with the hydroxyl groups. The DS can also be determined by titration of the hydroxyl groups following standard methods [64–66].

Infrared (IR) spectroscopy is also widely used to characterise CDs [57,59,67–70]. The IR spectrum and the main adsorption bands for βCD are shown in Figure 2.7. A strong adsorption band at 3400–3300 cm^{-1} is due to the stretching of hydroxyl groups. The peak at 2926 cm^{-1} is assigned to the stretching of the C-H bond in CH and CH_2 groups. The peaks at 1200–1400 cm^{-1} are assigned to the bending of C-H in the primary and secondary hydroxyl groups of βCD (1411, 1368, 1335, 1301 and 1246 cm^{-1}) [71]. The strong adsorption at 1030–1200 cm^{-1} is attributed to the stretching of the C-O-C bonds in the ether and hydroxyl groups. Finally, the absorption bands at 700–950 cm^{-1} show the bending vibrations of the C-H bonds and the stretching vibrations in the glucopyranose ring [72]. The peak at 1626 cm^{-1} is actually due the water absorption included in the CD molecule as reported for the spectrum of water elsewhere [57,73].
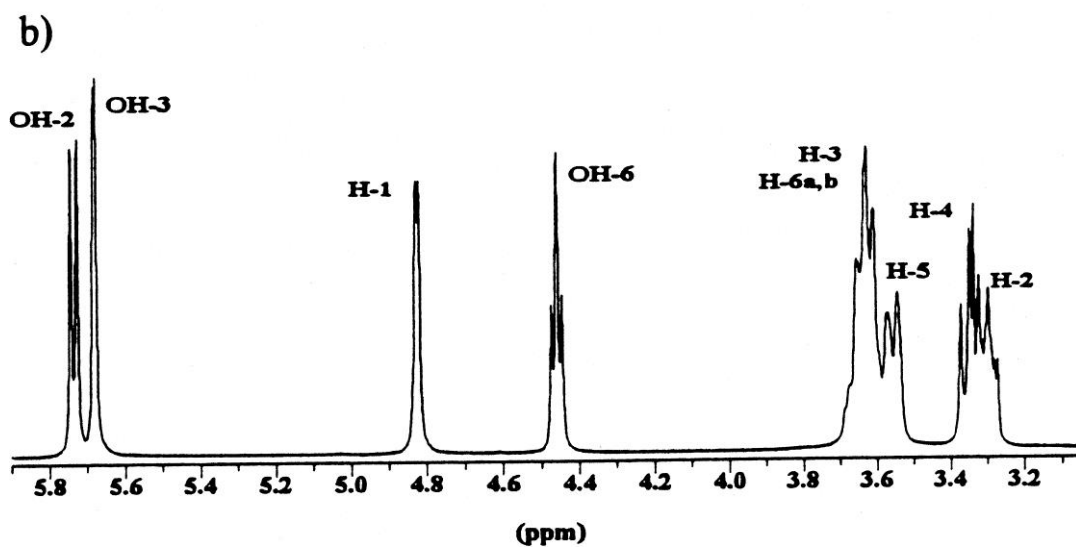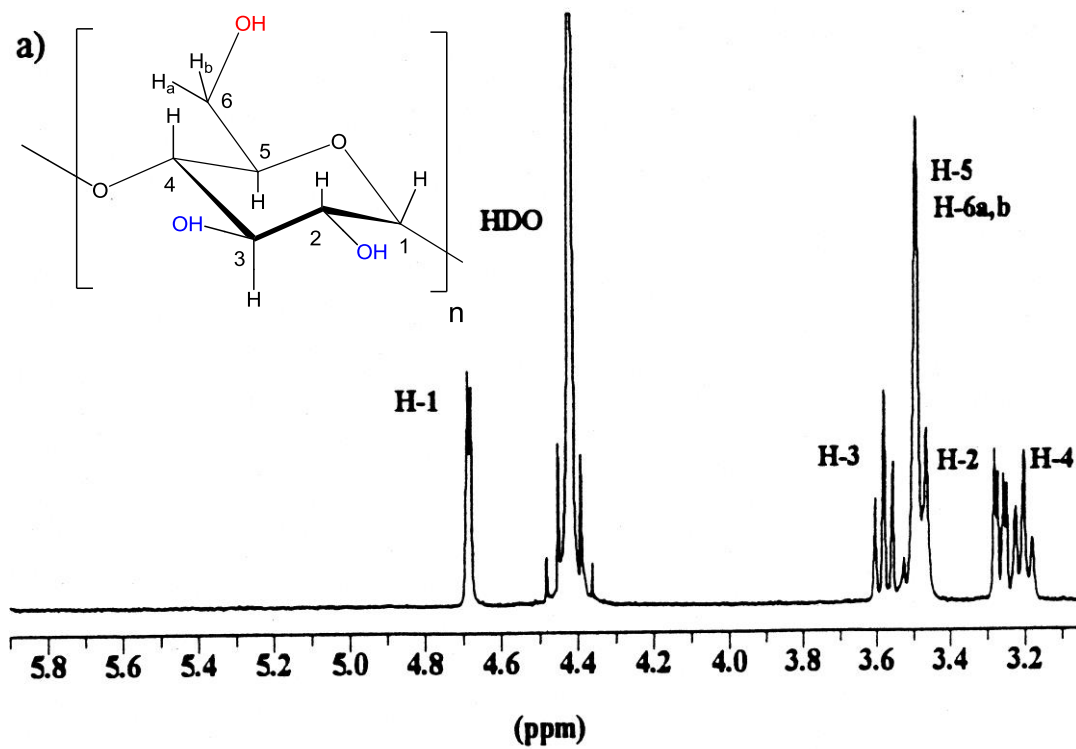
Figure 2.6 The ^{1}H-NMR spectra of CD (a) in D_2O and (b) in DMSO-d_6 [63].

Table 2.6 The ^{1}H-NMR chemical shifts of CD protons in D_2O and DMSO-d_6 [63].

Cyclodextrin	δ H-1	δ H-2	δ H-3	δ H-4	δ H-5	δ H-6a,b
D_2O						
αCD	4.60	3.19	3.57	3.08	3.39	3.44
βCD	4.68	3.26	3.58	3.19	3.47	3.49
γCD	4.53	3.08	3.35	3.00	3.26	3.30
DMSO-d_6						
αCD	4.79	3.29	3.78	3.40	3.59	3.65
βCD	4.82	3.29	3.64	3.34	3.59	3.64
γCD	4.89	3.32	3.65	3.36	3.56	3.65

Table 2.7 The ^{13}C NMR chemical shifts of CDs in D_2O [63].

Cyclodextrin	δ C-1	δ C-2	δ C-3	δ C-4	δ C-5	δ C-6
αCD	102.19	72.61	74.21	82.07	72.91	61.37
βCD	102.58	72.67	73.89	81.94	72.89	61.17
γCD	102.42	73.19	73.82	81.33	72.69	61.21
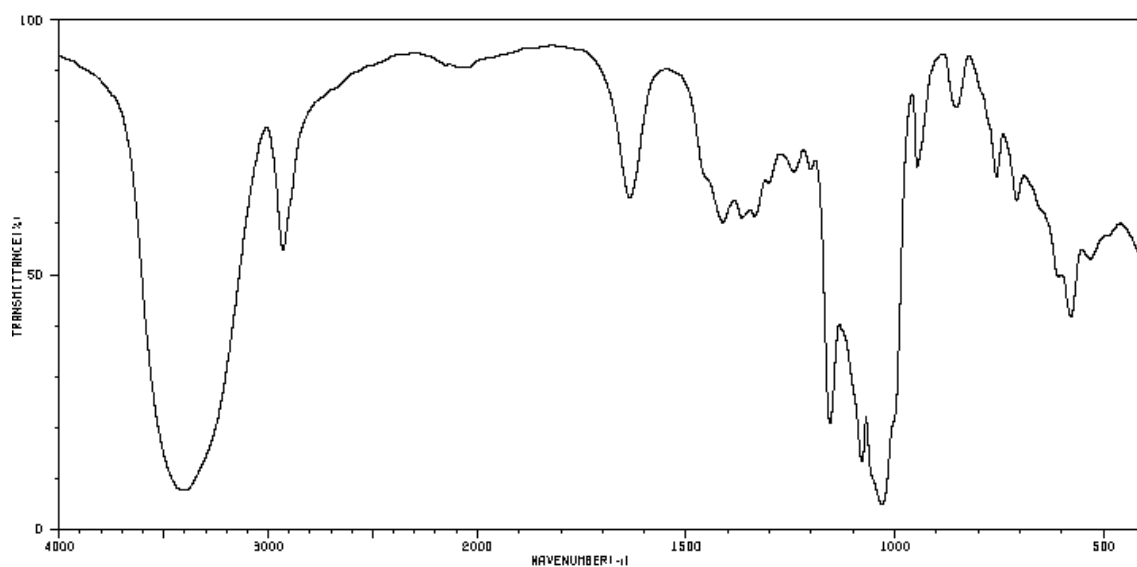
Figure 2.7 The infrared spectrum of βCD.

2.4.2 Synthesis of cyclodextrins

The enzyme CD glucosyltransferase (CGTase) converts starch into CDs. It is expressed by bacteria such as *Paenibacillus macerans*, *Klebsiella oxytoca*, *Bacillus circulans*, and alkalophilic *Bacillus* species [38,42,74]. CD synthesis begins with the liquefaction of starch by heating and hydrolysis to reduce the viscosity of the raw material. The enzyme is then mixed with the starch and different solvents are used as complexants to obtain the three CDs: toluene is used for βCD, 1-decanol for αCD, and cyclohexadecenol for γCD. The CDs are separated from the mixture by filtration, washed with water, and the organic solvent is removed by distillation or extraction in water. The resulting aqueous solution is treated with active carbon to remove trace impurities and filtered. The cost of production depends on how easy it is to remove the CDs from the organic solvent [38].

2.4.3 Cross-linking of cyclodextrins

CDs can be grafted to polymer chains, can form complexes with the branches of an existing polymer, or can be entrapped in a polymer lattice such as the polyrotaxane configuration (Figure 2.5). Polymeric CDs are formed primarily due to a reaction between the primary and/or secondary hydroxyl groups with functional groups of other molecules, or due to guest–host interactions. CD is often cross-linked using a variety of cross-linkers to form 3D structures that are usually insoluble in common solvents (Table 2.8).

The first cross-linked CDs were formed by reacting monomers with epichlorohydrin under basic conditions. Changing the reaction parameters (pH, solvent, temperature and time) led to different degrees of cross-linking [38]. The solubility of the resulting products varies depending on the cross-linker and reaction parameters [59,75,76]. The ability of polymers to swell depends on whether the polymer is linear [77] or branched [71]. The synthesis of different 3D networks leads to different degrees of swelling and chiral properties [75]. Many cross-linked CDs are insoluble due to their high molecular weight (Mw), so characterisation is restricted to methods such as solid-state NMR or Fourier transform infrared (FTIR) spectroscopy [71,78]. Other synthesis routes include

the living polymerisation of CDs to form the core of thermosensitive polymers [79].

Table 2.8 Applications of cross-linked CDs

Studies	Cross-linker used	Ref.
Removal of bisphenol A from water	1,2,3,4-butanetetracarboxylic dianhydride	[71]
Removal of pollutants such as 2-methylisoborneol and chlorinated disinfection by-products from water	4,4′ - methylenebis(cyclohexyl isocyanate), toluene diisocyanate	[80]
Absorption of phenol, methylene blue and aniline	Citric acid	[68,70]
Absorption of methylene blue and phenylalanine	Citric acid	[81]
Inclusion of aromatic compounds	Epichlorohydrin	[59]
Removal of urea from water	Epichlorohydrin	[51]
Manufacture of chromatographic stationary phase	Epichlorohydrin	[75] [77]
Removal of bisphenol A from water	Ethylene glycol diglycidyl ether	[78]
Solubility studies of the synthesised polymers	Poly(carboxylic acids)	[76]
Removal of bisphenol A from water	Poly(ethylene glycol diglycidyl) ether	[78]
Synthesis of thermosensitive star copolymers	Poly(N-isopropylacrylamide) and poly(N,N-dimethylacrylamide)	[79]
Manufacturing of antimicrobial packaging	Poly(vinyl alcohol) citric acid	[82]
Increasing the mechanical resistance of microneedles for drug injection	Poly(vinylpyrrolidone)	[83]
Control of drug release	Polyethyelene glycol	[84–88]

Cross-linked CD polymers have been extensively used to remove chemicals from solution as reported in Table 2.8. The advent of green chemistry led to the production of different water-insoluble CD polymers using citric or polycarboxylic acids as environmentally friendly cross-linkers for wastewater treatment [68,70,76,81]. The same cross-linking technique has been used to manufacture antimicrobial packaging [82]. The thermal characterisation of these compounds indicated that the presence of CDs increases the T_g of any polymers to which they are grafted. The glass transition is defined by IUPAC as the "*Process in which a polymer melt changes on cooling to a polymer glass or a polymer glass changes on heating to a polymer melt*" [89]. Long-chained cross-linkers are necessary to reduce the T_g of cross-linked CDs [82].

The synthesis of non-toxic materials is necessary when cross-linked CDs are used for drug delivery [40]. Many reactants produce non-toxic compounds when combined with CDs, expanding research into the synthesis of hydrogels for drug delivery. The solubility, pH response and membrane permeability of these systems can be tuned by adjusting the reaction conditions, making them ideal carriers to bind specific drug molecules in pharmaceutical applications [90]. Hydrogels are insoluble matrices of polymers that can adsorb large amounts of water, which cause them to swell [90]. This specific ability is valuable in other fields such as wastewater treatment, to trap pollutants [91].

One of the most widely-used hydrogels is based on CDs cross-linked with polyethylene glycol based cross-linkers [68,78,84–88,92]. The mechanical properties of hydrogels are also beneficial in pharmaceutical applications. The hydrogel must maintain its integrity to deliver the drug cargo to a specific target in the human body. Several hydrogels based on CDs can self-heal, which means they can at least completely or partially regenerate their mechanical strength after damage [93–95], and many of these are CD/PEG systems [92,96,97].

Self-healing is a characteristic possessed by many polymeric systems, in which a material can restore its structural integrity in a damaged area [98]. Different

polymers rely on different self-healing mechanisms that involve three different processes:

- Irreversible covalent bonds;
- Reversible covalent bonds;
- Reversible intermolecular interactions.

The first two processes require the presence of an encapsulated monomer reservoir in the polymer bulk. When damage occurs, the capsules break and release the healing agent into the fracture, followed by cross-linking to repair the damage. This relies on the formation of reversible or irreversible covalent bonds at sites where stress has caused the cleavage of bonds in the polymer network. Examples of irreversible mechanisms include ring-opening metathesis polymerisation (ROMP) and click chemistry [99], whereas reversible mechanisms include cross-linked poly(dimethylsiloxane), retro Diels-Alder reactions, and deformable/reformable disulfide and alkoxyamine bonds in response to stimuli such as temperature or irradiation [100].

The healing behaviour of CD/PEG systems is based on reversible supramolecular interactions, where various intermolecular forces can drive the self-healing process:
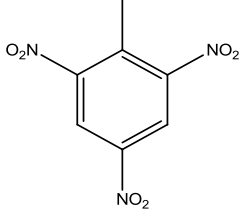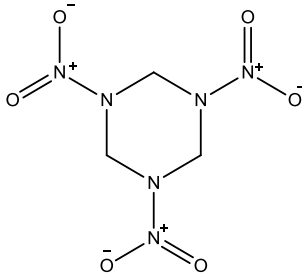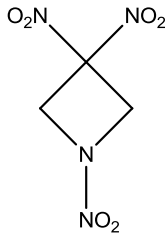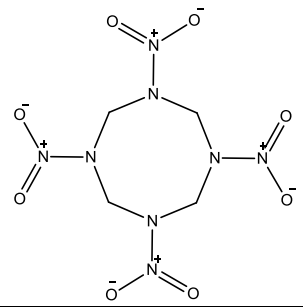
- Inclusion complexes form between the cross-linker and CD [95,96,101];
- Electrostatic interactions and intermolecular hydrogen bonding [50,94,102];
- Mobility of the polymeric chains in the bulk (reptation) [92,103,104];
- Mobility of the polymeric chains in the water of the hydrogel [105,106].
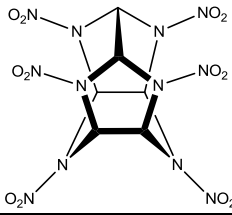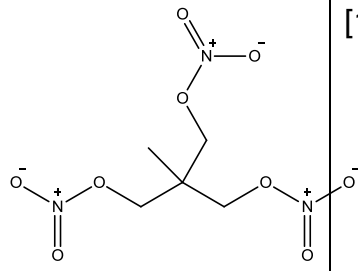
The combined effect of these driving forces allows the CD/PEG systems to heal, which is useful in applications that subject the materials to mechanical stress. In addition, the self-repairing ability of CD/PEG systems is enhanced when the compounds are exposed to heat due to the increased mobility of the polymer chains in water. Compounds that heal in response to external stimuli such as temperature or mechanical pressure are defined as healable or amendable [98,106].

2.4.4 Energetic applications of unlinked/cross-linked cyclodextrins

The ability of CDs to trap energetic molecules has been investigated in the past for the treatment of military waste streams [67,107]. A list of studies involving the energetic applications of CD is provided in Table 2.9.

Table 2.9 Applications of CDs functionalised with energetic molecules.

Application	CD type	Energetic		Ref
Removal of TNT from soil	βCD	**Trinitrotoluene** (TNT)		[67]
Removal of RDX from soil	βCD	**Cyclotrimethylene-** **trinitramine** (RDX)		[108,109]
Inclusion studies[1]	βCD			
High explosive manufacturing	βCD, γCD			
Inclusion studies[2]	αCD, βCD, γCD	**1,3,3-Trinitroazetidine** (TNAZ)		[110,111]
Inclusion studies[1]	βCD, γCD	**Cyclotetramethylene-tetranitramine** (HMX)		[110]

Application	CD type	Energetic		Ref
Inclusion studies[3]	γCD	**Hexanitrohexa azaiso- wurtzitane** (CL-20)		[112,113]
Manufacturing of gun propellants with nitrated βCDs (βNCDs)	βCD	**Trimethyloleth ane trinitrate** (TMETN)		[114]

1 ^{1}H-NMR solution studies.
2 Characterisation by IR spectroscopy and DSC.
3 Characterisation by IR spectroscopy.

CDs can be used as molecular sieves to remove nitroaromatic compounds such as TNT and RDX from soil. Dilute aqueous solutions of hydroxypropyl-βCD and methylated-βCD were used to absorb TNT from soil, achieving the removal of at least 25% of the pollutant. These studies directly demonstrated that βCDs can interact with and envelop aromatic explosive compounds [67,108].

The encapsulation of TNAZ, RDX and HMX has been attempted using α, β and γ CDs. Interactions were characterised by ^{1}H-NMR spectroscopy and showed that the degree of interaction was relative to the size of the macrocycle and its cavity, and the size of the molecule to be encapsulated. HMX only interacted with γCD (having the larger cavity), whereas RDX interacted with both βCD and γCD. In contrast, αCD did not interact with any of the energetics due to its relatively smaller cavity size. TNAZ formed a solid complex with βCD, that was also characterised by DSC, solid-state NMR, and Raman spectroscopy [111]. The physicochemical properties of this complex differed from those of the physical mixture: the volatility of TNAZ was reduced and the CD thermal decomposition profile was less exothermic, but the thermal stability of TNAZ was not affected by the complexation [111]. Other attempts to encapsulate

larger molecules such as CL-20 have been successful with the larger γCD, but not with βCD [112]. A more recent study showed that complexation also occurs between CL-20 and the nitrated derivative of γCD [113]. The inclusion studies offered insight into the ability of CDs to trap energetic molecules.

In addition, βNCD and βNCD cross-linked with epichlorohydrin and isocyanate have been used to develop energetic formulations that are less vulnerable to accidental stimuli [109,114]. These patents led to the registration of a warhead featuring nitrated cross-linked CDs as part of the main charge [115]. The first patent [109,114] claimed the use of βNCD to encapsulate trimethylolethane trinitrate (TMETN). Different nitration levels are possible because not all of the 21 βCD hydroxyl groups need to be nitrated. The level of nitration affects the energetic performance and physicochemical properties of the βNCD. When more than three hydroxyl groups are nitrated to form nitro groups, the βNCD becomes insoluble in water but remains soluble in organic solvents such as acetone, methylene chloride or tetrahydrofuran (THF) [116]. Consequently the βNCDs can be processed as acetone lacquers. The inventors tested different reaction conditions to obtain βNCDs that are listed in Table 2.10.

Table 2.10 Summary of βCD nitration conditions [114].

CD[1] (g)	90% HNO_3 Mass (g)	98% H_2SO_4 (g)	Time (min)	Extent of nitration (%)
200	1296	-	15	-[2]
50	291	480[3]	-[2]	-[2]
750	2650	550	120-180	12.96

1 Reaction temperature < 30 °C.
2 Values not reported.
3 Oleum.

The βNCD/TEMTN formulations were then used in hazard tests to determine their sensitivity towards accidental stimuli. Hazard tests are systematic studies to quantify the accidental initiation of energetic compounds using standardised methods [117]. Such methods were developed independently by several countries in the nineteenth century and the results differ in the way the

magnitude of the sensitivity is reported, which makes it difficult to compare studies carried out in different countries [117]. The formulated products were compared to pure TMETN and βNCD (Table 2.11), but no information on the methodology was reported, although the compounds were likely to have been tested under American standards.

The tests demonstrated that the addition of βNCD to TMETN reduced the vulnerability of almost all the all formulations to shock, with only the 6:1 ratio TMETN/βNCD formulation becoming more susceptible to impact than the single ingredients. The addition of βNCD as a binder to TMETN did not improve the thermal stability of the mixtures. The temperature of decomposition (T_{dec}) of the single ingredients was not reported, but the T_{dec} of the formulations was 4 °C lower than the T_{dec} of TMETN and 20 °C lower than the T_{dec} of βNCD as reported elsewhere. The sensitivity of βNCD to electrostatic discharge (ESD) was mitigated by the formulation with TMETN up to the safe value of 12.5 J. The TMETN/βNCD 2:1 propellant cured with R45M isocyanate was described as a flexible gum, but its characterisation was not reported in the patent [114].

The nitration of βCDs featuring different cross-linkers (such as epichlorohydrin, urethane and amines) was attempted to obtain softer binders less susceptible to impact and ESD, but still able to contribute to the energy of the system [109]. A cross-linked CD sample, obtained by cross-linking βCD with a large excess of epichlorohydrin (1:12 ratio) was nitrated with 98% HNO_3 and then formulated with RDX in different ratios. The sensitivity towards accidental stimuli was then determined in impact and ESD tests (Table 2.12).

Table 2.11 Performance of TEMTN:βNCD propellant formulations [114].

| Sample | Hazard tests | | | DTA[1] (Onset°C/ Exotherm°C) | Card gap |
	5 kg Impact (mm)	Friction (lb)	ESD (J)		
TMETN	≥ 600	≥ 980	≥ 12.5	182[2]	15–20
βNCD	≥ 600	≥ 980	0.0125	200–208[3]	0
TMETN:βNCD	≥ 600	≥ 980	≥ 12.5	140/178	0

Sample	Hazard tests			DTA[1] (Onset°C/ Exotherm°C)	Card gap
	5 kg Impact (mm)	Friction (lb)	ESD (J)		
2:1					
TMETN/βNCD 4:1	≥ 600	≥ 980	≥ 12.5	140/178	0
TMETN/βNCD 5:1	≥ 600	≥ 980	≥ 12.5	140/178	0
TMETN/βNCD 6:1	225	≥ 980	≥ 12.5	110/172	0

1 Values obtained from data thermal analysis (DTA): onset temperature of the decomposition and exotherm peak temperature.

2 Exotherm peak value from [118].

3 This work.

The nitrated cross-linked βCD (βNCCD) reduced the sensitiveness of RDX against impact depending on the amount of βNCCD used as the binder. The presence of the binder slightly reduced the susceptibility of the formulation to friction compared to pure RDX. Although the formulations also remained vulnerable to ESD, the energy input required for ignition increased to that of the binder (0.1288 J), which is much higher than the value for pure RDX (0.0585 J) and significantly lower than the 0.02 J that can potentially be accumulated by an operator [119] (Table 2.12).

Table 2.12 Sensitivity of nitrated cross-linked βCCD and RDX complexes [109]

Sample	RDX : βNCCD ratio	Hazard Tests		
		Impact Bruceton (cm)	Friction (kg)	ESD (joule)
RDX	-	19	9.6	0.0595
βNCCD	-	47	28.8	0.1288
RDX:βNCCD	1:1	42	12.8	0.1288
RDX:βNCCD	5:1	27	10.8	0.1288
RDX:βNCCD	10:1	30	10.8	0.1288

The CD derivatives used thus far still need design improvements before they are considered suitable as binders for energetic applications. There is a need to develop new systems that are more resistant to impact and ESD stimuli. To the best of our knowledge, βCD systems cross-linked with XEG segments and nitrated derivatives thereof have not yet been synthesised and characterised as potential binders for energetic applications. The research described in Chapters 4–6 therefore focuses on the development and testing of these novel formulations.

3 Experimental

3.1 Materials

The βCD used in this project (97%, Sigma-Aldrich) was used from stock with a 11–13% water content, based on TGA data. Polyethylene glycol diglycidyl ether (PEGDGE 500 Mw, Sigma-Aldrich), sodium hydroxide (Fisher Chemicals), benzylated dialysis membranes with a molecular weight cut-off (MWCO) of 2000 (Sigma-Aldrich), epichlorohydrin (Sigma-Aldrich), tetrabutyl ammonium bromide (Sigma-Aldrich), hexaethylene glycol (Sigma-Aldrich) and triethylene glycol (Sigma-Aldrich) were used without further purification. Triethylene glycol diglycidyl ether (TEGDGE, 262 g mol^{-1}) and hexaethylene glycol diglycidyl ether (HEGDGE, 394 g mol^{-1}) were synthesised as described in Section 3.3.

3.2 Methods

3.2.1 NMR spectroscopy

The ^{1}H NMR spectra were recorded on a Bruker Ascend (400 MHz) with a broad band fluorine observation (BBFO) probe in deuterated dimethyl sulfoxide (DMSO-d$_6$) and deuterium oxide (D$_2$O) solutions. Signals representing the solvents served as internal standards. The solvent peaks were referenced to 2.5 ppm (DMSO-d$_6$) and 4.7 ppm (HDO, D$_2$O). Peak multiplicities were described as follows: singlet (s), multiplet (m), and broad (br).

3.2.2 FTIR spectroscopy

FTIR spectra were collected using a Bruker Alpha in attenuated total reflection (ATR) mode, allowing the immediate characterisation of undiluted samples. The spectra were collected in the region between 400 and 4000 cm^{-1}.

3.2.3 Gel permeation chromatography

Gel permeation chromatography (GPC) was used to determine the Mw of the products on a Waters size-exclusion chromatography system equipped with a 2410 refractive index detector. The samples in water (1–0 mg mL^{-1}) were passed through two columns (PL aquagel-OH MIXED-M 1000–500,000 Da, 8

μm, 300 x 7.5 mm). The buffer was a solution of 0.01 M $LiNO_3$ and 0.5% (w/w) NaN_3 in distilled water. Nitrated samples in anhydrous THF (1.5 mg mL^{-1}) were passed through the column (10 μm PL-gel, Polymer Laboratories) at a flow rate of 1.0 mL min^{-1}. Calibration curves were created using polyethylene oxide/polyethylene glycol standards for aqueous buffers, and polystyrene standards for anhydrous THF.

3.2.4 Differential scanning calorimetry and thermal gravimetric analysis

Thermal analysis of the βCXCD samples and their precursors was carried out using a Mettler Toledo DSC3+ instrument for low-temperature profile studies and a combination of Mettler Toledo TGA/DSC3+ and DSC30 instruments for decomposition and compatibility studies. The temperature was cycled three times for the low-temperature regime: the first heating run was set from −100 to 130 °C to eliminate the water present in the samples, whereas the second and third runs were set from −100 to 120 °C, a higher temperature considered sufficient to dry the sample. The degradation of the samples was characterised in the temperature range 30–500 °C. A mass of 10 mg was placed in a 40-μL aluminium pan with a pierced lid to analyse the degradation of the inert materials, and low-temperature profiles of energetic and inert samples were also assessed with 10-mg samples. The decomposition of the energetic products was characterised using 1-mg samples. The DSC chamber was continuously purged with N_2 at a flow rate of 50 mL min^{-1}. The variation of the heat flow in the samples was recorded as a function of temperature and time.

3.2.5 Dynamic mechanical analysis

The thermo-mechanical properties of the βCXCDs were determined by dynamic mechanical analysis (DMA) using a Perkin Elmer DMA8000 device. The samples were subjected to a controlled sinusoidal displacement of 0.05 mm at frequencies of 1, 5 and 10 Hz in the single cantilever clamped bending configuration. The storage modulus (E′), loss modulus (E″) and damping factor (tanδ) were monitored as a function of temperature and time. The free sample length between the vibrating and fixed cantilever clamps was ~15 mm. The

testing temperature was cycled three times between −100 and 140 °C at a rate of either 2 or 10 °C min^{-1}. Each material was tested in triplicate under each condition. The samples were tested in aluminium pockets, a stainless steel mesh or aluminium pockets with polytetrafluoroethylene (PTFE) tape because the cross-linked CD samples were not capable of self-support. The aluminium pockets consisted of rectangular shims (30 x 14 mm) cut from a 0.1 mm thick aluminium strip (supplied by RS) and then folded lengthwise to form the pockets. About 25 mg of the cross-linked CD sample was placed in the centre of the pockets. This sample support was recommended by the DMA manufacturer when testing powders, gels and liquids. PTFE tape (30 x 15 mm) was used to fold the sample in the pocket and assess the bonding interaction between the sample and the metallic support during cooling. Rectangular strips of mesh (30 x 15 mm) were cut from a 0.65 mm thick sheet (supplied by RS). The wire forming the mesh had a diameter of 0.4 mm and the dimensions of the holes were 1 x 1 mm. About 30 mg of the crosslinked CD material was spread around and in the centre of the mesh strips.

3.2.6 Optical microscopy

The dynamic physical properties of the βCXCD materials under the influence of temperature were investigated by optical microscopy using a Leica DM microscope fitted with a temperature-controlled stage (Linkam THMS 600). The temperature was changed using a T95 controller and an automated LNP95 liquid N_2 pump (both from Linkam). The material was placed on a 0.5 mm thick quartz cover slip. The slide was placed in a carrier on the stage to allow visual scanning. The stage was cooled to −100 °C and then heated to 100 °C at either 2 or 10 °C min^{-1}. To prevent condensation forming on the windows of the cold stage, the interior was purged with dry N_2 gas prior to cooling. A digital Qicam Fast 1394 CCD camera (QImaging) was used to continuously record any changes in the samples during the temperature cycle. The sample was illuminated by a white light source set in transmission mode.

3.2.7 Scanning electron microscopy

Scanning electron microscopy (SEM) was conducted using a Hitachi SU3500 instrument which is a tungsten filament variable pressure device with an accelerating voltage of 20 kV at 80 Pa. Samples (5 mg) were pressed onto conductive carbon tabs and supported with specimen stubs.

3.3 Procedures

3.3.1 Triethylene glycol diglycidyl ether [120]

Sodium hydroxide (40.00 g, 1.00 mol) in water (50 mL), tetrabutylammonium bromide (1.19 g, 7.40 mmol) and epichlorohydrin (92.70 g, 1.00 mol) were placed in a three necked round bottomed flask. The reaction mixture was then stirred vigorously for 1 h at room temperature. Triethylene glycol (25.60 g, 0.17 mol) was added slowly over 3 h at room temperature with vigorous mechanical stirring. The reaction mixture was stirred at 40 °C for 1 h, allowed to cool and then filtered. The liquid phase was collected, dried overnight on sodium sulfate, and the excess epichlorohydrin was evaporated under high vacuum to leave a yellow-orange viscous liquid: ^{1}H-NMR (400 MHz, CDCl$_3$) : δ=4.00–3.40 (m, 16H, C$\underline{H}_2$-O), 3.15 (m, 2H, CH-C$\underline{H}_2$), 2.80 and 2.62 (2 m, 4H, C$\underline{H}_2$-CH); ^{13}C-NMR (CDCl$_3$): δ=72.0 ($\underline{C}$H$_2$-O), 70.9, 70.7 and 70.6 ($\underline{C}$H-CH$_2$-O), 50.8 ($\underline{C}$H-CH$_2$) and 44.4 ppm (CH$_2$-CH); DSC (10 °C min^{-1}, N$_2$) 203 °C (T$_{dec}$ onset); DSC (10 °C min^{-1}, N$_2$) Tg = 80 °C; yield 78%.

3.3.2 Hexaethylene glycol diglycidyl ether [120]

Sodium hydroxide (23.60 g, 0.59 mol) in water (29.5 mL), tetrabutylammonium bromide (0.70 g, 4.35 mmol) and epichlorohydrin (54.70 g, 0.59 mol) were placed in a three necked round bottomed flask. The reaction mixture was stirred vigorously for 1 h at room temperature. Hexaethyelene glycol (28.50 g, 0.10 mol) was added slowly over 3 h at room temperature with vigorous mechanical stirring. The reaction mixture was stirred at 40 °C for 1 h, allowed to cool and then filtered. The liquid phase was collected and dissolved in dichloromethane (50 mL). The solution was washed with half-saturated brine three times and dried overnight on sodium sulfate. The excess epichlorohydrin was evaporated

under high vacuum to leave a yellow-orange viscous liquid: ^{1}H-NMR (400 MHz, CDCl$_3$) : δ=4.00–3.40 (m, 26H, C$\underline{H}_2$-O), 3.15 (m, 2H, C$\underline{H}$-CH$_2$), 2.80 and 2.62 (2 m, 4H, C$\underline{H}_2$-CH); ^{13}C-NMR (CDCl$_3$): δ=72.0 ($\underline{C}$H$_2$-O), 70.9, 70.7 and 70.6 (CH-$\underline{C}$H$_2$-O), 50.8 ($\underline{C}$H-CH$_2$) and 44.4 ppm ($\underline{C}$H$_2$-CH); DSC (10 °C min^{-1},N$_2$) 273 °C (T$_{dec}$ onset); DSC (10 °C min^{-1}, N$_2$) Tg = 80 °C; yield 70%.

3.3.3 Cross-linked cyclodextrins (βCXCDs)

The reported procedure refers to the conditions optimised during this project. For the conditions tested, see the appendices (Table A 1, Table A 2 Table A 3). The βCD (5.00 g, 4.40 mmol) was dissolved in 5.6% w/w NaOH (21.0 mL) and stirred mechanically for 16 h. Diglycidyl ether (TEGDGE, HEGDGE or PEGDGE; 17.4–5.8 mL, 13.2–36.9 mmol) was then added dropwise over a period of 20 min with vigorous stirring. The reaction mixture was heated to 30 °C for 6 h with vigorous stirring. After cooling to room temperature for 20 min, the mixture was neutralised with HCl (6 M). The volume of solvent was reduced and the reaction mixture was precipitated in acetone. The solid was dissolved in distilled water and dialysed against water using a benzylated cellulose membrane (2000 MWCO) for 5 days. The dialysis water was replaced every day. The dialysed white solid was collected and the water was evaporated under reduced pressure. The final product was characterised by ^{1}H NMR and DSC. ^{1}H NMR (400 MHz, DMSO-d6, ppm): δ=5.9–5.6 (brm, C$_2$-O$\underline{H}$, C$_3$-O$\underline{H}$), 5.1–4.8 (m, $\underline{H}$-C$_1$), 4.7–4.5 (br m, O$\underline{H}_A$, O$\underline{H}_B$), 4.4 (br m, C$_6$-O$\underline{H}$), 4.0–3.2 (brm, βCDOC$\underline{H}_2$(C$\underline{H}$OH)C$\underline{H}_2$OC$\underline{H}_2$C$\underline{H}_2$). DSC 10°C min^{-1}, N$_2$: 240–250°C (T$_{dec}$); yield 45-72%.

3.3.4 Nitrated cross-linked cyclodextrins (βNCXCDs)

Nitric acid (100%, 2.1 mL) was poured into a round-bottomed flask and cooled below 10 °C in ice water. The bath was removed and βCXCD (200 mg) was added in small fractions over 5 min, ensuring that the temperature remained below 10 °C. The crude slurry or solution was then left stirring at room temperature for 1 h. The reaction mixture was crushed into ice/water (10 mL). The solid was decanted and rinsed with distilled water. The solid was dissolved in acetone (5 mL) and re-precipitated in a solution of half saturated brine and

Na$_2$CO$_3$ (5% w/w, 100 mL) three times. The crude product was filtered and dissolved in 10 mL acetone. The solution was filtered through Na$_2$CO$_3$ and dried under vacuum. Small portions of products were characterised by ^{1}H NMR and DSC and stored under dichloromethane. Then ^{1}H NMR spectroscopy was performed in DMSO-d$_6$ and used for comparison with the precursors. DSC (10 °C min^{-1}, N$_2$): 197–210 °C (T$_{dec}$); yield 80%.

3.3.5 Hazard testing

A set of small-scale hazard tests were performed according to Cranfield internal procedures and following the Energetic Materials Testing Assessment Policy (EMTAP) Manual of Tests.

3.3.5.1 Small scale hazard tests

Direct impact: steel hammer on steel anvil

A small amount of the synthesised compound (20 mg) was placed on the steel anvil and struck 10 times with the steel hammer. Signs of decomposition, such as smell, colour change and material consumption, were evaluated after each blow.

Glancing blow: steel hammer on steel anvil

A small amount of synthesised compound (20 mg) was placed on the steel anvil and struck with a glancing blow using the curved edge of the steel hammer. Signs of decomposition were evaluated after each blow as above.

High temperature test

A small amount of compound (20 mg) was placed on a steel plate at 100 °C for 30 min. Signs of decomposition were evaluated as above.

Room temperature test

A small amount of compound (20 mg) was placed on a steel plate at 30 °C for 24 h. Signs of decomposition were evaluated as above.

Flame test

A small amount of compound (20 mg) was placed on a steel spoon and ignited using a blow torch. The nature of the combustion process was described by an expert member of the Cranfield University "Synthesis and Formulation" group.

3.3.5.2 Hazard tests based on the Energetic Materials Testing Assessment Policy Manual of Tests

Electrostatic discharge test

Nylon spark test strips were filled with the material and sealed with copper tape. Fifty samples were tested using a certified ESD testing apparatus and a spark of 4.5 J was discharged through the composition. The samples were inspected for perforation or signs of decomposition.

Rotter direct impact test

Samples (30–40 mg) were placed in a concavity at the centre of the supporting frame of the Rotter tester apparatus. A free-fall weight (5 kg) and striker were suspended above. The tests followed the Bruceton "up and down" testing technique with 50 replicates and the results were based on the height at which the compound was initiated 50% of the time, with the mean height reported as the figure of insensitiveness (FoI) [119]. Initiation was determined by the observation of parameters such as sound, smoke, flash and volume of gas released immediately after impact, and is therefore affected by operator judgment.

3.3.6 Compatibility tests

The tests were based on Test 4 of STANAG 4147 [121]. Approximately 0.5–1.0 mg of each material was analysed by DSC at a heating rate of 2 °C min^{-1} under N_2 and then a mixture of the two materials was measured in the same manner. Any alteration in the shape, onset, or peak position of any measured thermal event can be indicative of incompatibility.

Under "Applicability" STANAG 4147 Test 4 states: "*This test is applicable to explosives likely to come into contact with plasticizers, fuels, additives,*

polymeric materials and other explosives." It also states: "*This test is not concerned with compatibility between ingredients in explosive compositions and the consequent stability of such compositions.*" Even so, the method allows a large number of mixtures to be investigated rapidly. As such, the results from this tests are useful but not conclusive, and further experiments are required, such as vacuum stability testing [122].

Edition 2 of STANAG 4147 Test 4 states that shifts in thermal events that vary by less than 4°C indicate compatibility. For shifts between 4 and 20 °C, the test is inconclusive and, as above, further experiments are required [122]. Shifts greater than 20 °C are considered conclusive evidence that materials are incompatible.

3.3.7 Stability analysis

The stability of the nitrated products was determined by heat flow calorimetry (HFC). The samples (1.0 g) were placed in sealed vials (10 mL) with glass beads to fill the head space. The samples were characterised by isothermal calorimetry at 80 °C on a TAM IV device with a dedicated software package.

4 Synthesis and characterisation of inert βCXCDs

This chapter describes the cross-linking of βCD with the diglycidyl ethers TEGDGE, HEGDGE or PEGDGE as a first step towards the synthesis of a new, inert binder for energetic applications. The cross-linking reaction conditions discussed below were investigated and optimised to obtain products that exhibited the following properties, in alignment with the statement of requirements developed by the PhD sponsor organisation, the Weapons Science and Technology Centre (WSTC):

- Low T_g (possibly below 0 °C) to reduce vulnerability to shocks, ensuring the cross-linked binder remains soft in a wide operative temperature range, down to the T_g.
- Soluble in organic solvents and/or water, allowing the formulations to be processed by preparing a lacquer with the binder. The lacquer and the solid ingredients mixed with it can be extruded as a paste and granulated in pellets [2]. Low-molecular-weight cross-linked products with a low cross-linking ratio would guarantee the preparation of an extrudable paste.
- Easily converted to energetic derivatives by nitration. The new requirement for binders in energetic formulations is to contribute to the energetic output of the main filler. A simple and safe nitration procedure would produce a suitable replacement for NC.
- Good chemical and thermal stability to avoid uncontrolled events during the shelf life of the formulation.
- Good compatibility with energetic fillers such as high explosives, oxidisers, and pyrotechnics to avoid undesirable reactions and instability when the binder is mixed with the other ingredients of an energetic formulation.

4.1 Synthesis and chemical characterisation

The effect of the reaction conditions discussed in sections 4.1.1–4.1.7 and the chemical characterisation of some of the βCXCDs by ^{1}H-NMR and FTIR spectroscopy have been published in a peer-reviewed article: Luppi F, Cavaye H, Dossi E (2018) Nitrated cross-linked β-cyclodextrin binders exhibiting low

glass transition temperatures. *Prop Expl Pyrotech* 43 (10) 1023–1031. The paper is attached at the end of the annex to this thesis.

The synthesis of βCXCDs was based on the cross-linking of βCD with polyethylene glycol diglycidyl ethers containing ethylene glycol units, according to Scheme 4.1. Triethylene glycol diglycidyl ether (TEGDGE) contains three ethylene glycol units and was a synthetic sample. Hexaethylene glycol diglycidyl ether (HEGDGE) contains six ethylene glycol units and was also a synthetic sample. Polyethylene glycol diglycidyl ether (PEGDGE) was obtained from a commercial source and was a polydisperse 500 Da preparation with an average of nine ethylene glycol units. The abbreviation XEG is used to collectively refer to the ethylene glycol segments in the cross-linkers and the βCXCD products.

To note that, TEG:βCD ratio, HEG:βCD ratio, PEG:βCD ratio is used refer to the ratio of XEG units to βCD units in the reaction products βCXCDs

TEGDGE was prepared according to a published procedure [120] by reacting triethylene glycol with an excess of epichlorohydrin under basic conditions to produce the diglycidyl ether derivative. The same experimental conditions were then used for the synthesis of HEGDGE. The synthesis of HEGDGE from hexaethylene glycol has been described in the past following a similar route, but gave a lower yield (55%) [123]. The yield using the method followed in this PhD project was 70%.

As shown in Scheme 4.1, βCD (**1**) is dissolved in NaOH (5.6–50%) to give the corresponding alkoxylated βCD (**2**). The equilibrium is strongly shifted towards (**1**) (Step 1, Scheme 4.1) due to the pK_a values of the acid dissociation of the βCD hydroxyl groups. The pK_a values for the βCD secondary alcohols in the literature vary from 12.1 to 13.5 [124]. There is no information about the pK_a values of the primary hydroxyl groups because this is difficult to measure directly [124]. The alcohol-alkoxide equilibrium (Step 1, Scheme 4.1) therefore cannot be evaluated accurately. When a solution of 1.5 M NaOH (5.6% w/w) is used, the amount of (**1**) is six orders of magnitude higher than the alkoxylated derivative (**2**). It can be inferred that the alkoxylation of **1** is the rate-limiting step in the cross-linking process.
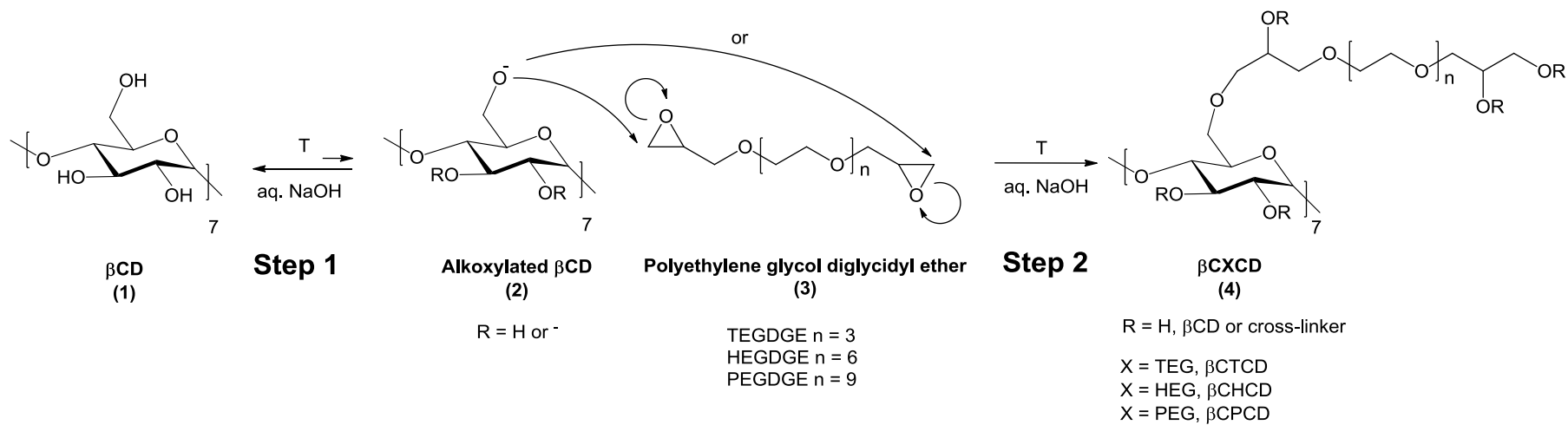
Scheme 4.1 The synthesis of cross-linked βCXCDs.

The reaction can be accelerated by modifying certain conditions, such as the temperature or concentration of NaOH or cross-linker, but a secondary reaction competes with the main reaction and its outcome is the loss of cross-linker. The competitive reaction is the opening of the diglycidyl rings of the cross-linker under basic conditions yielding the corresponding tetrahydroxyl derivative (Scheme 4.2).

Polyethylene glycol diglycidyl ether

n = 3, 6, 9

Tetrahydroxy poly ethylene glycol
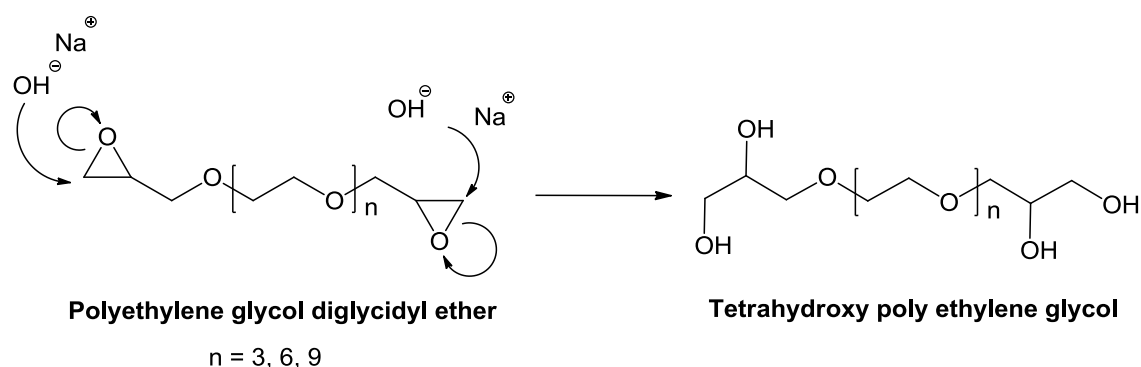
Scheme 4.2 Competitive hydrolysis of diglycidyl rings under basic reaction conditions.

Both the cross-linking and competitive hydrolysis reaction kinetics are strongly affected by:

- NaOH concentration
- Reaction time
- Temperature
- Effect of the βCD alkoxide formation
- Volume of NaOH aqueous solution
- Cross-linker:βCD ratio
- Addition rate of the cross-linker

Because all of these parameters affect the efficiency of cross-linking, it was necessary to optimise them in order to avoid the competitive reaction as far as possible and increase the yield of the desired product. PEGDGE is a commercially available chemical and was used for most of the cross-linking experiments, but a few tests were carried out using the TEGDGE produced in-house.

4.1.1 Effect of the NaOH concentration

The effect of the concentration of NaOH was tested to determine which conditions favoured the primary cross-linking reaction rather than the side reaction in which the cross-linker is degraded. The effect of the NaOH concentration was investigated at a high temperature (70 °C) for short reaction times (Step 2, 1 h) to enable rapid screening. All the NaOH concentrations that were tested resulted in a strongly alkaline environment, which can deprotonate the βCD hydroxyl groups. Four βCXCD samples (IP1–IP4) were prepared using 50%, 40%, 36% and 5.6% w/w NaOH solutions and a PEGDGE:βCD ratio of 9:1 (Table 4.1) [78]. Higher concentrations of NaOH were used for the synthesis of epichlorohydrin/βCD cross-linked systems [59,69,75], so these conditions were tested to determine their effect on the balance between cross-linking and PEGDGE degradation and also their effect on the solubility of the compounds. The results are summarised in Table 4.1.

Table 4.1 Effect of NaOH concentration on the yield of βCPCDs at a PEGDGE:βCD ratio of 9:1.

Sample ID[1]	NaOH[2] (% w/w)	Reaction Time (Step 2) (h)	Yield[3] (%)	Water solubility
IP1	50	1	<1	Y
IP2	40	1	<1	Y
IP3	36	1	<1	Y
IP4	5.6	0.66	88%	N

[1] PEGDGE:βCD ratio = 9:1.
[2] Reaction temperature = 70 °C.
[3] Yield measured as mass of products/mass of both reactants.

At 70 °C, the most dilute NaOH solution (5.6% w/w) promoted cross-linking whereas all the stronger NaOH solutions (36%, 40% and 50% w/w) favoured the rapid degradation of the cross-linker compared to the formation of the βCD alkoxide. When the NaOH concentration was low, the reaction reached the gelation point, thus causing a consistent change in viscosity of the reaction mixture accompanied by the appearance of an insoluble hydrogel. The speed of

gelation indicated that cross-linking with 5.6% NaOH at 70 °C is extremely fast and would make it difficult to recover soluble products. Accordingly, the studies proceeded by investigating the effect of the reaction time in the presence of 40% NaOH. However the optimisation of the temperature and the amount of cross-linker discussed in the following sections proved that this assumption was incorrect, and that 5.6% NaOH was a more effective choice at lower temperatures.

4.1.2 Effect of the reaction time

The slow step in the cross-linking mechanism is the formation of the alkoxide (Step 1, Scheme 4.1), only small amounts of which are available to react with the cross-linker. In order to increase the yield of βCPCDs, it appeared important to increase the reaction time to reform the alkoxides that reacted with the cross-linker and make more of these groups available for the cross-linking reaction. Two samples were synthesised, maintaining the earlier reaction conditions (40% NaOH, 70 °C) but extending the reaction time (Step 2) from 1 h (sample IP2, Table 4.2) to 5 h (sample IP5, Table 4.2).

Table 4.2 Effect of the reaction time (Step 2) on the yield of βCPCDs.

Sample ID[1]	NaOH[2] (% w/w)	Reaction Time (Step 2) (h)	Yield[3] (%)	Water solubility
IP2	40	1	<1	Y
IP5	40	5	12	Y

1 PEGDGE:βCD ratio = 9:1.
2 Reaction temperature = 70 °C.
3 Yield measured as mass of products/mass of reactants.

The product yield increased from negligible amounts to 12% when the reaction time was extended to 5 h (Step 2). This suggested that longer times are necessary to replenish the consumed alkoxide, allowing the cross-linking reaction to proceed. Although 12% was a significant improvement, it was not considered ideal and the reaction conditions were investigated in further detail. Accordingly, extending the time from 5 to 6 h improved the yield even further.

4.1.3 Effect of the temperature

Higher temperatures often accelerate endothermic reactions [125]. However, both the cross-linking reaction and the degradation of the cross-linker are likely to be accelerated by temperature. A trial was therefore carried out using the following conditions:

- The temperature was reduced from 70 °C to 50 °C
- A low concentration of NaOH (5.6% w/w)
- A time of 5 h for the cross-linking reaction (Step 2, Scheme 4.1)
- The amount of cross-linker was reduced to a 5:1 ratio, to avoid the gelation observed when the ratio was 9:1

The cross-linker appeared more stable at 50 °C when the reaction proceeded for 5 h in the presence of 5.6% NaOH (sample IP6, Table 4.3). The lower yield at 70 °C (sample IP7, Table 4.3) reflected the loss of cross-linker in the competing degradation reaction, which is favoured by the higher temperature, whereas lower temperatures favour cross-linking. Water-soluble polymers were produced in the tests, confirming that a lower PEGDGE:βCD ratio was necessary to generate soluble cross-linked βCPCDs.

Table 4.3 Effect of the temperature on the yield of βCPCDs, when the PEGDGE:βCD ratio is 5:1.

Sample ID[1]	T (°C)	Yield[2] (%)	Water solubility
IP6	70	1	Y
IP7	50	13	Y

1 PEGDGE:βCD ratio = 5:1, 5 h reaction time (Step 2), aq. NaOH 5.6% w/w.
2 Yield measured as mass of products/mass of reactants.

4.1.4 Effect of βCD alkoxide formation

The time allowed for the system to reach alcohol/alkoxide equilibrium (Step 1, Scheme 4.1) was extended by leaving the βCD stirring in 5.6% NaOH for 16 h, thus increasing the amount of alkoxide available to react with the cross-linker.

Table 4.4 Effect of the time allowed for βCD alkoxide formation (Step 1) on the yield of βCPCDs.

Sample ID[1]	Alcohol/alkoxide time (Step 1)	T (°C)	Yield[2] (%)	Water solubility
IP6		70	1	Y
	0 h			
IP7		50	13	Y
IP8		50	30	Y
	16 h			
IP9		30	33	Y

1 PEGDGE:βCD ratio = 5:1, 5 h reaction time (Step 2), aq. NaOH 5.6% w/w.
2 Yield measured as mass of products/mass of reactants.

The difference between samples IP6 and IP7, where no time was allowed for the system to reach alcohol/alkoxide equilibrium (Step 1, Scheme 4.1), and samples IP8 and IP9 (where Step 1 in Scheme 4.1 involved stirring for 16 h), revealed that the cross-linking process requires more time to increase the availability of alkoxide groups for the reaction (Step 2, Scheme 4.1). Samples IP8 and IP9 were obtained at higher yields (30% and 33%, respectively), with the best results achieved at 30 °C. The malleability of the products prompted thermal characterisation studies, revealing that the T_g of compounds IP8 and IP9 were –18 and –22 °C, respectively. This confirmed that the processability of crystalline βCD could be improved by the incorporation of soft polyethylene glycol segments.

4.1.5 Effect of the volume of NaOH solution

When the concentration of βCD was higher than 0.23 $g_{\beta CD}$ $mL^{-1}_{aq.NaOH}$ in the reaction mixture, the solubility of the cross-linked βCPCDs was reduced,

causing their gelation (sample IP9, Table 4.4). In all subsequent experiments, the safe value of 0.21 $g_{\beta CD}$ $mL^{-1}_{aq.NaOH}$ was used.

4.1.6 Effect of cross-linker:βCD ratio

The next set of trials (Table 4.5) tested the effect of the PEGDGE:βCD ratio on the yield and physical properties of the products, with the other parameters maintained at the optimal values established above:

- 5.6% w/w NaOH
- 30 °C
- 16 h for the formation of the alkoxide (Step 1, Scheme 4.1)
- 5 h for the completed cross-linking reaction (Step 2, Scheme 4.1)
- PEGDGE as the cross-linker

The PEGDGE:βCD ratio influenced the final thermal properties of the βCPCD products. As expected, increasing the amount of cross-linker from 2 to 5 molar equivalents increased the cross-linking ratio in the product (Table 4.5). The cross-linker consumed in the competitive degradation reaction negatively affected the mass economy of the reaction, with the difference attributed to the degradation of the PEGDGE. Thermal analysis of the cross-linked products confirmed that lower amounts of cross-linker generated βCPCD products with greater crystallinity and higher T_g values. The synthesis of sample IP11 achieved a higher yield than the other compounds, and led to a further investigation of the purification method, which generally involved dialysis against water.

Table 4.5 Effect of PEGDGE:βCD ratio on the yield of βCPCDs.

Sample ID[1]	PEGDGE:βCD feed ratio	Yield[2] (%)	Water solubility
IP9	5 : 1	34[3]	Y
IP10	4 : 1	36[3]	Y
IP11	3 : 1	68	Y
IP12	2 : 1	44[3]	Y

1 5.6% (w/w) NaOH, 30 °C, 16 h for alkoxide formation (Step 1), 5 h reaction time (Step 2).
2 Yield measured as mass of products/mass of reactants.

4.1.6.1 Purification of βCXCDs

A typical work up for the cross-linked compounds started with the recovery of the crude product from the reaction mixture after neutralising the excess NaOH with 6 M HCl. Most of the water was removed under vacuum and the product was reprecipitated in acetone to eliminate unreacted and degraded cross-linkers. The compound was dissolved again in a small amount of water and dialysed against water to remove:

- NaCl formed during the neutralisation step
- Unreacted starting compounds (βCD and cross-linker)
- Any residual degraded cross-linker
- Low-molecular-weight oligomers

Dialysis was carried out using a cellulose membrane with a MWCO of 2000 Da for 5 days at room temperature (Figure 4.1). The dialysate was changed daily. At the end of the process, the retentate containing the desired cross-linked product was NaCl-free, as assessed by $AgNO_3$ qualitative analysis. When characterised by ^{1}H-NMR in DMSO-d_6, the compounds were found to be free of impurities. The NMR characterisation of the product is discussed in detail in Section 4.2.

Figure 4.1 Dialysis apparatus for the purification of βCXCDs.

The dialysate residues were dried and weighed, revealing that 80–70% w/w of the expected impurities on the first day were dialysate, reaching 85–90% w/w on the second day. No residual NaCl was detected after replacing the water four times, leaving only the degraded cross-linker and oligomeric products with a Mw < 2000 Da. These were absent after 5 days of dialysis.

4.1.7 Effect of the duration of cross-linker addition

The duration of cross-linker addition to the reaction mixture containing the βCD alkoxide was tested, initially with prolonged exposure times of up to 7 h to determine whether generally lower amounts of cross-linker would react preferentially with the βCD alkoxide rather than undergoing degradation. The earlier results suggested that βCPCDs obtained with a PEGDGE:βCD ratio of 5:1 reflected the maximum ratio that still produced soluble compounds (Table 4.6). Considering a potential increase in the efficiency of the cross-linking reaction, the first test involved 16 h for the alkoxide formation (Step 1, Scheme 4.1) and 7 h for the addition of the cross-linker (Step 2, Scheme 4.1). The product obtained using the new reaction parameters (sample IP14) had a higher PEG:βCD ratio than a similar setup with a brief exposure time (sample IP13) reflecting an 8% higher cross-linking efficiency. No significant change in the

yield was observed, possibly due to losses of product during the purification dialysis (Table 4.6).

Table 4.6 Effect of cross-linker addition time.

Sample ID	PEGDGE:βCD ratio feed	PEG:βCD ratio by ^{1}H NMR	Addition time (h)	Yield[1] (%)	Cross-linker yield efficiency[2]	Water solubility
IP13	5 : 1	3.8 : 1	20 min	68	75	Y
IP14	3.8 : 1	3.2 : 1	7 h	71	83	Y

1 Yield measured as mass of products/mass of PEGDGE and βCD.
2 Cross-linker yield is measured as the molar ratio between the feed of cross-linker and the amount of polyethylene glycol units present in the product.

The longer cross-linker addition time improved the mass economy of the reaction, but it seemed to have a negligible effect on the reaction yield and the product solubility. A cross-linker addition time of 20 min was therefore used for subsequent tests.

4.2 **The synthesis of βCXCDs**

The screening tests discussed in Sections 4.1.1–4.1.7 revealed the optimal conditions for the cross-linking of βCD with diglycidyl ethers. The reaction time was duly increased to 6 h to ensure that more unreacted cross-linker was consumed. The optimised parameters are shown below:

- Low NaOH concentration (5.6% w/w) to reduce the competitive side reaction (degradation of the cross-linker)
- Concentration of βCD in NaOH = 0.21 $g_{βCD}$ $mL^{-1}_{aq.NaOH}$ to avoid gelation
- A 16 h (overnight) reaction for βCD alkoxide formation (Step 1, Scheme 4.1)
- Cross-linker:βCD feed ratio < 5:1 to avoid gelation
- Addition of the cross-linker in 20 min
- Low temperature (30 °C) to favour cross-linking over the degradation of the cross-linker
- A 6-h reaction time (Step 2, Scheme 4.1)

Three sets of βCXCDs were synthesised using TEGDGE, HEGDGE and PEGDGE cross-linkers, varying the feed cross-linker:βCD ratio from 2:1 to 5:1. The water content of βCD can reach (13–14% w/w) [38]. The water content was determined by TGA prior to each cross-linking reaction to maintain the βCD concentration at 0.21 $g_{\beta CD}$ $mL^{-1}_{aq.NaOH}$, as discussed above. In a typical synthesis reaction, 5 g of wet βCD was dissolved in 20.5 mL 5.6% $NaOH_{aq}$ w/w and left to react at 30 °C overnight to form the βCD alkoxide. The cross-linker was then added in 20 min and the reaction mixture was left for 6 h at 30 °C as shown in Figure 4.2.

Figure 4.2 Cross-linking apparatus for the synthesis of βCXCDs.

The reaction mixture was then neutralised with 6 M HCl to remove excess NaOH, reduced in volume and reprecipitated in acetone to eliminate organic impurities such as degraded and unreacted cross-linker (Scheme 4.2). The products were then purified by dialysis against water using a 2000 Da MWCO benzoylated cellulose membrane. The retentate was collected and dried under high vacuum for 48 h. The cross-linking of βCD with PEGDGE was replicated to produce enough sample mass for the tests discussed in the following chapters. No significant differences in the yield or properties of the synthesised products were observed when comparing the replicates (Table A 1).

The desired βCXCD products were obtained with yields of up to 68% when HEGDGE and PEGDGE cross-linkers were used, whereas slightly lower yields (63%) were achieved when TEGDGE was used. This may reflect the outcome of the dialysis step, with smaller βCTCD molecules not retained by the membrane. Table 4.7 summarises the results of representative cross-linking reactions with the best results in terms of yield and βCXCD properties. The remaining synthesis reactions are reported in Table A 1.

Table 4.7 Synthesis of βCXCDs: summary of the most successful water-soluble products.

Sample ID[1,2]	Cross-linker	Cross-linker :βCD ratio feed	XEG:βCD ratio by ^{1}H NMR	Yield[3] (%)	Physical appearance
IT1	TEGDGE	5 :1	3.6 :1	63	Friable solid
IT2		4 : 1	3.1 :1	52	Brittle solid
IT3		3 : 1	2.4 :1	56	Brittle solid
IT4		2 : 1	1.9 :1	45	Brittle solid
IH1	HEGDGE	5 : 1	4.0 :1	68	Soft gum
IH2		4 : 1	3.2 :1	72	Soft gum
IH3		3 : 1	2.6 :1	67	Brittle solid
IH4		2 : 1	1.8 :1	65	Brittle solid
IP13	PEGDGE	5 : 1	3.8 :1	68	Soft gum
IP15		4 : 1	3.0 :1	65	Soft gum
IP16		3 : 1	2.3 :1	68	Brittle solid
IP17		2 .1	1.6 :1	68	Brittle solid

1 5.6% (w/w) NaOH, 30°C, 16 h for the formation of βCD alkoxide, 6 h reaction time, 20 min for cross-linker addition.

2 Sample ID: I = inert (not nitrated), T/H/P = cross-link segment, numeral = unique sample reference.

3 Yield measured as mass of products/mass of cross-linker and βCD.

The off-white βCXCDs were soft and malleable at cross-linker ratios of 4:1 and 5:1, but powdery and fragile at cross-linker ratios of 3:1 and 2:1 (Figure 4.3).
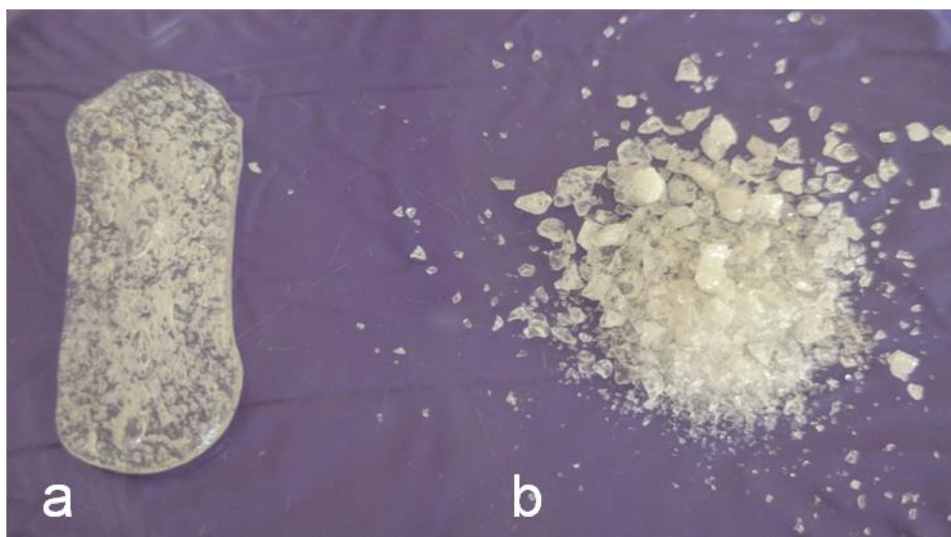
Figure 4.3 Physical characteristics of βCPCD. (a) Malleable IP13. (b) Powdery IP17.

Attempts to cross-link βCD using a greater ratio of cross-linker:βCD than 5:1 generated highly cross-linked βCXCD products that were insoluble in water. The βCXCDs produced with lower cross-link ratios were more soluble, and among the three sets of products those synthesised with TEGDGE were easier to dissolve than those synthesised with HEGDGE or PEGDGE. This is likely to reflect the lower Mw, generating a less intricate cross-linked network.

All the products were characterised by ^{1}H NMR:

- The NMR spectra were recorded in both DMSO-d_6 and D_2O solvents without a reference because βCD can encapsulate these reference compounds
- DMSO-d_6 was used as a solvent to investigate whether the hydroxyl groups of the βCDs at 4.4–5.5 ppm reacted with the cross-linker: a decrease in signal intensity would confirm this.
- D_2O was used as a solvent to determine the cross-linking ratio (this was not possible in DMSO-d_6 due to the overlapping water and product signals.

¹H-NMR analysis in DMSO-d₆

The ^{1}H-NMR analysis in DMSO-d$_6$ of the βCPCD sample IP13 and its precursors PEGDGE and βCD led to the proposed βCXCD general chemical structure shown in Figure 4.4. The corresponding ^{1}H-NMR spectra are shown in Figure 4.5.
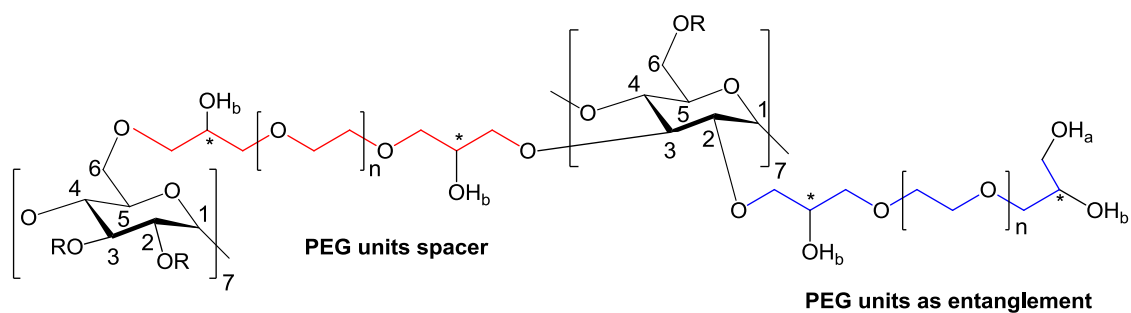
Figure 4.4 Proposed chemical structure of the βCXCD products based on IP13 incorporating PEG segments, underlining the co-existence of PEG units as spacers and as entanglements.
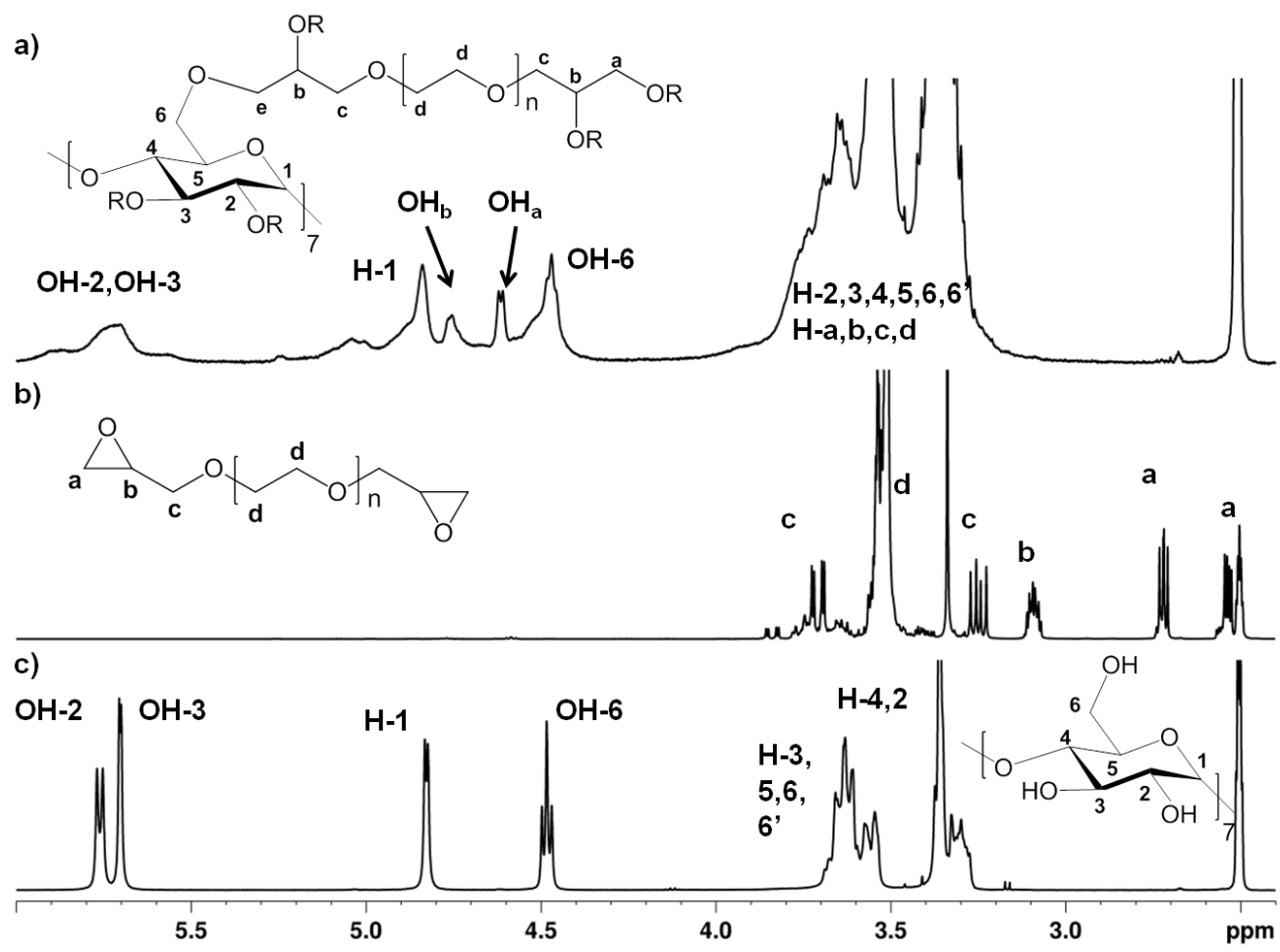
Figure 4.5 Comparative ^{1}H NMR spectra of (a) sample IP13 (PEG:βCD ratio = 3.8:1), (b) PEGDGE, and (c) βCD in DMSO-d_6 with assignments of signals. The DMSO reference peak is at 2.5 ppm. R= H, cross-linker C_a-OR = H or βCD.

The NMR spectra of βCD and PEGDGE match the values reported in the literature and discussed in Section 2.4.1 [63]. The spectrum of sample IP13 in DMSO-d_6 shows broadened peaks due to the macromolecular structure of the cross-linked product, given the complex chemical environment of protons in larger cross-linked molecules compared to the smaller βCD and cross-linkers. This is a general observation valid for all the synthesised βCXCD systems, confirming their polymeric nature. The integration of the NMR signals gave reliable indications for the chemical structure of the products, including the reduction of the integrals from OH groups at 5.9 ppm. The consumption of the OH-6 groups cannot be confirmed because they overlap with new signals between 5.0 and 4.6 ppm, which were attributed to the OH_b on the PEG spacer units after the opening of the diglycidyl ring of the PEGDGE (Scheme 4.2). The anomeric proton H-1 was found at 4.7 ppm broadened by the macromolecular structure and by its overlap with signals from OH_a and OH_b. The remaining proton signals from βCD and methylene protons from the PEG units were found between 3.9 and 3.2 ppm. Many signals overlap and peak attribution is therefore difficult. The absence of the characteristic diglycidyl group signals between 3.2 and 2.6 ppm excludes the presence of the cross-linker in the purified product (Figure 4.6a-c).

It was difficult to confirm the absence of degraded cross-linker (Figure 4.5b) in the final cross-linked products. In order to help with the assignment of the peaks, a sample of PEGDGE was left to react under the cross-linking reaction conditions, resulting in partial degradation and the formation of a blend of unreacted and degraded PEGDGE (Figure 4.6). During the synthesis of all βCXCDs, the by-products were removed during purification by reprecipitation in acetone followed by dialysis.

In addition, when only one of the glycidyl groups of PEGDGE reacts with βCD, a new pendant PEG unit is formed which contains two new hydroxyl groups (OH_b and OH_a) at the end of each entanglement. The NMR signals of the new OHs appear as a broad peak between 4.9 and 4.55 ppm (Figure 4.6).
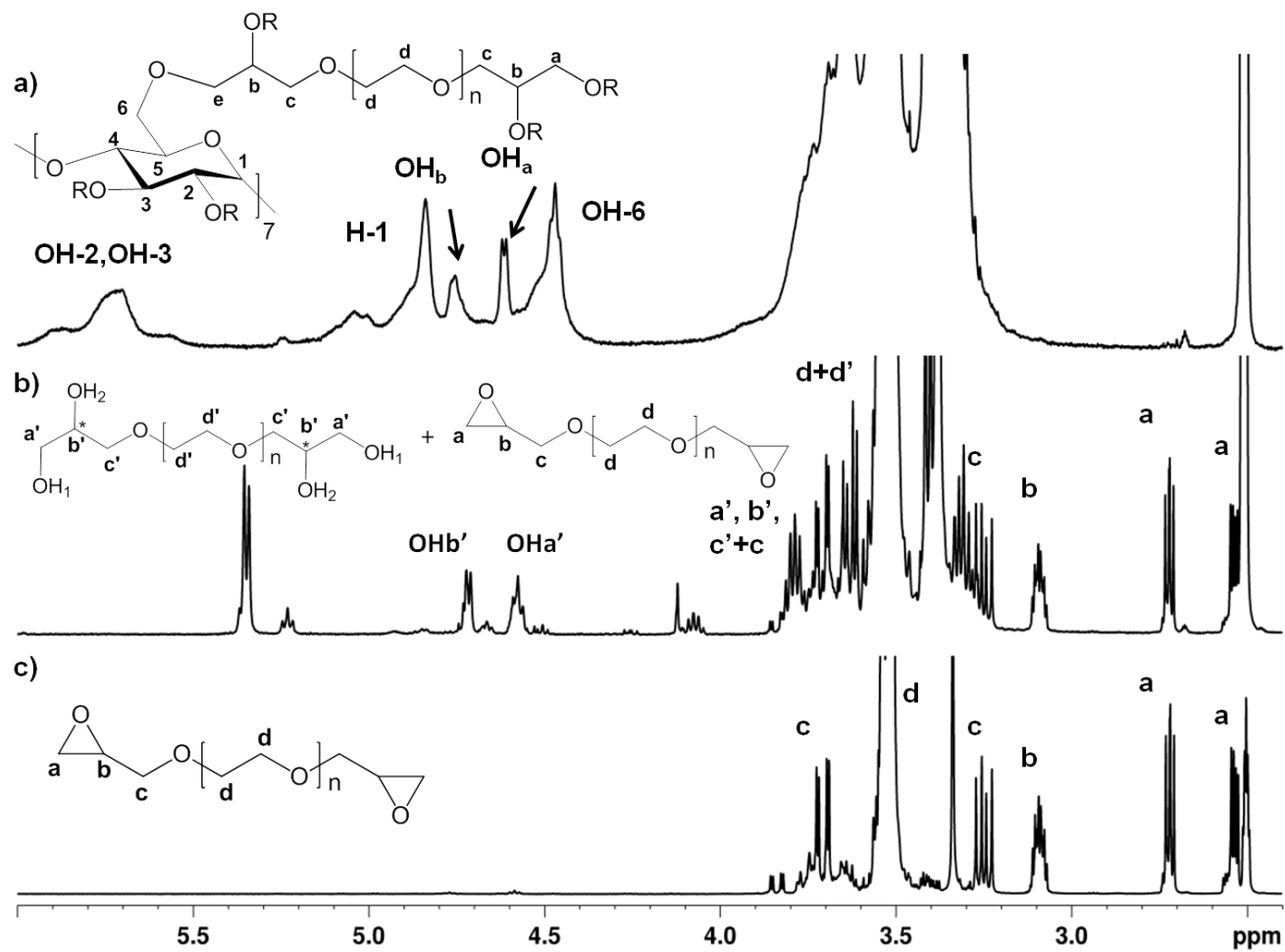
Figure 4.6 Comparative ^{1}H NMR spectra of (a) IP13 (PEG:βCD ratio = 3.8:1), (b) mixture of degraded/non degraded PEGDGE, and (c) PEGDGE in DMSO-d$_6$.

The ^{1}H-NMR spectra of the βCXCDs were then recorded in D_2O to determine the degree of cross-linking. The spectrum of the representative sample IP13 in Figure 4.7 is divided in two distinct regions: 5.2–4.6 ppm attributed to the chemical shift of the H-1 anomeric protons in two different situations as seen in Fig 4.7b and 4.1–3.4 ppm assigned to the chemical shift of the CH and CH_2 protons of both βCD and PEG units in the βCXCDs.
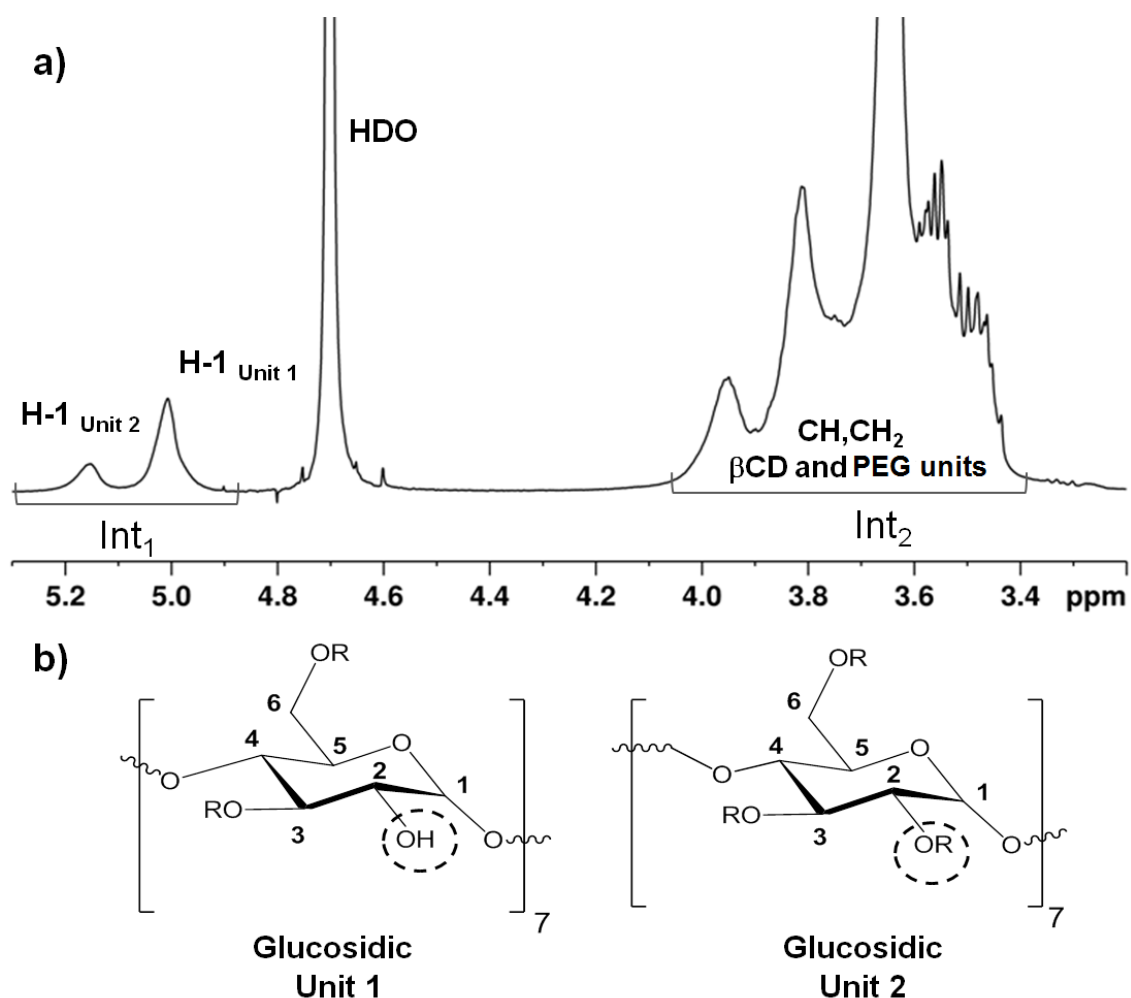
Figure 4.7 (a) The ^{1}H-NMR spectrum of IP13 (PEG:βCD ratio = 3.8:1) in D_2O and (b) the proposed chemical structure of βCXCDs highlighting the two different situations for the anomeric H-1, when in unit 1 or unit 2 of βCXCDs.

The broad signal centred at 5.00 ppm is assigned to the anomeric H-1 protons of the glucosidic unit 1 of βCD and represents the chemical environment of H-1

βCD when the protons of the OH-2 groups are not involved in the cross-linking. In contrast, when the protons of the OH-2 groups were substituted with PEG units (Figure 4.7, unit 2) the anomeric proton signal was shifted downfield at 5.18 ppm. The ratio between the two integrals in Figure 4.7 (Int_1 and Int_2) was used to determine the degree of cross-linking in βCXCDs (XEG:βCD molar ratio) [86]. Int_1 refers to the seven anomeric protons of βCD units, whereas Int_2 refers to all remaining protons in the βCXCD monomeric unit, specifically:

- 42 protons of βCD units
- Protons of the polyethylene glycol unit (X), namely
  - 22 protons when X = TEG
  - 34 when X = HEG
  - 44 when X = PEG

The following system of two equations was used

$$Int_1 = 7 \text{ H-1} \tag{1}$$

$$Int_2 = H\beta CD \text{ units} + nH_{PEG \text{ or } HEG \text{ or } TEG} \tag{2}$$

From the ^{1}H-NMR spectra, the calculated XEG:βCD ratios in the βCXCDs were 25% lower than the initial feed ratio of the reaction. Using sample IP13 as an example, the PEGDGE:βCD feed ratio was 5:1 but the PEG:βCD ratio in the product was 3.8:1 (Table 4.7) reflecting the degradation of the cross-linker as discussed in section 4.1.1. The PEG:βCD ratio was also confirmed by the integrals ratio of the H-1 signals in unit 2 and unit 1 (Figure 4.6b).

The calculation of the XEG:βCD ratio in the βCXCDs was also attempted by comparing Int_1 and Int_3, where Int_3 between 3.7 and 3.6 ppm is the integral of the four ethylene glycol CH$_2$ protons present in the XEG repeat units in βCXCD (Figure 4.8).

However, the cross-linking ratios obtained when comparing Int_1 and Int_3 were 5–10% higher in value in relation to the cited method (Equations 1 and 2) which uses Int_1 and Int_2 [86], reflecting the partial overlap of the βCD protons and the

methylene groups of the XEG chains. The values obtained via the cited method were therefore used for subsequent evaluations.
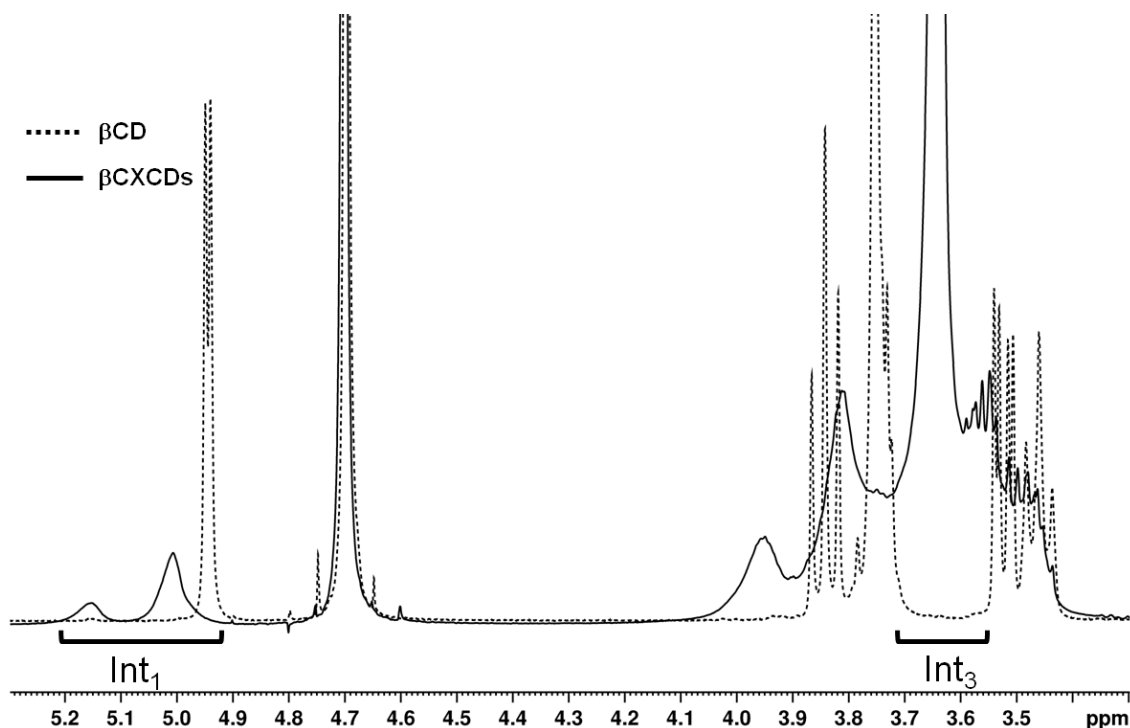
Figure 4.8 The ^{1}H-NMR spectrum of IP13 (PEG:βCD ratio = 3.8:1) in D$_2$O. Int$_1$ = anomeric H-1, Int$_3$ = CH$_2$ of PEG.

The NMR spectra of the three sets of βCXCDs prepared using PEGDGE were similar, as shown in Figure 4.9. However, the intensity of the signal between 5.2 and 4.9 ppm, attributed to unit 2 (the anomeric H next to cross-linking point), increased at higher PEG:βCD ratios. Three sharp signals attributed to the H-3 proton of βCD units appeared in the region between 3.6 and 3.4 ppm when the PEG:βCD ratio was lower than 2.6, due to the absence of the broad signals at high level of cross-linking (black arrows, Figure 4.9).
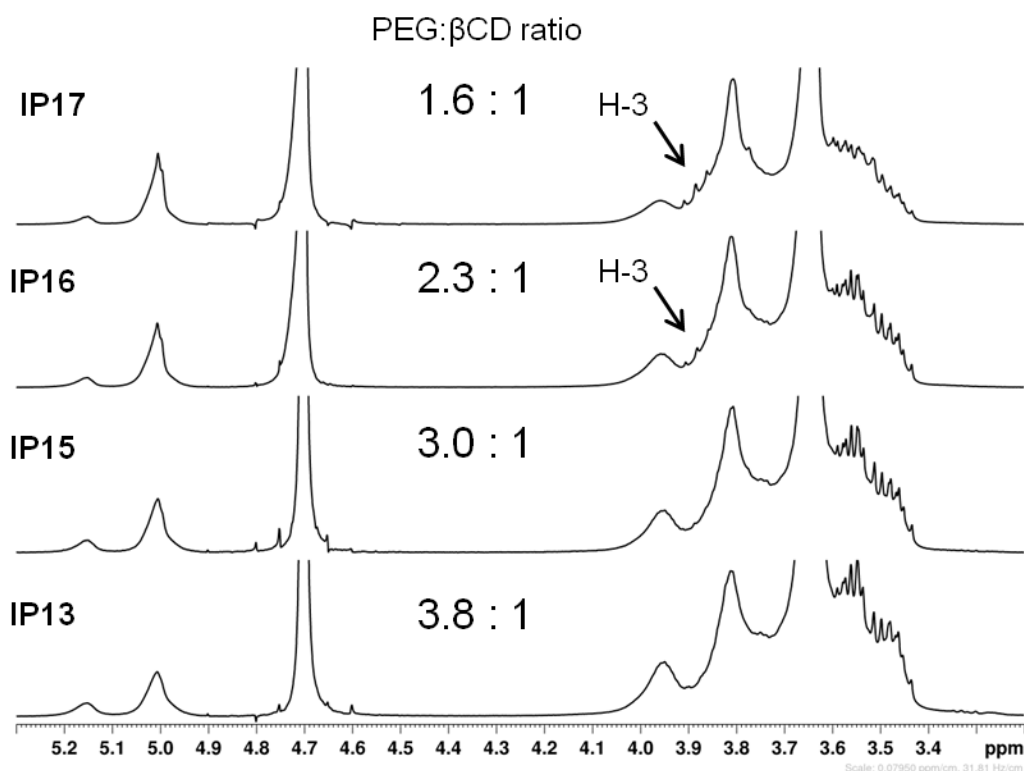
Figure 4.9 Comparative [^1]H-NMR spectra of βCPCD samples (IP13, IP15–IP17) with different PEG:βCD ratios. Lower ratios enhance the visibility of the βCD proton (marked with the arrow).

All βCXCDs were characterised by FTIR spectroscopy and the spectrum of a representative sample (IP13) was compared to those of the precursors βCD and PEGDGE (Figure 4.10). The strong absorption at 1077 and 1023 cm[^-1] (Figure 4.10, red curve) was attributed to the stretching of C-O-C cross-linking bonds in βCXCDs. The absorption intensity at 2940 cm[^-1] (symmetric stretching of CH_2 and CH), 2871 cm[^-1] (asymmetric stretching of CH_2 and CH), 1453 cm[^-1] (scissoring of CH_2) and 1349 cm[^-1] (bending of CH) in the βCXCDs was higher than in the βCD precursor, confirming the presence of the cross-links. The signals in all the spectra at 1642 cm[^-1] represented the secondary vibration of adsorbed water [73].
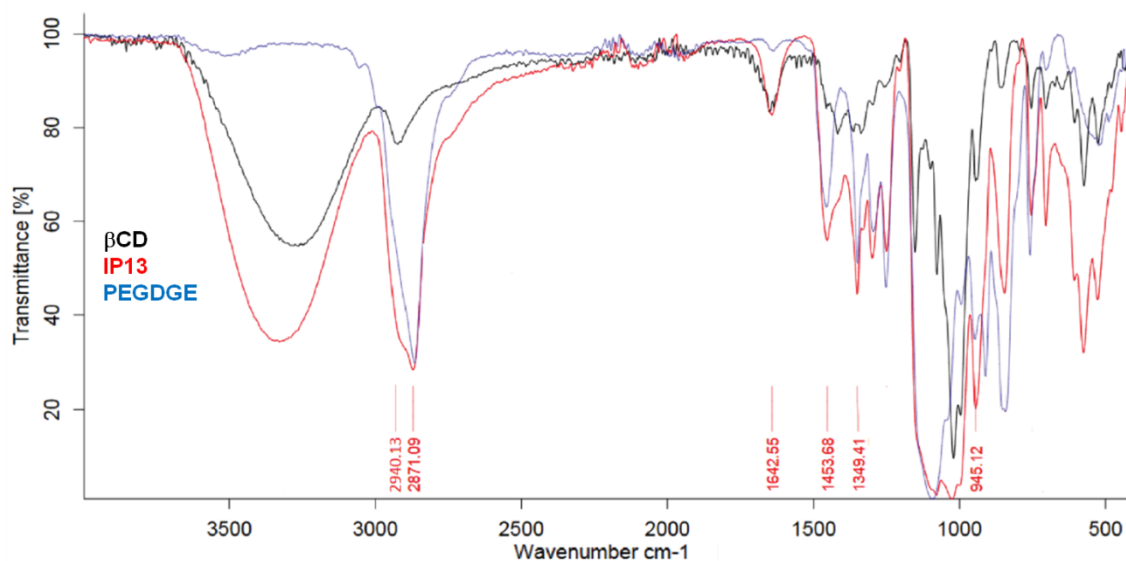
Figure 4.10 Comparative FTIR spectra of βCD (black curve), βCPCD sample IP13 (red curve), and PEGDGE (blue curve).

The Mw of water-soluble βCXCDs containing TEG, HEG or PEG units were determined by GPC. The samples were dissolved in aqueous 0.1 M $LiNO_3$ containing 0.05% w/w NaN_3, with polyethylene glycol/polyethylene oxide standards for nine-point calibration in the range 106 Da to 1 MDa. Therefore, all Mw values reported are standards equivalents. These standards were the nearest available to the chemical composition of the βCXCDs.

GPC analysis of the precursors βCD and PEGDGE was carried out under the same experimental conditions. The βCD chromatogram showed a peak at retention time 13.7 min (M_w=1134.98 g mol^{-1}, 200 Da standards equivalents) that fell outside the calibration curve of the standards (Figure 4.11). As expected, the standards eluted at different times compared to pure βCD. Their equivalents cannot be used to assess the Mw of the oligomers, but provide a useful qualitative estimate.
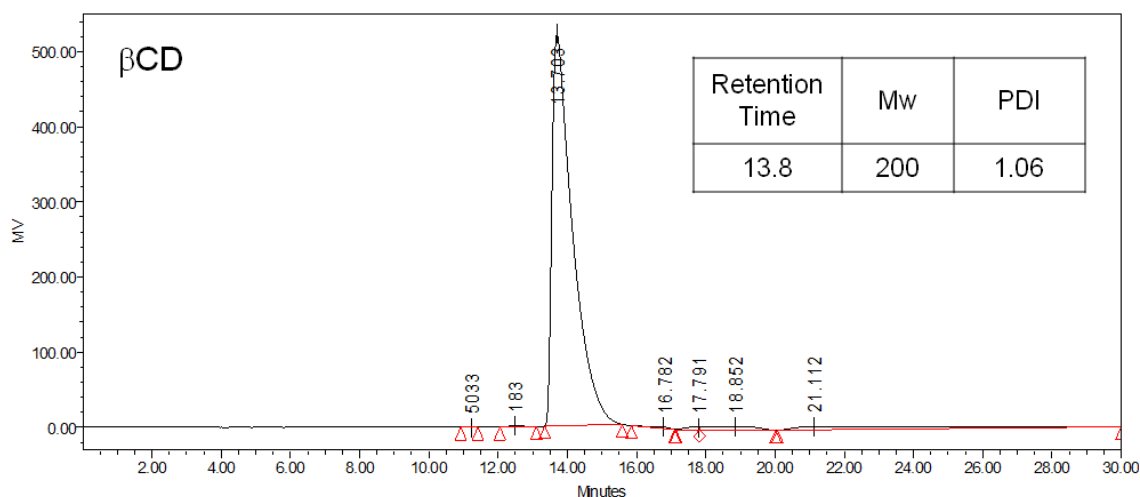
Figure 4.11 GPC analysis of βCD compared to polyethylene glycol/polyethylene oxide standards.

The chromatogram of PEGDGE (Figure 4.12) revealed the polydispersity of the compound as stated by the manufacturer (Sigma-Aldrich, average Mw=500). Two major fractions were detected, with retention times of 12.7 and 13.5 min, respectively (equivalent = 200 Da for the first fraction, with the other outside the calibration range). The TEGDGE and HEGDGE cross-linkers were not analysed by GPC because ^{1}H-NMR analysis confirmed their monodisperse nature (Mw = 262 and 394 Da, respectively; Figure A 2 and Figure A 3).
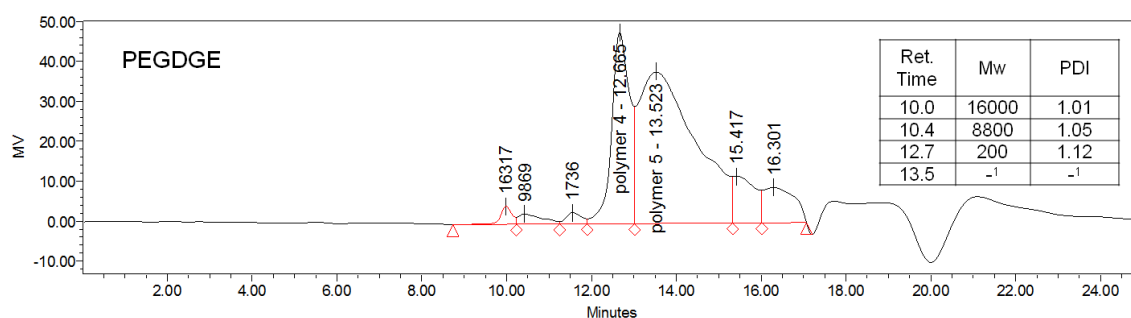
Figure 4.12 GPC analysis of PEGDGE compared to polyethylene glycol/polyethylene oxidestandards.

The βCXCD samples analysed by GPC (IT2I, IH2 and IP22) were synthesised using TEGDGE, HEGDE and PEGDGE, respectively. Their chromatograms (Figure 4.13) were composed of two major elusion peaks between 12 and 16 min. Sample IH2 presented a broader distribution of higher Mw, represented by

the onset of elution at 7.5 min corresponding to fractions with higher Mw (Figure 4.13b). The Mw of all βCXCDs, calculated using the elution times of the standards equivalents, were lower than expected. Again this reflected the different elution behaviour of the βCXCDs compared to the standards, due to the presence of βCD with a different hydrodynamic volume [125]. The peak at 13.7–14 min suggested the sample was contaminated with βCD and/or dimers that were not eliminated during the purification process.

GPC analysis of the βCXCDs confirmed that products with higher XEG:βCD ratios (3.6:1) eluted at lower retention times, corresponding to their higher Mw. Figure 4.14 shows the chromatograms of βCTCDs containing a decreasing ratio of TEG units.
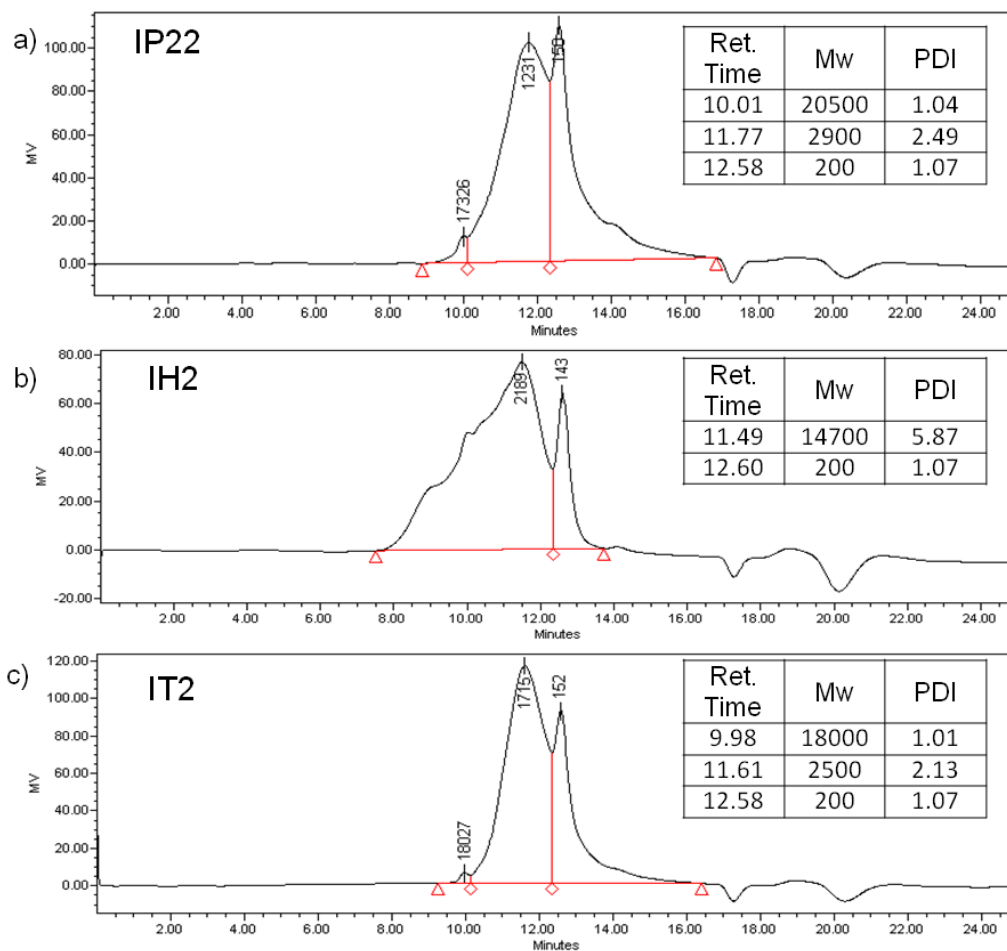
Figure 4.13 Analysis of βCXCDs by GPC compared to polyethylene glycol/polyethylene oxide standards. (a) Sample IP22 (PEG:βCD ratio = 2.9). (b) Sample IH2 (HEG:βCD ratio = 3.2). (c) Sample IT2 (TEG:βCD ratio = 3.1).
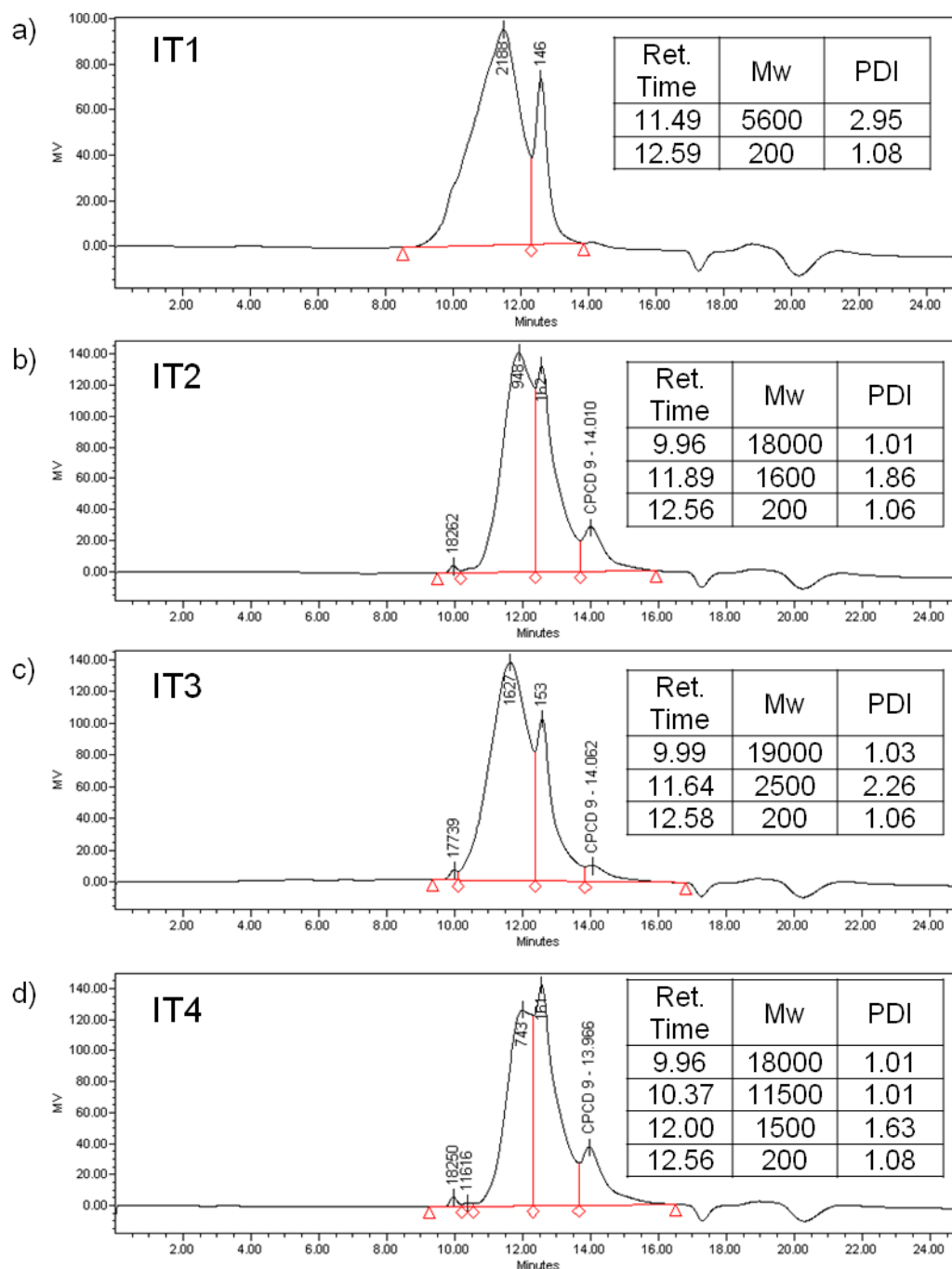
Figure 4.14 Analysis of βCTCDs by GPC compared to polyethylene glycol/polyethylene oxide standards. (a) Sample IT1 (TEG:βCD ratio = 3.6). (b) Sample IT2 (TEG:βCD ratio = 3.1). (c) Sample IT3 (TEG:βCD ratio = 2.4). (d) Sample IT4 (TEG:βCD ratio = 1.9).

4.3 Thermal and thermo-mechanical characterisation of βCXCDs

The thermo-mechanical characterisation of some of the βCPCDs synthesised using the PEGDGE cross-linker has been published as a peer-reviewed article: Luppi F, Kister G, Carpenter M, Dossi E (2019) Thermomechanical characterisation of cross-linked β-cyclodextrin polyether binders. *Polym Test* 73, 338–345 (see Appendix).

The thermo-mechanical properties of the βCXCDs were investigated to determine their suitability as binders for energetic formulations. Their thermal properties, specifically the decomposition temperature (T_{dec}), the enthalpy of decomposition and the glass transition temperature (T_g) were determined by DSC and DMA.

DSC was carried out using two temperature regimes: a low temperature range (–100 to 100 °C) to determine T_g and a high-temperature range (25–500 °C) to determine the T_{dec}. DMA was carried out solely in the low-temperature range.

The first task was the characterisation of the starting materials (βCD and the cross-linkers TEGDGE, HEGDGE, PEGDGE). The low-temperature heat flow changes were initially examined from –100 to 100 °C, but the upper temperature was later extended to 140 °C to detect thermal events attributed to βCD. The thermo-mechanical properties of βCD/ethylene glycol hydrogel systems have been investigated before, revealing their viscoelastic properties [86,87,92]. The βCXCDs were characterised to determine whether their viscoelasticity was sufficient to reduce their sensitivity to shocks and hence their vulnerability when used as binders.

In this chapter, the published data are combined with data for the βCTCDs and βCHCDs. This chapter also discusses the self-healing properties of the βCXCDs.

4.3.1 Thermo-mechanical characterisation of the starting materials

4.3.1.1 Thermal characterisation of βCD

The degradation of βCD under N_2 gas was observed in the temperature range 30–500 °C by the combined use of DSC and DSC + TGA techniques. The βCD thermogram is shown in Figure 4.15.
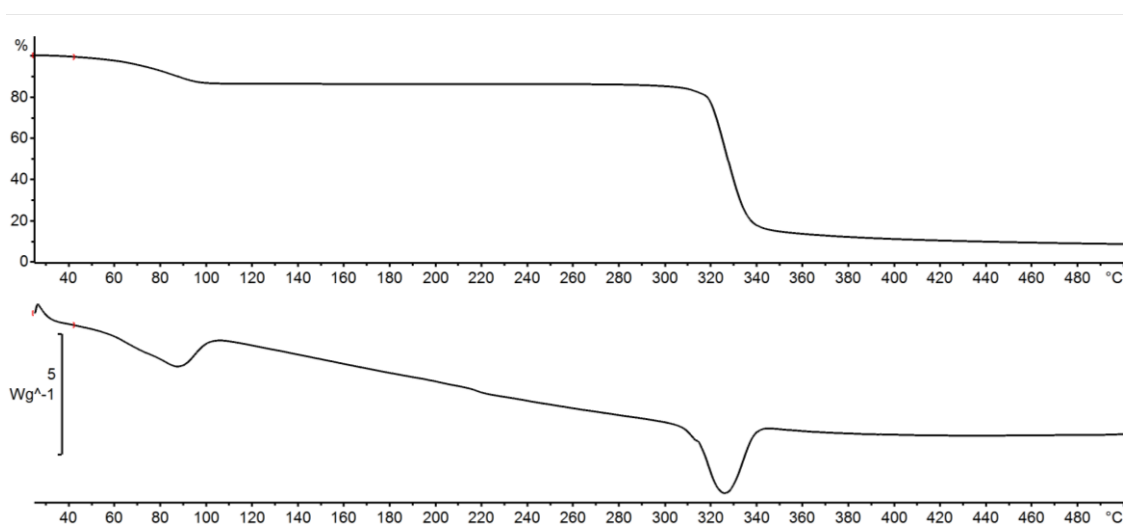
Figure 4.15 Combined TGA and DSC analysis of βCD (10 °C min^{-1}, 25–500 °C, aluminium crucible).

An endothermic event occurring before the temperature reached 110 °C was attributed to the presence of water in the βCD stock sample, confirming the precursor is hygroscopic. The mass loss percentage of 13.6% was similar to that reported in the literature [38,126]. This value varied by several percentage points depending on the moisture adsorbed daily by the βCD (13.1–13.7%). The major event indicated by DSC was an endothermic peak at 328 °C, which represented the degradation of βCD (Figure 4.15). Additional melting point analysis revealed that βCD degradation passes through a caramelisation phase, where the white βCD powder quickly undergoes three sequential stages of browning, melting and charring (Figure 4.16).
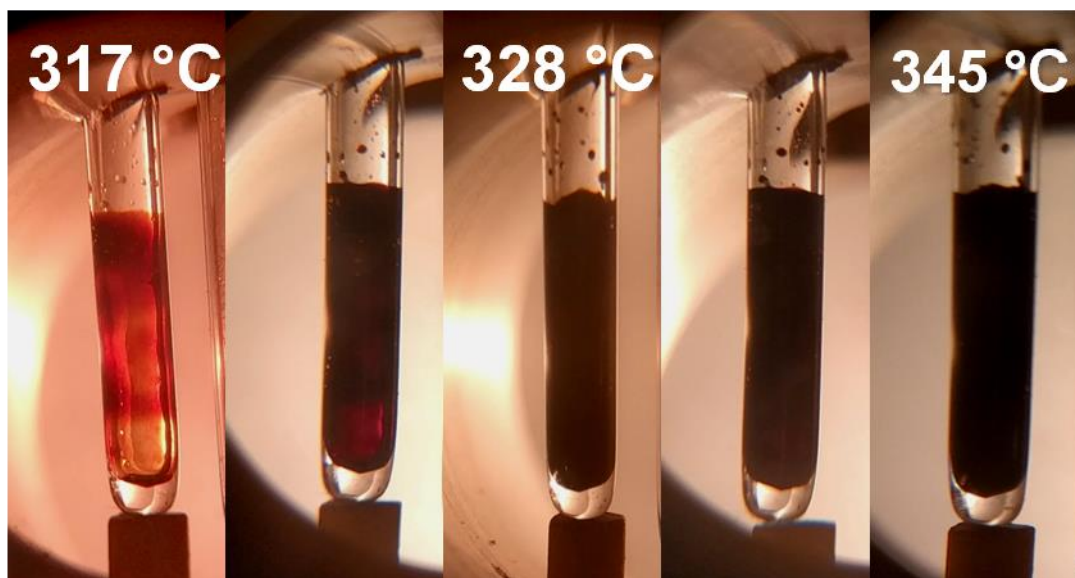
Figure 4.16 The decomposition of βCD observed by melting point analysis. At 317 °C, melting and caramelisation are dominant, but above 328 °C charring prevails.

The low-temperature scan to determine the T_g was initially cycled three times from –100 to 100 °C to eliminate effects caused by the presence of water in the thermogram (Figure 4.17). A second-order phase transition at 85 °C persisted during these temperature cycles. Earlier reports attributed this phenomenon to the dissolution of βCD crystals in water already present in the sample [45]. Molecular dynamics simulations predicted a T_g of 61 °C for βCD [127] whereas others determined an empirical T_g of 216 °C [128].

The temperature extreme was gradually increased by 10 °C up to a maximum of 140 °C (Figure 4.17). The phase transition stabilised at ~100 °C in all subsequent runs. The shifting of the transition to higher temperatures reflected the evaporation of water molecules within the βCD cavity, which requires more energy. This experiment suggested that the transition is not due to the dissolution of βCD in water, as previously suggested [45]. The second-order transition at 61 °C may represent the T_g of βCD predicted by modelling [127].
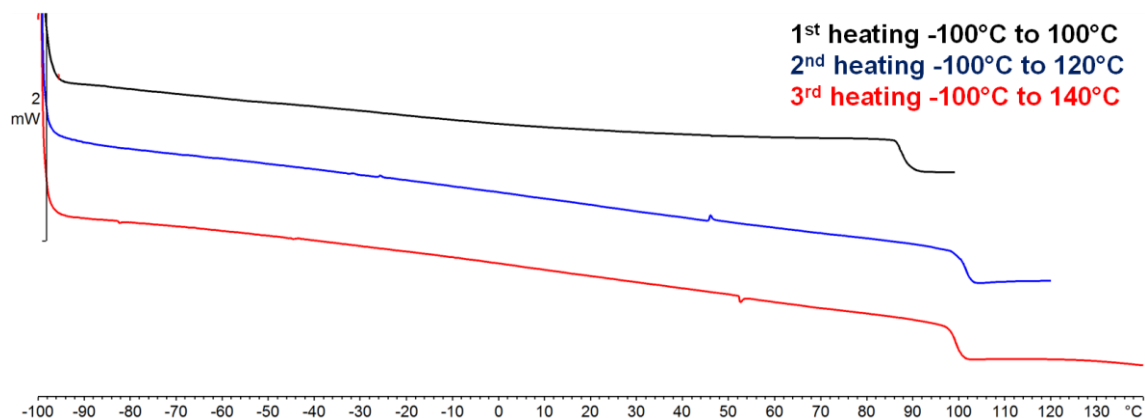
Figure 4.17 DSC heating curves of βCD (10 °C min^{-1}) from −100 to 100 °C in the first cycle (black), from −100 to 120 °C in the second cycle (blue), and from −100 to 140 °C in the third cycle (red).

4.3.1.2 Thermo-mechanical characterisation of βCD

DMA was used to determine the storage modulus (E′) and damping factor (tanδ) of βCD over three heating/cooling cycles. One difference between DSC and DMA is the higher temperature at which transition occurs due to the effect of the sinusoidal stress frequency during mechanical analysis [129]. The temperature range was then set from −100 to 140 °C at 10 °C min^{-1} in order to investigate the second-order transition due to the presence of βCD in the cross-linked compounds. There were no significant differences between the second and third thermal cycles. The last thermal cycle is shown in Figure 4.18.
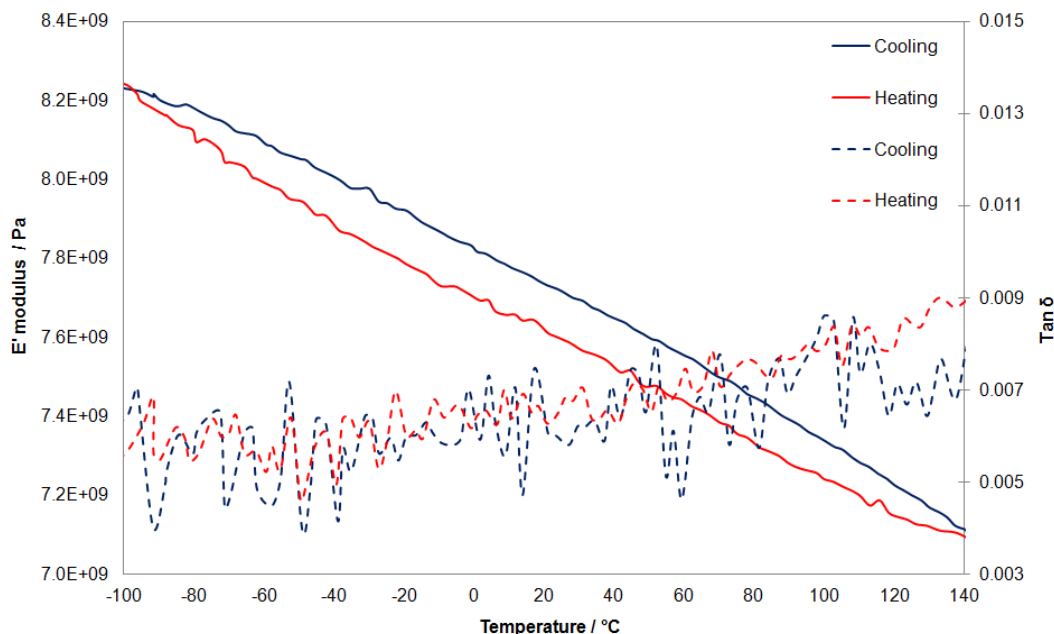
Figure 4.18 DMA showing variation in the storage modulus (E′, solid lines) and tanδ (dashed lines) of βCD (10 °C min^{-1}, 1 Hz, third temperature cycle, −100 to 140 °C, aluminium pocket).

The E′ values of the pure βCD sample were inversely related to the temperature, whereas the tanδ values remained relatively constant during each temperature cycle, showing there was no phase transition. This is consistent with earlier experiments that defined βCD as a crystalline compound [14]. A minor hysteresis was observed between cooling and heating. The lower E′ value during heating reflects the higher degree of relaxation in the material at high temperatures. Therefore, the higher E′ value during cooling is due to the stress generated by the high cooling rate.

The variation in E′ and tanδ was also investigated as a function of the oscillation frequency. The increase in frequency during the temperature cycle had no significant influence on either value. The corresponding thermogram is shown in Figure A 4.

4.3.1.3 Thermal characterisation of TEGDGE, HEGDGE, and PEGDGE

The cross-linkers were also characterised by DSC, and their degradation profiles (30–500 °C) and low-range temperature profiles (–100 to 140 °C) are compared below.
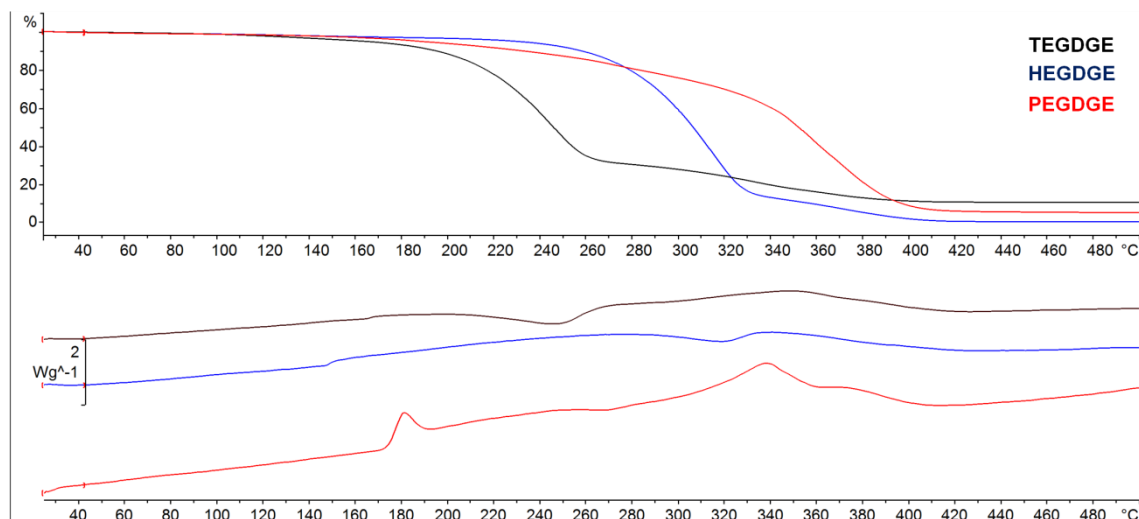
Figure 4.19 Combined DSC/TGA thermograms of the cross-linkers TEGDGE (black), HEGDGE (blue) and PEGDGE (red), from 30 to 500 °C (10 °C min^{-1}, third temperature cycle, aluminium crucible).

Heating the cross-linkers highlighted a continuous loss of substrate mass starting at 160 °C. Part of the mass of the cross-linkers was lost even before the onset of degradation (Table 4.8). The decomposition of TEGDGE was more endothermic than its longer analogues, but the degradation events cannot be analysed in detail using the available thermogram data. The TGA results (Table 4.8 and Figure 4.19) indicate that longer cross-linkers are more thermally stable, which reflects the degradation of PEGDGE at 312 °C compared to the shorter TEGDGE at 214 °C. The thermal stability of the longer chain can be attributed to the scission mechanism of the chain extremities that occurs before its complete decomposition. The PEGDGE cross-linker showed a mass loss of 27% before the main degradation event at 312 °C, which was greater than the 18–19% observed for the other cross-linkers. This can be attributed to the degradation of the shorter chains present in the blend, which degraded earlier

than the predominant long-chain fraction resulting in a higher initial loss compared to the two monodisperse cross-linkers (Table 4.8).

Table 4.8 Combined DSC/TGA data for the cross-linkers.

Cross-linker	Number of ethylene glycol units	Mw (g mol^{-1})	Mass loss before onset of degradation (% w/w)	Onset of degradation (°C)
TEGDGE	3	262	18	214
HEGDGE	6	394	19	278
PEGDGE	9	500	27	312

The T_g was initially characterised by three temperature cycles from −100 to 100 °C. Subsequently, the range was extended to 120 °C to completely remove any water in the samples. The increase in temperature did not change the T_g of the cross-linkers (Figure 4.20). There were no significant differences among the three runs and the third heating cycle of −100 to 120 °C is shown as an example in Figure 4.20.
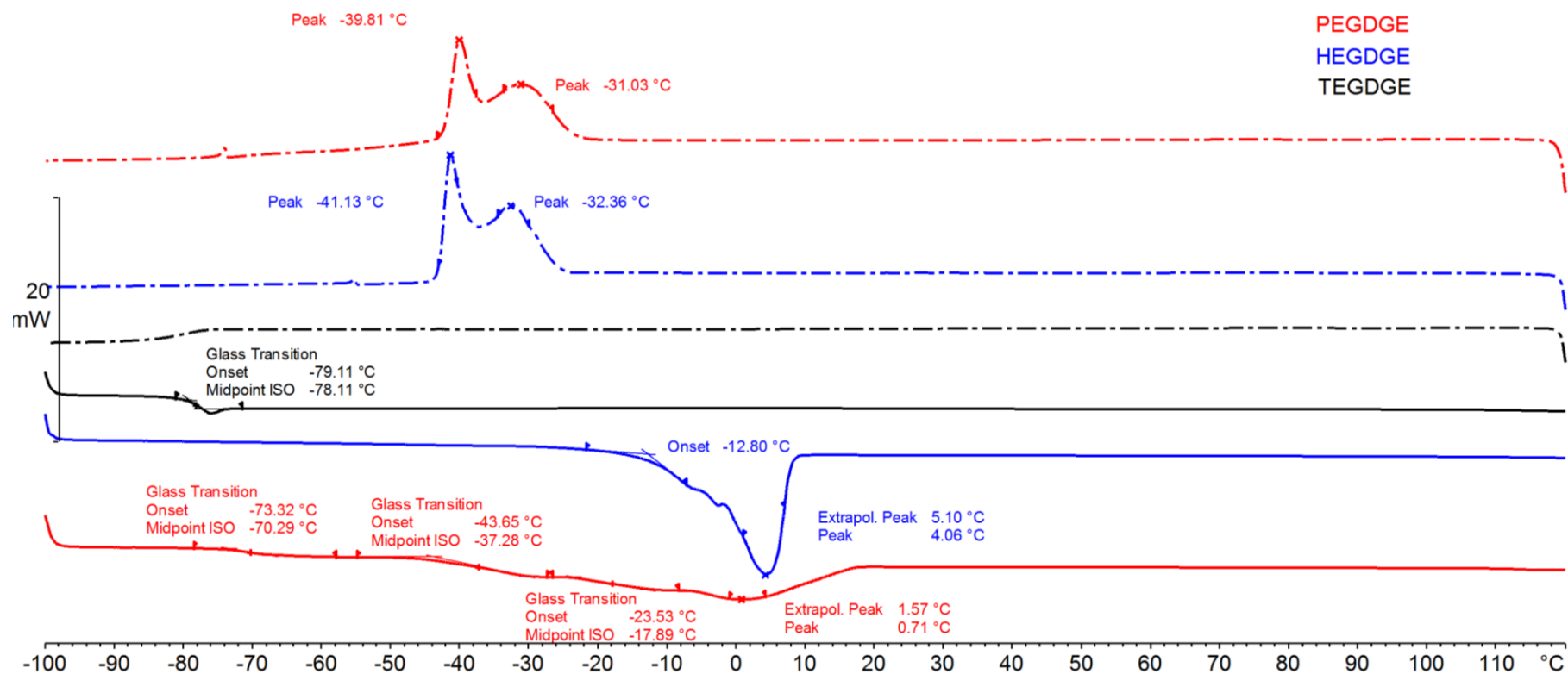
Figure 4.20 DSC thermogram of the cross-linkers: heating (solid) and cooling (dashed) of TEGDGE (black), HEGDGE (blue) and

PEGDGE (red) from –100 to 120 °C (10 °C min^{-1}, third temperature cycle, aluminium crucible).

DSC analysis indicated the presence of a single, well-defined T_g for TEGDGE at −78°C due to the monodisperse and pure nature of the sample. For HEGDGE, the thermogram highlighted the presence of a first-order transition attributed to chain melting as well as the glass transition beginning at −13 °C and peaking at 4 °C. Indeed, the baseline of the thermogram changes when the thermal event concludes. The cooling curve for HEGDGE also reflected the sum of the two transitions, with two crystallisation peaks centred at −41 °C and a lower baseline after the thermal transition.

During heating (−100 to 120 °C), the heat flow adsorption of PEGDGE increased between −70 and 10 °C in a multi-step transition that represented the polydispersity of the sample as described by the manufacturer, the combination of longer polymer chains melting (centred at 1 °C) and the increased mobility of the shorter and middle-length chains after the glass transitions at −70, −18°C and −37 °C, respectively. The multiple changes in the baseline from −71 °C reflected a series of glass transitions involving different middle-length and shorter polymer chains that can also act as plasticisers for the longer chains, as reported for polyethylene glycol based polymers [130].

During cooling, the longer chains of HEGDGE and PEGDGE crystallised within the temperature range from −23 to −50 °C, whereas the T_g of TEGDGE is reiterated at −80°C. The cooling curves support the hypothesis that exotherms during the crystallisation of HEGDGE and PEGDGE mask a vitrification event that would explain the change in the baseline of the heat flow.

4.3.1.4 Thermo-mechanical characterisation of TEGDGE, HEGDGE, PEGDGE

DMA was also used to determine the thermo-mechanical properties of the cross-linkers, with three heating/cooling cycles from −100 to 100 °C at 10 °C min^{-1}. When PEGDGE was analysed, there were no significant differences among the thermal cycles so only the third cycle is shown in Figure 4.21. The E′ value fell during heating, with two main transitions at −70 and −22 °C corresponding to the glass transitions of the PEGDGE sample. The broad and laddered decline in E′ reflects the specific properties of this commercial product,

a blend of PEG chains with an average molecular weight of 500 Da and a polydispersity index of 1.7.
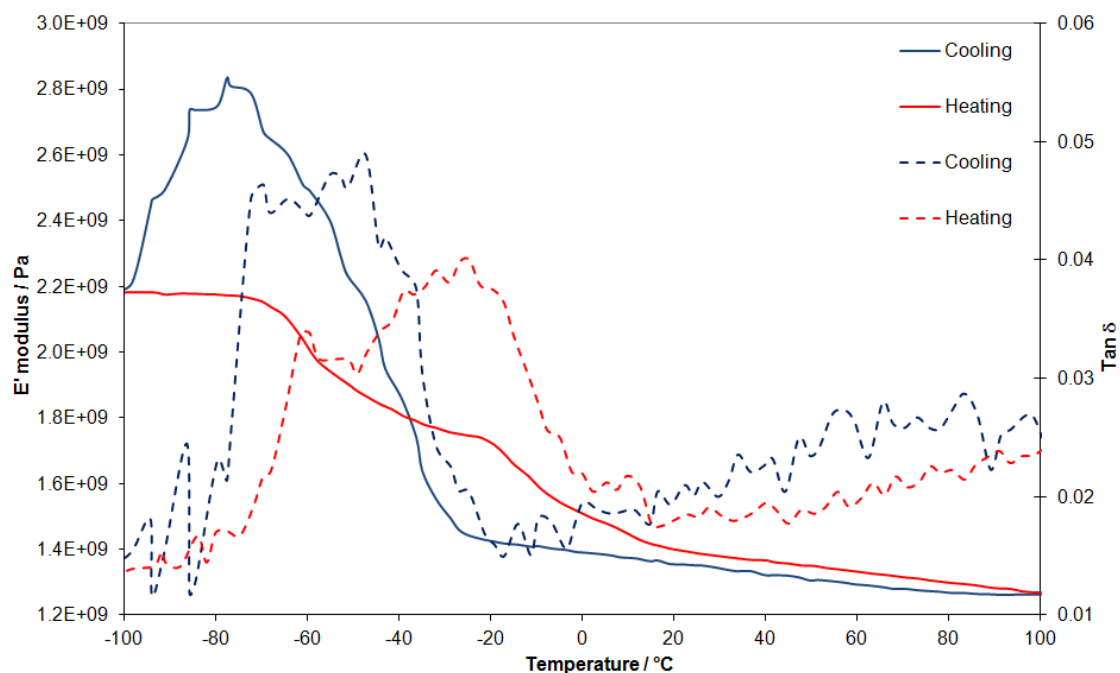
Figure 4.21 DMA showing variation in the storage modulus (E′, solid lines) and tanδ (dashed lines) of PEGDGE (10 °C min^{-1}, 1 Hz, third temperature cycle from –100 to 100 °C, aluminium pocket).

Previous studies have shown that the T_g of PEGDGE is inversely related to its polydispersity because the shortest polymer chains act as plasticisers, reducing the brittleness and tensile strength while increasing the overall impact strength of the material [46,47]. During cooling, PEGDGE underwent a single glass transition event, increasing its stiffness. However, the rapid increase in E′ from about –30 °C was followed by a sudden drop at about –75 °C, the latter corresponding to 28% of the maximum E′ value. This phenomenon also occurred in tests conducted at the lower heating/cooling rate of 2 °C min^{-1}. DMA was used to test the aluminium support in order to eliminate artefacts caused by the machine and/or support matrix (Figure A 5). The E′ value of the support showed linear variation within the experimental temperature range, suggesting that the observed phenomenon is caused by the viscoelastic behaviour of the PEGDGE and its strong interaction with the supporting pocket. Hydroxyl, epoxy and carboxyl groups in polymers allow the formation of

hydrogen bonds with metal and glass [48]. The strong adhesive interactions and the change in the stiffness of the PEGDGE sample during the glass transition promote internal stress which is suddenly released, initiating cracking and de-bonding of the sample from the support, recorded as a sudden drop in the E′ value. The physical damage (such as cracking) that emerged during the cooling cycle provided an interesting initial assessment of the adhesive strength between the sample and different support matrices. The same thermal profile during the second and third cycles confirmed that PEGDGE recovers its initial mechanical properties when heated above the T_g in each cycle, and the process is therefore reversible.

The effect of the oscillation frequency on the mechanical properties of PEGDGE was tested at 1, 5 and 10 Hz. The E′ curves at 1 and 10 Hz are shown in Figure 4.22. The cooling and heating curves at both frequencies diverge at the point of glass transition. During heating, the glass transition of the compound is complete at ~25 °C as confirmed by the small decrease in E′ and the overlapping of the curves at different frequencies. The T_g is directly proportional to the frequency during both heating and cooling, and thus increases at higher frequencies [49,50]. The drop in E′ value caused by cracking is also influenced by the oscillation frequency: the E′ peak at 1 Hz occurs at –78 °C whereas the 10 Hz peak occurs at –70 °C.
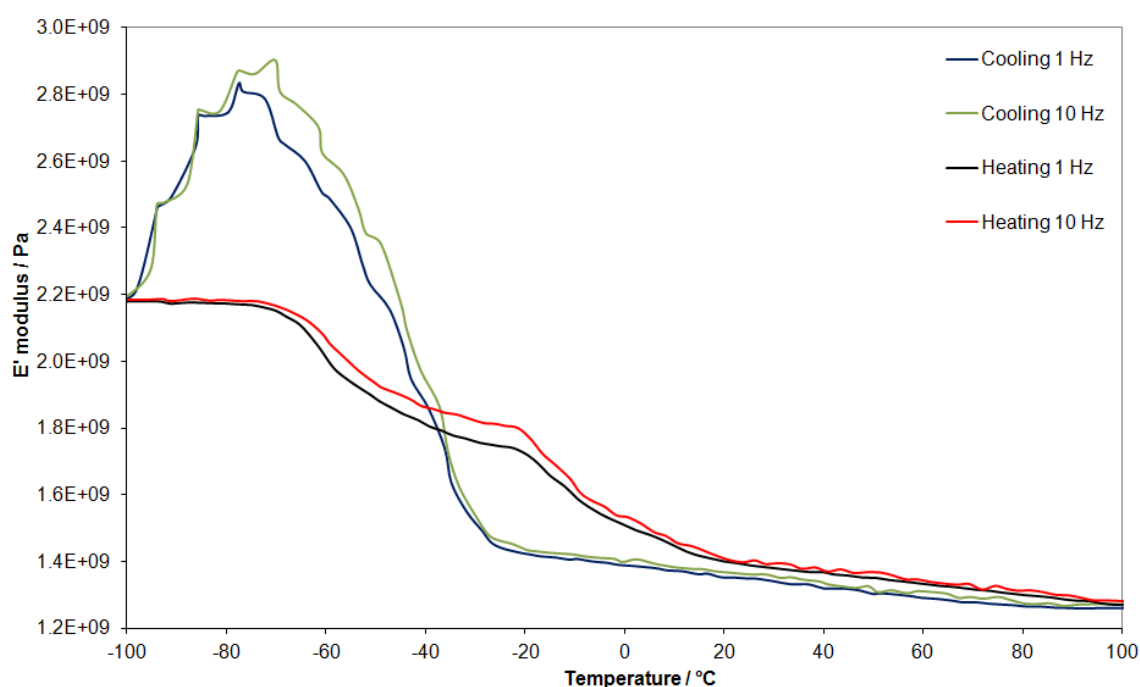
Figure 4.22 DMA showing variation in the storage modulus (E′) of PEGDGE with frequency (10 °C min^{-1}, 1 and 10 Hz, third temperature cycle from –100 to 100 °C, aluminium pocket).

DMA revealed that HEGDGE behaved similarly to PEGDGE (Figure 4.22). During cooling, HEGDGE underwent significant stiffening and the E′ and tanδ values increased below –20 °C. The E′ values dropped when HEGDGE passed the vitrification point, and it cracked due to adhesion with the support. When HEGDGE was heated, the rigidity decreased above –78 °C in a two-step transition that concluded at 20 °C. The tanδ value gradually increased when the sample was heated, reaching its maximum at 1 °C. The cross-linker undergoes a broad transition representing the sum of its glass transition and melting as observed by DSC (Figure 4.20). In addition, the drastic fall in tanδ at 1 °C revealed the point at which the compound becomes a liquid.

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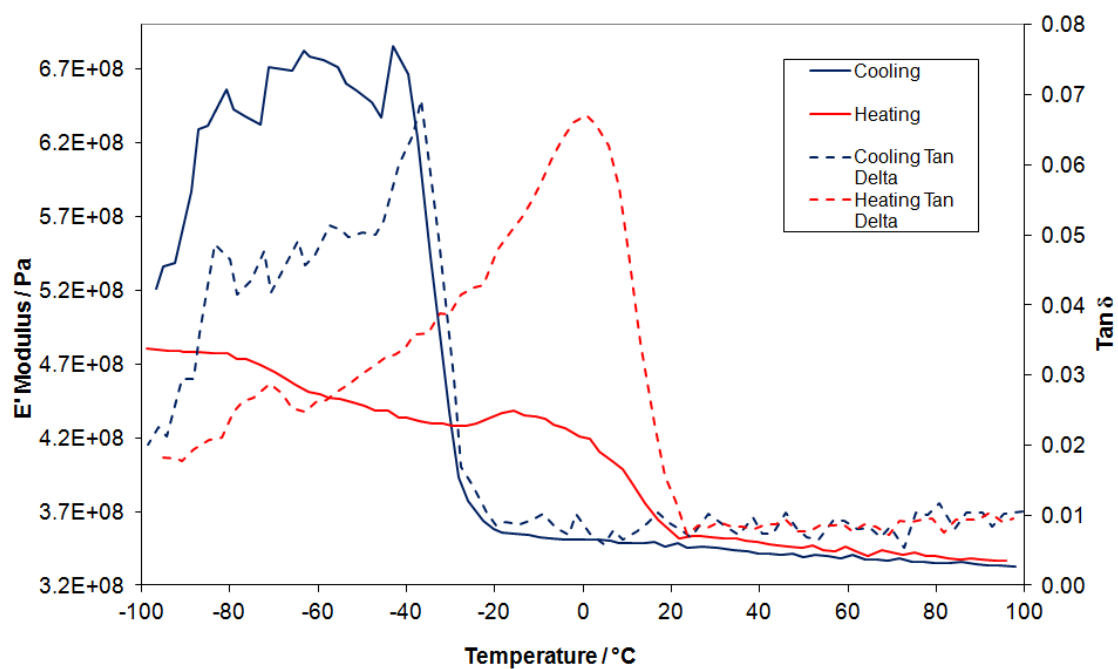
Figure 4.23 DMA showing variation in the storage modulus (E′, solid lines) and tanδ (dashed lines) of HEGDGE (10 °C min^{-1}, 1 Hz, third temperature cycle from −100 to 100 °C, aluminium pocket).

The transition was also affected by the frequency of oscillation: a higher frequency increased the E′ value by 2% up to 20°C (Figure 4.24).
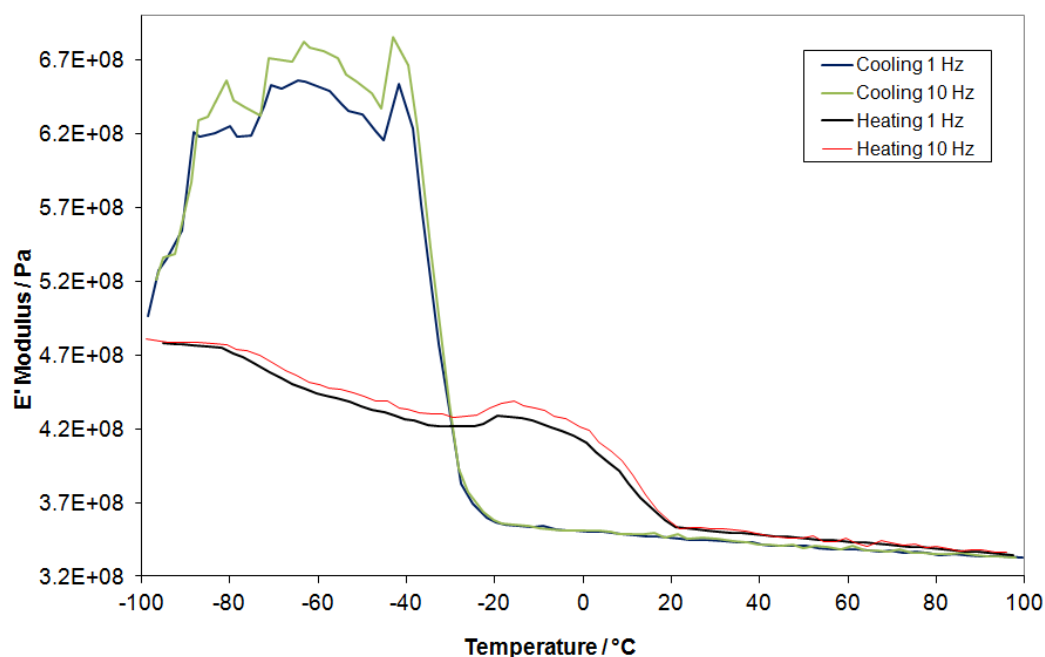
Figure 4.24 DMA showing variation in the storage modulus (E′, solid lines) of HEGDGE with the frequency (10 °C min^{-1}, 1 and 10 Hz, third temperature cycle from −100 to 100 °C, aluminium pocket).

The DMA data for TEGDGE (Figure 4.25) was compared with the DSC results (Figure 4.15). The T_g of the cross-linker was indicated by the tanδ peak at −71 °C and the transition was neat compared to the other cross-linkers, due to its monodispersity and the absence of crystallisation in this short-chained polymer.
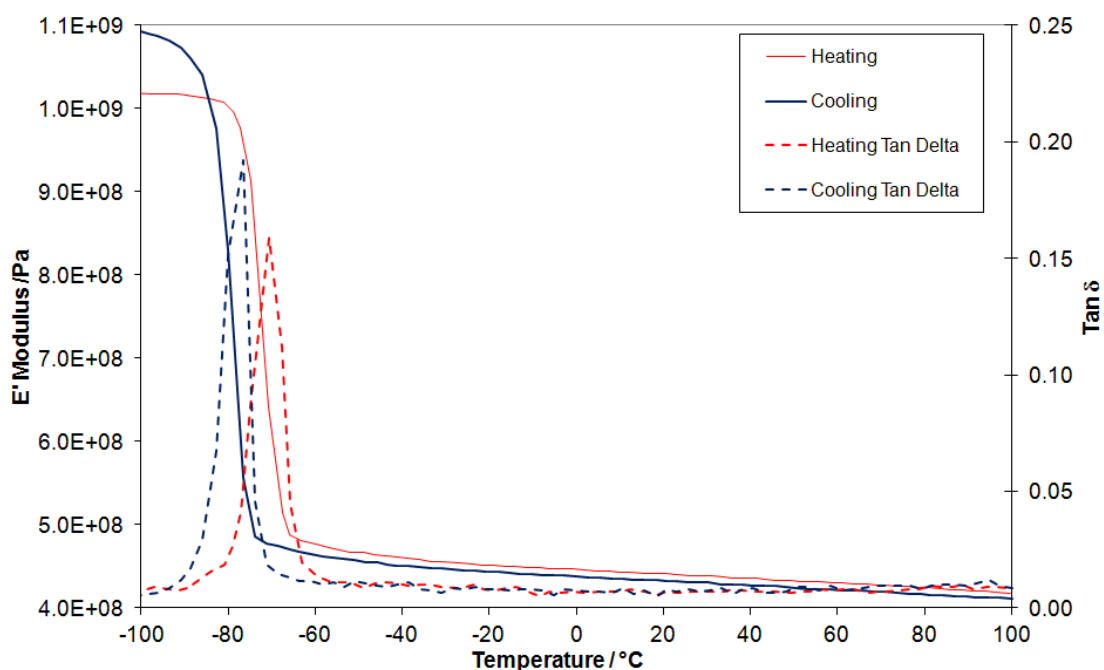
Figure 4.25 DMA showing variation in the storage modulus (E′, solid lines) and tanδ (dashed lines) of TEGDGE (10 °C min^{-1}, 1 Hz, third temperature cycle from −100 to 100 °C, aluminium pocket).

The T_g was found to be dependent on the frequency, as was the case for the other cross-linkers. Due to the extreme vicinity of the T_g to the lowest extreme, the temperature range was extended to the lower temperature of −140 °C to determine whether cracking occurred. Accordingly, TEGDGE began to crack at −100 °C (Figure 4.26).
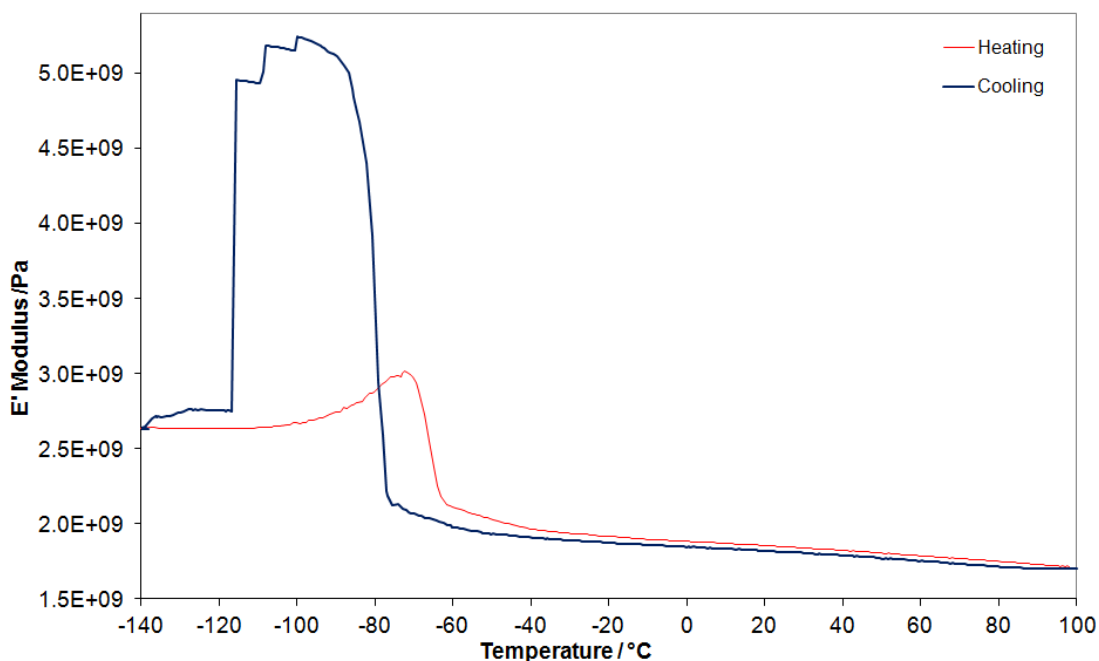
Figure 4.26 DMA showing variation in the storage modulus (E′, solid lines) and tanδ (dashed lines) of TEGDGE in an extended temperature scan (10 °C min^{-1}, 1 Hz, third temperature cycle from –140 to 100 °C, aluminium pocket).

4.3.2 Thermal and thermo-mechanical characterisation of inert βCXCDs

Thermal analysis using DSC, TGA and DMA as described above was also used to characterise the βCXCDs, to determine how the cross-linking conditions influenced the thermo-mechanical properties of each βCXCD system.

4.3.2.1 Thermal characterisation of inert βCXCDs

The thermal degradation of all βCXCDs revealed similar thermal properties. Table 4.9 summarises the T_{dec}, T_g and mass loss data. The cross-linking reaction increased the T_{dec} of βCXCDs compared to the single cross-linkers, reflecting the presence of βCD in the compounds, thus increasing the temperature at which thermolysis affected their stability. The effect was stronger in the βCTCD products (containing TEG units) due to their higher βCD content. The T_{dec} of the βCXCD products was linearly dependent on the length of the

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cross-linker, as seen for the single cross-linkers (Section 4.3.1.3). Accordingly, the βCHCDs (containing HEG units) were associated with higher T_{dec} values than the βCTCDs (containing TEG units). However, the βCPCDs (containing PEG units) did not follow this trend, with T_{dec} values lower than the βCTCDs. This reflects the presence of short chains in the polydisperse PEGDGE reagent and subsequently in the cross-linked products, which set up decomposition hotspots in the blend earlier than expected for a pure compound. A pure compound with longer chains would have a higher T_{dec} than HEGDGE.

Replicate samples produced using the same reaction conditions differed slightly in terms of their mean cross-linker ratio due to the uncontrolled nature of the reaction and the uncontrolled selection of hydroxyl groups that react with the cross-linkers. However, products with the same feed ratio showed similar thermal profiles (Table 4.9).

The glass transition event attributed to βCD was difficult to assess in the βCXCDs. The T_g was inconsistent in the replicates and was only visible in βCTCDs, and in the βCPCDs and βCHCDs with cross-link ratios of 3.8:1 or 1.8:1. This trend suggests that the transition is registered by DSC only when the amount of βCD exceeds 51 % w/w. The mass lost during decomposition did not differ significantly among the βCXCDs indicating similar thermodynamic decomposition behaviours.

Table 4.9 Summary of the thermal properties of the βCXCDs.

Sample	Cross-linker	Cross-linker:βCD feed ratio	XEG:βCD ratio by ^{1}H NMR	T_{dec} onset (°C)[1]	T_{dec} peak (°C)[1]	T_g midpoint (°C)	T_g βCD midpoint (°C)	Mass loss decomposition (%)
βCD	-	-	-	318	328	-	101	-
TEGDGE	-	-	-	203[1]	-	-79	-	-
HEGDGE	-	-	-	273[1]	-	-13[2]	-	-
PEGDGE	-	-	-	339[1]	-	-71[3]	-	-
IT1	TEGDGE	5 :1	3.6 :1	252	287	-	99	84
IT2		4 :1	3.1 :1	257	277	-	95	80
IT3		3 :1	2.4 :1	268	289	-	94	83
IT4		2 :1	1.9 :1	259	277	-	94	82
IH1	HEGDGE	5 :1	4.0 :1	278	308	-10	-	87
IH2		4 :1	3.2 :1	279	303	-6	-	84
IH3		3 :1	2.6 :1	276	307	-	-	80
IH4		2 :1	1.8 :1	274	301	-	101	74
IP18		5 :1	4.1 :1	248	257	-20	-	87
IP19		5 :1	4.0 :1	247	256	-18	-	88
IP13		5 :1	3.8 :1	252	261	-19	110	-

Sample	Cross-linker	Cross-linker:βCD feed ratio	XEG:βCD ratio by ^{1}H NMR	T_{dec} onset (°C)[1]	T_{dec} peak (°C)[1]	T_g midpoint (°C)	T_g βCD midpoint (°C)	Mass loss decomposition (%)
IP20	PEGDGE	5 :1	3.7 :1	250	256	-19	-	84
IP21		5 :1	3.6 :1	247	256	-13	104	84
IP9		5 :1	3.5 :1	237	254	-14	106	81
IP14		4 :1	3.2 :1	242	252	-8	96	81
IP15		4 :1	3.0 :1	236	250	-7	90	-
IP22		4 :1	2.9 :1	239	250	-3	90	80
IP23		4 :1	2.6 :1	239	246	-6	108	88
IP24		3 :1	2.5 :1	228	248	+5	106	82
IP25		3 :1	2.1 :1	226	243	-	102	84
IP17		2 :1	1.6 :1	221	233	-	90	75

1 DSC onset was used instead of TGA to determine the mass loss during decomposition (Figure 4.19, p. 83).

2 Onset of the transition of HEGDGE (Figure 4.19, p. 83).

3 First glass transition of PEGDGE (Figure 4.19, p. 83).

All DSC experiments were conducted in duplicate and the values shown in Table 4.9 are averages. However, the replicates gave consistent results differing by only ±1 °C from the average value.

The thermogram of product IP18 (PEG:βCD ratio = 4.1:1) compared to its precursors (PEGDGE and βCD) is shown as a representative of the other βCXCDs in Figure 4.27.
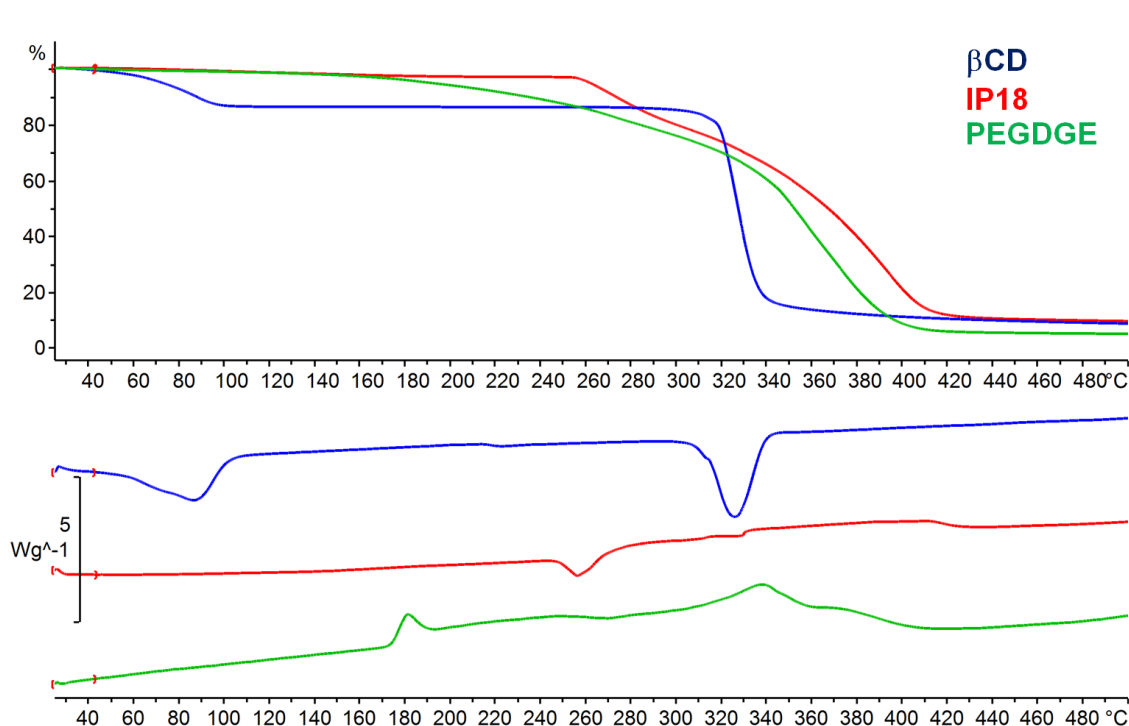
Figure 4.27 Combined DSC analysis and TGA of IP18 (PEG:βCD ratio = 4.1:1, red line) and its precursors βCD (blue) and PEGDGE (green) over the temperature range 30–500 °C (10 °C min^{-1}, aluminium crucible).

The thermogram of the product (red line) in each experiment indicates that degradation occurred at 257 °C, whereas βCD degraded at 328 °C (blue line) and PEGDGE initiated at 180 °C with a major drop at 338 °C (green line). The thermal stability of each βCXCD lies midway between that of its precursors (Table 4.9). Specifically, βCD improves the thermal stability of the short-chained cross-linked systems (βCTCDs and βCHCDs) but reduces the thermal stability of systems with longer cross-linkers (βCPCDs). The degradation of the compound resembled the βCD thermogram, with a major endothermic event at

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257 °C suggesting that the cross-linked products undergo a degradation/caramelisation process.
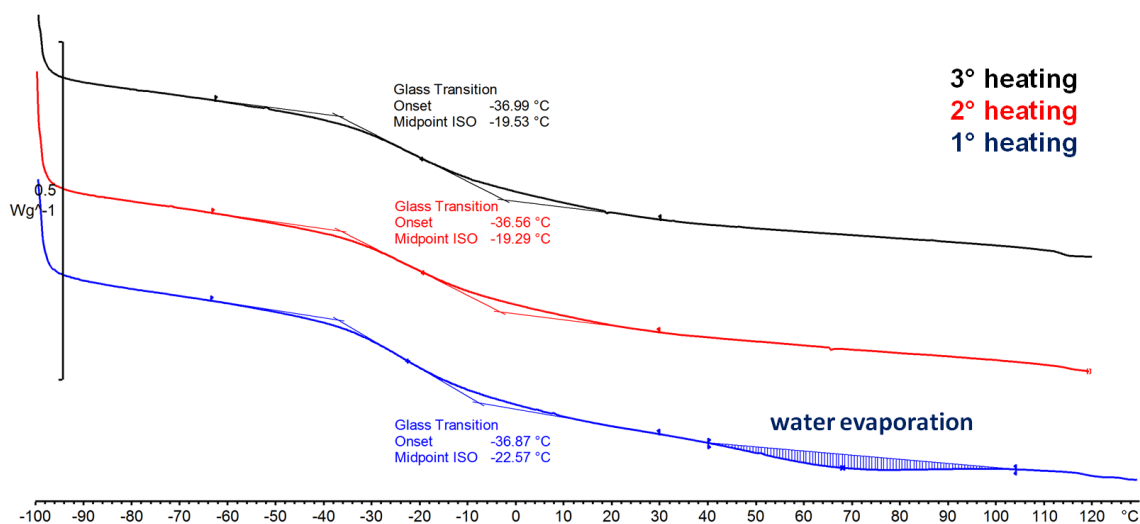
Figure 4.28 DSC analysis showing the plasticising effect of water in IP18 from −100 to 120 °C (10 °C min⁻¹, third temperature cycle, aluminium crucible).

The water entrapped by βCD affected the T_g of βCD and βCXCD (IP18) in a similar manner, hence the water was eliminated during a first heating cycle up to 130 °C to achieve the T_g of the pure compounds without the plasticising effect of the water. The iterative heating cycles eliminated the endotherm present in the first heating curve caused by the evaporation of water. The second and third heating runs were stopped at 120 °C to reduce the thermal shock on the βCXCDs. The absence of water therefore caused the T_g to increase from approximately −23 to −20 °C, confirming its plasticising effect in the βCXCDs. The third heating of each compound was used to report the T_g of the dry product (Table 4.9). Comparison of the three cross-linked products IT1, IH1 and IP13, which feature high cross-link ratios of 3.6:1, 4.0:1 and 3.8:1, respectively (Table 4.9), indicated that the cross-linker type affects the thermal properties of the products. The T_g of the three different βCXCD products based on a temperature scan from −100 to 120 °C is shown in Figure 4.29.
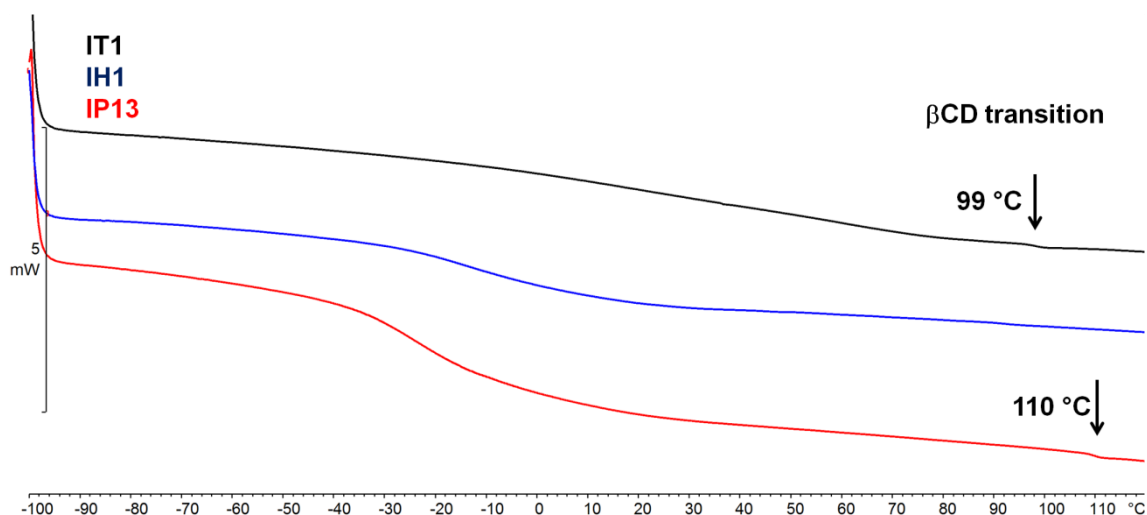
Figure 4.29 DSC analysis of βCXCD products with high XEG:βCD ratios, namely IT1 (3.6:1, black line), IH1 (4.0:1, blue line) and IP13 (3.8:1, red line) from –100 to 120 °C (10 °C min^{-1}, third temperature cycle, aluminium crucible).

The cross-linker chains dominated the behaviour of the cross-linked samples at low temperatures. A glass transition occurred in at least part of the products with a notable shift towards positive temperatures compared to the cross-linkers alone (Table 4.9). However, softening was observed in all the tested products even when no evident glass transition occurred, as represented by the black curve in Figure 4.29 related to the βCTCDs. The T_g was absent from products cross-linked with TEGDGE, and general softening occurred in the entire thermal spectrum. The products synthesised with the longer cross-linkers retained the glass transition if the HEG:βCD ratio exceeded 3:1 or the PEG:βCD ratio exceede 2.5:1 (Table 4.9). The heating curve revealed that the glass transition of the βCXCDs was broad and gradual, as seen in the PEGDGE cross-linkers. The broadness of the transition depended on the polydispersity of the products, as also highlighted by GPC experiments. The secondary transition attributed to βCD occurred at lower temperatures in the products cross-linked with TEGDGE and PEGDGE, with few exceptions (Table 4.9). The βCHCD curves showed no evidence of a secondary transition other than IH4 (HEG:βCD ratio = 1.8), which contains the least amount of cross-linker. This general trend suggests that the small secondary transition becomes visible by DSC only when a significant proportion of βCD is present in the system.

4.3.2.2 Thermo-mechanical characterisation of the inert βCXCDs

The cross-linked βCPCD samples were tested with three different supports to determine whether the adhesion of the material to the supports influenced the tendency to crack and/or affected the thermal transitions. The supports were aluminium pockets (Figure 4.30a), a stainless steel mesh (Figure 4.30b), or aluminium pockets with PTFE tape (Figure 4.30c).
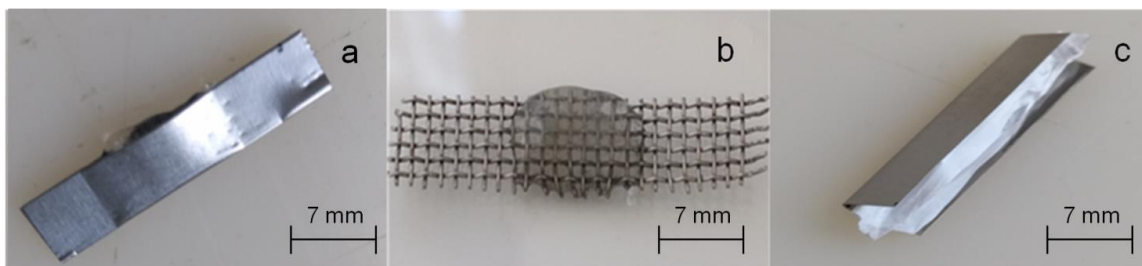
Figure 4.30 Photographs of βCPCD samples supported by (a) an aluminium pocket, (b) a stainless-steel mesh, and (c) an aluminium pocket wrapped in PTFE tape.

4.3.2.2.1 Analysis of the βCXCD product in aluminium pockets

DMA was used to determine if the type of cross-linker and amount (XEG:βCD ratios ranging from 4.3:1 to 1.6:1) affected the thermo-mechanical properties of βCXCD. Initially the tests were performed with the samples held in aluminium pockets as recommended by the DMA manufacturer for materials incapable of self-support. The temperature was extended from 100 to 140 °C at 10 °C min^{-1} in order to cover the shift in temperatures for the minor second-order transition identified by DSC. The DMA and DSC data are compared in Table 4.10.

The change in heat flow of the T_g recorded by DMA reduced as the amount of βCD present in the βCXCDs increased. Furthermore, the secondary transition captured by DSC was not detected by DMA up to 140 °C. The temperature range was not extended any further to avoid the degradation of the βCXCDs. The thermogram of IP9 (PEG:βCD ratio = 3.5) is used as an example to discuss the significant changes in E′ and tanδ values at T_g (Figure 4.31).

Table 4.10 Comparison of DMA and DSC results for βCXCD samples and their precursors.

Sample	Cross-link ratio	T_g (°C)		
		tanδ DMA[1]	STD[2]	DSC
IT1	3.6	-		-
IT2	3.1	-		-
IT3	2.4	-		-
IT4	1.9	-		-
IH1	4.0	31	6.4	-10
IH2	3.2	53	4.5	-6
IH3	2.6	72	4.0	Soft
IH4	1.8	104	7.0	Soft
IP18	4.1	16	1.2	-19
IP19	4.0	41	4.8	-18
IP13	3.8	44	3.6	-19
IP20	3.7	47	3.1	-19
IP9	3.5	27	3.9	-16
IP15	3.0	67	7.5	-7
IP22	2.9	48	3.6	-3
IP17	1.6	-		-

1 Third cooling cycle at 1 Hz, T_g determined as the tanδ peak.
2 Standard deviation (STD) of three replicates.
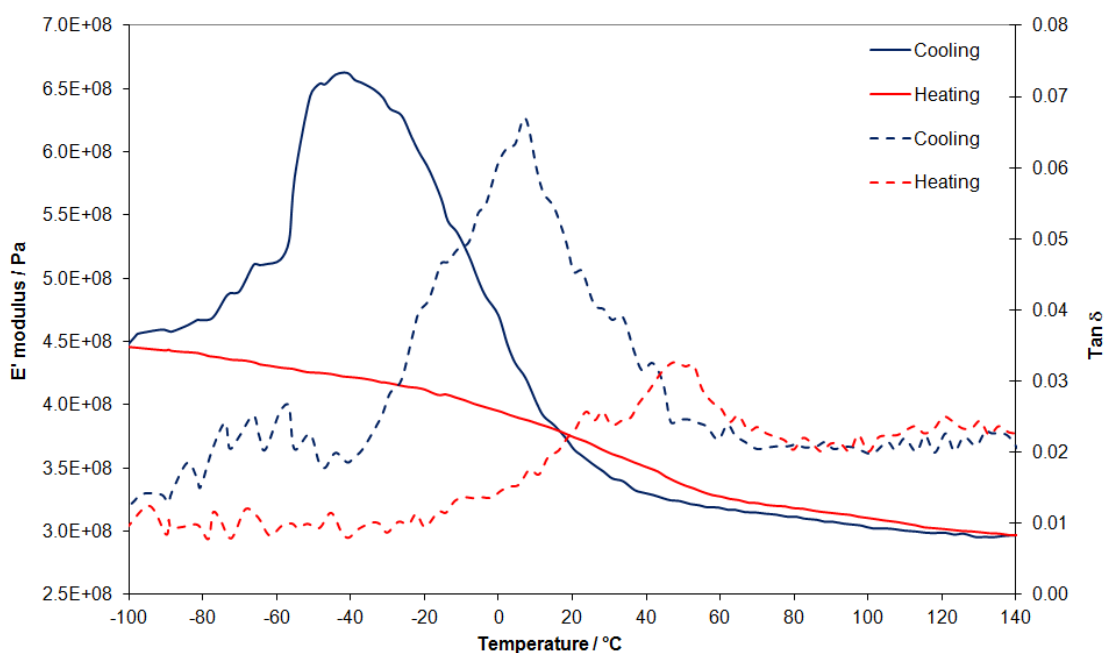
Figure 4.31 DMA showing variation in the storage modulus (E′, solid lines) and tanδ (dashed lines) of sample IP9 (10 °C min^{-1}, 1 Hz, third temperature cycle from –100 to 140 °C, aluminium pocket).

Figure 4.31 shows the E′ and tanδ values for sample IP9 (containing 67% w/w PEGDGE) during the third temperature cycle from –100 to 140 °C. There were minor differences in each value between the first cycle and the second and third cycles, suggesting that the cross-linked system retained water adsorbed from the air and during the purification process.

During heating, DMA revealed a gradual stepwise decrease in E′ between the temperature extremes with a major step at 55 °C coinciding with a tanδ peak. This broad transition was frequency dependent, suggesting it represented a glass transition event for sample IP9 highlighted at –10 °C by DSC. The softening of the IP9 product was represented by a change in the slope of the E′ curve at –31 °C, matching the onset of the tanδ peak, and this relates to the viscoelasticity of the PEG soft segments present in all the cross-linkers. The difference in T_g determined by DSC and DMA was much larger than the typical shift of 10–20 °C often reported in the literature at 10 Hz [131,132].

With an aluminium support in place, the DMA thermogram for IP9 showed a similar profile to PEGDGE during the cooling phase, which can be attributed to the cracking of the sample. This was shown by the sudden drop in E′ from its maximum value to 31% at around –30 °C. The temperature at which cracks begin to appear in the IP9 sample was not significantly dependent on the oscillation frequency, whereas cracking of the PEG chains in PEGDGE shifted from –78 °C at 1 Hz to –70 °C at 10 Hz. The cracking temperature was not dependent on the material used, but was dependent on overall changes in the sample preparation method and differences in stress dissipation within the bulk compound. The lower mobility of the cross-linked samples reflects the existence of a cross-linked matrix compared to the viscous PEGDGE liquid, which has a higher adhesive surface area.
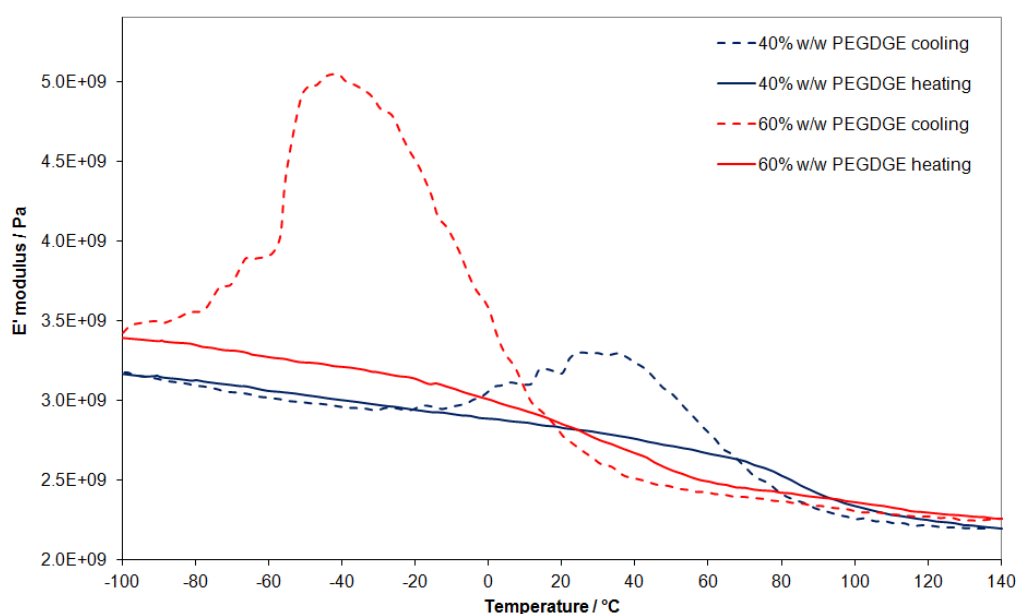
Figure 4.32 DMA showing variation in the storage modulus (E′) and tanδ of sample IP9 (PEG:βCD ratio = 3.5, solid and dotted red lines) and IP17 (PEG:βCD ratio = 1.6, solid and dotted blue lines) (10 °C min^{-1}, 1 Hz, third temperature cycle from –100 to 140 °C, aluminium pocket).

The DMA curves of samples IP9 (PEG:βCD ratio = 3.5) and IP17 (PEG:βCD ratio = 1.6) are compared in Figure 4.32. The lower PEG content of IP17 resulted in cracks appearing at a much higher temperature (35 °C) and the E′

value dropped to 10% of its maximum value. In comparison, the E′ value of IP9 with the higher PEG content fell to only 30% of its maximum. The relatively low cross-linker content of sample IP17 therefore appears to cause earlier cracking compared to sample IP9 and reduces its viscoelastic behaviour, also limiting its binding strength given that the low E′ value is related to the strength of adhesion to the metallic support. The glass transitions determined from the peak tanδ values shift to higher temperatures when the PEG content is low. The absence of first-order transitions in the βCPCD samples during cooling was confirmed by DSC (Figure A 6) suggesting that βCPCD products are completely amorphous at temperatures between −100 and 140 °C.

4.3.2.2.2 Analysis of the βCXCD product on a steel mesh support

The interaction between the βCXCDs and the support had a noticeable effect in the cooling thermogram. Sample IP9 (PEG:βCD ratio = 3.5) was analysed with a stainless-steel mesh in lieu of the aluminium pocket. The sample was spread over the mesh prior to analysis (Figure 4.30). The glass transition of IP9 as determined by DMA was interrupted by stress relaxation at 15 °C (Figure 4.33). Cracking was still observed during cooling, but the phenomenon was less severe compared to the sample held in an aluminium pocket (Figure 4.33). The cracking manifested itself over a wider temperature range (−14 to −70 °C) compared to the sudden drop observed with the aluminium pocket. The characteristic drop in E′ began at about −17 °C and reached 3% of the maximum value. The drop was visible during each cycle, confirming the stress relaxation effect that occurs with each round of heating. The metallic mesh changed the manner in which the stress introduced during each cooling cycle was dissipated. The mesh had a greater surface area to which IP9 could bind (362 mm^2) compared to the aluminium pocket (180 mm^2) but nevertheless allowed effective stress dissipation within the bulk sample.
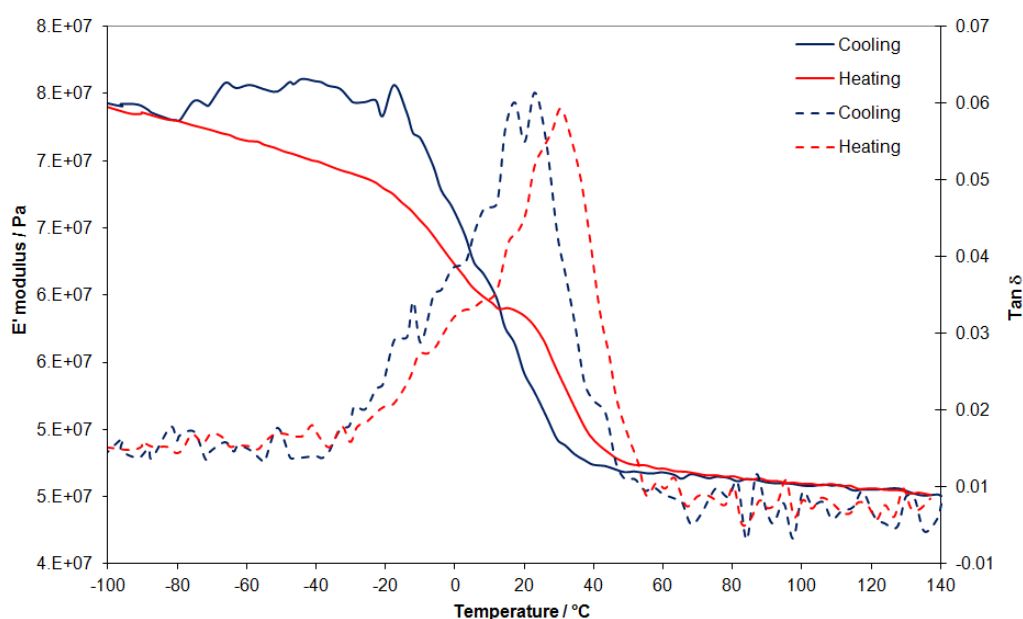
Figure 4.33 DMA showing variation in the storage modulus (E′, solid lines) and tanδ (dashed lines) of IP9 (10 °C min^{-1}, 1 Hz, third temperature cycle, −100 to 140 °C, stainless-steel mesh).

4.3.2.2.3 Analysis of the βCXCD product in aluminium pockets with PTFE tape

In order to confirm that the drop in the E′ values during cooling was due to the de-bonding of the sample from its support, PTFE tape was used to hold βCPCD1 samples within an aluminium pocket, thus allowing the samples to contract freely as the temperature declined. Preliminary DMA characterisation of the PTFE tape (blank) showed a softening at the onset temperature of 18 °C (Figure A 7). The absence of adhesion between sample IP9 and the support when the sample was enfolded by PTFE tape was confirmed by the drop in E′ during cooling (Figure 4.34).
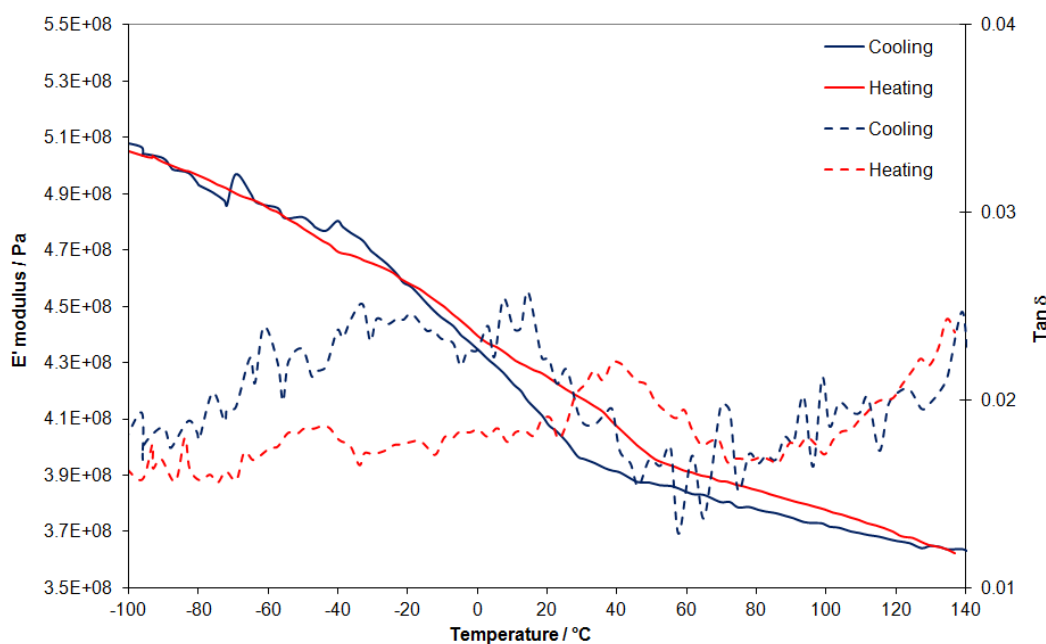
Figure 4.34 DMA showing variation in the storage modulus (E′, solid lines) and tanδ (dashed lines) of IP9 (10 °C min⁻¹, 1 Hz, third temperature cycle, −100 to 140 °C, aluminium pocket and PTFE tape).

The hysteresis between the heating and cooling curves during the same temperature cycle diminished with each cycle. Therefore, the PTFE tape almost completely eliminated the de-bonding phenomenon and the thermal stress in the sample during the cooling phase. The T_g of IP9 under these conditions was 41°C, identical to the value recorded in the aluminium pocket without tape, confirming that the experimental setup does not affect the T_g.

4.3.2.3 Analysis of the βCXCDs by optical microscopy

Optical microscopy was used to characterise the cracking of the IP9 product (PEG:βCD ratio = 3.5) in more detail during cooling (Figure 4.35). A glass support was considered adequate as a transparent substitute for the metallic support we used to investigate the adhesion of the compound. The sample was cooled from 25 °C (Figure 4.35a) and began to crack at about −55 °C (Figure 4.35b), with the cracks propagating further as the temperatures was reduced to −100 °C (Figure 4.35c,d). The same sample was then heated to 100 °C and the cracks began to self-repair, starting at 0 °C (Figure 4.35e) until healing was complete at ~80 °C (Figure 4.35h).

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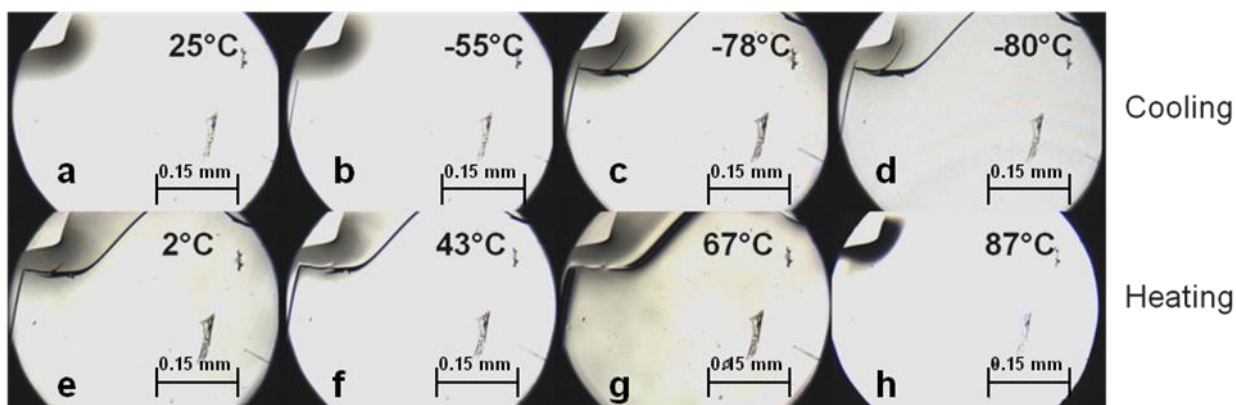
Figure 4.35 Optical microscope images of IP9 (PEG:βCD ratio = 3.5) during the first temperature cycle from –100 to 100 °C. The top row (a-d) shows the cooling phase captured at 25 °C, –55 °C, –78 °C and –80 °C and the bottom row (e-h) shows the heating phase captured at 2 °C, 43 °C, 67 °C and 87 °C .

During the second thermal cycle in the same sample, cracking began at –58°C and initiated at a different location (Figure 4.36c). This confirms the evidence provided by the similar E′ values in each thermal cycle, i.e. the thermal history is erased by heating as previously reported for a hydrogel CD/PEG system [33]. During the second cycle, sample healing occurred at ~80 °C as in the first cycle (Figure 4.36h). Furthermore, IP9 placed on PTFE tape showed no evidence of cracking during the cooling phase, confirming that stress relief by cracking was due to the bonding of IP9 to the glass support (Figure A 8).
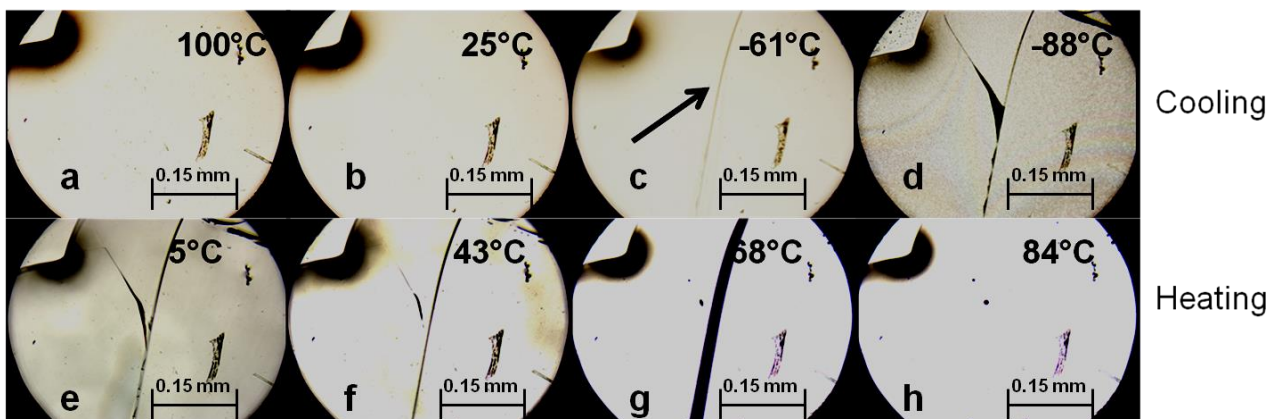
Figure 4.36 Optical microscope images of IP9 (PEG:βCD ratio = 3.5) during the second temperature cycle from –100 to 100°C. The top row (a-d) shows the cooling phase captured at 100 °C, 25 °C, –61 °C and –88 °C and the bottom row (e-h) shows the heating phase captured at 5 °C, 43 °C, 68 °C and 84 °C.

This experiment confirmed the self-healing of the compound and explained why the E′ curves are identical during multiple temperature cycles. The self-healing behaviour is thought to reflect the reformation of hydrogen bonds and host–guest interactions as seen in CD hydrogel systems due to the lower viscosity of the cross-linked system when heated above the T_g [33,52–54]. The physical transformation occurs at the onset of material flow behaviour, allowing the crack to be filled in, and probably involves a rheological model involving the snake-like displacement of the polymeric chains, described as reptation [55].

4.3.2.4 Qualitative assessment of the self-healing properties
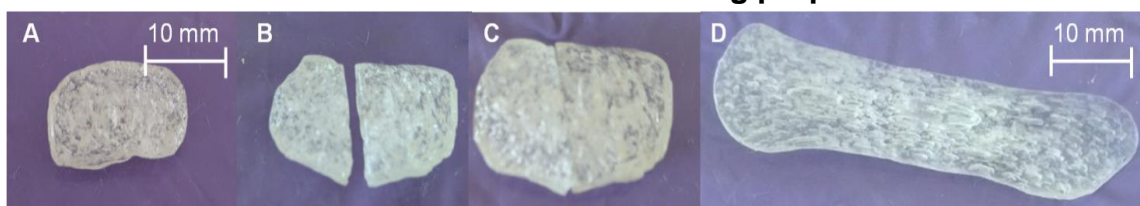
Figure 4.37 Self-healing of IP13 (PEG:βCD ratio = 3.8). (a) Sample after solvent evaporation. (b) Sample after cutting. (c) The parts are placed in contact. (d) The sample is heated to 70 °C for 30 min and pulled by the extremities.

The rupture strength of sample IP13 was qualitatively assessed by intentionally cutting the sample (Figure 4.37b). The parts were subsequently rejoined and annealed in the oven at 70 °C for 30 min (Figure 4.37c). The joined parts were found to be cohesive after this qualitative test (Figure 4.37d). The sample was gripped at its extremities and pulled gently at room temperature. The sample showed considerable elongation. Diffusion of the polymeric chains by reptation and the reforming of hydrogen bonds in the fracture allowed the material to qualitatively self-repair and self-heal.

4.3.2.5 Scanning electron microscopy

The surface morphology of the βCXCDs was explored by scanning electron microscopy (SEM) and compared to the precursor βCD, which is a crystalline material with roughly square particles of different sizes (Figure 4.38).

ß-CD 15.0kV X300 BSE-3D 60Pa   100µm

Figure 4.38 Scanning electron micrograph of βCD crystals.

In contrast to the precursor, the surface of the βCXCDs was more amorphous due to the cross-linking reaction. The foamy appearance of the surface was due to the evaporation of water during the drying process. The βCTCD samples with various TEG:βCD ratios showed significant differences when analysed by SEM (Figure 4.39). The surface of IT1 (TEG:βCD ratio = 3.6) was amorphous with large aggregates, whereas the higher TEG content of samples IT2 (TEG:βCD ratio = 3.2), IT3 (TEG:βCD ratio = 2.4) and IT4 (TEG:βCD ratio = 1.8) caused the particles to appear progressively less amorphous and to resemble the crystalline morphology of native βCD.
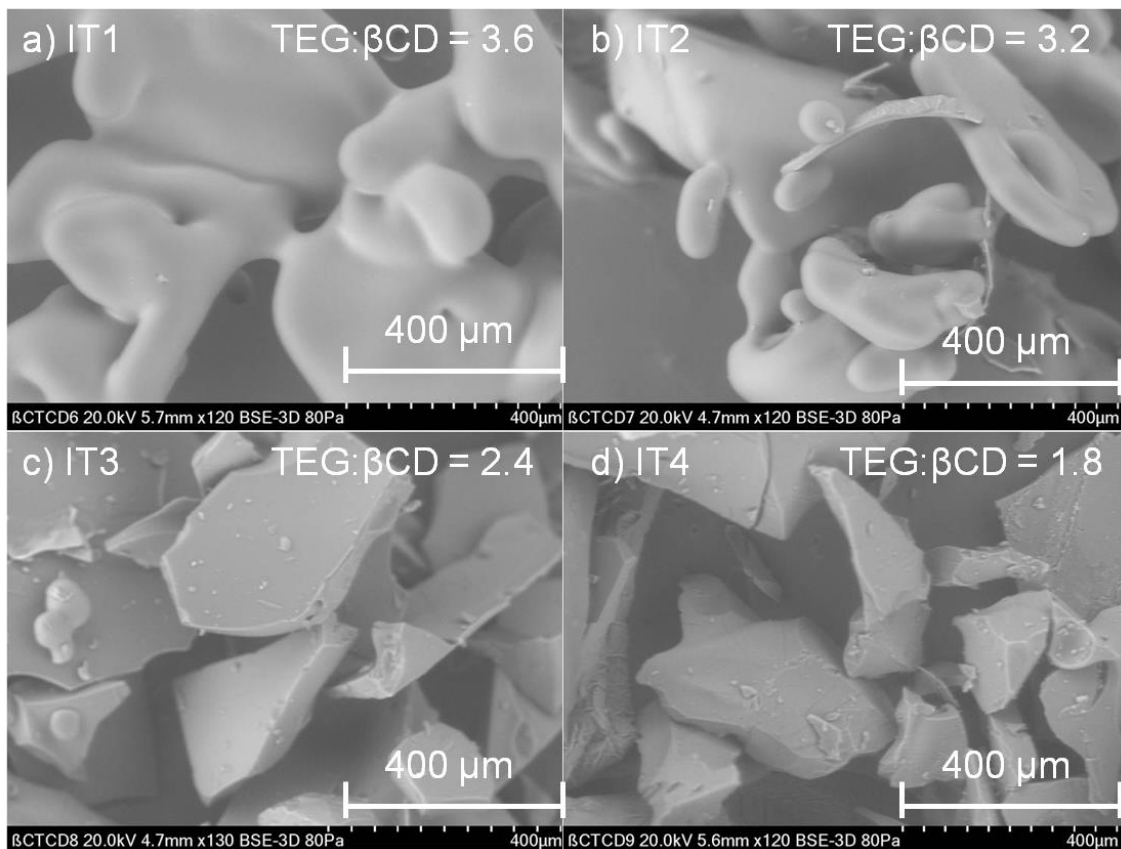
Figure 4.39 Scanning electron micrographs of the βCTCDs (a) IT1 (b) IT2 (c) IT3 and (d) IT4.

The βCXCDs containing HEG and PEG units were not significantly affected by the degree of cross-linking and were characterised by a homogeneous smooth surface (Figure 4.40). Crystalline domains were observed in the βCPCDs with fewer cross-links (Figure 4.40d).

The upper part of Figure 4.40 compares the surface morphology of sample IH1 (HEG:βCD ratio = 4.0) and IH4 (HEG:βCD ratio = 1.8), whereas the lower part compares samples IP19 (PEG:βCD ratio = 4.0) and IP17 (PEG:βCD ratio = 1.6). The crystalline domains in the less cross-linked sample IP17 may have a higher βCD content given their similarity to native βCD. The exposure of these regions to the electron beam for a few minutes in the vacuum chamber generated a honeycomb structure, due to the evaporation of water and/or the degradation of these regions.
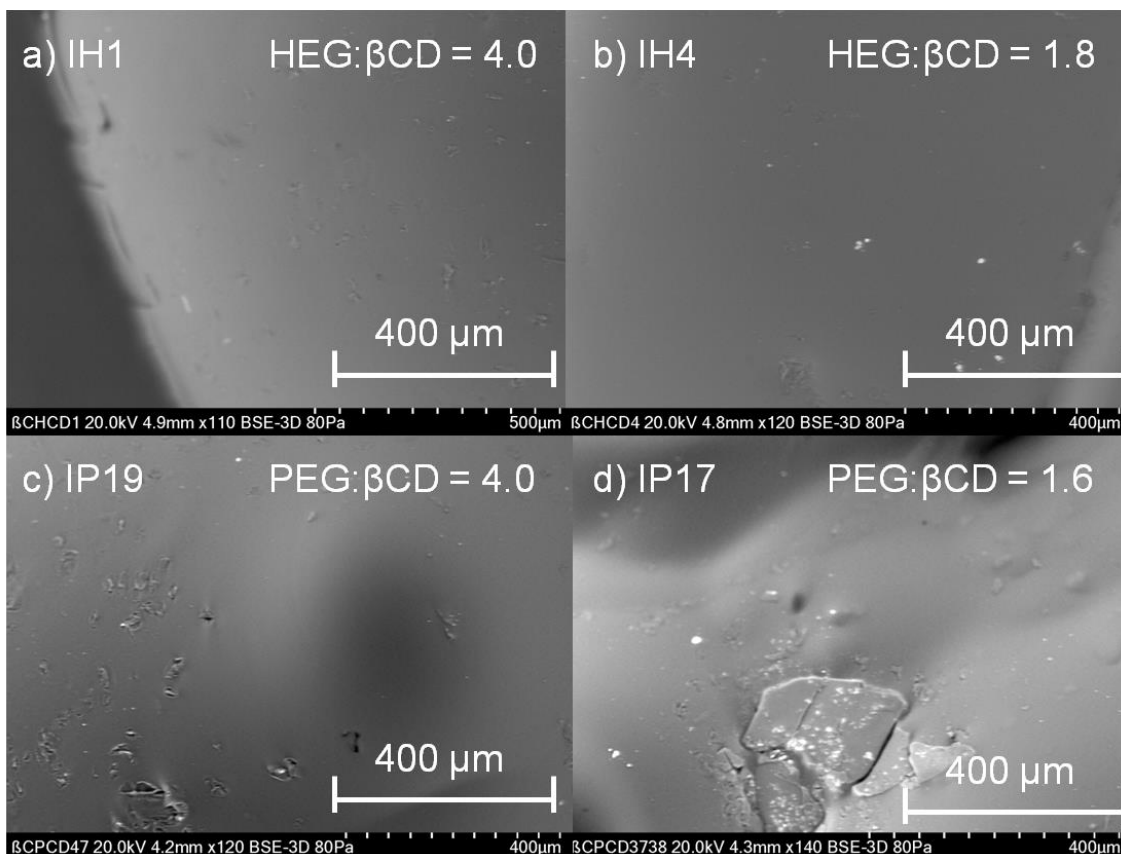
Figure 4.40 Scanning electron micrographs of the βCHCDs (a) IH1 and (b) IH4, and the βCPCDs (c) IP19 and (d) IP17.

4.3.2.6 The βCXCD product in an early-stage formulation

A basic formulation was prepared to study the effect of the inert binder on the formulation's mechanical properties. Sample IP17 (10% w/w) was mixed with melamine in water. The melamine was used as inert substitute for RDX given the similarities in their particle sizes. The mixture was left stirring for 1 h at room temperature before drying under vacuum. The dry mixture contained aggregates rather than finely-dispersed melamine. DMA experiments were conducted, resulting in the thermogram shown in Figure 4.41.
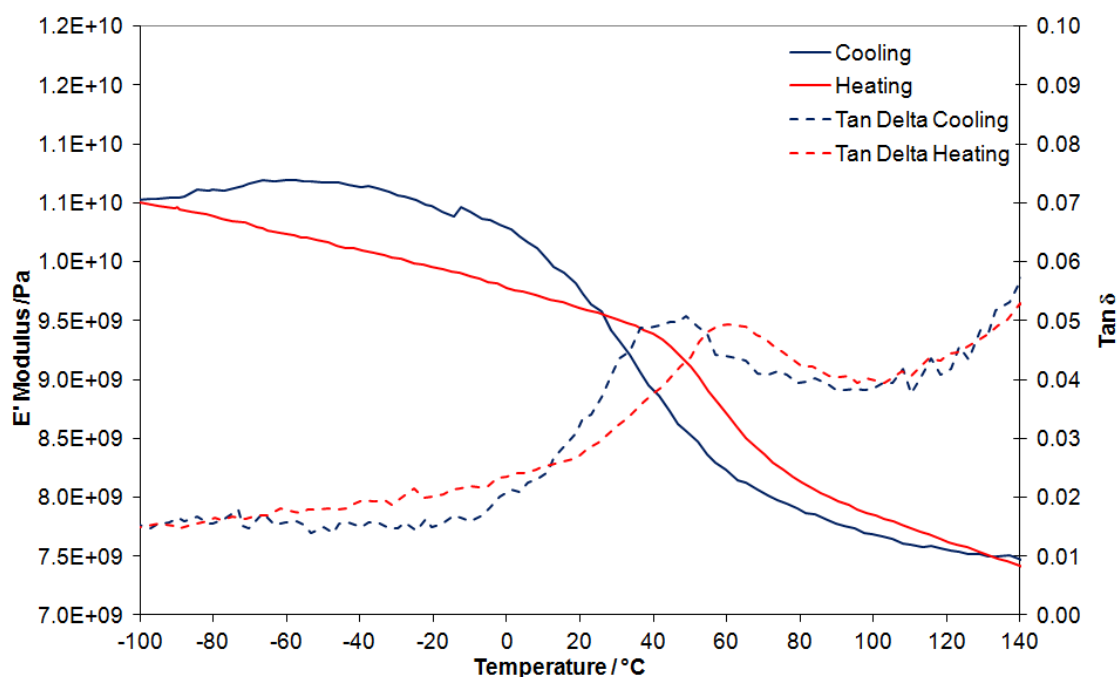
Figure 4.41 DMA showing variation in the storage modulus (E′, solid lines) and tanδ (dashed lines) of sample IP17 (10% w/w) formulated with 90% w/w melamine (10 °C min^{-1}, 1 Hz, third temperature cycle from –100 to 140 °C, aluminium pocket).

The formulation inherited some of the mechanical properties of the binder given the T_g highlighted by the tanδ peak at 60 °C and the drop in E′ at -45 °C, matching the values of the binder alone (Figure 4.31). The cracking attributed to IP17 was not abolished in the formulation and a small drop in E′ was observed at –12°C. The drop in E′ was lower than the equivalent drop for the pure cross-linker.

4.4 Conclusions

This chapter summarised the outcome of cross-linking βCD with polyethylene glycol diglycidyl ethers containing three, six and nine repeat units, as a first step towards the synthesis of a new inert semi-synthetic binder for energetic applications. The investigation focused on the optimisation of the cross-linking reaction, which was strongly affected by several factors including NaOH concentration and volume, reaction time, temperature, βCD alkoxide formation, cross-linker:βCD ratio, and the addition rate of the cross-linker in the βCD alkoxide solution. The optimal conditions for the reaction were 5.6% NaOH,

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0.21 $g_{\beta CD}$ $mL^{-1}_{aq.NaOH}$, 30 °C, 16 h to form the βCD alkoxide, 20 min for the addition of the cross-linker, a cross-linker:βCD feed ratio < 5:1, and 6 h for the cross-linking. A unique synthesis procedure was adopted for all βCXCDs. Samples with different cross-linker:βCD feed ratios (5:1, 4:1, 3:1 and 2:1) were synthesised using the three different cross-linkers. Up to 25% of the cross-linker was consumed in a parallel degradation reaction. Characterisation by ^{1}H-NMR and FTIR spectroscopy confirmed the formation of βCXCDs containing units of βCD and XEG chains. Characterisation by ^{1}H-NMR in D_2O allowed the XEG:βCD ratio in the repeat unit of the macromolecule to be calculated. Samples with XEG:βCD ratios between 4:1 and 3:1 were malleable whereas compounds with lower ratios were friable.

The compounds synthesised using the shorter cross-linker TEGDGE were friable and easy to dissolve in water regardless of the TEG:βCD ratio. The βCXCDs synthesised using longer cross-linkers (HEGDGE and PEGDGE) took longer to dissolve when the XEG:βCD ratio defined by ^{1}H-NMR was > 3.4:1.

The thermal and mechanical properties of the precursor βCD were tuned by the cross-linking, giving βCXCDs with low T_g values (from –20 to 5 °C). The softness of the βCXCD samples was dependent on the quantity and length of the polyethylene glycol units. In products with a XEG:βCD ratio > 3.7:1, the T_g was as low as –20 °C, whereas the glass transition was absent in the βCXCDs with the lowest number of cross-links. No glass transition was observed in βCTCDs, which contained the shorter TEG units.

The βCXCD samples were found to crack when cooled during DMA due to the formation of strong hydrogen bonds with the metallic support. The βCXCDs also healed rapidly when heated, retaining some of the healing properties of hydrogels synthesised with βCD and polyethylene glycol reported in pharmaceutical research projects. The characterisation of βCHCDs and βCPCDs by SEM confirmed their amorphous nature, but the βCTCDs increasingly resembled the crystalline morphology of native βCD when the TEG:βCD ratio was < 2.4:1.

Having established a robust synthesis route for βCXCDs and investigated the properties of the water-soluble products, the project moved on to the synthesis and characterisation of nitrated derivatives, as described in Chapter 5.

5 Synthesis and characterisation of energetic cross-linked βNCXCDs

In order to produce new binders that provide energy to energetic formulations, the cross-linked βCXCDs systems described in Chapter 4 were nitrated using conventional protocols. The nitration procedure was initially developed at a scale of 200 mg. The energetic properties of the nitrated products were assessed by Cranfield Defence and Security experts before synthesis was scaled up to 1 g.

The number of βCD hydroxyl groups that can be nitrated, i.e. converted to nitrato groups (ONO_2), can vary from 1–3 per glucosidic unit of βCD and 1–21 per βCD molecule (Scheme 5.1). The available hydroxyl groups could become sterically hindered when the precursor molecules are cross-linked to form βCXCDs. Therefore, to ensure a high degree of nitration, a large excess of the nitrating mixture was used as discussed below.

Two conventional synthesis routes used for the preparation of other nitro-esters were tested [21]. Route 1 used a mixture of concentrated sulfuric acid (98%) and nitric acid (95%) whereas route 2 used fuming nitric acid (Scheme 5.1).

route 1

HNO_3, H_2SO_4, 1 h, <20°C

route 2

HNO_3, 1 h, <20°C

(β**CXCD**)   (β**NCXCD**)

R= cross-linker; OH   R= cross-linker; OH; ONO_2
X= TEG, HEG, PEG   X= TEG, HEG, PEG
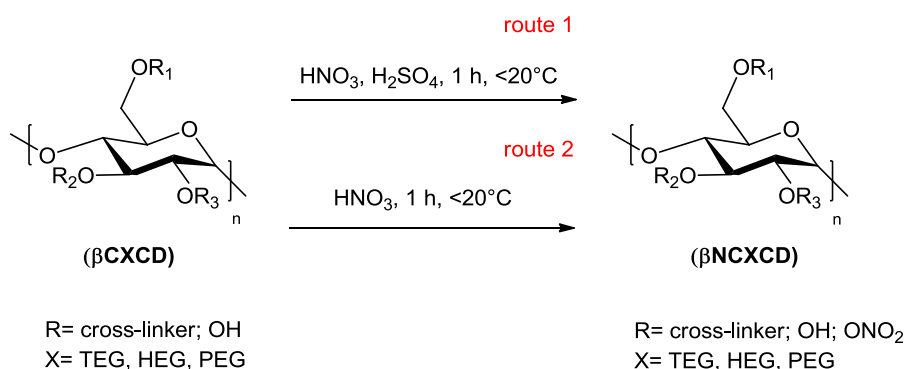
Scheme 5.1 Synthesis routes selected to achieve the nitration of βCXCDs.

Route 1 is typically used for the synthesis of NC [27]. The sulfuric acid catalyses the formation of the nitronium ion, resulting in an electrophilic attack on the organic substrate, and its desiccant power removes the water generated during nitration as shown in Scheme 5.2. The removal of water is a highly exothermic

process and has the potential to degrade βCD if not properly controlled. During the synthesis of NC, sulfuric acid can also promote the formation of sulfate esters during the nitration process, which affect the yield and stability of the nitrated product. The presence of sulfate esters, which are sensitive to moisture and temperature, could reverse the nitration reaction thus degrading the nitroesters. This negatively affects the physicochemical properties and stability of the products, as reported for NC [27].

a)

i) $HNO_3 + H_2SO_4 \rightleftharpoons H_2NO_3^+ + HSO_4^-$

ii) $H_2NO_3^+ \rightleftharpoons H_2O + NO_2^+$

iii) $H_2O + H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^-$

$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2HSO_4^-$

b)
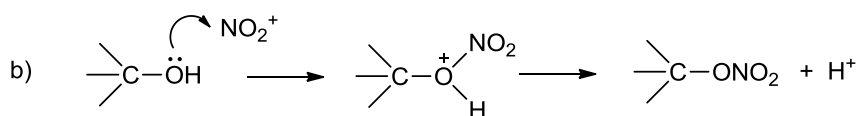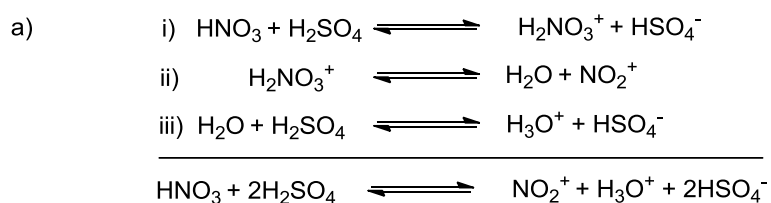
Scheme 5.2 Nitration of βCD units: (a) the sulfuric acid catalyses the formation of nitronium ions, and (b) the formation of nitroesters.

In route 2, fuming nitric acid was used as the nitrating mixture. This procedure has already been used for the synthesis of nitrated βCD and the experimental data from this PhD project can therefore be compared with data reported in the literature [109,114,116].

Two-phase nitration was also attempted for the nitration of βCXCDs using the halogenated solvent dichloromethane, which can act as a heat sink, removing the nitrated product from the nitrating medium and increasing the yield. This approach is commonly used in the synthesis of polymeric nitroesters such as polyNIMMO and polyGLYN [133]. Two-phase nitration is also used to extract nitrated organic substrates such as nitroglycerine from the nitrating mixture [133]. However, dichloromethane was found to be inefficient for the nitration of βCXCDs because neither the cross-linked precursors nor the nitrated products dissolved in this solvent. Therefore, two-phase nitration was considered unsuitable as method to produce nitrated βCD derivatives.

The βCXCD systems containing TEG, HEG and PEG were nitrated using fuming HNO$_3$. The conditions and work-up were optimised primarily using the water-soluble βCPCD products, given the commercial availability of PEGDGE. However, the insoluble products generated by cross-linking with TEGDGE and PEGDGE were initially used to assess the efficiency of nitration of insoluble precursors, as described in Section 5.1.

5.1 Attempts to nitrate the insoluble βCXCD precursors

The first nitration attempts targeted the insoluble products synthesised during the optimisation of the cross-linking reaction conditions. The nitration of the cross-linked products was influenced by three parameters:

- The physical properties of the starting material;
- The strength of the nitrating medium;
- The duration of the nitration reaction.

Four insoluble βCXCDs were chosen, namely samples IP26 and IT5–IT7 containing PEG and TEG units, respectively (Appendix, Table A 4) and nitrated using the sulfuric and nitric acid mixture (Route 1, Scheme 5.1) or fuming nitric acid (Route 2, Scheme 5.1). The degree of cross-linking reflected on the swelling power of the two precursors in water. The optimisation of the synthesis parameters was guided by the data collected during the characterisation of the thermal properties of the βNCXCD products, as discussed below.

Figure 5.1 Physical appearance of the insoluble IP26 and IT5–IT7 precursors.

The insoluble βCXCDs were mixed with a large excess of the nitrating mixture or fuming nitric acid (~1 mL) relative to the mass of cross-linked substrate (200 mg). The samples were crushed into small pieces before nitration to increase the available surface area for the nitration. The nitration mixtures were stirred at 200–900 rpm during the trials to grind the largest particles and guarantee good contact with the acids. The starting materials physically disintegrated under these conditions to give a cloudy suspension, indicating that the insoluble compounds were not efficiently converted to soluble nitrated derivatives. The nitration reaction was interrupted after 1 h at room temperature by quenching the mixture in excess water and ice. The crude slurry was rinsed with large amounts of water to dilute and eliminate the acids and the solids were partially extracted with acetone. The insoluble solid products were rinsed with water and then acetone. Small fractions were recovered when rinsing with acetone and these were dried. Both fractions were characterised by ^{1}H-NMR spectroscopy and DSC.

Several replicates of the nitration of βCTCDs containing TEG units (samples IT5–IT7) led only to insoluble βNCTCDs, whereas the βNCPCD mixtures generated small amounts of acetone-soluble material comprising highly-nitrated derivatives. The nitrated samples were not soluble in acetone (Appendix, Table A 5) and they showed good thermal stability with a decomposition peak at ~200 °C. The energy content of the samples was relatively low for energetic binders,

at 450–800 J g^{-1} (Table 5.2), and seemed to be independent of the nitration conditions. Generally, the yields of the nitration reactions of βCTCDs were high (450–1400 J g^{-1}, Table 5.2). In contrast, the synthesis of βCPCDs from insoluble precursors was more difficult given the physical properties of the starting material, which was less gummy and friable. Nitration thus produced a variety of nitrated insoluble compounds with different thermal properties, as well as some acetone-soluble fractions.

In conclusion, the properties of the nitrated products were strongly dependent on the method used to disperse the insoluble particles of the inert βCXCD precursors in the nitration medium. The βCTCD precursors were well-dispersed fine powders whereas the βCPCD precursors were hydrogels that were difficult to penetrate and wet by the acids. The traces of βNCPCD soluble in acetone consisted of highly nitrated oligomers with crystalline properties, similar to the nitrated βCD (Table 5.1) and were not pursued further.

5.2 Attempts to nitrate the soluble βCXCD precursors

Initial tests revealed that the solubility of the βCXCD precursors in the nitrating media was inversely proportional to the degree of cross-linking. The dissolution of βCXCD substrates took up to 1 h at room temperature for derivatives with a XEG:βCD ratio of 3:1, and less than 20 min when the XEG:βCD ratio was < 3:1. (As stated in Chapter 4, the abbreviation XEG is used here to refer collectively to the TEG, HEG and PEG segments in the cross-linked products.) The volume of nitric acid used per 200 mg of βCXCD was therefore increased to 2.1 mL, and most precursors took less than 40 min to fully dissolve. Subsequently, all reaction mixtures were left to stir at room temperature for 1 h before quenching in excess ice-water. The liquid was decanted and the solid residue was washed several times with water, dissolved in a minimum amount of acetone, and re-precipitated in water (450 mL). The product was dispersed in the water, making it difficult to recover, so a half-saturated solution of brine was used instead of distilled water in order to change the zeta potential of the solution and promote the flocculation of product particles. The precipitate was subsequently re-dissolved in acetone, the inorganic components were filtered off and the

βNCXCDs were dried under high vacuum. Small portions were then used for chemical and thermal characterisation. The βNCXCD samples obtained from soluble βCXCD precursors showed a high thermal stability (T_{dec} ~200°C, E_{dec} ~1700 J g^{-1}; Table 5.3). These values were also consistent when compared to the nitrated products of the insoluble precursors, as discussed above.

The compounds emitted a smell consistent with traces of acid (NOx) when briefly stored (hours) in a vial, indicating the purification method was inefficient. Subsequent tests were therefore carried out to assess the efficiency of three variations of the purification method for βNCXCDs:

- Multiple re-precipitations from acetone in water;
- Re-precipitation from acetone in boiling water;
- Re-precipitation from acetone in an aqueous $CaCO_3$ suspension (100 or 25 °C).

When the compounds were purified by multiple re-precipitations in boiling water, they retained the characteristic smell of NOx albeit less pungent compared to the original purification method. The use of a boiling water/$CaCO_3$ mixture was adopted from the NC manufacturing process and was considered an unnecessary extreme choice at this initial stage of research, where the stability of the βNCXCDs was not fully understood. The crude nitrated products from the initial ice-water wash were rinsed several times with water, re-dissolved in small amounts of acetone and re-precipitated in an excess of water containing 1% (w/w) $CaCO_3$. The resulting products lacked the NOx smell suggesting that the latter purification method was the most efficient.

A side experiment using a strong base (NaOH) at room temperature as a neutralising agent resulted in the degradation of the product, with the release of NOx from the nitrated product and absorption onto its surface (Figure 5.2).
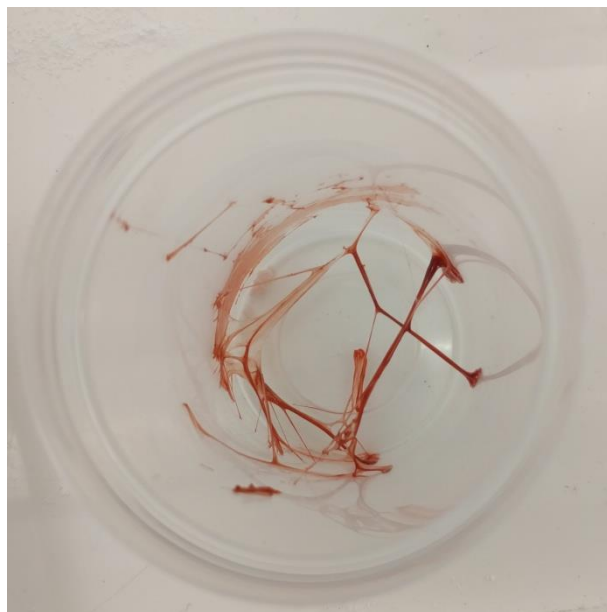
Figure 5.2 Nitrated product degraded by the use of NaOH during purification.

A number of replicates confirmed that re-precipitation from acetone in 0.5% w/w CaCO$_3$ in water at room temperature gave consistent results with clean, acid-free βNCXCDs, and this purification method was adopted for their preparation.

5.3 **Synthesis and chemical characterisation of βNCXCDs**

Based on the pilot studies described above, several βCXCD samples were nitrated and extracted in acetone using the following general procedure. Nitric acid (2.1 mL, 100%) was cooled below 10 °C in an ice-water bath, and 200 mg of βCXCD was added in small portions over 5 min, ensuring that the temperature remained below 10 °C. The crude slurry was then stirred at room temperature for 1 h and the nitration mixture changed from the slurry to a clear solution, indicating complete dissolution of the βNCXCD products. To quench the reaction, the nitrating mixture was poured into excess ice-water and the solid compounds were collected and washed with distilled water to eliminate acid residues. The products were then re-dissolved in a small amount of acetone and precipitated in an excess of half-saturated brine. Subsequent re-precipitation from acetone in a 0.5% w/w aqueous CaCO$_3$ suspension at room temperature gave a crude precipitate which was dissolved in a small amount of acetone and filtered to remove the inorganic salts. The βNCXCDs

were then chemically characterised by ^{1}H-NMR spectroscopy. The nitrated products were soluble in acetone-d_6 and DMSO-d_6 allowing the nitrogen content to be determined (Table 5.1). The NMR spectra of the βNCXCDs were compared with those of the βCXCD precursors, revealing similar profiles although lower chemical shifts for the nitrated derivatives due to the presence of the nitro groups.

An attempt was made to attribute the signals to specific protons or groups of protons in the βNCXCD molecules. The literature provides a number of assignments for the parent nitrated βCD molecule (βNCD), and the corresponding ^{1}H NMR and FTIR spectra were used as references. However, the chemical characterisation of similar cross-linked systems has not been published [116,134]. In order to facilitate the assignment of peaks, a sample of βCD precursor was nitrated as an internal comparison using the method described above for the nitration of βCXCDs. Figure 5.3 compares the ^{1}H NMR spectra of βNCD and sample NP1, prepared from the inert precursor IP18 with a PEG:βCD ratio of 4.0:1. The similarities between the spectra confirmed the formation of βNCPCDs.
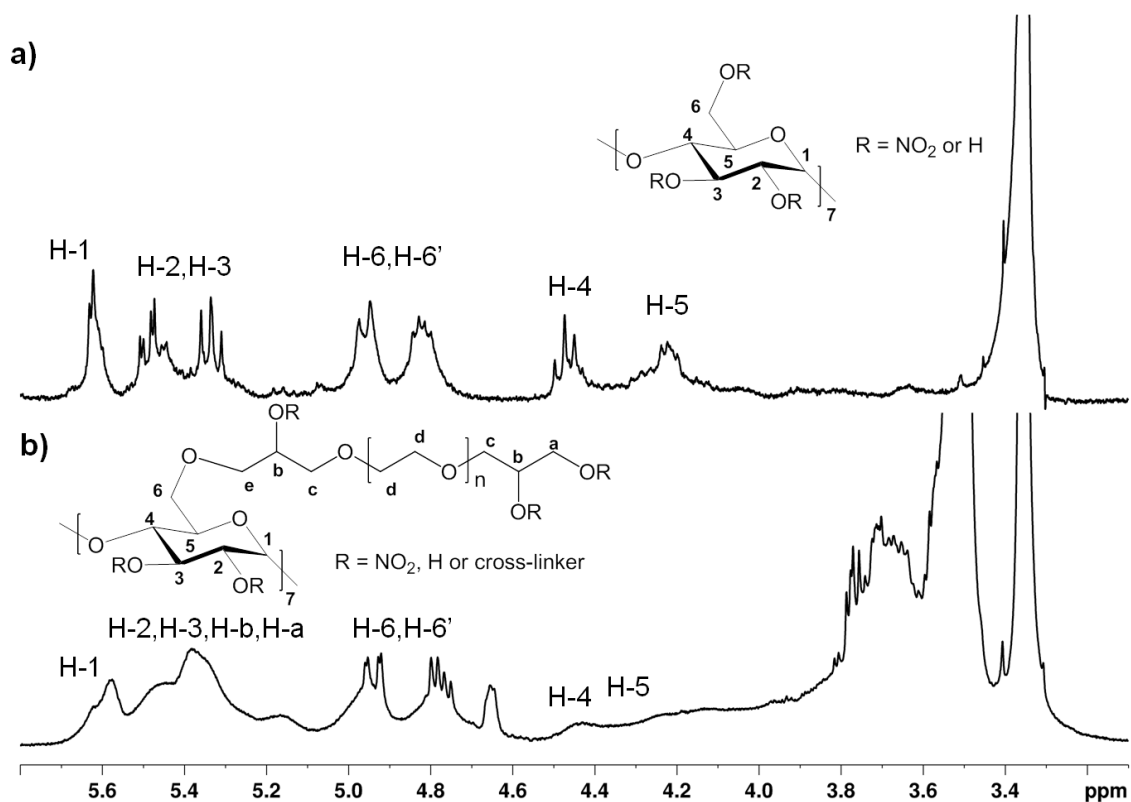
Figure 5.3 The ^{1}H NMR spectra of (a) βNCD [116] and (b) NP1 in DMSO-d$_{6}$.

Figure 5.4 compares the ^{1}H-NMR spectra of the inert precursor IP18 and a representative nitrated sample NP1. The detailed properties of both samples are summarised in Appendix A (Table A 1 and Table A 6).
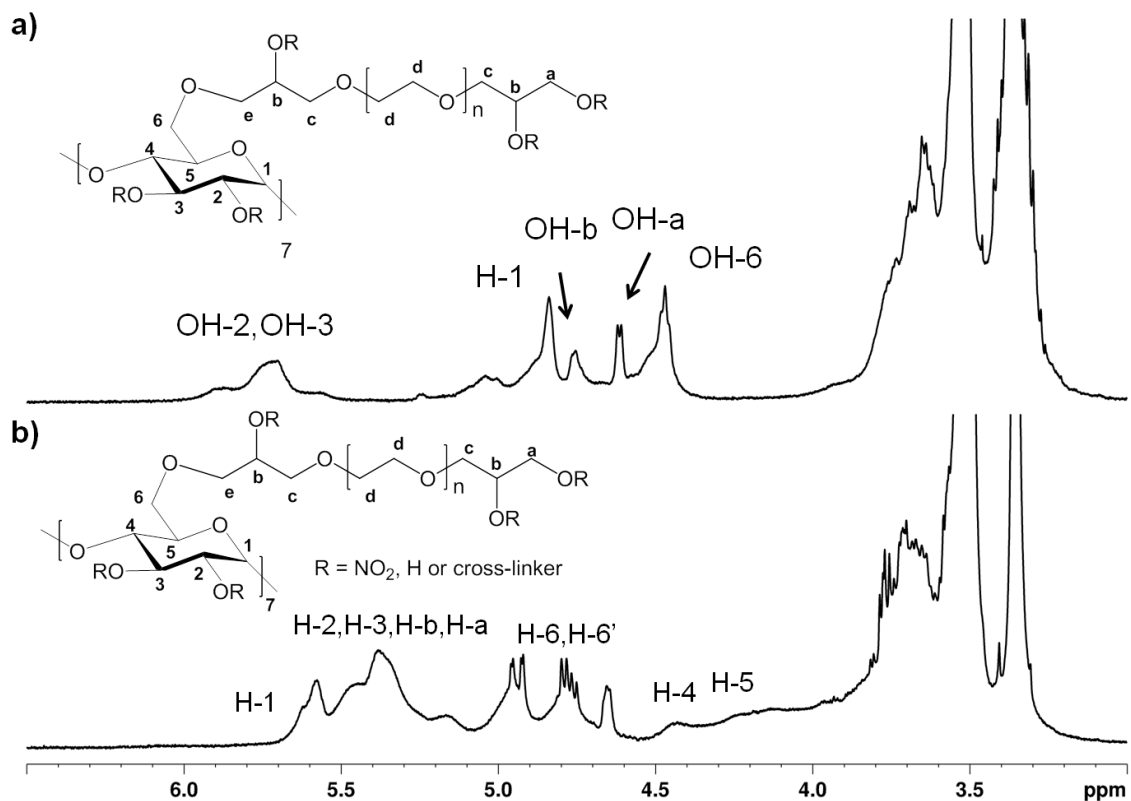
Figure 5.4 Comparative ^{1}H-NMR spectra of (a) inert precursor IP18 (PEG:βCD ratio = 2.5:1) and (b) its nitrated product NP1, both in DMSO-d_6.

The assignment of ^{1}H-NMR signals in the βNCXCD spectra was complex. The spectrum of the nitrated sample is characterised by three sets of broad signals at 5.70–5.20 ppm, 5.10–4.00 ppm and 3.80-3.40 ppm. The first set of peaks at 5.70–5.20 ppm indicated different chemical environments in the nitrated macromolecule due to the presence of the stronger electro-withdrawing nitrato groups. The anomeric proton H-1 of sample IP18 with a chemical shift centred at 4.8 ppm was shifted at 5.60 ppm in the NP1 spectrum. The shoulder at 5.60 ppm is possibly the H-1 signal when the cross-link was added at position OH-2 of unit 2, as described in Scheme 5.1. The broad signals centred at 5.45 and 5.35 ppm can be assigned to protons H-2 and H-3 of the βCD units and H-b, next to a chiral centre in the PEG chain. The region 5.10–4.00 ppm represents the modified chemical shift of all the βCD and PEG units protons situated close to the nitrato groups. The two broad signals between 5.15 and 4.65 ppm can be assigned to Ha and H6 protons. The set of small, broad signals at 4.60–3.80 ppm can be assigned to all CH$_2$ protons belonging to βCD and PEG units that

are not adjacent to a nitrato group, but are close enough to be influenced by them. The complex environment between 3.80 and 3.40 ppm can be assigned to the remaining βCD protons which are situated far enough away from the nitrato groups to maintain the chemical shifts of their precursors.

No significant differences were observed among the spectra for βCTCDs, βCHCDs and βCPCDs, containing TEG, HEG and PEG units, respectively, and with similar XEG:βCD ratios (Figure 5.5).
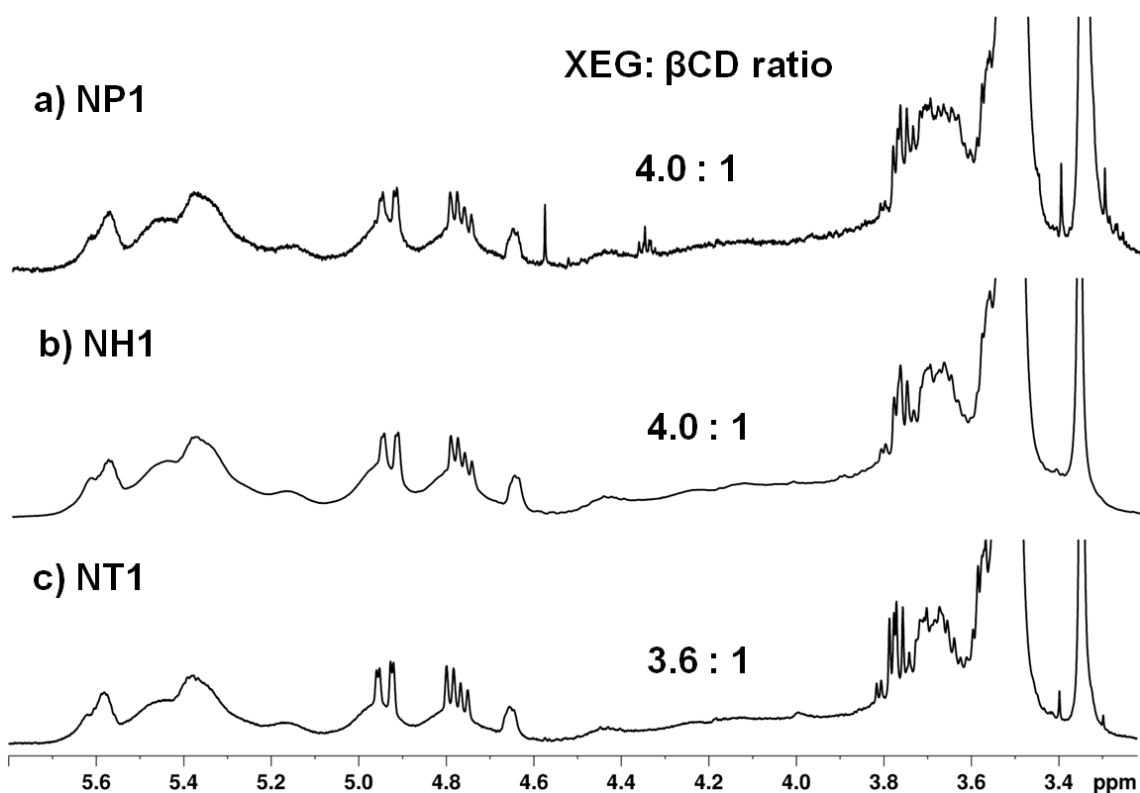
Figure 5.5 The ^{1}H NMR spectra of products (a) NP1, (b) NH1 and (c) NT1 in DMSO-d_6. The XEG:βCD ratios were previously determined by NMR spectroscopy.

The compounds with fewer cross-links featured a sharper H-1 anomeric signal at 5.7–5.5 ppm (Figure 5.6). Fewer cross-links promote the comparable conversion of all three available hydroxyl groups in the βCD unit into ONO_2 groups (Figure 5.6d), whereas the conversion of OH-2 was more frequent in the highly cross-linked products as highlighted by the presence of the shoulder at 5.7–5-6 ppm (Figure 5.6a).
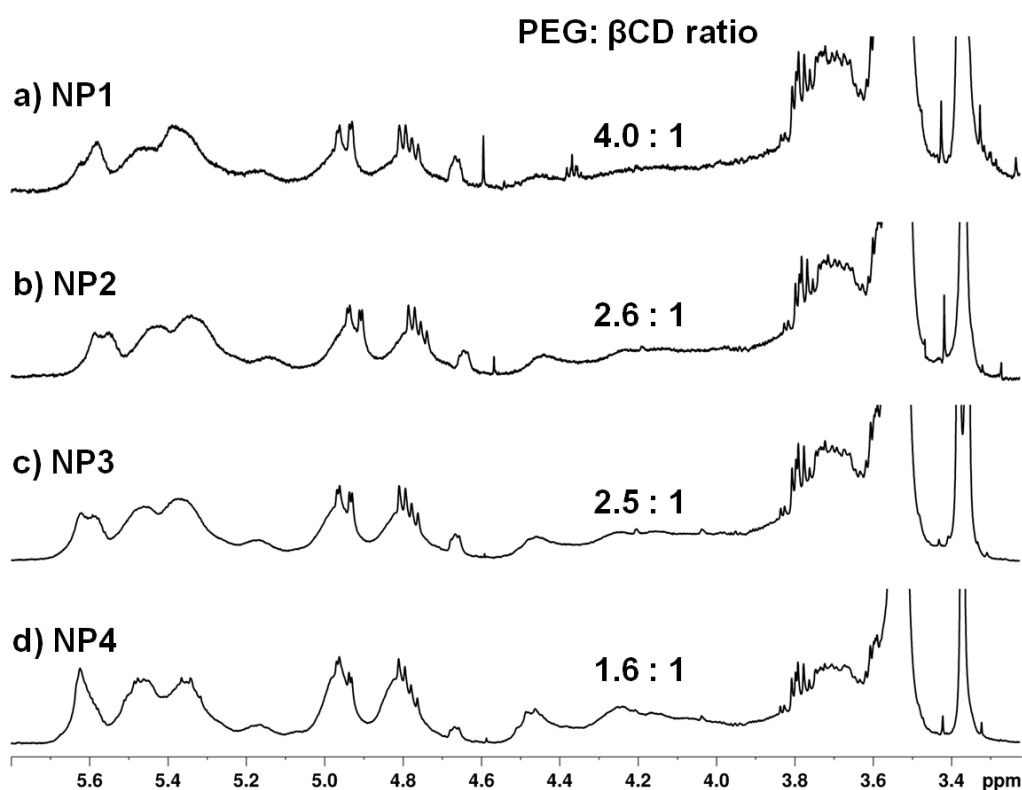
Figure 5.6 The ^{1}H NMR spectra of products (a) NP1, (b) NP2, (c) NP3 and (d) NP4, which show a gradually decreasing PEG:βCD ratio.

The degree of substitution (DS) of the hydroxyl groups in βNCD was determined by NMR spectroscopy as described in the literature [116], revealing that 2.6 of the 3 hydroxyl groups available per βCD repeat unit were nitrated under the adopted reaction conditions. The technique has an error of ± 2.5% in terms of the nitrogen content [116] and the values were assessed also by iron sulfate titration (Table 5.1) [135]. The nitrogen content of βNCD was also determined by titration to confirm the consistency of the results.

The iron sulfate titration method is based on the hydrolysis of nitrato groups in excess 98% sulfuric acid while stirring for 1 h at room temperature. The nitric acid generated in this reaction forms NO_x complexes with the iron titrant and turns the solution pink, allowing quantification by colour change [135]. KNO_3 is used as a standard to determine the correction factor (F) from ideal to real titration conditions using (3:

$$F = \frac{A \ x \ 13.833}{B} \qquad \textbf{(3)}$$

where 13.833 is the nitrogen content of KNO_3 (g mol^{-1}), A is the weight of NT or NH or NP (g), and B is the amount of titrant used to reach the endpoint (mL).

Several βNCXCDs were subsequently titrated and the nitrogen content then determined using (44:

$$N\% = \frac{V \ X \ F}{m_{NC}} \qquad \textbf{(4)}$$

where N% is the nitrogen content, m_{NC} is the weight of the NT, NH or NP samples (g), V is the amount of titrant required to reach equivalency (mL), and F is the correction factor from Equation 3.

The nitrogen content was inversely dependent on two factors:

- The XEG:βCD ratio (degree of cross-linking);
- The length of the polyethylene glycol repeat unit in the βNCXCDs.

The TEG, HEG and PEG units increase the overall mass of carbon atoms in the βNCXCDs and therefore reduce the percentage of nitrogen in the total mass of the macromolecule. The only exception was NT4, which diverged from the trend in all three triplicates and further investigation is therefore needed. The DS in the βNCXCDs was generally greater than 2.1/3. The lower DS in the βNCPCDs can be attributed to the lower efficiency of nitration in the less-soluble βNCXCDs, which take longer to dissolve in the nitrating medium.

Table 5.1 Nitrogen content of the βNCXCDs.

Sample ID	Inert precursor		Nitrogen content		DS per βCD unit
	Name	XEG:βCD ratio	(% w/w)[1]	Error (%)	(ideal max = 3)
βNCD	-	-	11.6	11	2.1
NT1	IT1	3.6	8.2	2	2.4
NT2	IT2	3.1	9.4	8	2.7
NT3	IT3	2.4	9.5	8	2.4
NT4	IT4	1.9	6.3	15	1.3
NH1	IH1	4.0	5.6	20	3.1
NH2	IH2	3.2	7.2	5	2.2
NH3	IH3	2.6	9.0	4	2.8
NH4	IH4	1.8	9.4	13	2.5
NP1	IP18	4.0	6.3	3	2.4
NP5	IP13/20	3.7	6.2	2	2.4
NP6	IP13/20	3.7	6.8	25	2.5
NP2	IP23	2.6	7.0	5	2.2
NP3	IP33	2.5	6.9	12	2.2
NP4	IP32	1.6	8.8	28	2.4

1 Values are means of three replicate experiments with a variance of ±0.2%.

The nitrated products were then characterised by FTIR spectroscopy in attenuated total reflectance (ATR) mode for the rapid analysis of solid-phase samples. A representative sample NP1 is compared with its precursor in Figure 5.7.
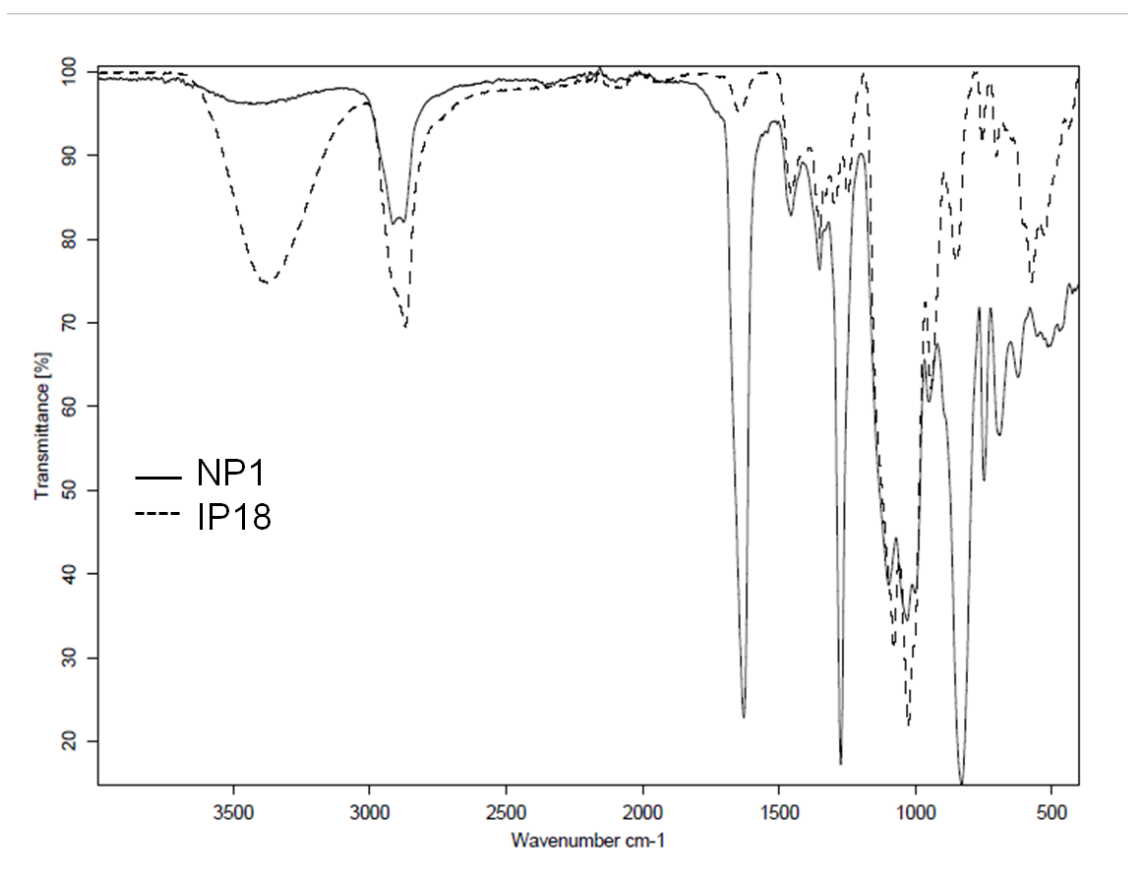
Figure 5.7 Comparative FTIR spectra of sample NP1 (solid line) and its inert precursor IP18 (dashed line).

The absorption peak at 3440 cm^{-1} was assigned to the O-H stretching vibration of the remaining hydroxyl groups in the cross-linked system, and the peak at 2900 cm^{-1} was assigned to the C-H stretching vibration. The absorbance was significantly reduced at 3440 cm^{-1} and strong absorption peaks, attributed to the introduction of nitrato groups, appeared at 1646, 1274 and 831 cm^{-1}. Sample NP8 was also compared with βNCD to identify any differences in the absorption spectrum (Figure 5.8).
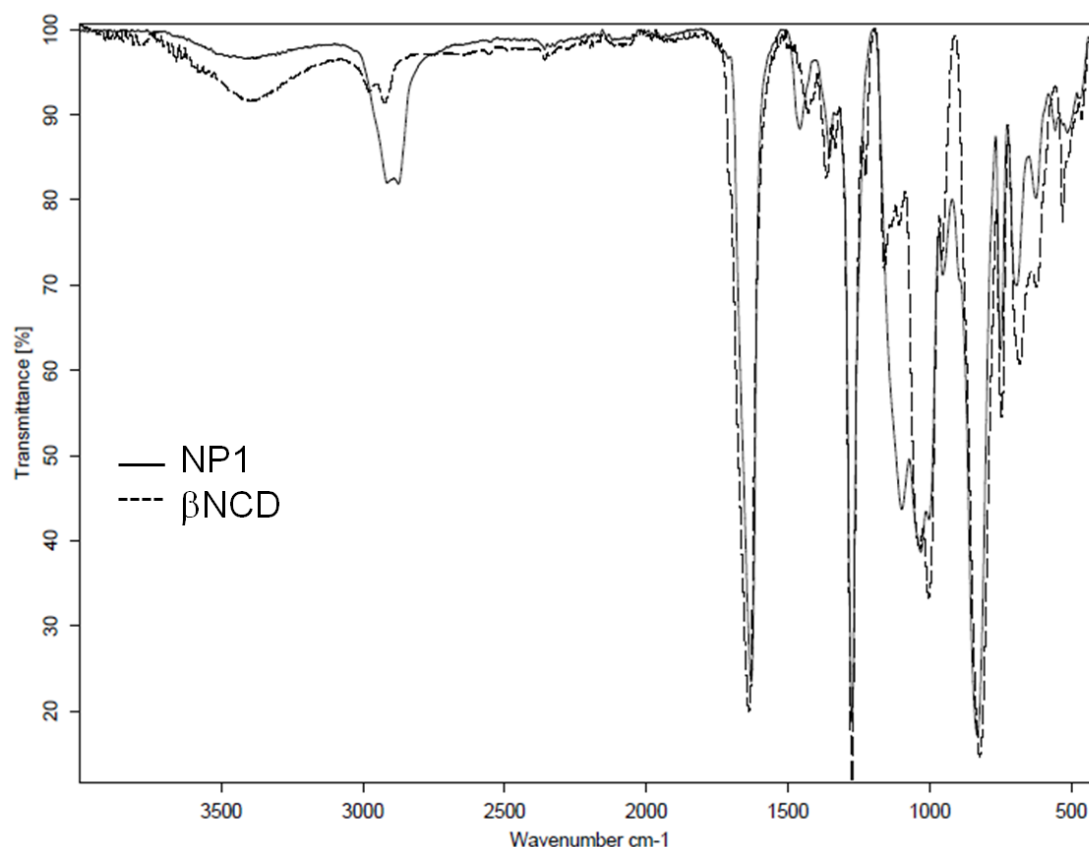
Figure 5.8 Comparative FTIR spectra of sample NP1 (solid line) and βNCD (dashed line).

The NP1 spectrum revealed stronger absorption peaks at 2900 and 2800 cm^{-1} due to the vibration of the C-H bond of the methylene groups (symmetric and asymmetric stretching) and weaker absorption by the OH groups (bending) at 3400 cm^{-1}. This last difference in the OH bond vibration can be attributed to the Mw of the two materials: free OH groups in βCD have a greater mass than the same groups in the macromolecule.

The peaks at 1460 cm^{-1} and 1100 cm^{-1} were more intense in NP1 than βNCD and were assigned to the bending vibrations of the C-H bond of the methylene groups in the PEG units of NP1. There were no significant differences between the nitrated systems with different XEG:βCD ratios (Appendix, Figure A 9).

The molecular weights of the βNCXCD derivatives were determined by GPC in the solvent THF. Polystyrene standards were used for a nine-point calibration

(600 Da to 1.7 MDa) and all Mw values are reported are polystyrene equivalents.

The broad chromatograms of the βNCXCDs were similar to their precursors and confirmed the polymeric structure of the nitrated products (Figure 5.9). The Mw distribution in the three βNCXCD systems is compared in Figure 5.9. The systems have similar XEG:βCD ratios (~3.8) but contain different repeat units, namely PEG (Figure 5.9a), HEG (Figure 5.9b) or TEG (Figure 5.9c). All samples had a broad Mw distribution with the elution of high-Mw fractions beginning at 12 min. Sample NP1 displayed a broader profile, whereas NH1 and NT1 differed slightly due to the presence of two major elution peaks as observed following the GPC analysis of βCXCD.
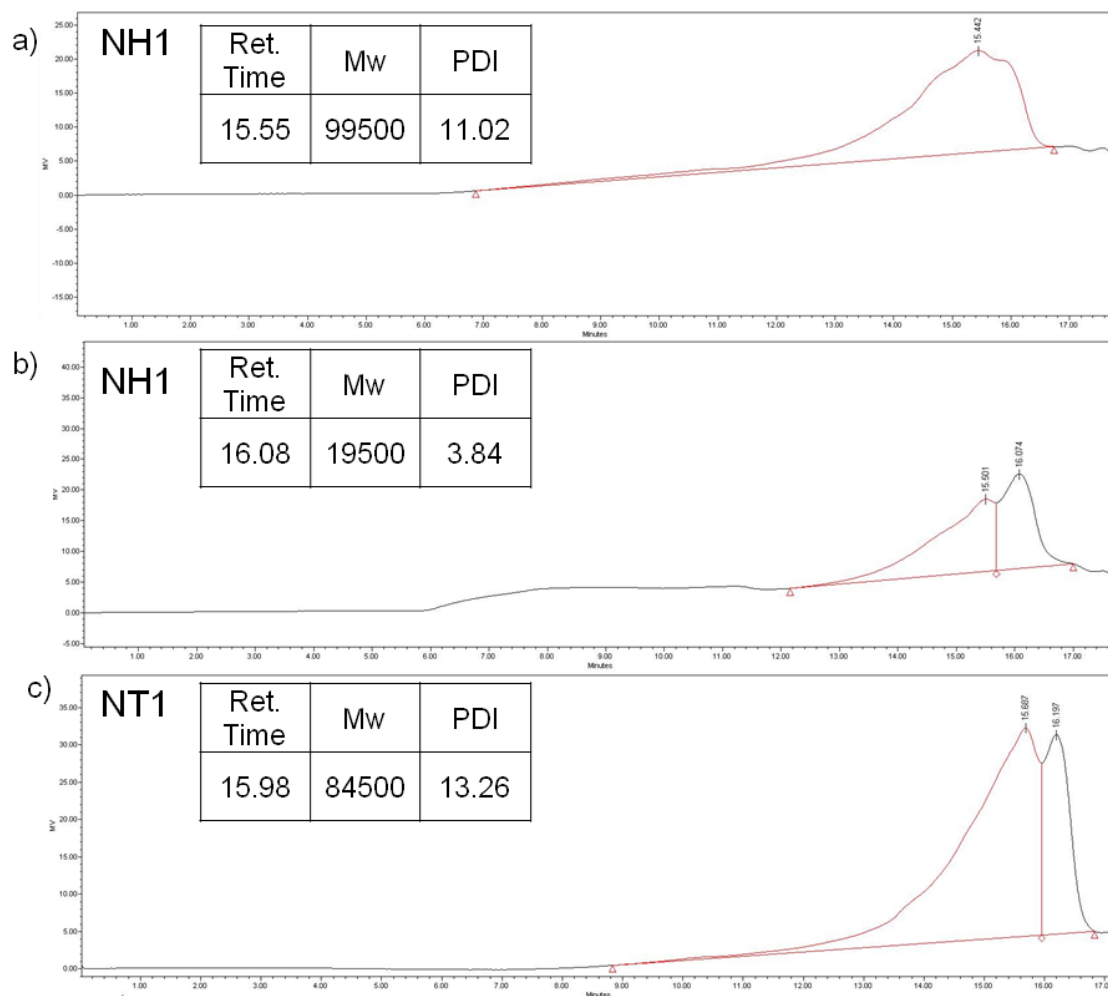
Figure 5.9 Comparative GPC analysis of βNXCDs: (a) NP1 (PEG:βCD ratio = 3.8), (b) NH1 (HEG:βCD ratio = 4.0), and (c) NT1 (TEG:βCD ratio = 3.8).

As expected, both the Mw distribution and polydispersity index of the samples were dependent on the XEG:βCD ratio. As observed for the inert βCXCDs, the GPC analysis of βNCXCDs confirmed that products with higher XEG:βCD ratios (3.8:1) eluted at lower retention times corresponding to their higher Mw (Figure 5.10).
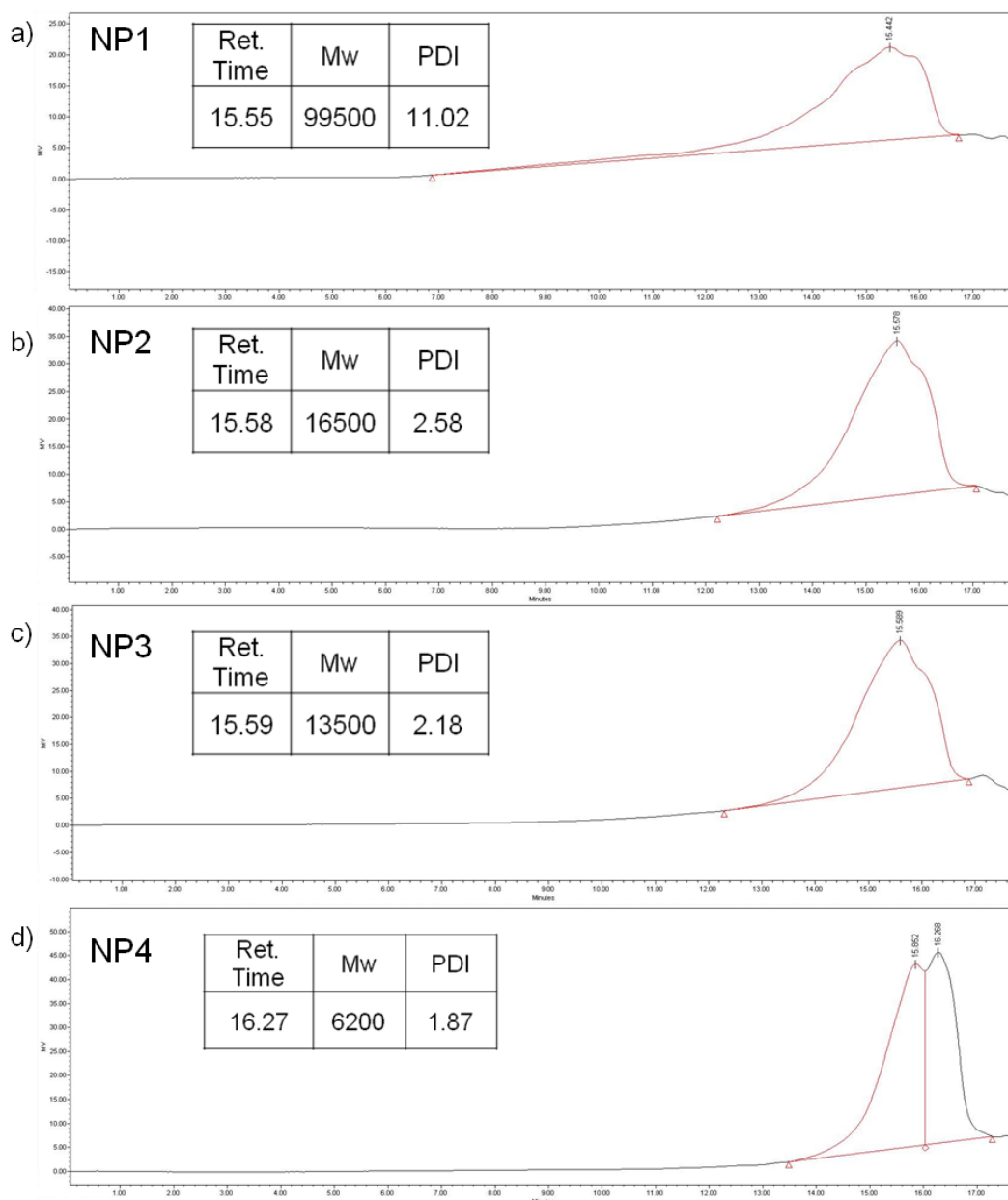
Figure 5.10 Comparative GPC chromatograms of βNPCDs with decreasing PEG:βCD ratios: (a) NP1 (PEG:βCD ratio = 3.8), (b) NP2 (PEG:βCD ratio = 2.6), (c) NP3 (PEG:βCD ratio = 2.1), and (d) NP4 (PEG:βCD ratio = 1.6).

5.4 Thermal and thermo-mechanical characterisation of energetic βNCXCDs

As discussed above, two sets of βNCXCDs were synthesised from inert precursors having differing in terms of their solubility in water. The thermo-

mechanical characterisation of the inert βCXCDs by DSC, TGA and DMA (Chapter 4) was therefore extended to the nitrated derivatives, the βNCXCDs.

5.4.1 Thermal characterisation of βNCXCDs prepared from insoluble precursors

The thermal behaviour of βNCXCDs obtained by nitrating the insoluble βCXCDs was variable. The thermal stability of the nitrated products was affected by a combination of four different factors:

- Strength of the nitrating medium;
- Cross-link ratio of the inert precursor;
- Nitration reaction time;
- Physicochemical properties of the inert precursors.

The conditions used for the synthesis of the βNCPCDs (samples NP7–NP11) and βNCTCDs (samples NT5–NT15) from inert precursors containing PEG and TEG units, respectively, are summarised in Appendix A (Table A 4 and Table A 5, respectively). The nitration of the insoluble βCTCDs released similar amounts of energy in every trial, but this was variable and random in the βNCPCDs.

The thermal profiles of samples NP7–NP11 synthesised from the same precursor (IP26) were found to be inconsistent during decomposition due to the insolubility of the precursor in the nitrating medium. However, longer nitration times promoted higher degrees of nitration and higher decomposition enthalpies compared to analogues NT1–NT10 containing TEG units (Appendix A, Table A 5). The reaction conditions were changed in each trial to increase the efficiency of the reaction, but the nitration was strongly affected by the gel-like physical properties of the βCPCD precursors. Increasing the nitration time to 2 h (NP7–NP12) and the stirring speed (900 rpm), facilitated the dispersion of the hydrogel. The products demonstrated greater thermal stability up to T_{dec} (peak = 200 °C) which were attributed to the more efficient purification. However, the thermal properties of the compounds still appeared to be random, with NP8 and NP9 exceeding 1000 J g^{-1} (Figure 5.11), but NP7 and NP10–NP12 falling within the range 400–600 J g^{-1} (Table 5.2).
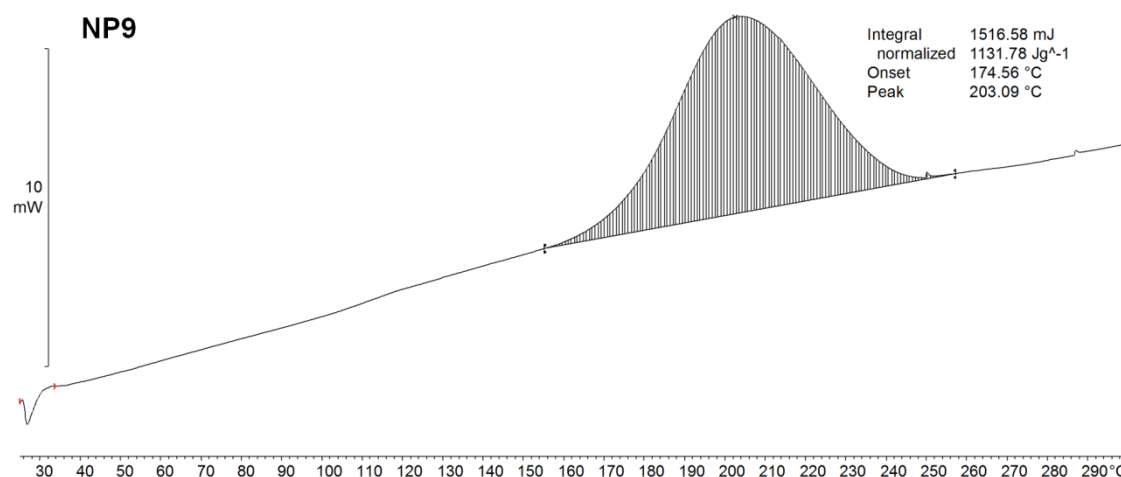
Figure 5.11 DSC thermogram of NP9, from 30 to 300 °C (10 °C min^{-1}, aluminium crucible).

All the βNCTCDs containing TEG segments showed similar thermal stabilities, with a decomposition peak centred at ~200 °C (Figure 5.12).
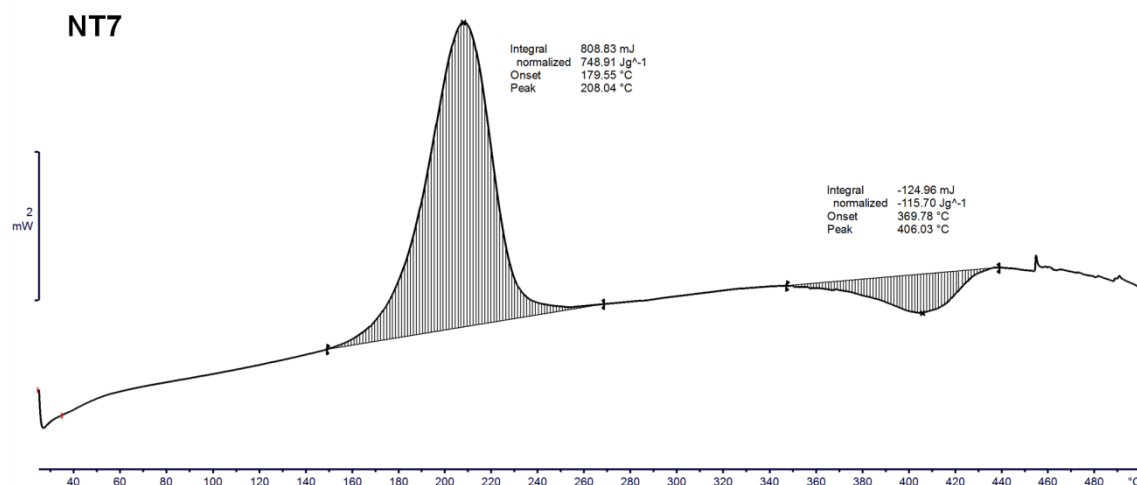
Figure 5.12 DSC thermogram of NT7, from 30 to 500 °C (10 °C min^{-1}, aluminium crucible).

The energy associated with the decomposition of NT5–NT14 was always in the range 430–810 J g^{-1} regardless of the nitration conditions (Table 5.2) and the thermal profiles were quite similar when characterised by DSC. The decomposition energy was low compared to the values for NC (~2000 J g^{-1}

when measured under the same conditions [28]), indicating a low degree of nitration in the samples. The residue began to char at 370 °C.

Table 5.2 Thermal properties of the energetic derivatives of gel-like insoluble βCPCDs and insoluble βCTCD powders.

| Sample ID | Inert Precursor | | Product | | | |
| | ID | Cross-linker: βCD feed ratio[1] | T_{dec} (°C) | | ΔH_{dec} (J g^{-1}) | T_g (°C) |
			Onset	Peak		
NP7	IP26	9:1	100	108	690	-
NP8	IP26	9:1	129	135, 139[2]	1400	-
NP9	IP26	9:1	174	203	1132	-8
NP10	IP26	9:1	181	208	460	-8
NP11	IP26	9:1	109	208	460	-28
NT5	IT5	9:1	183	210	530	-24
NT6	IT5	9:1	183	208	650	-19
NT7[3]	IT5	9:1	179	208	760	-19
NT8[3]	IT5	9:1	179	208	810	-18
NT9[3]	IT5	9:1	179	208	760	-22
NT10[3]	IT6	3:1	182	209	430	-22
NT11[3]	IT7	6:1	175	206	570	-22
NT12[3]	IT5	9:1	175	208	590	-21
NT13	IT6	3:1	181	208	570	-22
NT14	IT7	6:1	176	207	510	-21
NT15	IT5	9:1	183	210	530	-24

1 Double spiked decomposition.
2 Compounds are insoluble. The cross-linker:βCD feed ratio is reported.
3 Nitration time = 2 h.

The low-temperature characterisation of the compounds was achieved by cycling the temperature from −100 to 100 °C three times. The βNCXCDs derived from insoluble precursors appeared to be hygroscopic, retaining water in their structures. This affected the T_g of the product which fell to −26 °C

(Figure 5.13). By heating the sample, the water evaporated allowing the real T_g to be determined in the second heating cycle, revealing a value of –22 °C. The transition at 80 °C attributed to the βCD units in βNCXCDs was also recorded in several nitrated samples (Figure 5.10).
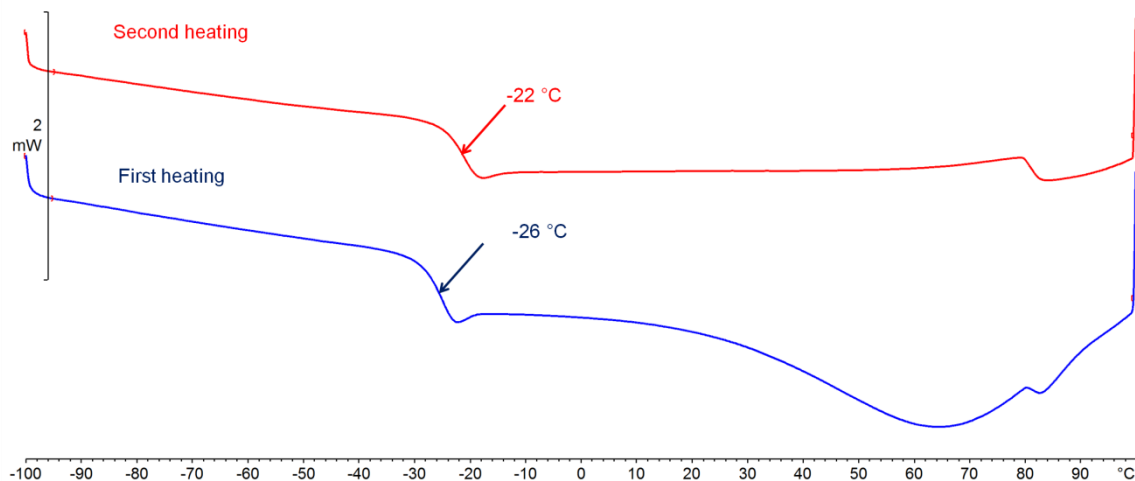
Figure 5.13 DSC thermogram of NT9 from –100 to 100 °C (10 °C min⁻¹, third temperature cycle, aluminium crucible).

In conclusion, the nitration of insoluble precursors generated sparsely nitrated products. It was not possible to control the degree of nitration and thus the thermal properties of the βNCXCDs so these products were not considered in the subsequent experiments.

5.4.2 Thermal characterisation of βNCXCDs prepared from soluble precursors

The βNCXCDs prepared from water-soluble βCXCDs were soluble in organic solvents such as acetone and THF. The thermal properties were duly investigated by DSC and TGA, and the nitrogen content was determined by titration (Table 5.3).

Table 5.3 Thermal properties of βNCXCDs prepared from water-soluble βCXCDs.

Sample	Inert precursor		Nitrated product					
ID	XEG:βCD ratio	T_g (°C)	T_{dec} (°C)		ΔH_{dec} (J.g^{-1})	Nitrogen content %	Ω (%)	T_g (°C)
			Onset	Peak				
βNCD	-	-	193	207	1990	11.6	-40	-
NT1	3.6	-[1]	180	196	2080	8.2	-81	-[1]
NT2	3.2	-[1]	180	203	1430	9.4	-71	-[1]
NT3	2.5	-[1]	179	200	1690	9.3	-69	-[1]
NT4	1.6	-	176	198	1850	6.2	-87	-
NH1	4	-10	179	191	1750	8.2	-87	+6
NH2	3.2	-6	174	198	1730	7.1	-93	+26
NH3	2.6	-[1]	178	199	1720	9.0	-76	+47
NH4	1.8	-[1]	174	196	1720	9.4	-70	+65
NP1	4.0	-20	176	198	1750	6.2	-109	-14
NP5	3.7	-19	178	190	1800	6.2	-101	+7
NP6	3.7	-19	175	190	1540	6.6	-105	+7
NP2	2.8	-6	172	196	1840	6.8	-97	+31
NP3	2.5	+5	174	197	1630	7.0	-94	+23
NP4	1.6	-	174	193	1730	8.7	-76	+45

1 Change in heat flow due to the softening of the compound.

The offsets for βNCXCD decomposition fell within the range 172–193 °C (Table 5.3) whereas the degradation peaks were in the range 190–203 °C and were comparable to those of the corresponding products obtained from insoluble βCXCD precursors in water and also to NC (201–205 °C) [28]. The ΔH_{dec} values were 1360–2080 J g^{-1}, lower than the 2200–1800 J g^{-1} released by the less fuel-rich NC [28]. Some general observations were made for the three sets of βNCXCDs and are reported below.

For samples NT1–NT4 containing TEG units, the decomposition temperatures were very close to 200 °C regardless of the TEG content whereas the decomposition enthalpies fell within the range 1430–2080 J g^{-1}. No glass transition was observed, confirming that the length of TEG units was insufficient to make the βNCTCD products soft and rubbery.

For samples NH1–NH4 containing HEG units, the decomposition temperatures were variable (191–199 °C) whereas the decomposition enthalpies were stable at 1700 J g^{-1}. A glass transition occurred between 6 and 65 °C confirming that the length of the HEG units was sufficient to influence the thermo-mechanical properties of the βNCHCD products.

For samples NP1–NP6 containing PEG units, the decomposition temperatures were again variable (190–197 °C) and the decomposition enthalpies varied in the range 1360–1840 J g^{-1}. A glass transition occurred between 7 and 45 °C confirming that the length of PEG units was also sufficient to influence the thermo-mechanical properties of the βNCPCD products. Exceptionally, NP1 was found to undergo a glass transition at −14°C.

Finally, the T_g of the βNCXCDs appeared to be linearly dependant on the HEG/PEG content, as shown in Figure 5.16.

NP1

Integral	1629.98 mJ
normalized	1752.67 Jg^-1
Onset	175.91 °C
Peak	198.40 °C
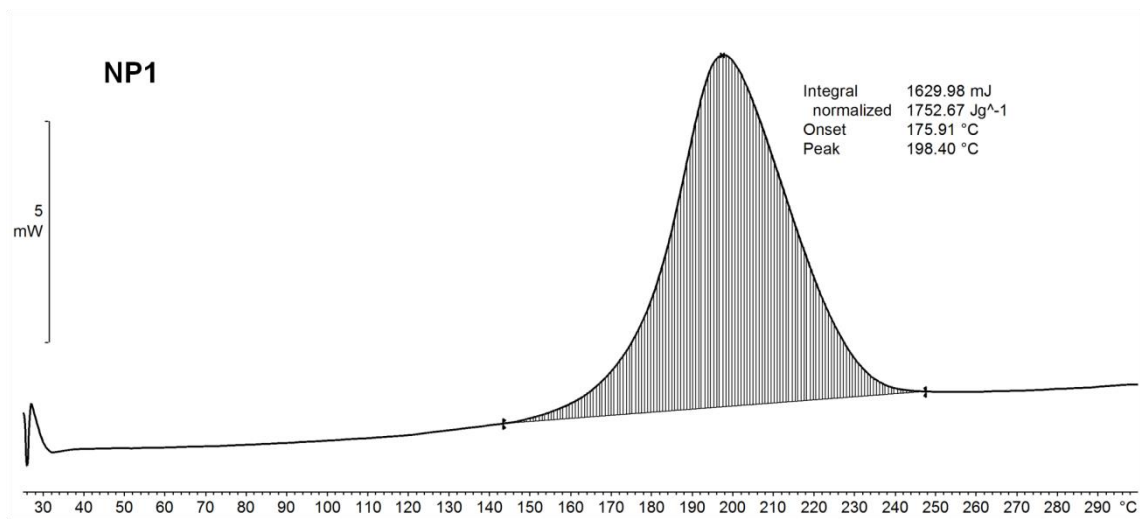
Figure 5.14 DSC thermogram of NP1 from 25 to 300 °C (10 °C min^{-1}, aluminium crucible).

The T_g of the βNCXCDs was 20–30 °C higher than that of the precursors (Table 5.3). The presence of hydrogen bonds increases the T_g [136]. The replacement of hydroxyl groups with nitrato groups in the βNCXCDs should reduce the number of hydrogen bonds but the T_g nevertheless increased. One potential explanation is that the nitrato groups expanded the polar surface area of the compounds, therefore increasing their cohesive energy and limiting chain mobility to an even greater extent than hydrogen bonds [137]. The cohesive energy is the increase in internal energy when all intermolecular forces are eliminated [137]. The trend in T_g values could be evaluated by Hildebrand or Hansen solubility parameter modelling to assess the effect of hydroxyl and nitrato groups on the cohesive energy of the βNCXCDs [138].
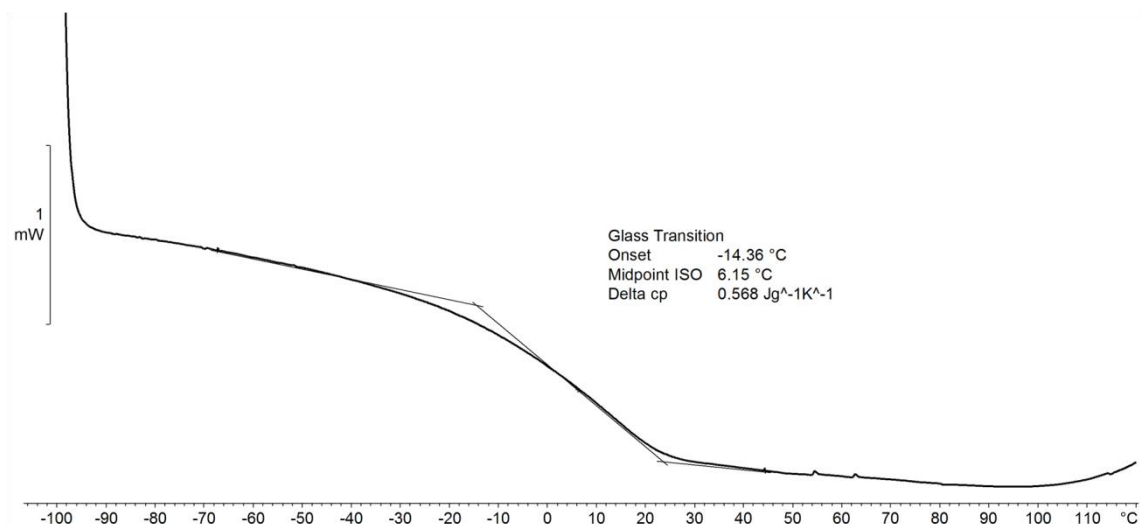
Figure 5.15 DSC thermogram of NP1 from –100 to 100 °C showing the pronounced glass transition of the highly cross-linked products (10 °C min^{-1}, aluminium crucible).

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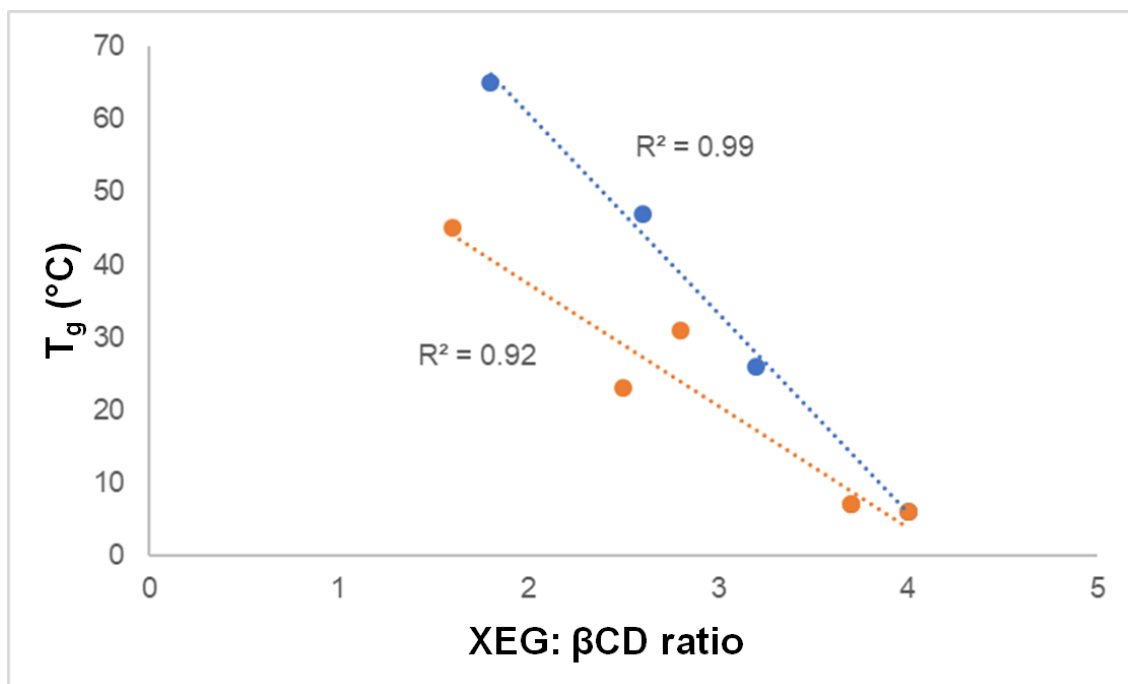
Figure 5.16 Plot of T_g against XEG:βCD ratio for βCHCDs (blue line) and βCPCDs (orange line).

The nitrogen content of the βNCXCDs was determined by titration as discussed above and was found to be inversely proportional to the length of the PEG segment. The βNCPCDs contained less nitrogen (6.5%) than the βNCTCDs and βNCHCDs (8–9%). The longer polyethylene glycol chains reduced the nitrogen content because the spacer increases the proportion of C, H and O relative to N. Furthermore, the βCPCDs are less soluble than the analogous molecules synthesised with the HEGDGE and TEGDGE cross-linkers, reducing the efficiency of the nitration reaction.

The nitrogen content of the βNCXCDs was needed to determine the chemical formula of each compound and thus its contribution to the combustion of energetic formulations. The difference between inert and energetic binders is the contribution to the overall energetic output of the formulation. The power of an explosive is proportional to the amount of molecular oxygen it contains, which determines the gaseous products produced during detonation. This is expressed as the oxygen balance (Ω), as shown in Equation 5:

$$\Omega = \frac{\left(d - 2a - \frac{b}{2}\right) x\ 1600}{Mw}\ \% \qquad \textbf{(5)}$$

where d is the number of oxygen atoms in the compound, a is the number of carbon atoms, b is the number of hydrogen atoms and Mw is the molecular weight of the compound.

Equation 5 indicates the ability of the compound to produce gaseous products and release energy as heat [2]. Positive Ω values correspond to the complete oxidation of the compounds in the formulation and the production of large quantities of gases such as CO_2 and hence more energy, whereas negative Ω values indicate the compound is deficient in oxygen, does not achieve complete oxidation, and that there is a higher yield of gases such as CO and solid residues rich in carbon, and hence less energy.

The Ω values for all βNCXCDs were negative due to the high proportion of carbon compared to oxygen. Furthermore, the Ω value of βNCD is –40%, which is identical to NC with a nitrogen content of 11.6%. The XEG units in the βNCXCDs reduced Ω even further, yielding values of –69% to –109%.

5.4.3 Thermo-mechanical characterisation of βNCXCDs

Due to the energetic properties of βNCXCDs, only one sample containing PEG units (NP1) was characterised by DMA. Preliminary small-scale hazard tests were completed before the characterisation and sample NP1 was declared safe for testing under the induced stresses generated by the DMA measurement conditions. NP1 was not susceptible to ignition during the impact and friction mallet tests as described in Chapter 6. The T_g of NP1 was similar to that of its precursor IP18, with an onset at 15 °C and a tanδ peak at 25 °C (Figure 5.17). The nitrated derivative interacted strongly with the support, just like its precursors (Section 4.3.2.2) and accordingly, cracking was observed at –51 °C during the cooling cycle at the onset of E′.
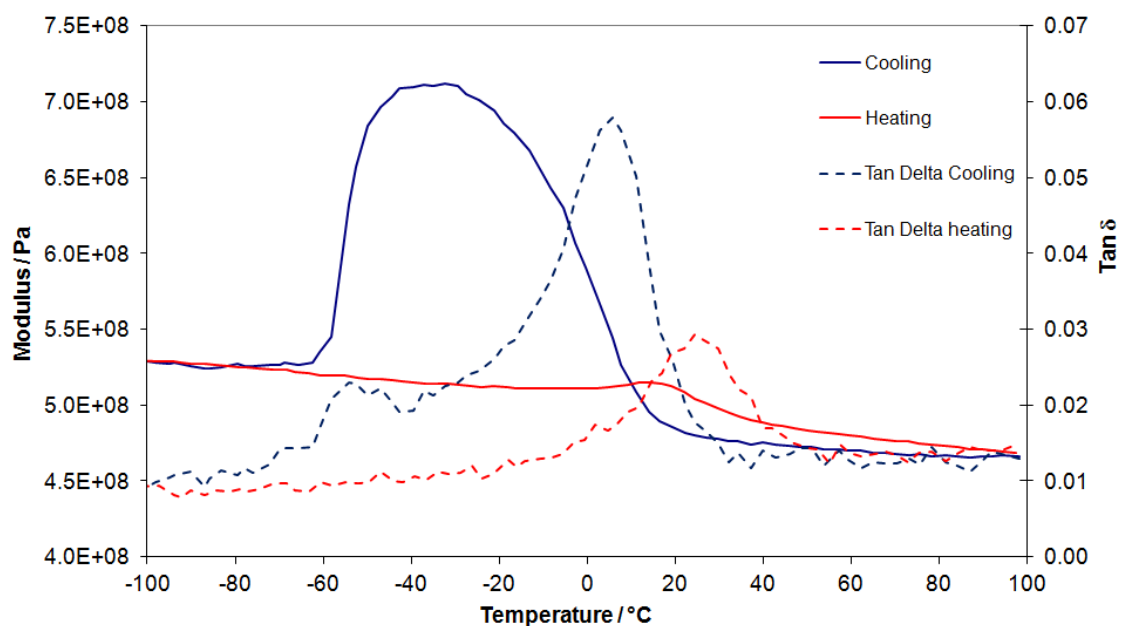
Figure 5.17 DMA showing variation in the storage modulus (E′, solid lines) and tanδ (dashed lines) of NP1 (10 °C min^{-1}, 1 Hz, third temperature cycle from –100 to 140 °C, aluminium pocket).

5.4.4 Qualitative analysis of the self-healing properties of βNCPCD34

The self-healing ability of NP1 was qualitatively visible, as for the inert βCPCDs (Chapter 4). NP1 was assessed by first cutting the sample (Figure 5.18a,b) and then re-joining the parts by leaving it at rest for 4 h (Figure 5.18c). The sample was then pulled gently by its extremities, showing a high degree of elongation (Figure 5.18d).
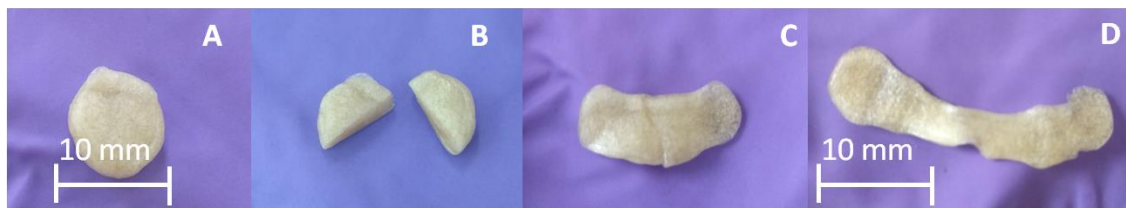
Figure 5.18 Self-healing ability of NP1 (PEG:βCD ratio = 4:1).

These experiments showed that the loss of some hydrogen bonds due to the replacement of hydroxyl groups with nitrato groups did not inhibit the mobility of the polymer chains in NP1 and did not eliminate its thermal healability. The healing of NP1 was driven by supramolecular interactions, such as hydrogen bonds and Van der Walls forces, as was the case for its precursor. The higher mobility of the dangling PEG chains accelerated the self-healing of these compounds.

5.5 Conclusions

The results presented in this chapter provide key data required for the nitration of βCXCDs, which are produced from βCD and diglycidyl ethers such as TEGDGE, HEGDGE and PEGDGE, and thus for the preparation of βNCXCDs as new energetic binders. The nitration reaction with fuming nitric acid led to two sets of βNCXCDs differing in terms of their solubility in water and other organic solvents, and their properties were strongly dependent on the physicochemical characteristics of the βCXCD precursors.

Insoluble βCXCD systems yielded cross-linked derivatives with various degrees of nitration that were insoluble in acetone, whereas water-soluble βCXCD precursors produced βNCXCDs that were soluble in acetone and easy to

characterise and process. The degree of nitration in these products was not only dependent on the properties of the precursor, but also the duration of the nitration reaction and the XEG:βCD ratio of the products. Better control of the properties of the βNCXCD products was achieved when soluble βCXCD precursors were used, and the workup was simpler compared to the insoluble precursors. A purification method based on the NC manufacturing process removed acid traces from the nitration reaction more efficiently, stabilising the compound during storage.

All of the synthesised products were characterised by ^{1}H-NMR and FTIR spectroscopy to confirm their effective nitration. No significant differences in the degree of nitration were observed for systems containing variable quantities of the linkers TEG, HEG and PEG. The nitrogen content of the βNCXCDs was determined by the titration of free hydroxyl groups in the molecules and was dependent on the degree of cross-linking and the length of the polyethylene glycol chains in the βNCXCDs. A lower degree of nitration was observed in derivatives containing PEG segments compared to those containing TEG or HEG segments due to the lower solubility of the βCPCD precursors in the nitration media.

The thermal stability of the βNCXCDs (T_{dec} = 190–200 °C) was independent of the degree of cross-linking and type of linker segment in the macromolecule, whereas ΔH_{dec} was influenced by the type of linker segment and ranged from 1300 to 2100 J g^{-1}. The βNCXCDs retained much of the softness of their βCXCD precursors, with T_g values in the range 6–65 °C. The analysis of one βNCPCD sample showed that it retained the self-healing characteristics of its precursor after 4 h at room temperature.

6 Compatibility, hazard and stability studies

It is expected that the main constituents of munitions, such as explosives, oxidisers and pyrotechnic fillers, would be less susceptible to external stimuli when embedded in a βCD binder, making the formulation safer and easier to handle. Compatibility, hazard and stability testing help to ensure the safety of an energetic formulation during manufacturing and storage. Compatibility tests determine whether materials such as binders, plasticisers and other additives in energetic formulations have an adverse effect on stability when in contact with each other. The tests check for chemical compatibility between the constituents of a formulation and with the tools used during manufacturing and storage. The effect of ageing on the stability of the materials is determined by accelerated ageing at high temperatures. Hazard tests offer a comprehensive understanding of the sensitiveness of formulations and their components against thermal, mechanical and electrostatic stimuli, and help with the development of guidelines for safe manufacturing, storage, transport and use.

This chapter discusses the compatibility, hazard and stability testing of the inert βCXCDs and nitrated βNCPXCDs developed in Chapters 4 and 5, according to NATO STANAG 4147 Test 4 S [121] and EMTAP guidelines [119]. Any changes in the shape, onset, or peak position of any thermal event may be indicative of incompatibility.

6.1 Compatibility tests – βCXCDs

A set of preliminary compatibility tests was carried out by mixing sample IP19 (an inert βCPCD with a PEG:βCD ratio of 4:1) with a set of inert, oxidising and energetic materials following the procedure described in Chapter 3. The decomposition temperatures of the pure compounds and 50:50 w/w mixtures were determined by DSC, and the results are summarised in Table 6.1. All DSC tests for compatibility were carried out with a heating rate of 2 °C min^{-1} rather than the 10 °C min^{-1} used to record the thermal properties in Chapters 4 and 5. The differences in thermal behaviour between the pure compounds and mixtures were taken as indications of compatibility/incompatibility as per

STANAG 4147 (Ed.2) Test 4 (see Section 3.3.6). Specifically, shifts of less than 4 °C generally indicate compatibility, shifts of more than 20 °C generally indicate incompatibility, and values between are inconclusive and warrant further testing.

Table 6.1 Compatibility of inert βCPCD (sample IP19, PEG:βCD ratio = 4.0:1) with various energetics.

Formulation	T_{dec} (°C)		ΔT (°C)	Shape change
	Energetic	Mixture		
IP19/HMX	279	279	0	Significant
IP19/RDX	226	212	−14	Significant
IP19/PETN	185	184	−1	Minor
IP19/ADN	172	149	−23	Significant
IP19/KClO$_3$	-[1]	-[1]	0	None
IP19/KNO$_3$	-[1]	-[1]	0	None
IP19/NH$_4$ClO$_4$	264	260	−4	Minor
IP19/NH$_4$NO$_3$	-[1]	188	0	Significant
IP19/RedP	400/492	404/471	+4/−11	Significant

1 No decomposition

Pure HMX decomposed at 279 °C (Figure 6.1) and there was no shift in the position of the decomposition peak when mixed with IP19. However, the shape and onset of the decomposition curve changed slightly in the mixture, with a broader degradation ramp starting at 10 °C, which is earlier than pure HMX. Further evaluation of the compatibility is therefore required according to NATO STANAG recommendations.
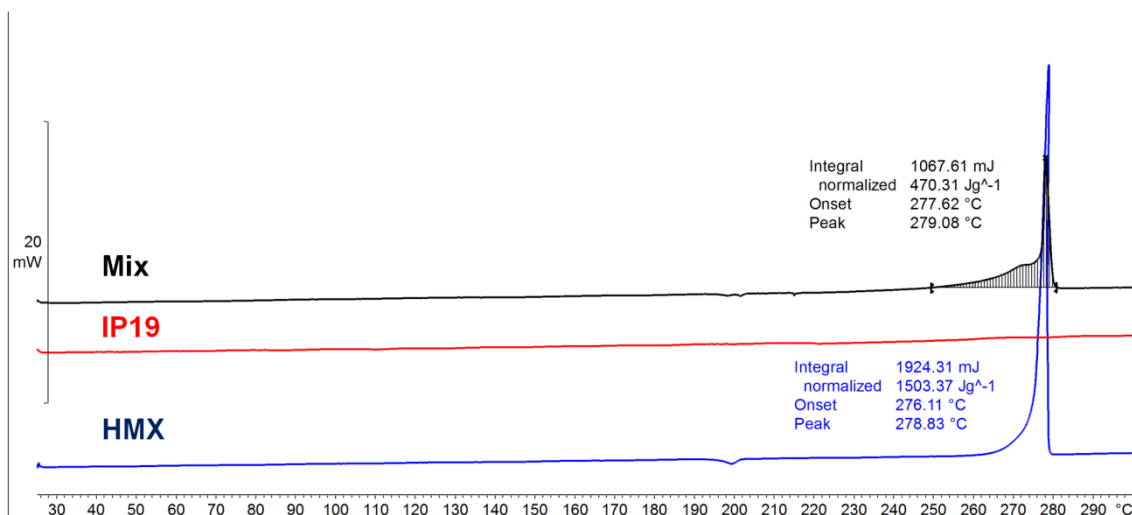
Figure 6.1 DSC thermogram of HMX (blue line), IP19 (red line), and a 50/50 (w/w) mixture (black line) from 30 to 300 °C (1 mg, 2 °C min^{-1}, aluminium crucible).

Pure RDX melted at 204 °C before decomposing at 226 °C (Figure 6.2, blue curve) whereas the mixture with IP19 decomposed directly at 212 °C with a lower onset of decomposition at 30 °C (Figure 6.1, black curve). The 14 °C shift in the decomposition temperature between pure RDX and the RDX/IP19 mixture suggests a degree of incompatibility and further investigation is needed. There was a significant difference in compatibility between the IP19 formulations with RDX and HMX, which may reflect the relative size of the two nitramines. RDX is the smallest (4–5 Å) and can be partially encapsulated by the βCD cavity (6–6.5 Å), which translates to the small hump in the degradation curve. In contrast, HMX remains free due to its larger size (5–8 Å). The βCD-based binder was therefore anticipated to encapsulate energetic fillers but no direct chemical reaction was expected.

Figure 6.2 DSC thermogram of RDX (blue line), IP19 (red line), and a 50/50 (w/w) mixture (black line) from 30 to 300 °C (1 mg, 2 °C min^{-1}, aluminium crucible).

Pentaerythritol tetranitrate (PETN) melted at 142 °C and decomposed at 185 °C (Figure 6.3, blue curve) and these properties were not affected by mixing with IP19 (Figure 6.3, black curve). The energy of the mixture increased, suggesting that the binder had a synergistic effect on the energy output of the system during decomposition.

Figure 6.3 DSC thermogram of PETN (blue line), IP19 (red line), and a 50/50 (w/w) mixture (black line) from 30 to 300 °C (1 mg, 2 °C min^{-1}, aluminium crucible).

Neat ammonium dinitramide oxidiser (ADN) melted at 93 °C (Figure 6.4, blue curve), and this did not change in the mixture with IP19 (Figure 6.4, black curve). ADN decomposed at 172 °C, but the mixture showed a biphasic decomposition curve with major peaks at 149 and 172 °C. This indicated a degree of incompatibility between the two compounds, perhaps reflecting the encapsulation of some of the ADN molecules within the βCD cavity, as proposed for RDX.
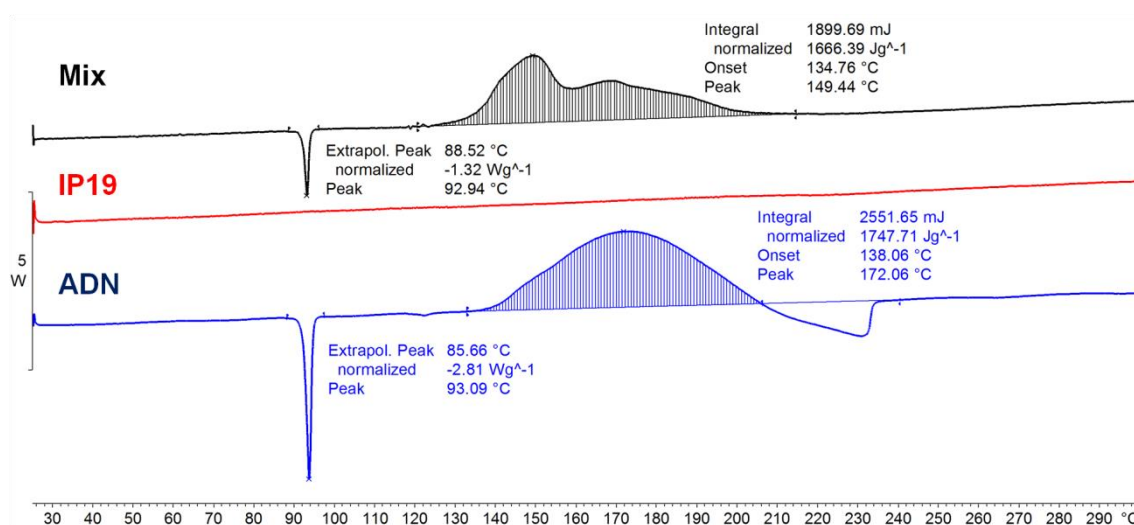
Figure 6.4 DSC thermogram of ADN (blue line), IP19 (red line), and a 50/50 (w/w) mixture (black line) from 30 to 300 °C (1 mg, 2 °C min^{-1}, aluminium crucible).

$KClO_3$ showed no exothermic peaks below 400 °C with a small endotherm visible at 303 °C (Figure 6.5, blue curve), possibly due to the compound melting. The mixture with IP19 exhibited the same endotherm and a tiny additional endotherm at 214 °C, suggesting good compatibility between these components (Figure 6.5, black curve).
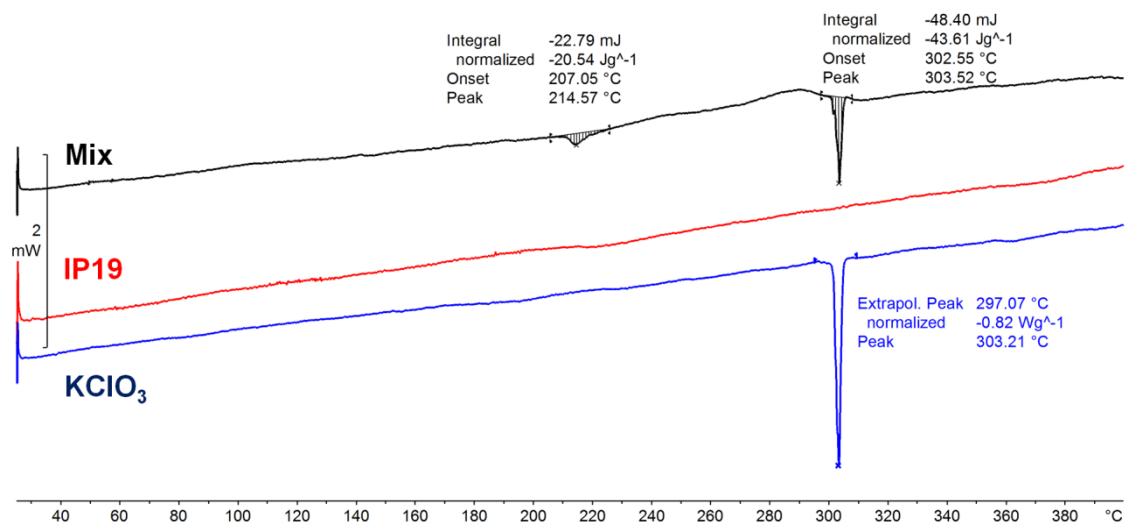
Figure 6.5 DSC thermogram of $KClO_3$ (blue line), IP19 (red line), and a 50/50 (w/w) mixture (black line) from 30 to 400 °C (1 mg, 2 °C min^{-1}, aluminium crucible).

KNO_3 melted at 335 °C (Figure 6.6, blue curve) and no changes were observed in the mixture with IP19 (Figure 6.6, black curve). These components were therefore considered to be compatible.
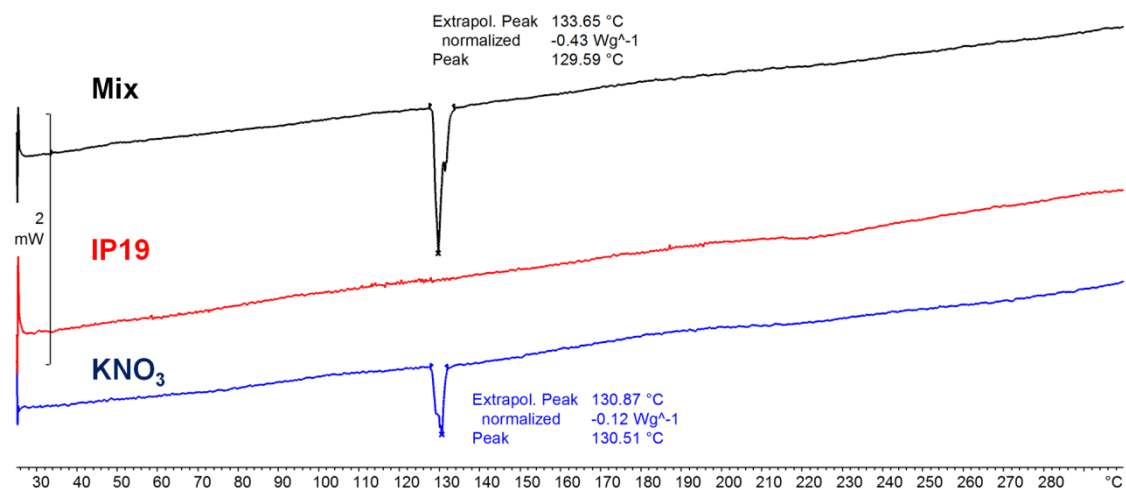
Figure 6.6 DSC thermogram of KNO_3 (blue line), IP19 (red line), and a 50/50 (w/w) mixture (black line) from 30 to 300 °C (1 mg, 2 °C min^{-1}, aluminium crucible).

The thermal profile of pure NH_4ClO_4 showed a melting point at 242 °C and decomposition at 264 °C (Figure 6.7, blue curve). These values were unchanged in the mixture with IP19 (Figure 6.7, black curve). Decomposition involved a principal event followed by two minor exothermic peaks. These results indicated that the two components were compatible.
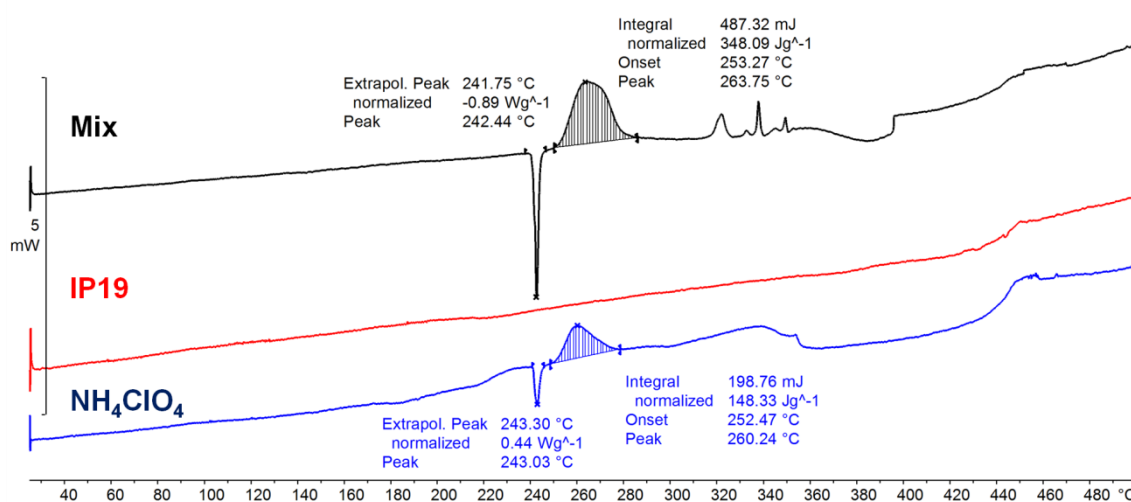
Figure 6.7 DSC thermogram of NH_4ClO_4 (blue line), IP19 (red line), and a 50/50 (w/w) mixture (black line) from 30 to 500 °C (1 mg, 2 °C min^{-1}, aluminium crucible).

Pure NH_4NO_3 showed a broad endotherm above ~200 °C caused by the volatile compound evaporating after melting (Figure 6.8, blue curve). When mixed with IP19, one endotherm became an exotherm with a peak at 188 °C (Figure 6.8, black curve), possibly indicating chemical reactivity between molten ammonium nitrate and the binder. This indicates the two ingredients are likely to be incompatible.
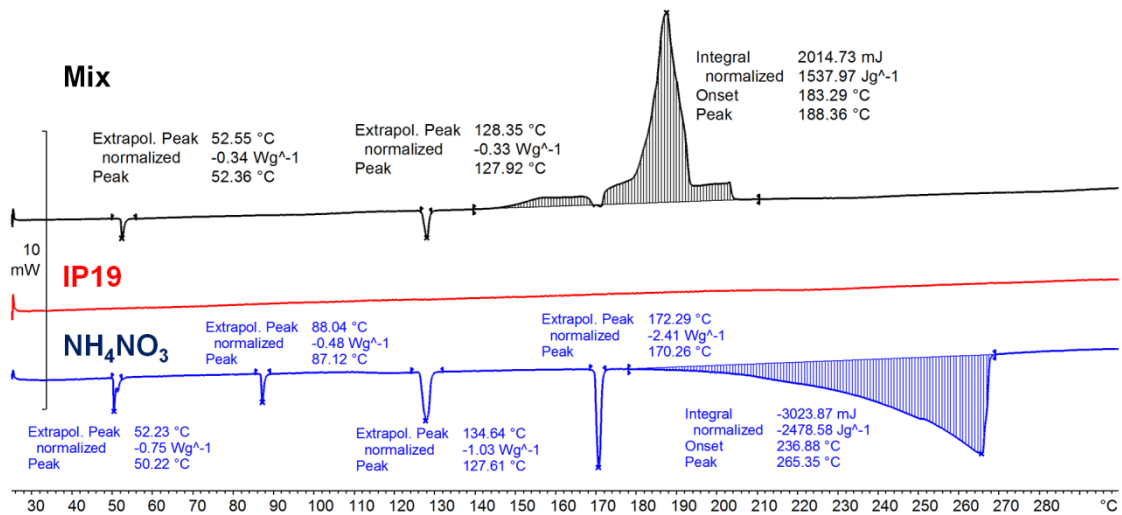
Figure 6.8 DSC thermogram of NH_4NO_3 (blue line), IP19 (red line), and a 50/50 (w/w) mixture (black line) from 30 to 300 °C (1 mg, 2 °C min^{-1}, aluminium crucible).

Two decompositions were observed for pure red phosphorous (RedP) at 400 and 492 °C (Figure 6.9, blue curve) but the mixture with IP19 showed a broader decomposition profile with maxima at 409 and 471 °C (Figure 6.9, black curve). Much more energy is released when RedP is mixed with the binder. The two ingredients could therefore be described as compatible, with reservations.
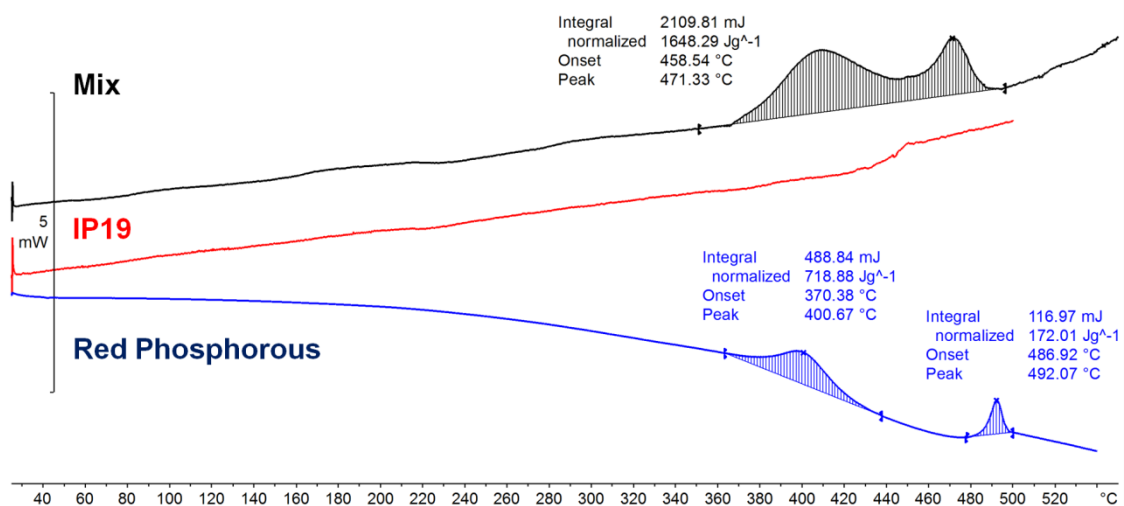
Figure 6.9 DSC thermogram of red phosphorus (blue line), IP19 (red line), and a 50/50 (w/w) mixture (black line) from 30 to 550 °C (1 mg, 2 °C min^{-1}, aluminium crucible).

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6.2 **Compatibility tests – βNCXCDs**

In the next set of compatibility tests, sample NP13 (a nitrated βNCPCD with a PEG:βCD ratio of 3.8:1) was mixed with a set of inert, oxidising and energetic materials and analysed by DSC to determine their compatibility in accordance with STANAG 4147 guidelines as described above for the inert precursor IP10. Like NC, the βNCXCDs are nitroesters and need to be mixed with stabilisers to ensure an adequate shelf life [139,140]. Therefore, the widely-used stabilisers diphenylamine (DPA) and N,N′-diethyl-N,N′-diphenylurea (Centralite) were also tested in the compatibility tests, as well as 2,4-nitrodiphenylamine (2,4-NDPA), which is an intermediate product of DPA. Due to the small-scale synthesis (200 mg) of the βNCXCD compounds, the compatibility tests with the stabilisers were conducted using a different sample (NP1), although this has the same chemical composition as NP13. The decomposition temperatures of the pure compounds and mixtures were determined by DSC, and the results are summarised in Table 6.2.

Table 6.2 Compatibility of nitrated βNCPCD (samples NP13 and NP1, PEG:βCD ratio = 3.8:1) with various energetics and stabilisers.

Formulation	$T_{dec}{}^2$ (°C)		ΔT (°C)	Shape change
	Energetic	Mixture		
NP13/NP11	186	-	-	-
HMX	279	278	−1	Significant
RDX	226	210	−13	Significant
PETN	185	187	+2	Minor
ADN	172	161	−11	significant
KClO3	-3	-3	0	none
KNO3	-3	1853	−13	minor
NH4ClO3	264	265	+1	minor
NH4NO3		1893	+34	Significant
RedP	400/492	404/481	+4/−11	minor

NP1	184	-	-	-
DPA		140^4	−44	
2,4-NDPA		190^4	+6	
Centralite		185^4	+1	

1 PEG:βCD ratio = 3.8:1

2 At 2 °C min^{-1}, N$_2$ atmosphere.

3 No decomposition.

4 Decomposition is related to the solely energetic binder.

The decomposition peaks of pure HMX at 279 °C (Figure 6.10, blue line) and the energetic binder NP13 at 186 °C (Figure 6.10, red line) were not affected when the two components were mixed (Figure 6.10, black line). As discussed for the inert precursor IP19, the onset of degradation remained the same, but a portion of the HMX started to degrade earlier, causing an initial step at 272 °C. This revealed a degree of incompatibility between NP13 and HMX that warrants further investigation.

Mix
Integral 960.19 mJ
normalized 711.25 Jg^-1
Onset 158.51 °C
Peak 185.12 °C

Integral 540.00 mJ
normalized 400.00 Jg^-1
Onset 277.24 °C
Peak 278.72 °C

NP13
Integral 1744.72 mJ
normalized 1586.11 Jg^-1
Onset 158.58 °C
Peak 185.98 °C

HMX
Integral 1911.04 mJ
normalized 1493.00 Jg^-1
Onset 276.11 °C
Peak 278.83 °C

20 Wg^-1

30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280 290 °C

Figure 6.10 DSC thermograms of HMX (blue line), NP13 (red line), and a 50/50 (w/w) mixture (black line) from 30 to 300 °C (1 mg, 2 °C min^{-1}, aluminium crucible).

Pure RDX melted at 204 °C before decomposition with a major peak at 226 °C (Figure 6.11, blue line). When mixed, RDX and NP13 decomposed in the same temperature range between 140 and 230 °C. The RDX decomposition moved from 226 to 210 °C, with the shift of −16°C suggesting a degree of incompatibility which needs investigation. In contrast, the NP13 was 5 °C more

stable when mixed with RDX, with its T_{dec} shifted from 186 to 191 °C. As for the inert binder, there was a noticeable difference between NP13 formulations containing RDX and HMX, which likewise can be attributed to the different sizes of the nitramines and resulting differences in their degree of encapsulation by the βCD units of the energetic binder.
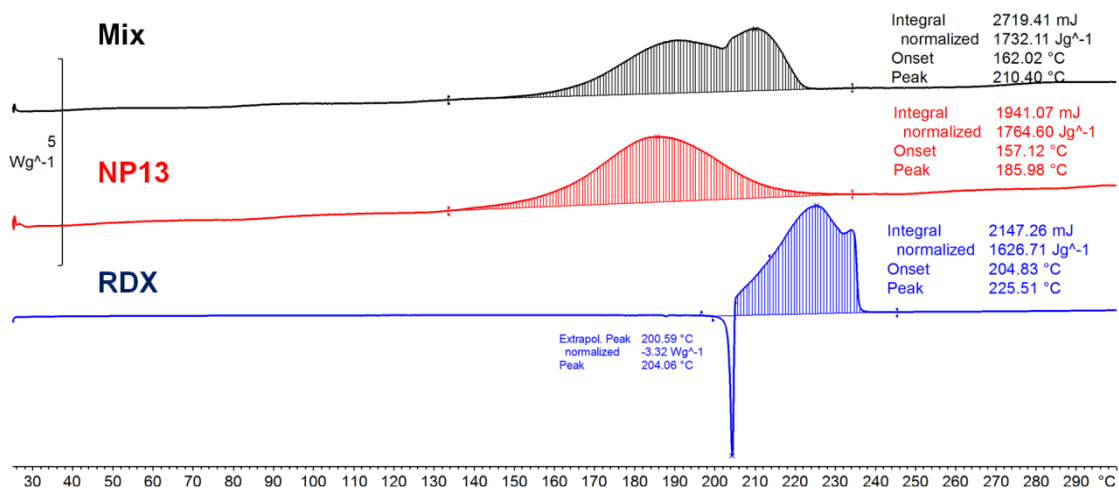
Figure 6.11 DSC thermograms of RDX (blue line), NP13 (red line), and a 50/50 (w/w) mixture (black line) from 30 to 300 °C (1 mg, 2 °C min^{-1}, aluminium crucible).

PETN and NP13 are both nitroesters containing nitrato groups and this is reflected in their very similar decomposition profiles (Figure 6.12, blue and red curves respectively). The melting of PETN at 141 °C was unchanged in the mixture. Furthermore, the mixture produced more energy than either of the components alone (Figure 6.12, black curve). The two components were therefore declared compatible.
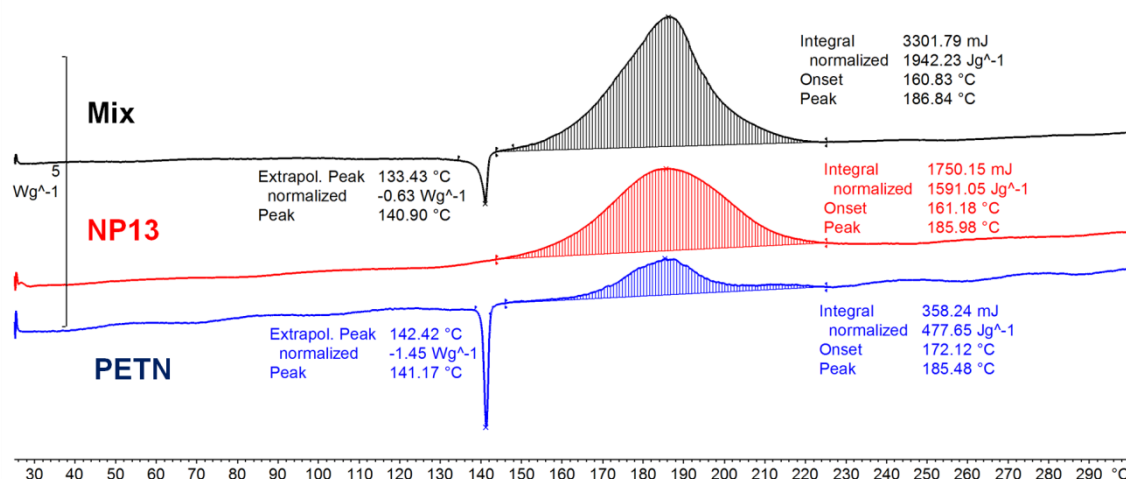
Figure 6.12 DSC thermograms of PETN (blue line), NP13 (red line), and a 50/50 (w/w) mixture (black line) from 30 to 300 °C (1 mg, 2 °C min^{-1}, aluminium crucible).

ADN melted at 93°C, a feature retained in the mixture with NP13 (Figure 6.13, blue and black curves). The ADN profile featured an exothermic decomposition with an onset at 137 °C and a peak at 172 °C, but in the mixture the onset shifted to 142 °C with a major peak at 161 °C, and a secondary peak at 157 °C matching the decomposition temperature of NP13 (Figure 6.13, red and black curves). The shape of the mixture's decomposition diverged from the profile of the pure compounds and became more indented, with a shift of +9 °C compared to ADN. This indicated a degree of incompatibility between the two components, and also suggested there was a ~20% increase in the amount of energy released by the mixture.
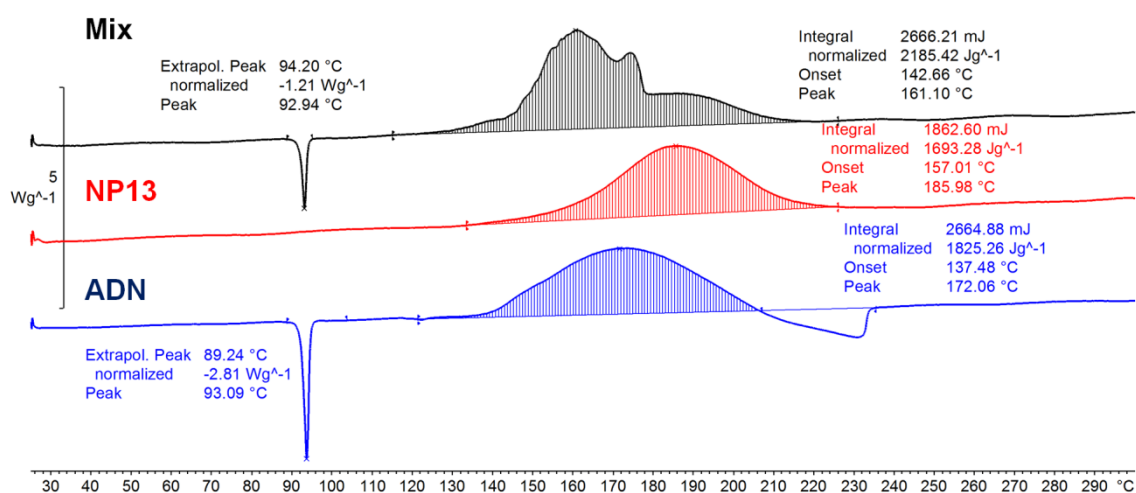
Figure 6.13 DSC thermograms of ADN (blue line), NP13 (red line), and a 50/50 (w/w) mixture (black line) from 30 to 300 °C (1 mg, 2 °C min⁻¹, aluminium crucible).

$KClO_3$ consistently melted at 303 °C (Figure 6.13, blue curve). The mixture displayed the same endotherm at 305 °C, as well as a shoulder in the very sharp exotherm (Figure 6.13, black curve). The data suggested these two compounds are highly compatible, as seen for the analogous experiments with IP19.
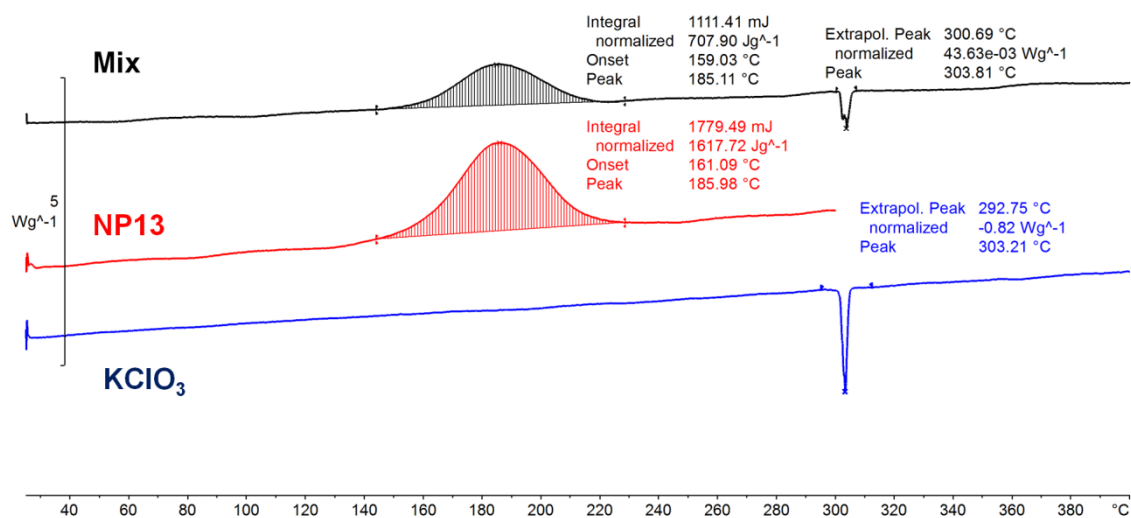
Figure 6.14 DSC thermograms of $KClO_3$ (blue line), NP13 (red line), and a 50/50 (w/w) mixture (black line) from 30 to 400 °C (1 mg, 2 °C min⁻¹, aluminium crucible).

KNO_3 showed no evidence of decomposition below 550 °C but melted at 335°C (Figure 6.15, blue curve). When the mixture was tested, there was no change in

the thermal profile (Figure 6.15, black curve). This indicated that the two components were compatible.
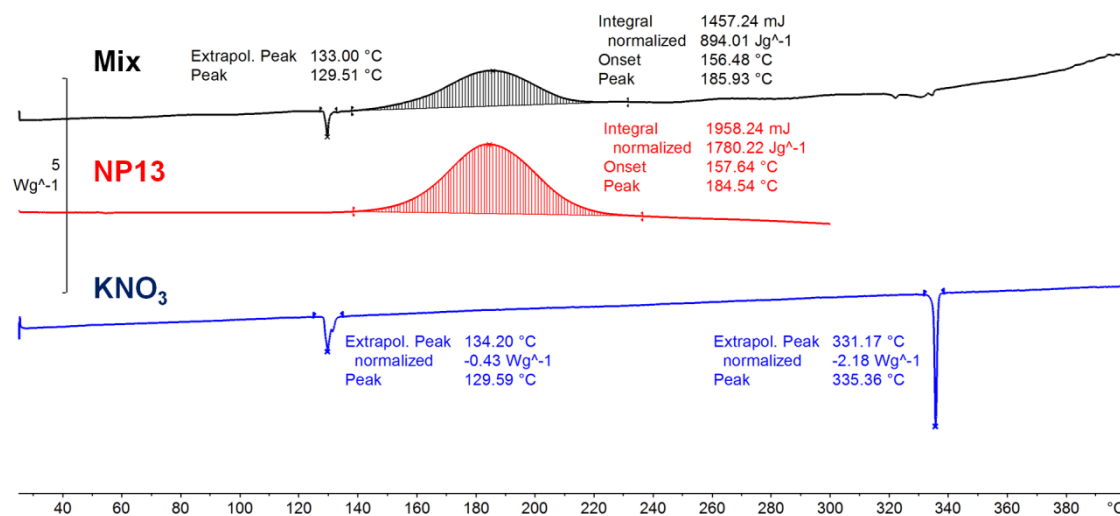
Figure 6.15 DSC thermograms of KNO_3 (blue line), NP13 (red line), and a 50/50 (w/w) mixture (black line) from 30 to 400 °C (1 mg, 2 °C min^{-1}, aluminium crucible).

NH_4ClO_4 melted at 242 °C and this property did not change in the mixture with NP13 (Figure 6.16, blue and black curves). The subsequent decomposition consisted of a main decomposition event at 264 °C followed by small exothermic peaks. The thermograms of the individual components and the mixture were comparable, suggesting the components were compatible.
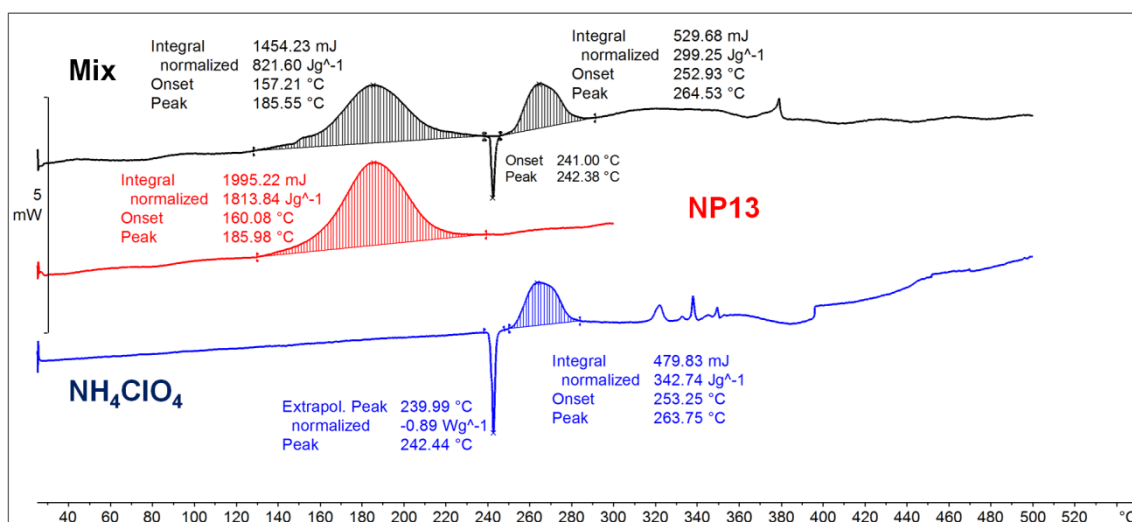
Figure 6.16 DSC thermograms of NH_4ClO_4 (blue line), NP13 (red line), and a 50/50 (w/w) mixture (black line) from 30 to 500 °C (1 mg, 2 °C min^{-1}, aluminium crucible).

NH$_4$NO$_3$ displayed an endothermic peak at 67 °C (Figure 6.15, blue curve) but this disappeared in the mixture (Figure 6.17, black curve). Furthermore, the endotherm at 265 °C (caused by the evaporation of NH$_4$NO$_3$) led to a strong exothermic event at 208 °C. This may have been caused by a reaction between the NH$_4$NO3 vapour and the binder NP13, indicating that the two components are likely to be incompatible.
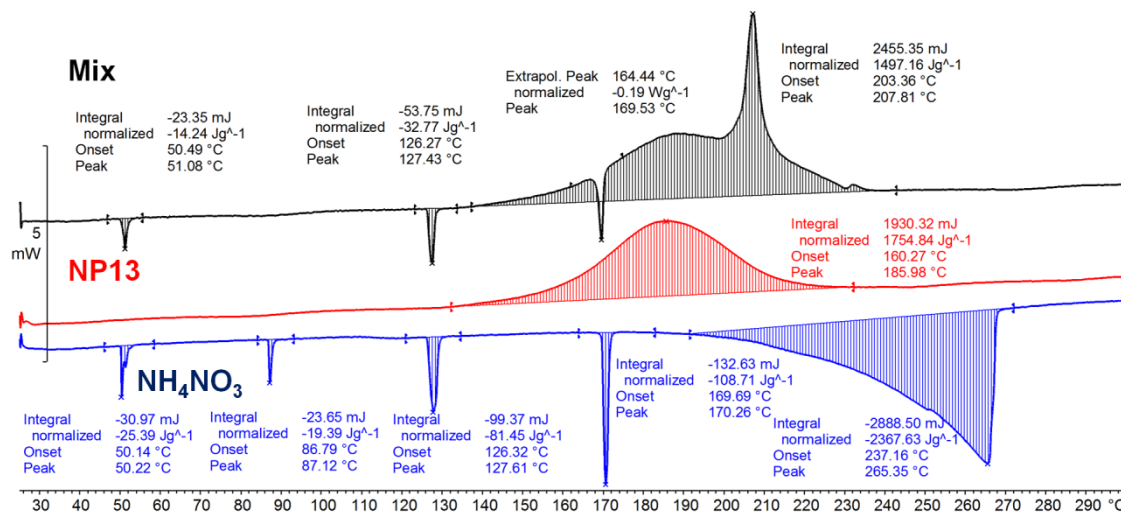
Figure 6.17 DSC thermograms of NH$_4$NO$_3$ (blue line), NP13 (red line), and a 50/50 (w/w) mixture (black line) from 30 to 300 °C (1 mg, 2 °C min^{-1}, aluminium crucible).

The decomposition of the mixture of RedP and NP13 differed very slightly from the individual components due to the drop in the baseline (Figure 6.18). The first RedP decomposition event shifted from 400 to 404 °C, whereas the second shifted from 492 to 481 °C. Despite the changes in the mixture, it is unlikely that any in-service munition containing these two components would reach such temperatures. Therefore, the components can be considered as compatible.
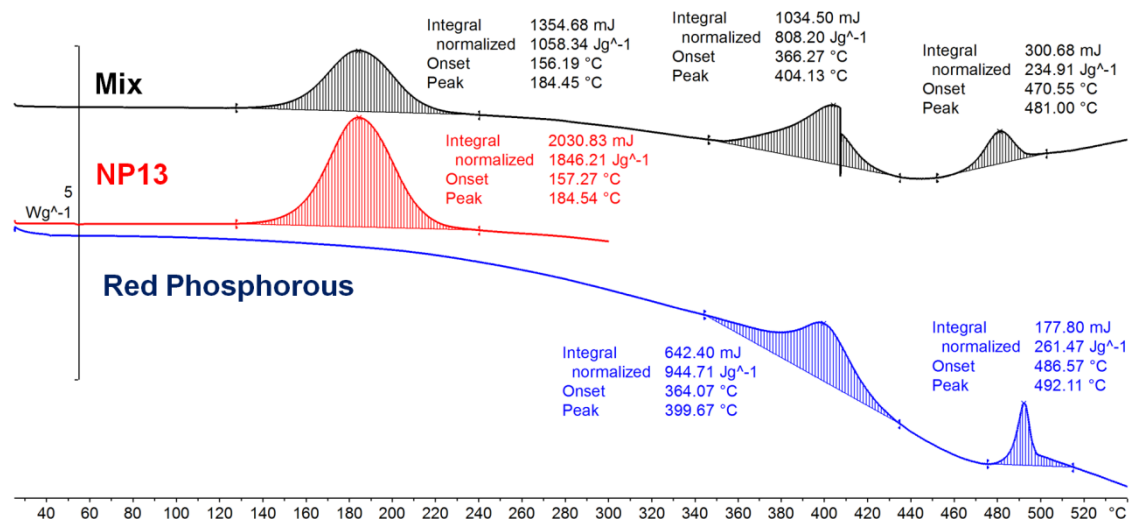
**Figure 6.18** DSC thermograms of RedP (blue line), NP13 (red line), and a 50/50 (w/w) mixture (black line) from 30 to 550 °C (1 mg, 2 °C min^{-1}, aluminium crucible).

The pure DPA stabiliser melted at 54 °C (Figure 6.19, blue curve) and this did not change in the mixture (Figure 6.19, black curve). Evaporation of the DPA from the pin hole in the crucible commenced as soon as the sample was heated above 100 °C due to the flow of nitrogen in the experiment. The development of vapours caused the early decomposition of NP1, from 157 to 130 °C. The DPA was not gassed away from the nitrogen purge when the crucible was sealed. The mixture was tested with sealed and unsealed vessels and the thermograms were identical, confirming that the evaporation of DPA causes NP1 to decompose at a lower temperature. This means that the DPA vapour does not stabilise NP1 but actually accelerates its decomposition.
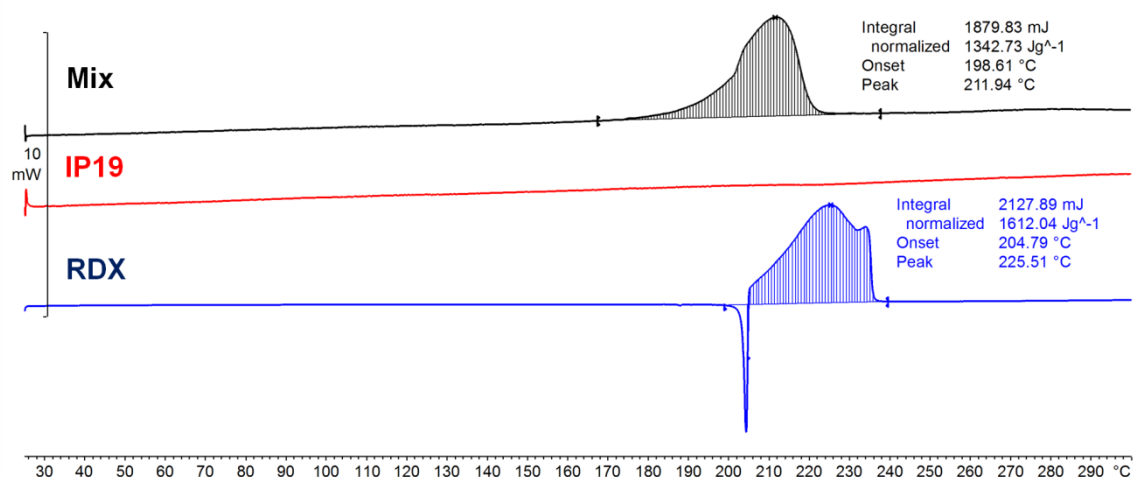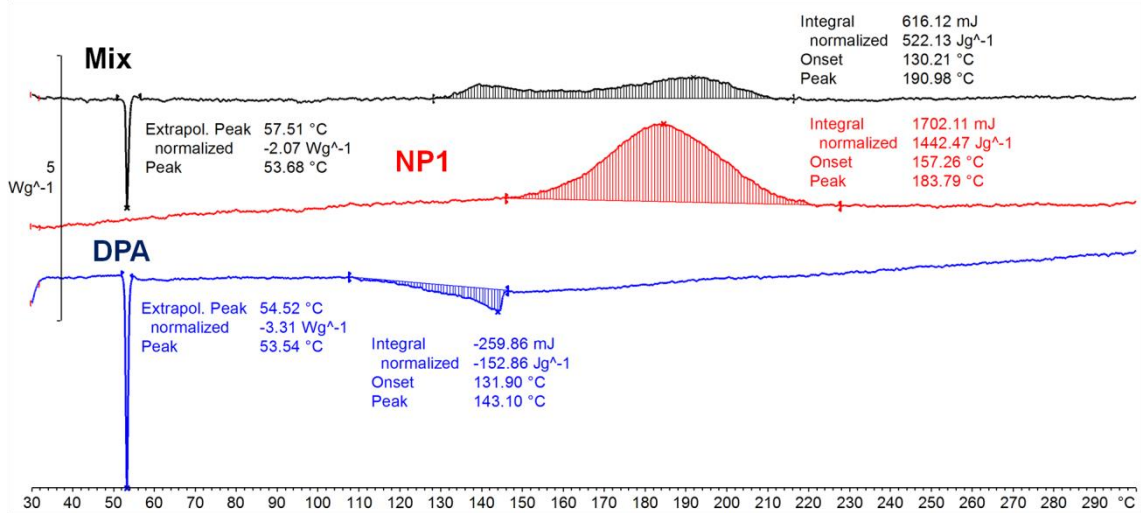
Figure 6.19 DSC thermograms of DPA (blue line), NP1 (red line), and a 50/50 (w/w) mixture (black line) from 30 to 300 °C (1 mg, 2 °C min⁻¹, aluminium crucible).

The 2,4-NDPA melted at 157 °C (Figure 6.20, blue curve) and the same melting peak was also present in the mixture (Figure 6.20, black curve). Unlike DPA, the 2,4-NDPA was found to stabilise NP1, shifting the degradation of the binder from 184 to 190 °C.
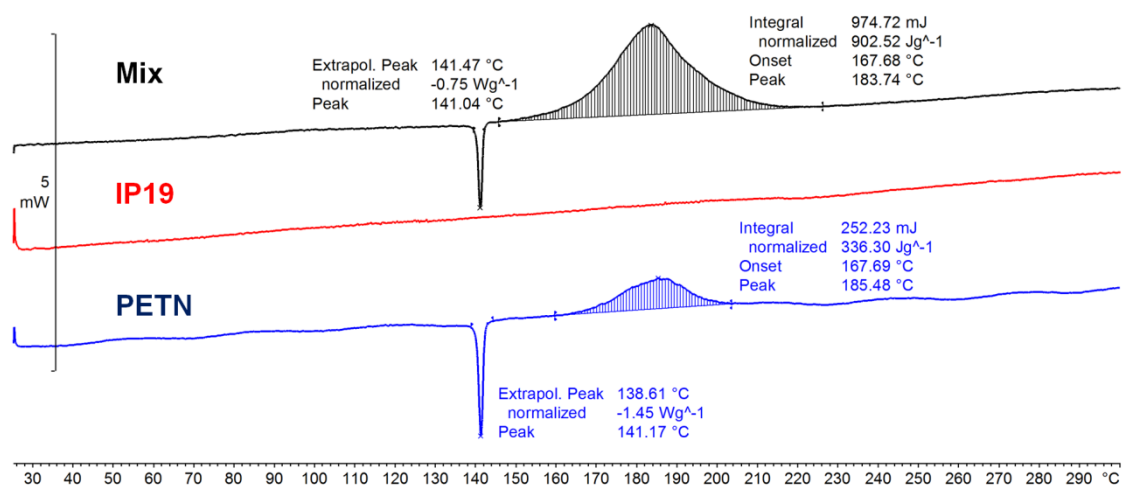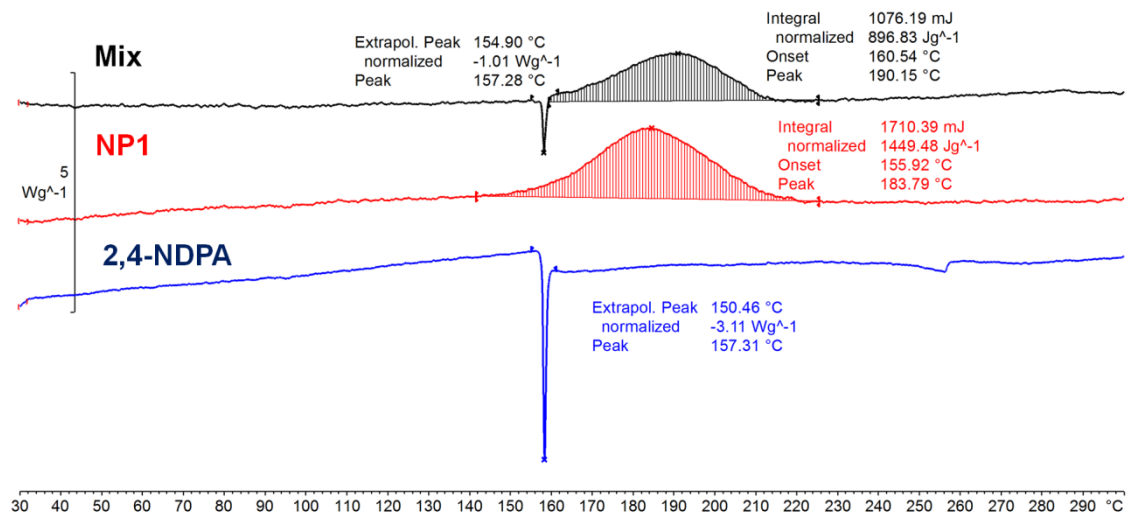

Figure 6.20 DSC thermograms of 2,4-NDPA (blue line), NP1 (red line), and a 50/50 (w/w) mixture (black line) from 30 to 300 °C (1 mg, 2 °C min⁻¹, aluminium crucible).

Centralite melted at 73 °C (Figure 6.21, blue curve) and this did not change when it was mixed with NP1 (Figure 6.21, black curve). Centralite also evaporated in the temperature range 130–154 °C, as observed above for DPA.

A second test with sealed crucibles showed no change in the thermogram of the mixture. Therefore, the degradation of the binder was not affected by the presence of Centralite, making it a suitable stabiliser.
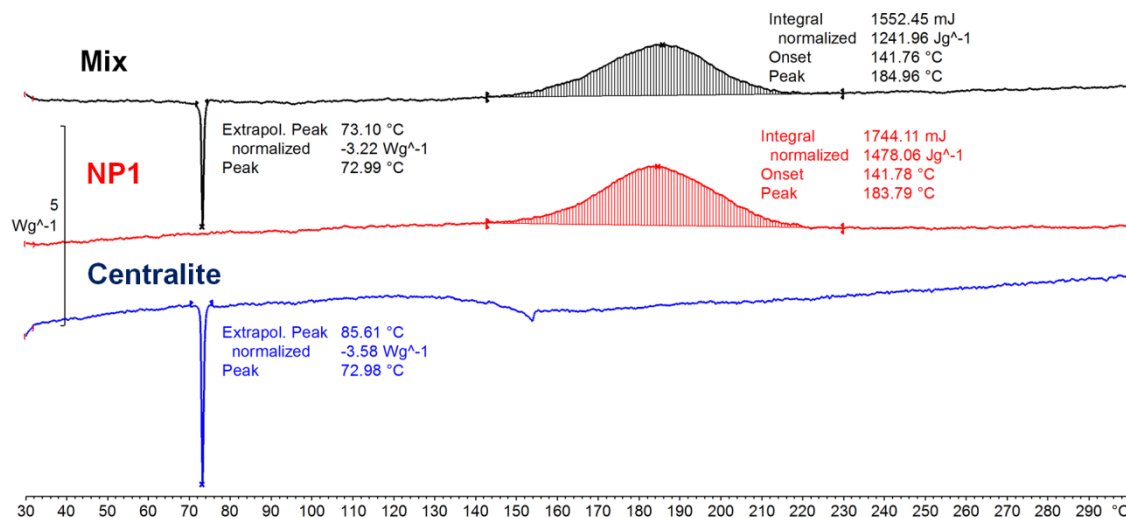

Figure 6.21 DSC thermograms of Centralite (blue line), NP1 (red line), and a 50/50 (w/w) mixture (black line) from 30 to 550 °C (1 mg, 2 °C min⁻¹, aluminium crucible).

6.3 **Hazard tests – βNCXCDs**

The new energetic βNCXCDs were characterised using internal hazard tests at Cranfield Defence and Security School to determine the conditions under which the energetic binders are likely to ignite. Two sets of small-scale (20 mg) hazard tests were performed using two different types of βNCXCDs.

The first set of tests was carried out on insoluble nitrated products synthesised from insoluble βCDTCD and βCDPCD precursors, containing TEG and PEG units respectively. These experiments are described in the appendix: samples NT1–NT5 (Table A 5) and samples NP13–NP15 (Table A 4).

The second set of tests was carried out on acetone-soluble βNCPCD samples NP1, NP5, NP6 and NP16–NP17 (Table 6.3). These were synthesised from βCPCDs with PEG:βCD ratios > 3.5:1, and their softness makes them promising in terms of processability. Sample NP16, with a low PEG:βCD ratio of 2.6:1 was characterised as well as βNCD to determine any increase in hazards

caused by the crystalline structure (Table A6). The following tests were performed:

- Impact and friction sensitivity test;
- Colour change tests to assess thermal stability;
- Temperature ignition test to assess combustion properties.

Materials which clearly failed these tests were considered too hazardous for manual handling and were not considered further. These tests were not standardised methods to characterise the energetic properties of a material, but were carried out to provide a degree of confidence in handling before full Energetic Materials Testing and Assessment Policy (EMTAP) tests on a larger scale. The test results are summarised in Table 6.3.

Table 6.3 Preliminary small-scale compatibility tests performed on βNCTCDs and βNCTCDs containing TEG and PEG units, respectively.

Sample	Polyethylene glycol:βCD feed ratio[1]	Colour change RT 24 h	Colour change 100 °C 30 min	Impact (GO)	Friction	Ignition[4]	Evaluated[5]
βNCD	-	No change	Browning	7/10	No response	HVB	Hazardous
NP13	6:1	No change	Browning	2/10	No response	HVB	Hazardous
NP15	9:1	No change	Browning	0/10 (smell)	No response	VB[4]	Not hazardous
NP16	3:1	No change	Browning	3/10	No response	HVB[2]	Hazardous
NP5	5:1	No change	Browning[2]	0/10	No response	VB	Not hazardous
NP6	5:1	No change	Browning[2]	0/10	No response	VB	Not hazardous
NP17	5:1	No change	Browning[2]	0/10	No response	VB	Not hazardous
NP1	5:1	No change	Browning[2]	0/10	No response	VB	Not hazardous
NT1	9:1	No change	Browning	0/10	No response	VB	Not hazardous
NT2	9:1	No change	Browning	0/10	No response	VB	Not hazardous
NT3	9:1	No change	Browning	0/10	No response	VB	Not hazardous
NT4	9:1	No change	Browning	0/10	No response	VB	Not hazardous
NT5	9:1	No change	Browning	0/10	No response	VB	Not hazardous

1. Feed ratio of cross-linker TEGDGE or PEGDGE, as appropriate to βCD.
2. The compound softened when heated.
3. HVB - Highly vigorous burning, similar to the ignition of a match.
4. VB - Vigorous burning, like the flame of a candle.

5. Assessed by CDS experts.

Colour change test

A colour change generally indicates that a decomposition reaction occurs (Table 6.3). The effect of temperature on the colour of each compound was assessed using two methods. In the first method, 20 mg of each sample was heated to 100 °C and maintained at this temperature for 30 min. In the second method, the samples were left at room temperature for 24 h. Samples NP1, NP5, NP6 and NP13–17 displayed a change in viscosity when heated to 100 °C, as anticipated from their thermal profiles. In contrast, the viscosity of the insoluble gels NT5–NT8 did not change as the temperature increased. All the samples became slightly brown during the test reflecting the decomposition of the nitroesters to form NOx, which was adsorbed by the samples. The inert precursor IP19 (PEG:βCD ratio = 4.0) was also heated to exclude the possibility that browning reflected the caramelisation of the βCD or the ageing of the PEG segments in the cross-linked system. IP19 showed no signs of browning after 30 min, but browning was observed when this inert sample was kept at 100 °C for 24 h.

Impact and friction test

The impact and friction sensitivity of insoluble gels NT5–NT10 and NP15, and acetone-soluble samples NP1, NP5, NP6 and NP13–NP17 was assessed using the steel-on-steel mallet test (Table 6.3). The detection of smell, flash or sound was left to the judgment of an operator trained for the test. This determined whether the compound was recorded as *go* (decomposition detected) or *no-go* (no decomposition detected). The βNCD control was quite susceptible to impact (7/10 *go*) whereas almost all of the synthesised compounds showed no evidence of decomposition, the exceptions being samples NP13, NP15 and NP16. This was attributed to the purification method, which left traces of acid, and the low degree of cross-linking of these products. However, the three sensitive samples showed evidence of a localised initiation that did not consume the entire sample mass. The soft samples (NP1, NP5, NP6 and NP17) were not sensitive to impact but underwent deformation due to the

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impact itself of the heat thus generated, confirming the softness of these compounds.

Ignition test

The samples were burnt over an open flame and the energy of the flame was qualitatively described to evaluate the susceptibility of the compound to burning. Fast burning refers to a type of combustion that is often compared to the ignition of a safety match, and vigorous burning is like the flame produced by wood burning. As expected from the earlier hazard tests, samples NP13, NP16 and βNCD burnt more vigorously than the others, with a sparking flame. The intensity of the ignition was directly dependent on the Ω value of the compound, with the less cross-linked compounds (less rich in carbon chains) burning more vigorously.

6.3.1 EMTAP tests

The EMTAP tests described below followed the certificated methods presented in the *EMTAP Manual of Tests*, which sets the British Standards relevant to the qualification of energetic materials and associated technical assessments [119]. Each test is based on the repetition of several forms of analysis to increase confidence in the result. The Rotter impact test (Test No. 1A) and electrostatic discharge (ESD) test (Test No. 4) were performed on sample NP17 (Table 6.4). Due to the large quantity of sample required and the safety restrictions applied at Cranfield University, the NP17 sample was obtained by dissolving and blending in acetone the products of four nitration reactions at the 2.5-g scale (Table A 6) using a precursor with a PEG:βCD ratio of 3.8:1. The resulting blend passed the small-scale tests described above and was considered safe for EMTAP testing. Given the properties of the sample, the material was soft and malleable, making it a promising candidate for future processing. Further work is needed to collect more data for the scaled-up manufacturing of this compound and to increase confidence in the assessment of its sensitivity.

Table 6.4 EMTAP test data for sample NP17 based on Rotter impact and ESD values.

Energetic sample	Impact by drop-weight input (cm)[1]	ESD[2] 4.5 J
NP17	29.3	0/50

1 Impact value is the mean of 50 tests.
2 ESD value is the mean of 50 tests at 4.5 J.

The Rotter impact test indicated a figure of insensitiveness (FoI) of 29 for NP17 with a release of 1 mL gas per test. The initiated samples were not completely consumed, indicating a localised initiation as seen in the small-scale tests described above.

The FoI value indicated that the compound was highly sensitive to impact, given that sensitive compounds have values in the range 100 ≥ FoI ≥ 30, and initiators have FoI values < 30. Dry βNCD has an FoI value of 60 [114] but this value is not comparable to the FoI of NP17 described here because it was based on the results of an impact test conducted under American standards that differ from the British system. Furthermore, the FoI value reported for a similar epichlorohydrin:βCD cross-linked nitrated product was 47 [109]. The values determined in the Rotter impact test therefore provide an indication of the potential sensitivity of NP17 but should not be considered conclusive. The test is affected by several factors, including the homogeneity of the blend and the presence of impurities. Given that this was the first attempt to synthesise a significant quantity of the nitrated product, more tests are required to achieve a confident result.

The ESD test (spark sensitivity test) determines the sensitivity of a sample to initiation by electrostatic discharges. NP17 was not susceptible to ESD up to an energy input of 4.5 J, which is a significant improvement compared to βNCD, which initiates at 0.0125 J [114], and the epichlorohydrin:βCD cross-linked nitrated product discussed above, which initiates at 0.1288 J [109].

6.4 **Stability of βNCXCDs determined by heat flow calorimetry**

The single-temperature stability test is a standardised technique in STANAG 4582 that uses heat flow calorimetry (HFC) to determine the shelf life of energetic formulations [139]. The test was repurposed in this project as a method to obtain indicative data about the lifetime thermal stability of βNCXCDs.

Four lots (~1 g) of sample NP1 were prepared, with a PEG:βCD ratio of 4:1. One lot was kept pure, and the others were mixed with one of three stabilisers (DPA, 2,4-NDPA or Centralite) as a 1% w/w formulation. A sample of pure (non-stabilised) NC with a nitrogen content of 12.6% was used as benchmark.

The heat flow from of the samples was measured at a constant temperature of 80 °C. At this temperature, the STANAG criterion is that the sample should have a heat flow less than a tabulated value of 114 µW g^{-1} (Figure 6.22, dashed line) for a time of 10.6 days, in order to be defined as stable. The heat flow is recorded after the release of the first 5 J of energy. Therefore, the thermograms do not present the initial stabilisation of the temperature when the samples are introduced in the machine. The results are summarised in Figure 6.22.
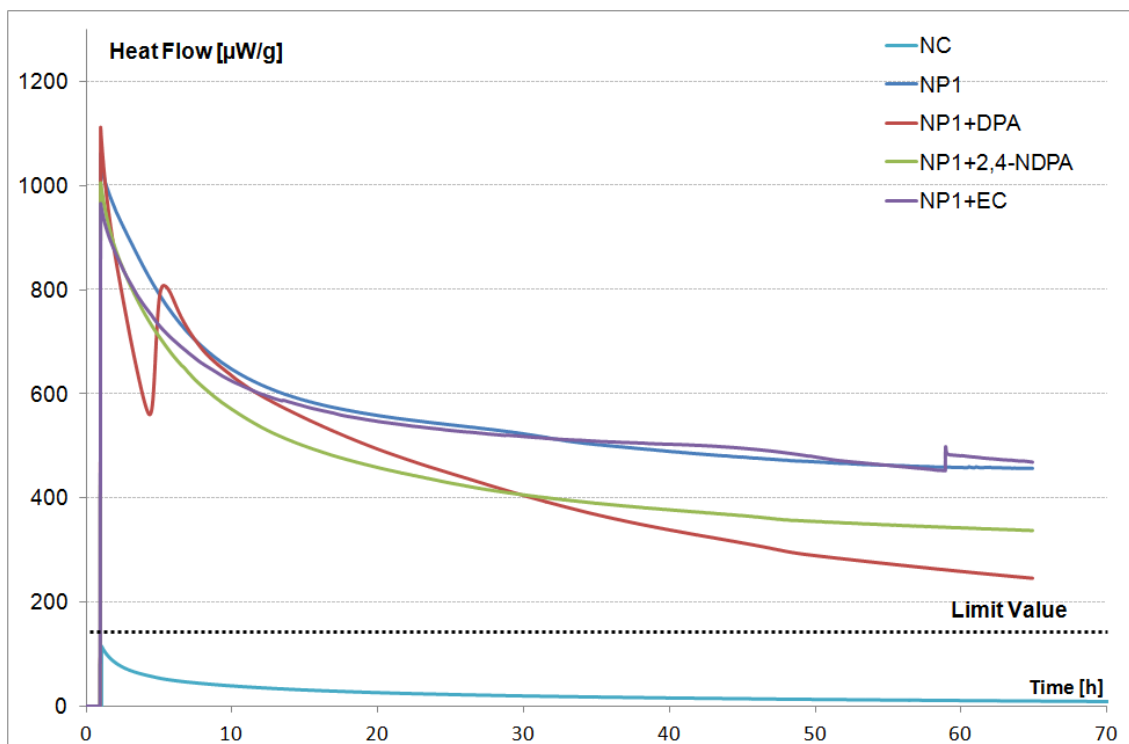
Figure 6.22 Thermal stability of pure NP1 and the same compound in the presence of three different stabilisers (1% w/w).

The experiment was automatically halted after 70 h by the safety control of the HFC instrument due to the high heat flow values that were registered. All samples containing the energetic binder NP1 were unstable throughout the recording (Figure 6.22). The heat flow from NC was lower than the limit value of 114 $\mu W \cdot g^{-1}$ (light blue curve). The viscous consistency of the sample is thought to influence its stability because gaseous and liquid materials decompose more quickly than crystalline solids [141,142]. The air and moisture trapped in the spongy matrix of the samples, as well as that in the head space of the vials, probably accelerated the decomposition, as reported for other nitroesters [140].

The highest heat flow was recorded for the pure NP1 sample. The presence of a stabiliser reduced the heat flow during decomposition, indicating that NP1 can be stabilised. Interestingly, DPA reduced the heat flow particularly during the first 4 h, but this was followed by an increase at ~4.5 h probably reflecting the consumption of the stabiliser. Despite the consumption of the DPA, a residual stabilising effect was observed, probably conferred by DPA nitro-derivatives,

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which include 2,4-NDPA in the latter stages of decomposition [143]. This explains why DPA has a greater stabilising effect than 2,4 NDPA alone.

The addition of Centralite did not influence the stability of the binder, as shown by the similar heat flow curves over time with and without this additive. It would be interesting to determine the quantity of stabiliser remaining throughout the experiment, but the specialised chromatography technique required for this type of experiment was not available [139]. However, the samples were analysed before and after testing by ^{1}H-NMR spectroscopy, which showed that the stabilisers decomposed during the experiment (Figure A 10, Figure A 11 and Figure A 12). The aged samples were also thermally characterised by DSC. The T_{dec} was not significantly changed following exposure to a constant temperature of 80 °C for 3 days under HFC testing conditions (Table 6.6). The presence of stabilisers slightly improved the stability of NP1, increasing the T_{dec} marginally compared to the pure sample, but the variations were small and within the range of experimental error.

Table 6.5 DSC analysis of the decomposition temperatures of sample NP1 before and after HFC tests.

Sample	T_{dec} before HFC tests (°C)	T_{dec} (after 3 days at 80 °C) (°C)
NP1	195	195
NP1/DPA	198	197
NP1/2,4-NDPA	198	196
NP1/Centralite	198	195

6.5 **Conclusion**

Energetic βNCXCDs were characterised by compatibility, hazard and stability tests to determine their suitability for energetic applications. Most of the studies were performed on the βNCPCD derivatives containing PEG segments because these had superior mechanical properties making them potentially suitable for

industrial exploitation. The compatibility studies determined whether the binder was likely to initiate unwanted reactions among the other constituents.

The βCPCDs and βNCPCDs behaved similarly in the tests. They were compatible with several pyrotechnic ingredients such as $KClO_3$, KNO_3 and NH_4ClO_4, as well as explosives such as HMX and PETN. A degree of incompatibility of both inert and nitrated compounds was observed with RDX, possibly due to the size of the nitramines, which were small enough to be encapsulated within the βCD macrocycles. Centralite was also compatible with the energetic βNCPCDs, but DPA reduced the T_{dec} of the binder by 44 °C (specifically when the DPA evaporated at 143 °C) suggesting that DPA vapours are incompatible with the binder.

Small-scale hazard tests were performed on a set of the new energetic binders differing in terms of their cross-linker ratio. The most malleable βNCPCD compounds (PEG:βCD ratio > 3.0) were insensitive to impact and friction with a mallet. In contrast, samples with PEG:βCD ratios < 3.0 were susceptible to impact due to the low cross-linker content and thus greater crystallinity. All the compounds underwent a colour change when left at 100 °C for 30 min. At this temperature, the nitroesters undergo rapid thermal cleavage to form NOx molecules that are adsorbed into the matrix of the compound.

A highly cross-linked βNCPCD product (PEG:βCD ratio = 3.8:1) was subjected to EMTAP tests for impact and ESD resistance. The recorded FoI value of 29 indicated that the nitrated products can be sensitive to impact, but the same sample was insensitive to ESD stimuli up to 4.5 J, which is a considerable improvement.

HFC-based stability tests were performed on the soft nitrated compound NP1, either in pristine form or mixed with 1% (w/w) of one of three different stabilisers (DPA, 2,4-NDPA or Centralite). The results indicated that the softer compounds were unstable when incubated at 80 °C for 3 days even in the presence of stabiliser, with heat flow exceeding 200 µW g^{-1}. The inherent viscosity of these materials is thought to accelerate the degradation of the nitroester groups. The

T_{dec} of the samples did not change significantly after the HFC tests, although DPA showed a stronger stabilising effect on the βNCXCDs.

7 Conclusion and recommendations

Conclusions

This PhD project has contributed to the development of new inert and energetic binders for energetic applications. The function of the binder is to hold together the constituents of an energetic formulation, improving its response to external stimuli and, when possible, contributing to the energy of the system. The project focussed on the use of βCD, a cyclic polysaccharide that has been investigated as a drug delivery vehicle due to its ability to envelop guest molecules. The design and synthesis of a set of inert and nitrated cross-linked βCD systems was achieved by the cross-linking of βCD with diglycidyl ethers containing a variety of polyethylene glycol units followed by a nitration reaction.

Three polyethylene glycol diglycidyl ethers (TEGDGE, HEGDGE and PEGDGE, containing three, six and an average of nine ethylene glycol units, respectively) were used to generate βCXCD products containing TEG, HEG or PEG segments. The abbreviation XEG is used to describe these segments collectively.

The cross-linkers were used to tune the properties of βCD and generate malleable cross-linked βCXCD compounds suitable for processing. The investigation focused on the optimisation of the cross-linking reaction, which was strongly affected by several factors including NaOH concentration and volume, reaction time, temperature, βCD alkoxide formation, cross-linker:βCD feed ratio, and the addition rate of the cross-linker in the βCD alkoxide solution.

The optimal experimental conditions for the cross-linking of βCD were investigated extensively using PEGDGE as the cross-linker due to its low cost and commercial availability. Cross-linked βCPCD products that were insoluble in water and other common solvents were produced using PEGDGE:βCD feed ratios higher than 5:1. The optimal conditions were a PEGDGE:βCD ratio of up to 5:1, 5.6% NaOH aqueous solution, 16 h to form the βCD alkoxide, 20 min for the addition of the cross-linker, and 6 h reaction time at 30 °C. Under these conditions, several βCPCDs containing different quantities of PEG units were

synthesised. The same procedure was then adopted for the synthesis of the other βCXCD systems. The products were characterised by ^{1}H-NMR and FTIR spectroscopy, confirming the polymeric nature of the βCXCDs. In all trials, up to 25% of the cross-linker was consumed in a parallel degradation reaction resulting in a lower XEG:βCD ratio in the products compared to the feed ratio. The XEG:βCD ratio in the βCXCDs was determined by ^{1}H-NMR in D_2O. The length of the XEG segments and the degree of cross-linking influenced the physical appearance of the βCXCDs. Samples with PEG:βCD ratios between 4:1 and 3:1 were malleable whereas those with PEG:βCD ratios below 3:1 were friable. Samples containing TEG units were friable and easy to dissolve regardless of the TEG:βCD ratio. Also, βCXCDs containing HEG and PEG units took longer to dissolve if the XEG:βCD ratio was higher than 3.4:1, as determined by ^{1}H-NMR spectroscopy.

As expected from the design of the materials, the thermal and thermo-mechanical properties of βCD precursors were affected by the cross-linking reaction, yielding βCXCDs with low T_g values. The softness of the βCXCD samples was directly dependent on the length of the XEG unit and the XEG:βCD ratio. Therefore, βCXCDs containing HEG and PEG segments with a XEG:βCD ratio exceeding 3.7:1 were characterised by T_g values as low as –20 °C. No glass transition was observed for the βCXCDs with few cross-links or for those containing TEG segments.

Cracking was observed in βCXCD samples cooled below their T_g during DMA experiments due to strong interactions with the metallic supports via hydrogen bonds. This was also confirmed by optical microscopy using glass supports. The βCXCDs demonstrated accelerated healing when heated above room temperature, much like the healing properties of hydrogels containing PEG and βCD segments, which are used in pharmaceutical applications.

The research project then focused on the synthesis and characterisation of nitrated derivatives of βCXCDs, aiming to improve the binder's contribution to the energy of the formulation. The nitration reaction with fuming nitric acid yielded two sets of βNCXCDs differing in terms of their solubility in water and

other organic solvents, and properties correlated to the physicochemical characteristics of the βCXCD precursors. Insoluble βCXCD systems yielded cross-linked derivatives with various degrees of nitration that were insoluble in acetone, whereas water-soluble βCXCD precursors produced βNCXCDs that were soluble in acetone and easy to characterise and process. A purification method adopted from the NC manufacturing process removed acid traces from the nitration reaction more efficiently, stabilising the compound during storage.

The βNCXCDs were characterised by ^{1}H-NMR and FTIR spectroscopy to determine the degree of nitration, which was found to be dependent on the nitration reaction time, the length of the cross-linker and the cross-linker:βCD feed ratio. This was confirmed by measuring the nitrogen content of the products. The more soluble products generally featured a lower degree of nitration.

The thermal stability of βNCXCDs (T_{dec} = 190–200 °C) was independent of the length of the XEG unit and the XEG:βCD ratio whereas the ΔH_{dec} of each system (1300–2100 J g^{-1}) was dependent on the length of the XEG segment.

The βNCXCDs retained a certain degree of softness from their βCXCD precursors with T_g values in the range –14 to +65 °C. The higher T_g values probably reflected the higher polarity of the system, which increases the cohesive energy of the compounds and inhibits the mobility of the XEG chains. One βNCXCD product containing PEG units retained the self-healing ability of its precursor after 4 h at room temperature.

The suitability of βNCXCDs as binders in energetic formulations was determined by conducting compatibility, hazard and stability tests using NATO STANAG and EMTAP protocols. Most of these studies were performed on the βNCPCD derivatives containing PEG segments. The compatibility studies determined the likelihood that the binder would initiate undesirable reactions in the other constituents of the energetic formulations.

Both βCPCD and βNCPCD behaved similarly when tested and were found to be compatible with several pyrotechnic ingredients (including $KClO_3$, KNO_3 and

NH_4ClO_4) as well as explosives such as HMX and PETN. The degree of incompatibility determined for RDX, needs further investigation. The different behaviour of mixtures containing HMX and RDX was attributed to the difference in the size of these energetic nitramines, promoting different interactions with the cavities of βCPCDs and βNCPCDs. Only Centralite was compatible with the energetic βNCPCD binders among three common stabilisers used with nitroesters

Small-scale laboratory hazard tests performed on a set of βNCPCD binders with different degrees of cross-linking showed that the most malleable compounds were insensitive to impact and friction with a mallet, but reducing the degree of cross-linking increased their sensitivity to impact. All the compounds changed colour when left for 30 min at 100 °C suggesting they produced NOx which was subsequently absorbed.

A highly cross-linked βNCPCD sample was found to be sensitive to impact (FoI = 29) but insensitive to ESD stimuli up to 4.5 J. The ESD test result is very significant because nitrated βCD is highly sensitive to ESD (0.0125 J) and the low sensitivity of βNCPCDs indicates they could be promising as a new generation of energetic binders.

Stability tests indicated that softer βNCPCD compounds are unstable when placed at 80 °C for 3 days even in the presence of a stabiliser. This may be due to the inherent viscosity of these materials, which is thought to speed up the degradation of the nitroester groups.

In conclusion, the new inert and nitrated βCD-based binders designed and developed during this PhD project offer a promising alternative to current binders for energetic formulations. The greatest strengths of the project are the use of and environmentally sustainable βCD precursor, the absence of flammable organic solvents in the synthesis method, and the easy synthesis and processability of the inert and energetic products. The highlight of the nitrated derivatives is their insensitivity to ESD at values up to 4.5 J compared to the low value of 0.12555 J for similar compounds reported in literature.

Notably, an inert βCPCD derivative with a PEG:βCD ratio of 3.7:1 is now being exploited by BAE Systems in Glascoed as a potential alternative to NC in propellant formulations.

Recommendations

The scope for future work in the area covered by this PhD project is considerable. Areas worthy of further investigation include, but are not limited to:

1. Investigating the inclusion properties of βCXCDs, which are widely exploited in pharmaceutical research because they can change the physical properties of encapsulated materials. These tests could help to optimise the manufacturing process for energetics containing βCXCDs and their nitrated derivatives. The characterisation of M_w during this project was not ideal due to the limited resources available for this task. Studying the M_w of the products should be extended to determine the effect of the reaction conditions and the consistency of the properties in each trial. GPC/MALDI-TOF (matrix-assisted laser desorption/ionisation time of flight) mass spectrometry could also be applied to confirm the results of the GPC/refractive index studies with the βCXCDs.
2. The phenomenon of thermal healability looks interesting for manufacturing purposes and further investigations of the healing process are needed to determine the degree of healing inherited by the formulations.
3. Curing is another step towards the manufacturing of energetic devices. Appendix A1 describes the first attempted curing experiments in the project to obtain polymer-bonded explosive (PBX) formulations from the remaining free hydroxyl groups in the βCXCDs, although the results are still preliminary.
4. Scaling up the formulations even further (500 g mixes) and investigating the effects of plasticisers, filler particle size distributions and automated mixing

processes on the mechanical properties and sensitivity of pressed/cast PBX pellets.

5. Further compatibility testing is necessary to determine the differences in compatibility between the βCXCDs and βNCXCDs when the XEG:βCD ratio varies. In addition, compatibility with nitroglycerine and NC should be assessed.

6. All forms of analysis should be extended to the level of triplicates in order to increase confidence in the results.

7. Scaling up the synthesis of the energetic derivatives for EMTAP tests should be extended to all compounds in order to correlate the mechanical characteristics and hazard properties of the βNCXCDs. In addition, hazard tests should be extended to real formulations to determine the suitability of the binders for real-world applications.

8. Stabilisation studies were performed on only one βNCXCD compound. Stability tests should be extended to obtain data for all the compounds synthesised in the project, to determine how the rheology of the products affects their stability.

The starting material was βCD cyclodextrin because it is less expensive than γCD. However, the studies performed with βCD should be replicated with γCD so that the complexation of energetic molecules with this larger macrocycle can be exploited.

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Appendix A

Table A 1 List of βCPCDs synthesised using PEGDGE as the cross-linker.

Sample ID	Logbook ref.	Feed ratio	βCD (g)[1]	Water (%)	PEGDGE (mL)	NaOH (% w/w)	NaOH (mL)	Time alkox. (h)	T (°C)	Cross-linker addition time.	Time reaction	Yield (%)	Solubility
IP3	βCPCD1	9:1	5.00	N.d	17.4	36	21	0	70	~20min	0.5	1	Water
IP24	βCPCD2	9:1	5.00	N.d	17.4	50	21	0	70	~20min	0.5+4.5 RT	1	Water
IP27	βCPCD3	9:1	5.00	N.d	17.4	5.6	21	0	70	~20min	0.66	88	Insoluble
IP4	βCPCD4	3:1	5.00	N.d	5.8	5.6	21	0	70	~20min	1	5	Water
IP26	βCPCD5	6:1	5.00	N.d	11.6	5.6	21	0	70	~20min	0.66	91	Insoluble
IP28	βCPCD6	9:1	5.00	N.d	17.4	5.6	21	0	70	~20min	1	1	Water
IP1	βCPCD7	9:1	5.00	N.d	17.4	50	21	0	70	~20min	0.5	1	Water
IP2	βCPCD8	9:1	5.00	N.d	17.4	40	21	1	70	~20min	1	1	Water
IP5	βCPCD9	9:1	5.00	N.d	17.4	40	21	1	70	~20min	5	12	Water
IP29	βCPCD10	1:1	5.00	N.d	1.9	40	21	3	70	~20min	1	1	Water
IP6	βCPCD11	5:1	5.00	N.d	9.7	5.6	21	1	70	~20min	5	1	Water

Sample ID	Logbook ref.	Feed ratio	βCD (g)[1]	Water (%)	PEGDGE (mL)	NaOH (% w/w)	NaOH (mL)	Time alkox. (h)	T (°C)	Cross-linker addition time.	Time reaction	Yield (%)	Solubility
IP7	βCPCD12	5:1	5.00	N.d	9.7	5.6	21	0	50	~20min	5	13	Water
IP30	βCPCD13	5:1	5.00	N.d	9.7	5.6	21	0	50	~20min	2	9	Water
IP8	βCPCD14	5:1	5.00	N.d	9.7	5.6	21	16	50	~20min	5	30	Water
IP31	βCPCD15	5:1	5.00	N.d	9.7	5.6	21	16	30	~20min	7.5	23.6	Insoluble
IP32	βCPCD16	5:1	5.00	N.d	9.7	5.6	21	16	30	5 hours	1	23.9	Water
IP9	βCPCD17	5:1	5.00	N.d	9.7	5.6	21	16	30	~20min	6	33.6	Water
IP33	βCPCD18	5:1	5.00	N.d	9.7	5.6	21	16	30	~20min	7	33.2	Water
IP34	βCPCD19	5:1	2.5	N.d	4.8	20	10.5	16	70	~20min	6	15	Water
IP35	βCPCD20	5:1	2.5	N.d	4.8	5.6 KOH	10.5	16	30	5 hours	1.5	Not recovered	Insoluble
IP36	βCPCD21	1:1	2.5	N.d	9.7	5.6	100	16	30	~20min	7.5	not recovered	Water
IP37	βCPCD22	5:1	2.5	N.d	4.8	5.6	10+42.5	16	30	~20min	24	48	Water
IP11	βCPCD23	3:1	2.5	N.d	2.9	5.6	10.5	16	30	~20min	24	68	Water
IP38	βCPCD24	4:1	5.00	N.d	7.7	5.6	21	16	30*	~20min	24	39	Water

Sample ID	Logbook ref.	Feed ratio	βCD (g)[1]	Water (%)	PEGDGE (mL)	NaOH (% w/w)	NaOH (mL)	Time alkox. (h)	T (°C)	Cross-linker addition time.	Time reaction	Yield (%)	Solubility
IP10	βCPCD25	4:1	5.00	N.d	7.7	5.6	21	16	30	~20min	24	36	Water
IP39	βCPCD26	4:1	5.00	N.d	7.7	5.6	21	16	30	7 hours	17	Not recovered	Insoluble
IP40	βCPCD27	3:1	5.00	N.d	5.8	5.6	21	16	30	7 hours	17	48	Water
IP12	βCPCD28	2:1	5.00	N.d	3.9	5.6	21	16	30	7 hours	17	44	Water
IP41	βCPCD29	3.5:1	5.67	0.12	9.7	5.6	21	16	30	7 hours	17	not recovered	Insoluble
IP42	βCPCD30	5:1	5.63	0.12	9.7	5.6	21	16	30	~20min	6	61	Insoluble
IP43	βCPCD31	5:1	5.63	0.12	9.7	5.6	21	16	30	~20min	5	not recovered	Insoluble
IP44	βCPCD32	5:1	5.64	0.12	9.7	5.6	21	16	30	~20min	5	not recovered	Insoluble
IP13	βCPCD33	5:1	4.35	0.13	8.4	5.6	20.7	16	30	~20min	6	68	Water
IP20	βCPCD34	5:1	4.35	0.13	8.4	5.6	20.7	16	30	~20min	6	64	water
IP22	βCPCD35	4:1	4.40	0.12	6.8	5.6	20.8	16	30	~20min	6	63	water
IP15	βCPCD36	4:1	4.40	0.12	6.8	5.6	20.8	16	30	~20min	6	65	water
IP45	βCPCD37	2:1	4.15	0.17	3.2	5.6	18.7	16	30	~20min	6	68	water

Sample ID	Logbook ref.	Feed ratio	βCD (g)[1]	Water (%)	PEGDGE (mL)	NaOH (% w/w)	NaOH (mL)	Time alkox. (h)	T (°C)	Cross-linker addition time.	Time reaction	Yield (%)	Solubility
IP17	βCPCD38	2:1	4.15	0.17	3.2	5.6	18.7	16	30	~20min	6	68	water
IP46	βCPCD39	6:1	4.34	0.13	8.4	5.6	19.8	16	30	~20min	6	gel	Insoluble
IP47	βCPCD40	6:1	4.34	0.13	8.4	5.6	20.7	16	30	~20min	6	37%+gel	Insoluble
IP16	βCPCD41	3:1	4.15	0.17	4.8	5.6	20.7	16	30	~20min	6	73	water
IP48	βCPCD42	3:1	4.15	0.17	4.8	5.6	19.8	16	30	~20min	6	68	water
IP14	βCPCD43	3.8:1	4.34	0.13	8.4	5.6	19.8	16	30	7 hours	6	71	water
IP21	βCPCD44	5:1	4.34	0.13	8.4	5.6	19.8	16	30	~20min	6	68	water
IP25	βCPCD45	3:1	4.34	0.13	5	5.6	19.8	16	30	~20min	6	67	water
IP23	βCPCD46	4:1	4.34	0.13	6.7	5.6	19.8	16	30	~20min	6	69	water
IP19	βCPCD47	5:1	4.34	0.13	8.4	5.6	19.8	16	30	~20min	6	67	water
IP18	βCPCD48	5:1	4.34	0.13	8.4	5.6	19.8	16	30	~20min	6	68	water

1 Dry mass of βCD determined by TGA after sample βCDPCD28.

Table A 2 List of βCHCDs using HEGDGE as the cross-linker.

Sample ID	Logbook ref.	Feed ratio	βCD (g)[1]	Water (%)	HEGDGE (g)	NaOH (% w/w)	NaOH (mL)	Time alkox. (h)	T (°C)	Cross-linker addition time	Time reaction	Yield (%)	Sol.
IH1	βCHCD1	5:1	4.00	0.12	6.9	5.6	19	16	30	~20min	6	68	water
IH2	βCHCD2	4:1	4.00	0.12	5.6	5.6	19	16	30	~20min	6	72	water
IH3	βCHCD3	2:1	4.00	0.13	2.8	5.6	14.3	16	30	~20min	6	65	water
IH4	βCHCD4	3:1	4.00	0.13	4.2	5.6	14.3	16	30	~20min	6	67	water

1 Dry mass of βCD determined by TGA.

Table A 3 List of βCTCDs synthesised using TEGDGE as the cross-linker.

Sample ID	Logbook ref.	Feed ratio	βCD (g)	Water (%)	TEGDGE (g)	NaOH (% w/w)	NaOH (mL)	Time alkox. (h)	T (°C)	Cross-linker addition time	Time reaction	Yield (%)	Sol.
IT5	βCTCD1	9:1	5	N.d	9.35	40	21	1	70	~20min	5	35	Insoluble
IT6	βCTCD2	3:1	5	N.d	3.1	40	21	1	70	~20min	5	40	Insoluble
IT7	βCTCD3	6:1	5	N.d	6.2	40	21	1	70	~20min	5	33	Insoluble
IT8	βCTCD4	5:1	5	N.d	5.76	5.6	21	1	70	~20min	5	10	water
IT9	βCTCD5	5:1	5	N.d	5.76	5.6	21	16	30	~20min	5	38	water

Sample ID	Logbook ref.	Feed ratio	βCD (g)	Water (%)	TEGDGE (g)	NaOH (% w/w)	NaOH (mL)	Time alkox. (h)	T (°C)	Cross-linker addition time	Time reaction	Yield (%)	Sol.
IT1	βCTCD6	5:1	2.00	0.12	2.3	5.6	9.5	16	30	~20min	6	63	water
IT2	βCTCD7	4:1	2.00	0.12	1.84	5.6	9.5	16	30	~20min	6	52	water
IT3	βCTCD8	3:1	2.00	0.12	1.39	5.6	9.5	16	30	~20min	6	56	water
IT4	βCTCD9	2:1	2.00	0.12	0.93	5.6	9.5	16	30	~20min	6	45	water

1 Dry mass of βCD determined by TGA.

Table A 4 Nitration of insoluble βCPCD precursor, sample IP26.

Sample ID	Logbook ref.	Precursor		HNO$_3$ %	Volume HNO$_3$ (mL)	H$_2$SO$_4$ %	Volume H$_2$SO$_4$ (mL)	Time (h)	DCM (mL)	Stirr rpm	Yield (%)
		Name	Solubility								
NP9	βNCPCD3	IP26	N	100	0.5	100	0.5	1.0	0.0	200	32[1,2]
NP10	βNCPCD4	IP26	N	100	0.5	100	0.5	2.0	0.0	400	30[1,2]
NP11	βNCPCD5	IP26	N	100	0.5	100	0.5	1.5	1.8	900	44[1,2]
NP12	βNCPCD6	IP26	N	100	0.5	100	0.5	1.5	0.0	900	37[1,2]
NP13	βNCPCD7	IP26	N	100	0.5	100	0.5	1.5	1.8	900	90
NP14	βNCPCD8	IP26	N	100	0.5	100	0.5	2.0	1.8	900	87

1 Low degree of nitration, gum-like βCPCD precursors.
2 Purification process affected the yield of the reaction.

Table A 5 Nitration of insoluble βCTCD precursors.

Sample ID	Logbook ref.	Precursor		HNO$_3$ %	Volume HNO$_3$ (mL)	H$_2$SO$_4$ %	Volume H$_2$SO$_4$ (mL)	Time (h)	DCM (mL)	Stirr rpm	Yield (%)
		Name	Solubility								
NT5	βNCTCD1	IT5	N	95	1.0	0	0.0	1.0	0.0	200	87

NT6	βNCTCD2	IT5	N	100	1.0	0	0.0	1.0	0.0	200	80
NT7	βNCTCD3	IT5	N	100	0.5	100	0.5	1.0	0.0	200	35
NT8	βNCTCD4	IT5	N	100	0.5	100	0.5	0.5	1.8	400	85
NT9	βNCTCD5	IT5	N	100	0.5	100	0.5	1.0	0.0	900	88
NT10	βNCTCD6	IT7	N	100	0.5	100	0.5	1.0	0.0	900	88
NT11	βNCTCD7	IT6	N	100	0.5	100	0.5	1.0	0.0	900	84
NT12	βNCTCD8	IT5	N	100	0.5	100	0.5	1.0	1.8	900	86
NT13	βNCTCD9	IT6	N	100	0.5	100	0.5	1.0	1.8	900	91
NT14	βNCTCD10	IT7	N	100	0.5	100	0.5	1.0	1.8	900	92

Table A 6 Nitration of βCPCD precursors.

Sample ID	Logbook ref.	Precursor name	HNO$_3$		Mass of precursor (mg)	Volume HNO$_3$ (mL)	H$_2$SO$_4$		Time (h)	DCM (mL)	Stirr	Yield[1]		Sol
			Sol.	%			%	(mL)			rpm	Mass mg	%	
NP14	βNCPCD1	IP5	Y	100	200	0.5	100	0.5	0.5	1.8	200	163		
NP15	βNCPCD2	IP5	Y	95	200	1	0	0	1	0	200	199		

Sample ID	Logbook ref.	Precursor name	HNO₃		Mass of precursor (mg)	Volume HNO₃ (mL)	H₂SO₄		Time (h)	DCM (mL)	Stirr rpm	Yield[1]		Sol
			Sol.	%			%	(mL)				Mass mg	%	
NP7	βNCPCD3	IP26	N	100	200	0.5	100	0.5	1	0	200			purification is difficult, insoluble precursor
NP8	βNCPCD4	IP26	N	100	200	0.5	100	0.5	2	0	400			purification is difficult, insoluble precursor
NP9	βNCPCD5	IP26	N	100	200	0.5	100	0.5	1.5	1.8	900	70		purification is difficult, insoluble precursor
NP10	βNCPCD6	IP26	N	100	3000	0.5	100	0.5	1.5	0	900	300		purification is difficult, insoluble precursor
NP11	βNCPCD7	IP26	N	100	200	0.5	100	0.5	1.5	1.8	900	103		purification is difficult, insoluble precursor
NP12	βNCPCD8	IP26	N	100	200	0.5	100	0.5	2	1.8	900	169		purification is difficult, insoluble precursor
NP18	βNCPCD9	IP8	Y	100	200	1			1		700	180		

Sample ID	Logbook ref.	Precursor name	HNO₃		Mass of precursor (mg)	Volume HNO₃ (mL)	H₂SO₄		Time (h)	DCM (mL)	Stirr	Yield[1]		Sol
			Sol.	%			%	(mL)			rpm	Mass mg	%	
NP19	βNCPCD10	IP8	Y	95	200	1			1		700	187		
NP20	βNCPCD11	IP8	N	100	200	1			1		700			almost nothing recovered (filter paper problem)
NP21	βNCPCD12	IP11	Y	100	200	1			1		700	190		
NP22	βNCPCD13	IP10	Y	100	1000	5			1+(15min dis)		700	1070		
NP16	βNCPCD14	βCPCD27	Y	100	1000	5			1		700	1230		
NP23	βNCPCD15	IP10	Y	100	200	1			1		700	103		
NP24	βNCPCD16	IP10	Y	100	200	1			1		700	117		compound is not easy to purify cloud solution
NP25	βNCPCD17	IP13/20 blend	Y	100	1000	5			1		700	451		
NP13	βNCPCD18	IP13/20 blend	Y	100	500	2.5			1		700	476		

Sample ID	Logbook ref.	Precursor name	HNO₃ Sol.	HNO₃ %	Mass of precursor (mg)	Volume HNO₃ (mL)	H₂SO₄ %	H₂SO₄ (mL)	Time (h)	DCM (mL)	Stirr rpm	Yield[1] Mass mg	Yield[1] %	Sol
NP26	βNCPCD19	IP13/20 blend	Y	100	2000	10			1		700	1637		
NP27	βNCPCD20	IP13/20 blend	Y	100	1000	10			1		700	656		
NP28	βNCPCD21	IP13/20 blend	Y	100	1000	10			1		700	395		
NP29	βNCPCD22	IP13/20 blend	Y	100	500	5			1		700	NA		samples damaged trying to use Na₂CO₃
NP30	βNCPCD23	IP13/20 blend	Y	100	500	5			1		700	NA		
NP31	βNCPCD24	IP13/20 blend	Y	100	300	2.1			1		700	150		
NP32	βNCPCD25	IP13/20 blend	Y	100	300	2.1			1		700	98		
NP33	βNCPCD26	IP13/20	Y	100	300	2.1			1		700	72		

Sample ID	Logbook ref.	Precursor name	HNO₃ Sol.	HNO₃ %	Mass of precursor (mg)	Volume HNO₃ (mL)	H₂SO₄ %	H₂SO₄ (mL)	Time (h)	DCM (mL)	Stirr rpm	Yield[1] Mass mg	Yield[1] %	Sol
		blend												
NP5	βNCPCD27	IP13/20 blend	Y	100	2000				1		700	1301		N% 6.2
NP6	βNCPCD28	IP13/20 blend	Y	100	2000	14			1		700	1755		N% 6.6
NP34	βNCPCD29	IP21	Y	100	2000	14			1		700	1562		
NP17	βNCPCD30	IP18/19 blend	Y	100	2500X4	17.5X4			1		700	9000		
NP2	βNCPCD31	IP23	Y	100	2500	17.5			1		700	2760		N% 6.8
NP4	βNCPCD32	IP17	Y	100	2100	14.7			1		700	1556		N% 7
NP3	βNCPCD33	IP25	Y	100	2200	15			1		700	2294		N% 8.7
NP1	βNCPCD34	IP18	Y	100	6000	28			1		700	4764	62	

1 Where yield is not reported, masses are less than required to determine the nitrogen content, thus were not calculated.

Table A 7 Nitration of βCHCD precursors.

Sample ID	Logbook ref.	Precursor name	Solubility	Mass of precursor (mg)	Volume 100% HNO$_3$ (mL)	Time (h)	Stirr	Yield		N (%)
							rpm	Mass mg	(%)	
NH1	βNCHCD1	IH1	Y	2000	14	1	700	1683	60	8.2
NH2	βNCHCD2	IH2	Y	2060	14	1	700	1897	71	7.1
NH3	βNCHCD3	IH3	Y	2000	14	1	700	1798	62	9.0
NH4	βNCHCD4	IH4	Y	2000	14	1	700	1939	66	7.4

Table A 8 Nitration of soluble βCTCD precursors.

Sample ID	Logbook ref.	Precursor name	HNO$_3$		Mass of precursor (mg)	Volume HNO$_3$ (mL)	H$_2$SO$_4$ %	Volume H$_2$SO$_4$ (mL)	Time (h)	DCM (mL)	Stirr	Yield[1]		N (%)
			Sol.	%							rpm	Mass mg	(%)	
NT5	βNCTCD1	NT5	N	95	200	1	0	0	1	0	200	170		
NT6	βNCTCD2	NT5	N	100	200	1	0	0	1	0	200	112		
NT7	βNCTCD3	NT5	N	100	200	0.5	100	0.5	1	0	200	146		
NT8	βNCTCD4	NT5	N	100	200	0.5	100	0.5	0.5	1.8	400	148		
NT9	βNCTCD5	NT5	N	100	200	0.5	100	0.5	1	0	900	103		

NT10	βNCTCD6	NT7	N	100	200	0.5	100	0.5	1	0	900	157		
NT11	βNCTCD7	NT6	N	100	200	0.5	100	0.5	1	0	900			
NT12	βNCTCD8	NT5	N	100	200	0.5	100	0.5	1	1.8	900	126		
NT13	βNCTCD9	NT6	N	100	200	0.5	100	0.5	1	1.8	900	110		
NT14	βNCTCD10	NT7	N	100	200	0.5	100	0.5	1	1.8	900	196		
NT1	βNCTCD11	NT10	Y	100	1000	7	0	0	1	0	700	1038	74	8.2
NT2	βNCTCD12	NT11	Y	100	1000	7	0	0	1	0	700	886	60	9.4
NT3	βNCTCD13	NT12	Y	100	1000	7	0	0	1	0	700	884	60	9.3
NT4	βNCTCD14	NT13	Y	100	1000	7	0	0	1	0	700	870	68	6.2

1Where yield is not reported, masses are less than required to determine the nitrogen content, thus were not calculated.
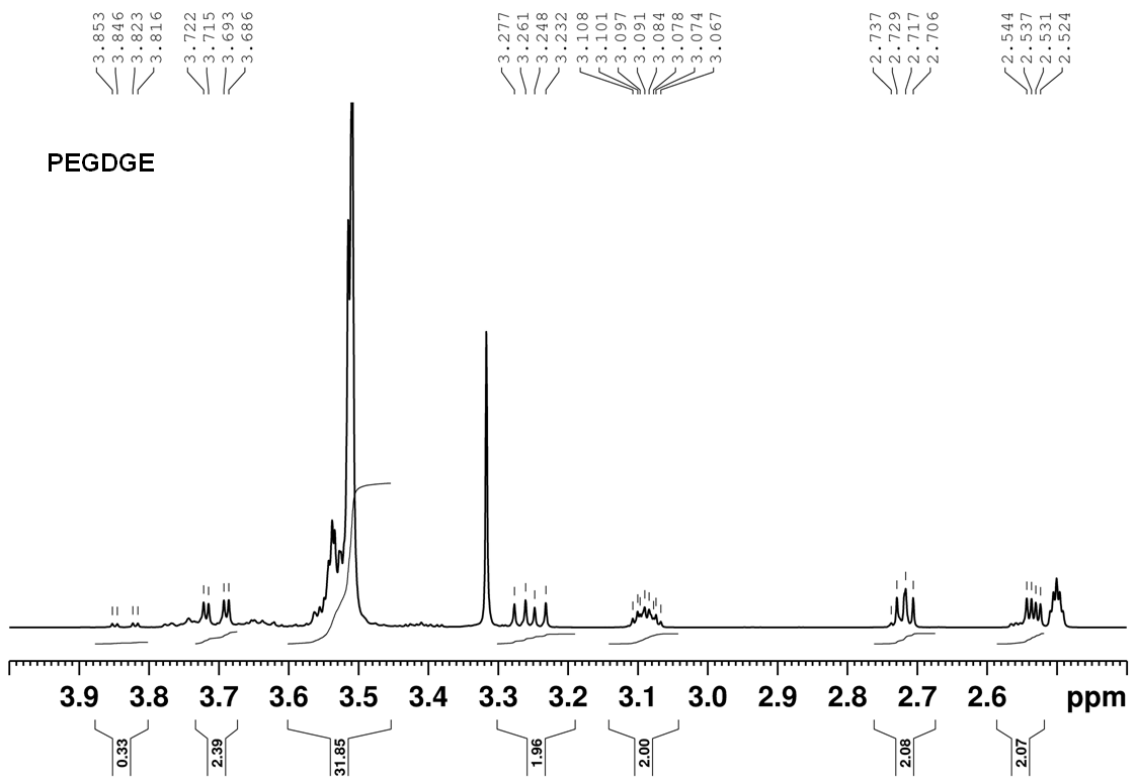
Figure A 1 ^{1}H-NMR spectrum of PEGDGE in DMSO-d$_6$.
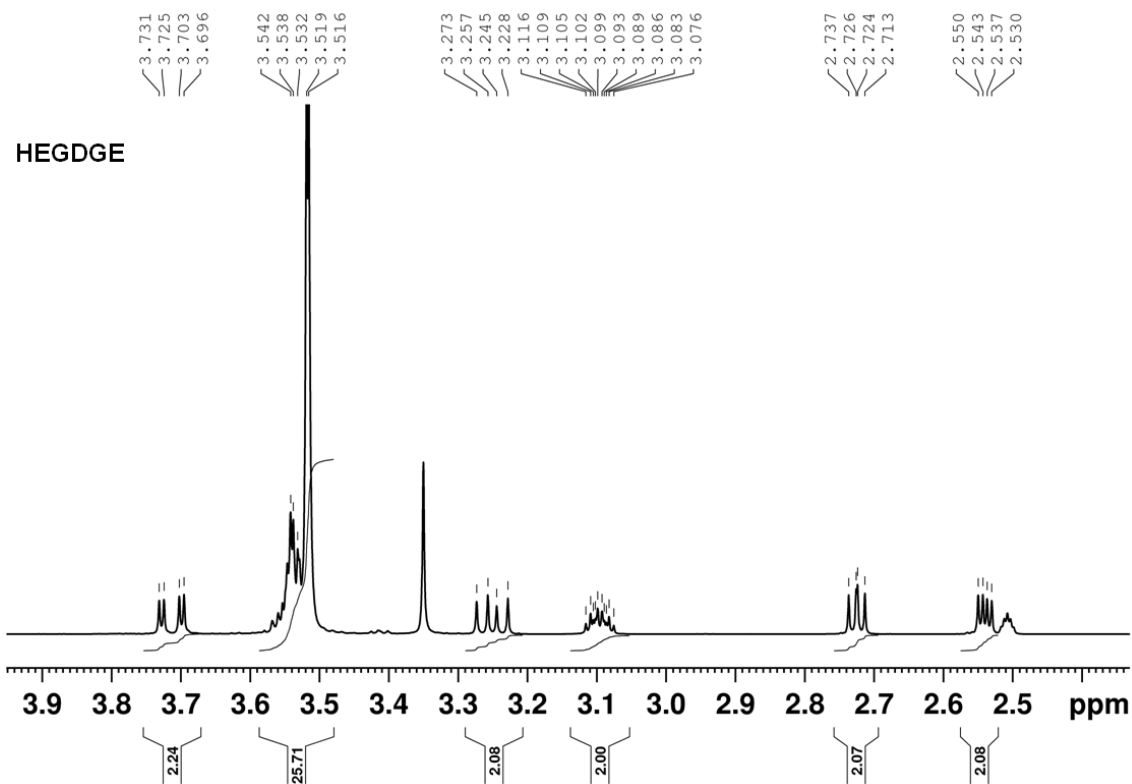
Figure A 2 ^{1}H-NMR spectrum of HEGDGE in DMSO-d[6].
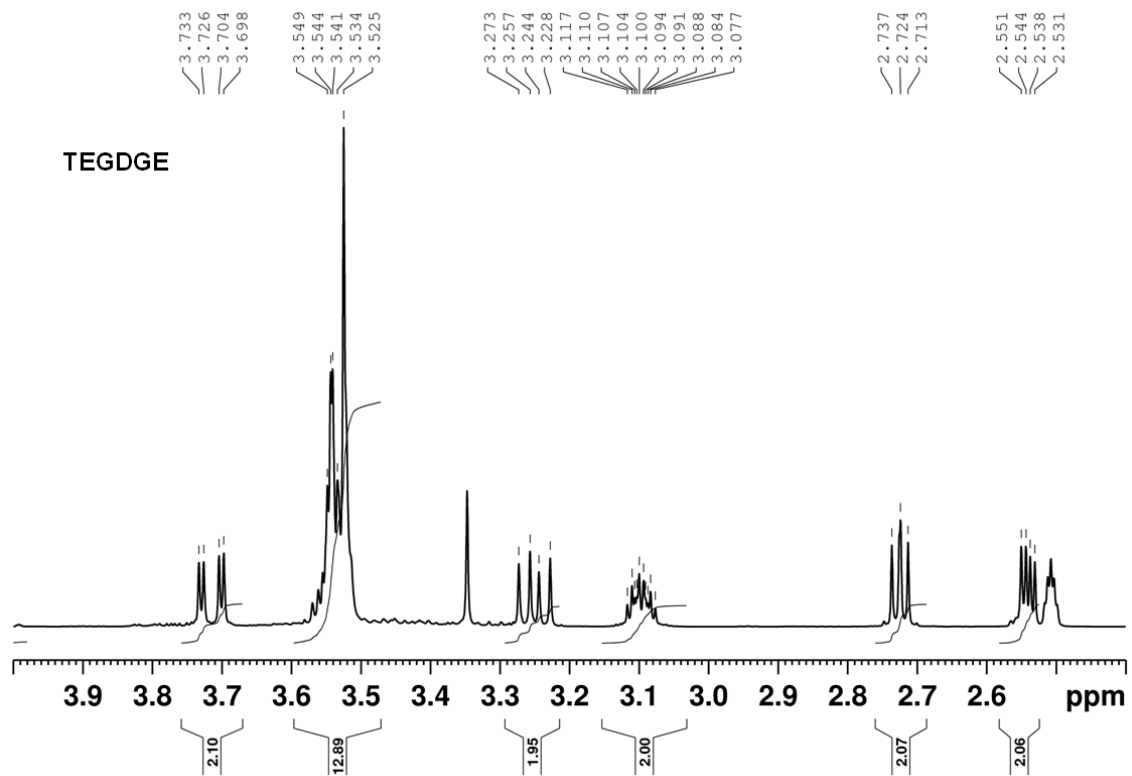
Figure A 3 ^{1}H-NMR spectrum of TEGDGE in DMSO-d[6].
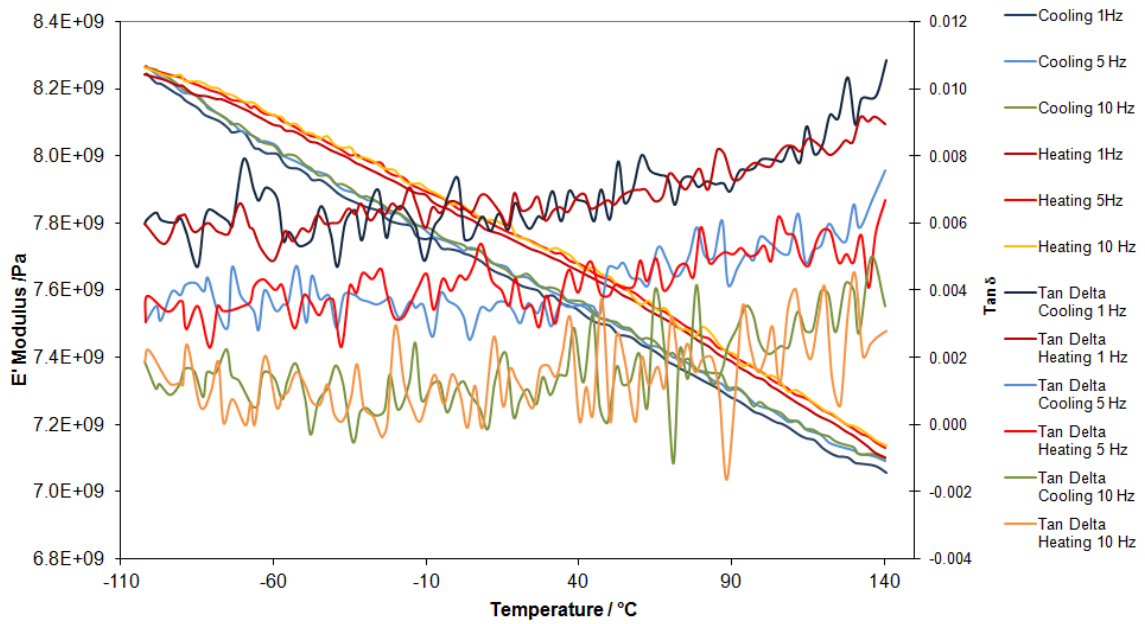
Figure A 4 DMA showing variation in the storage modulus (E′) and tanδ of βCD at 1, 5 and 10 Hz (10 °C min^{-1}, third temperature cycle from −100 to 140 °C, aluminium pocket).
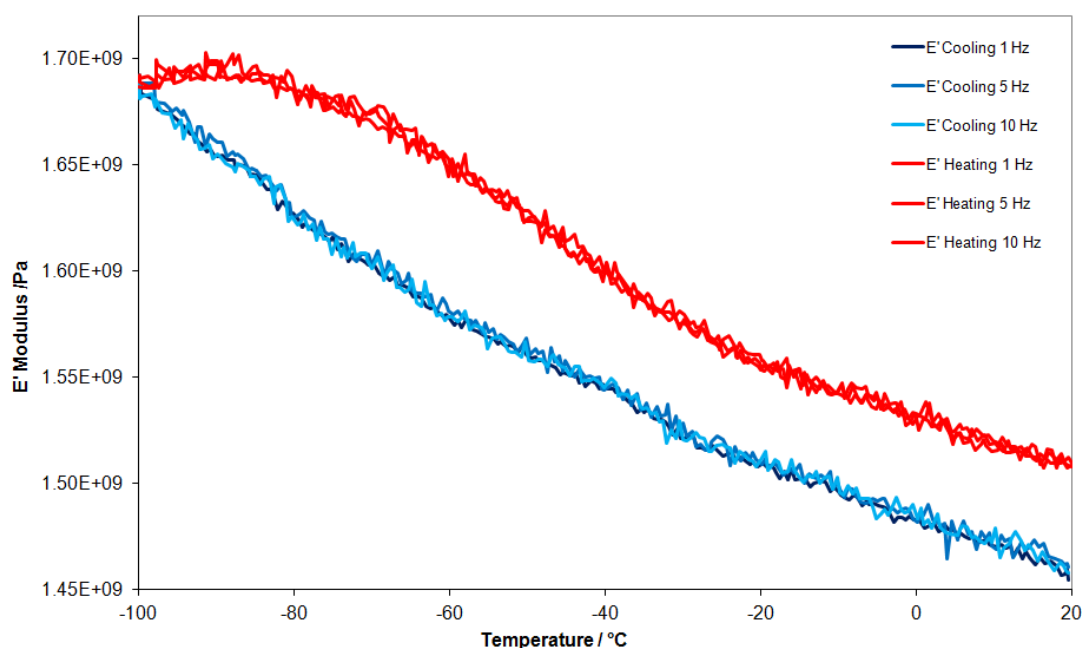
Figure A 5 DMA showing variation in the storage modulus (E′) of the aluminium support (10 °C min^{-1}, 1 Hz, third temperature cycle from –100 to 140 °C, aluminium pocket).
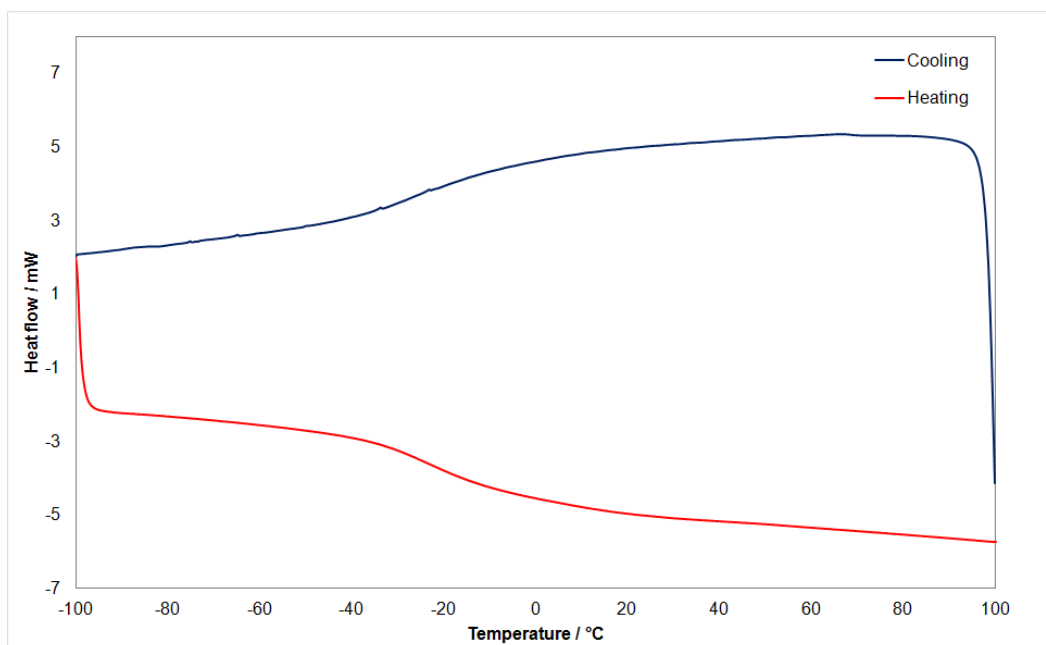
Figure A 6 DSC showing cooling of IP13 from –100 to 100 °C (10 °C min^{-1}, third temperature cycle, aluminium crucible).
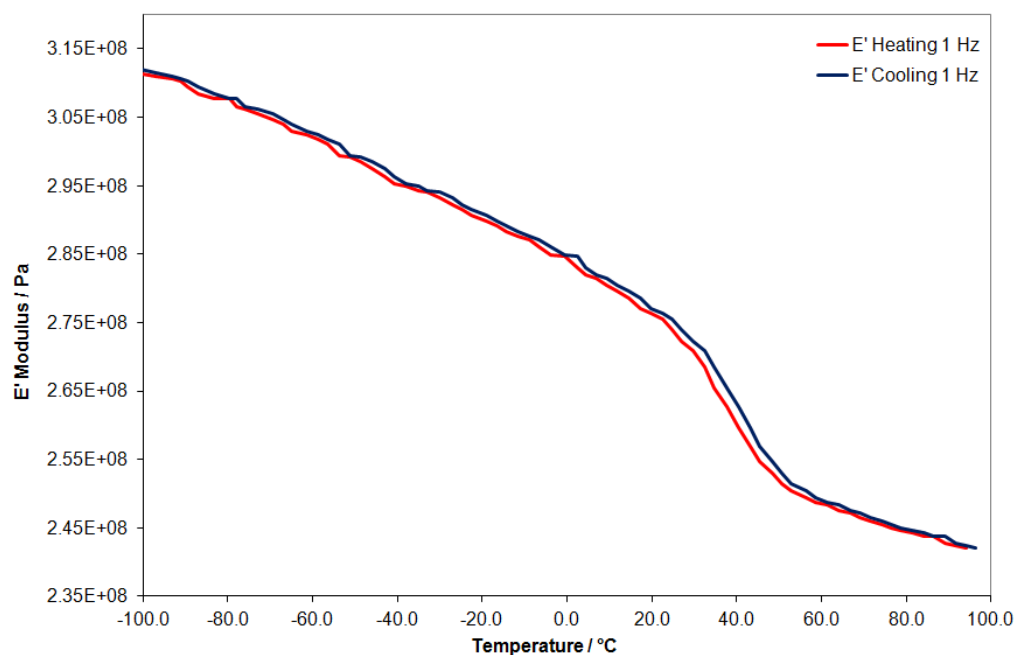
Figure A 7 DMA showing variation in the storage modulus (E′) of the aluminium support and PTFE (10 °C min^{-1}, 1 Hz, third temperature cycle from −100 to 140 °C, aluminium pocket).
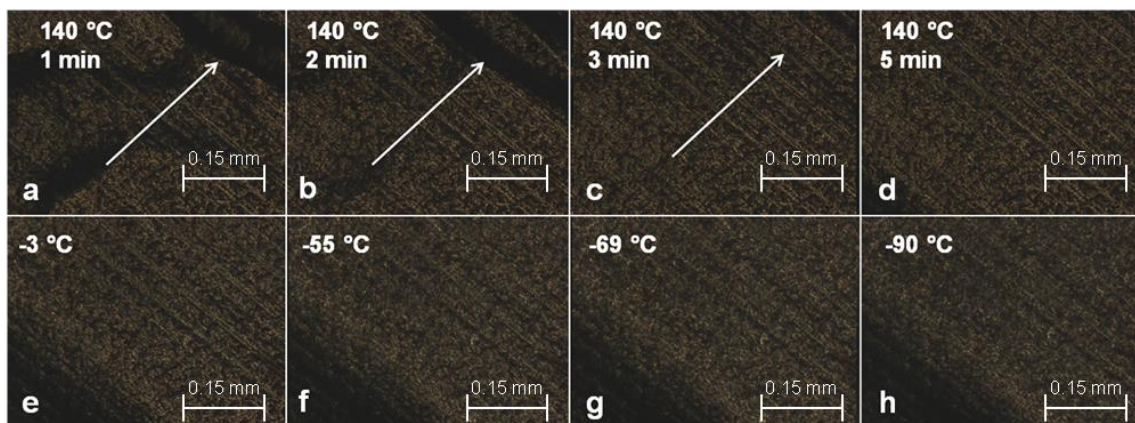
Figure A 8 Optical microscope images of IP9 (PEG:βCD ratio = 3.5) placed on PTFE tape. The sample was annealed at 140 °C for 5 min, top row (a-d), to remove any physical defects (a-b, black shades). The arrow indicates the disappearance of the black shades. The bottom row (e-h) shows the cooling phase captured at −3, −55, −69 and −90 °C and confirms the absence of cracking. The dark shapes on the bottom left of the picture represent condensed water in the cooling chamber.
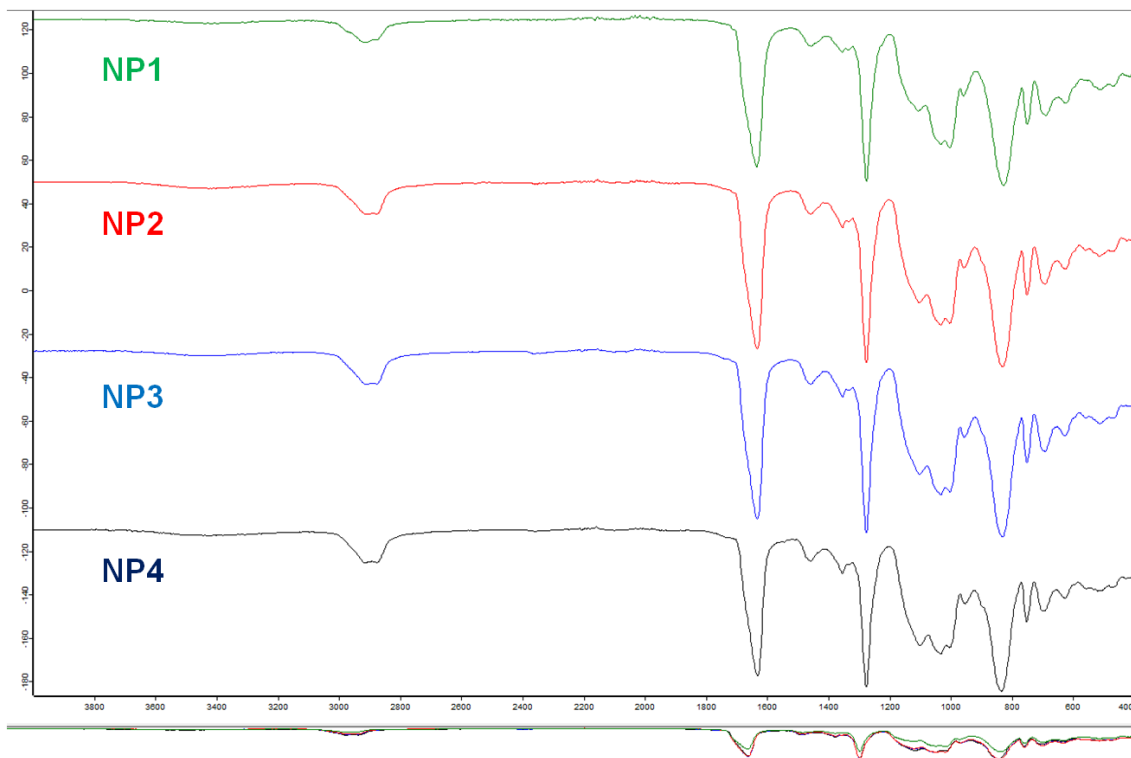
Figure A 9 FTIR spectra of the βNCPCD samples NP1–NP4 containing PEG spacer units.
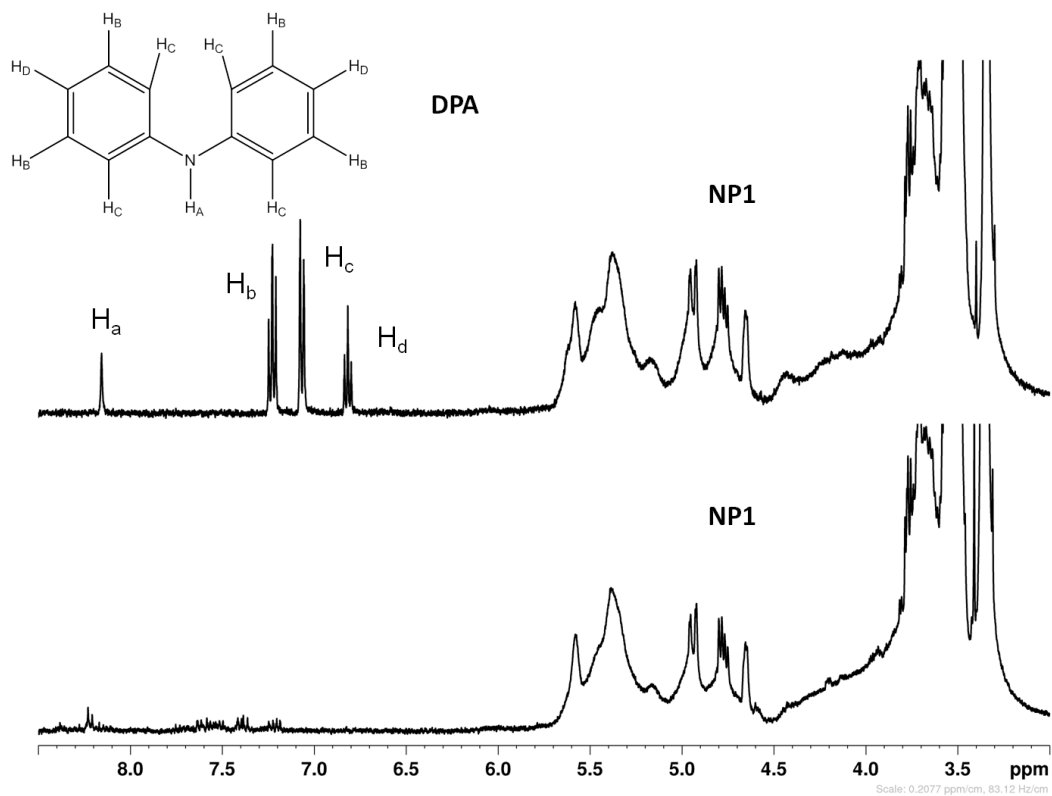
Figure A 10 ^{1}H NMR spectra of (a) NP1 + 1% w/w DPA at time 0, and (b) NP1 + 1% w/w DPA at time 3 d at 80 °C in DMSO-d_6.
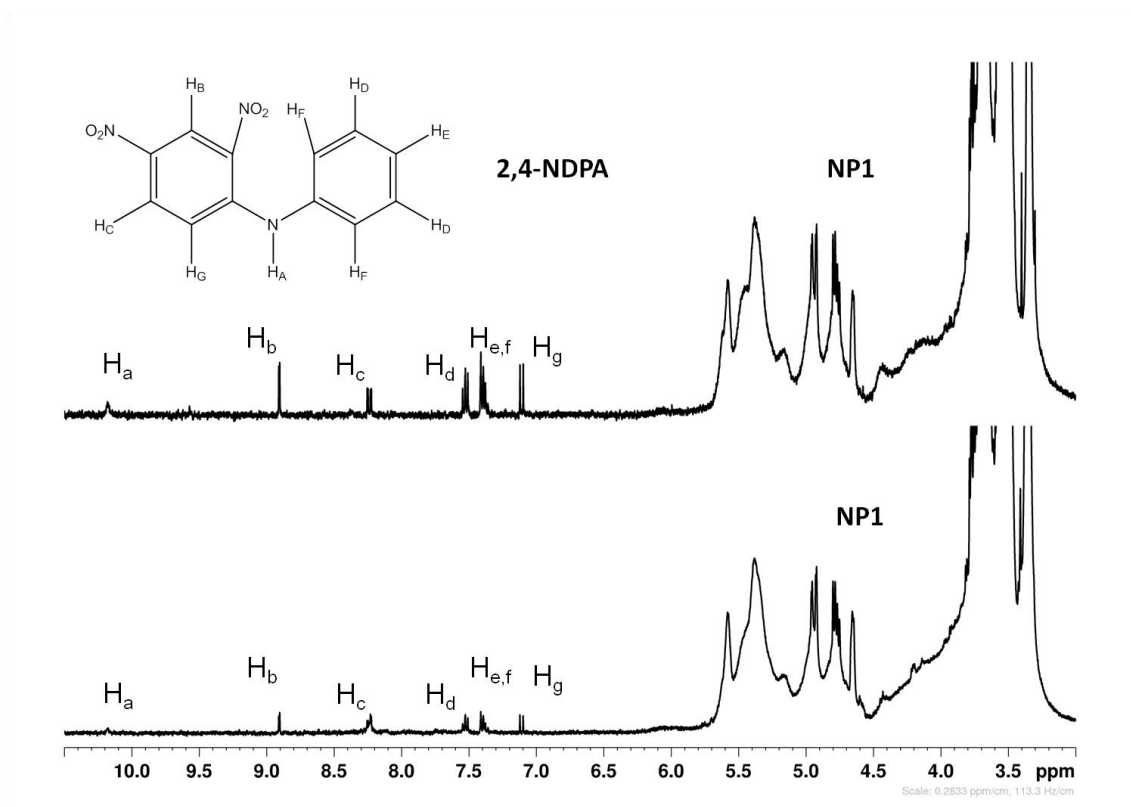
Figure A 11 ^{1}H NMR spectra of (a) NP1 + 1% w/w 2,4-NDPA at time 0, and (b) NP1 + 1% w/w 2,4-NDPA at time 3 d at 80 °C in DMSO-d_6.
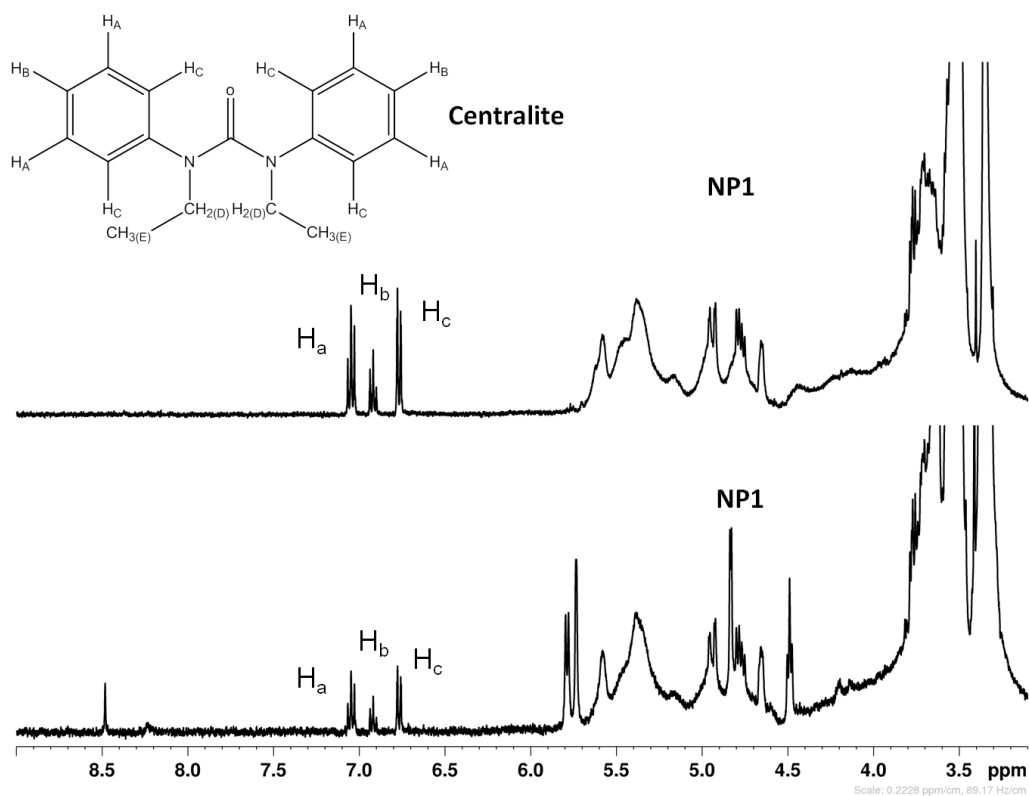
Figure A 12 ^{1}H NMR spectra of (a) NP1 + 1% w/w Centralite at time 0 and (b) NP1 + 1% w/w Centralite a time 3 d at 80 °C in DMSO-d_6.

A.1 Preliminary curing tests of inert βCXCDs and energetic βNCXCDs

Initial tests were performed on inert βCPCD and energetic samples βNCPCD to investigate further cross-linking in the presence of TEGDGE. The curing tests at 70 °C were designed to check the possibility that cured products could be used during the formulation process.

Preliminary curing tests using inert IP18 and nitrated NP1 samples (PEG:βCD ratio = 4.1) were performed with TEGDGE as the curing agent at a βCPCD:TEGDGE ratio of 1:0.2 (Figure A 13). The curing mixtures were prepared by dissolving IP18 or NP1 and the cross-linker in acetone. The samples were stirred for 10 min, the acetone was removed under high vacuum at 40 °C and the samples were left to cure in sealed flasks in the oven at 70 °C for 20 days. The analysis of the sample involved checking the solubility of a

small fraction of the curing samples and analysing the consumption of the cross-linker by ^{1}H-NMR spectroscopy.
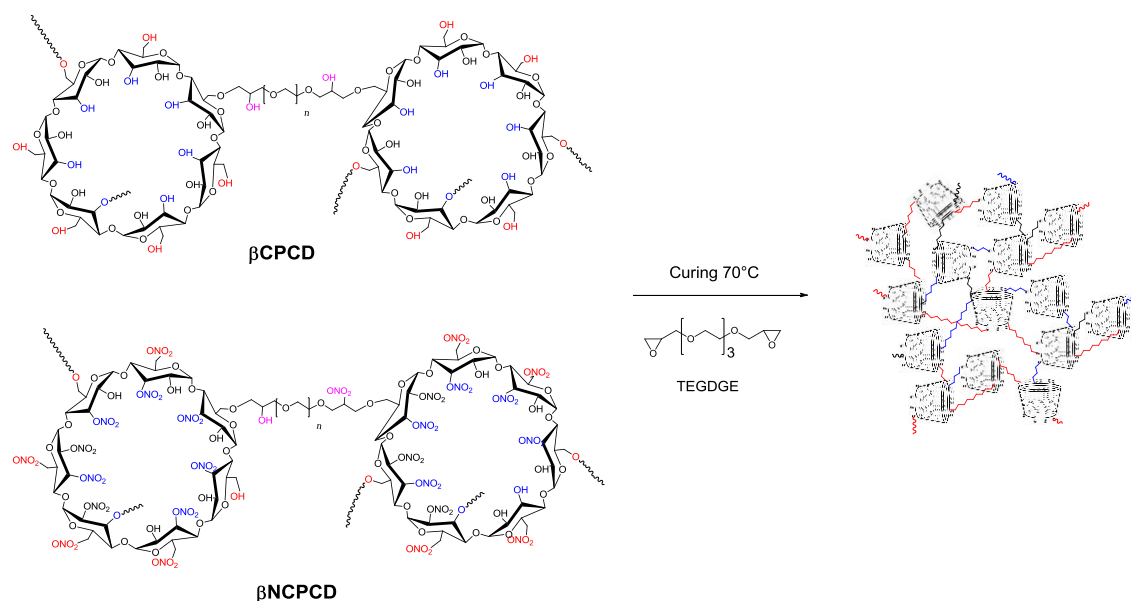
Scheme A 1 Schematic representation of the curing of βCPCD and βNCPCD binders using TEGDGE as the cross-linker.

A visible change in the colour of the mixture was observed after 2 days at 70 °C (Figure A.13b) which was attributed to the ageing of the compounds in the oven. The IP18 sample became partially insoluble in water after 3 days. Characterisation by ^{1}H-NMR revealed that the cross-linker was consumed and/or degraded under curing conditions, suggesting that cross-linking had occurred.
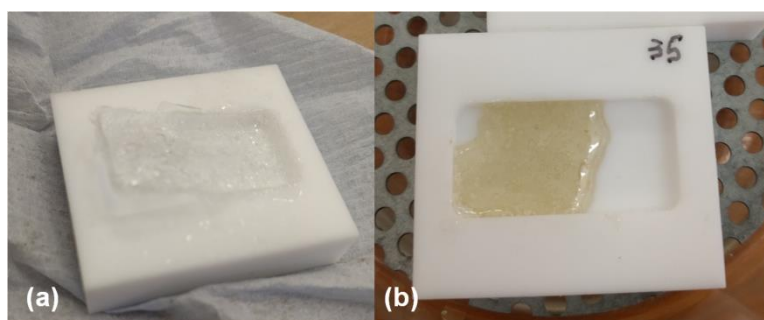
Figure A 13 (a) IP18 before curing and (b) after curing for 2 days at 70 °C.

A colour change was also observed after curing NP1 for 1 day at 70 °C (Figure A.14b,c). This was attributed primarily to the degradation of the nitrate esters, in

addition to the ageing of the compound in the oven. The NP1 sample was still soluble in acetone after 3 days. Characterisation by ^{1}H-NMR revealed that the cross-linker was consumed and/or degraded under curing conditions, suggesting that no cross-linking occurred.

Additional curing tests for the βCXCDs and βNCXCDs are necessary, potentially including the use of curing accelerators.
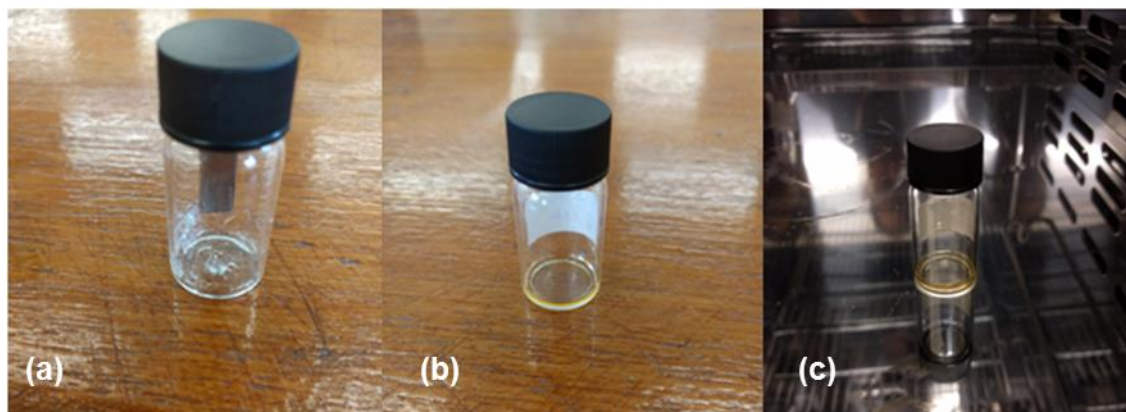
Figure A 14 Comparison of (a) NP1 and the NP1/TEGDGE curing mixture at (b) the mixing time, and (c) after 20 days at 70 °C.

Full Paper

Propellants, Explosives, Pyrotechnics

Nitrated Cross-linked β-Cyclodextrin Binders Exhibiting Low Glass Transition Temperatures

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Abstract: Polymeric binders such as β-cyclodextrins (βCDs) are used to bind with other constituents of energetic formulations and to prevent accidental ignition. One of the advantages of βCDs is the ability to tune their properties by chemical modification. Here, we synthesised nitrated cross-linked βCDs (βNCXCDs) to produce new binders for energetic formulations. The cross-linking of βCD with non-toxic triethylene glycol diglycidyl ether (TEGDGE, X=T) and poly(ethylene glycol) diglycidyl ethers (PEGDGE, X=P) yielded soft, water soluble oligomeric compounds (βCXCDs) which can improve the processability of energetic formulations and contribute to their desensitisation. When the PEGDGE cross-linker was used, lower glass transition temperatures were achieved, which extended the operative range of the βCPCD binder to −20 °C. The analogous nitrated systems (βNCXCDs) were therefore synthesised using a 1:1 (v/v) ratio of 98% sulfuric acid/100% nitric acid or 100% fuming nitric acid, increasing their solubility in acetone and tetrahydrofuran. The nitrated derivatives were characterised by decomposition temperatures (200 °C) and energies (up to 1750 J g^{-1}) comparable to nitrocellulose. Moreover, the glass transition of the inert βCXCDs at low temperatures (<0 °C) was conserved in the corresponding nitrated βNCXCDs, ensuring the desensitisation of energetic compositions even at low temperatures. This is the first time that nitrated derivatives of βCD with glass transition temperatures below 0 °C have been reported, suggesting such derivatives could make suitable replacements for nitrocellulose and other binders in energetic formulations.

Keywords: cross-linked β-cyclodextrin · diglycidyl ethers · energetic binder · low T_g

1 Introduction

Synthetic and semi-synthetic polymeric binders are important components of most energetic formulations [1]. The role of the binder is to improve the overall mechanical properties of the formulation and to coat the energetic molecules, thus shielding them from accidental stimuli and environmental degradation. Nitrocellulose, produced by the nitration of natural cellulose, is the most frequently used semi-synthetic polymer in energetic formulations [1].

During the past three decades, cyclodextrins (CDs) have been introduced as energetic binders in a small number of studies because they are natural molecules with a composition similar to cellulose and they have useful molecular inclusion properties [1,2]. Typical CDs are cyclic compounds containing six, seven or eight sugar rings (α, β and γCDs, respectively) linked together via α-glycosidic bonds. They are particularly useful in the food, cosmetic and pharmaceutical industries because they form complexes within their toroidal cavities with a wide range of molecules [2]. The physical properties of the CDs can be tuned to satisfy specific applications such as shielding other molecules from external stimuli [2,3], which is important in explosive applications [4–5]. The availability of hydroxyl functional groups allows the functionalisation of the macrocycles to further tune their physicochemical properties [2,3].

The inclusion properties of βCD and γCD binders can lead to stabilisation of energetic molecules because these molecules have larger cavities than αCDs [3–5]. Furthermore, nitrated cyclodextrins (NCDs) have been developed as energetic components, although fully-nitrated cyclodextrins are sensitive to electrostatic discharge (ESD), e.g. βCD nitrated to 85% is sensitive to ESD ignition at 0.0125 J [6]. To reduce the ESD hazard, pre-functionalisation before nitration can be achieved using inert molecules as cross-linkers [7,8]. NCDs initially cross-linked with epichlorohydrin in NaOH, polyallylamine in KOH or isocyanate in DMSO, are less sensitive to ESD ignition at 0.1288 J [8], which is a 10-fold reduction in sensitivity. In contrast, longer inert cross-linkers such as poly(ethylene glycol) (PEG) have been used in CD systems for pharmaceutical applications, resulting in the formation of insoluble gels [9,10]. Water-

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soluble CD polymers were obtained when acyl chloride PEG derivatives were used [11] but to the best of our knowledge these derivatives have never been converted to nitrated derivatives.

One of the most important properties of binders in energetic formulations is the glass transition temperature (T_g), at which the rubbery binder becomes glassy and brittle. PEG-based cross-linkers are favoured for their low glass transition temperatures because this increases the operative temperature range within which the cross-linked materials can successfully contribute as a binder [12] and desensitise the energetic formulation. The replacement of highly toxic cross-linkers with non-toxic materials is one of the requirements for new energetic formulations. The REACH regulation of the European Union, has introduced restrictions on the usage of certain isocyanates to improve the protection of human health and the environment from the risks that can be posed by chemicals [13, 14]. In this context, the use of CDs and non-toxic ethylene glycol diglycidyl ethers ensures relatively mild and environmentally sustainable cross-linking conditions: CDs are obtained from natural and sustainable sources, water is used as the reaction solvent, and the reaction temperatures are kept low. The formation of stable ether linkages (C—O—C) between CDs and the diglycidyl ethers also supports further functionalisation such as the nitration of the cross-linked cyclodextrins (CXCDs). Several nitration methods for pure or cross-linked CDs have been reported, ranging from pure nitric acid or nitric/sulfuric acid mixtures to stronger and more advanced systems such as nitration in liquid CO_2 with nitrogen pentoxide [8, 15]. The latest methods achieve full nitration whereas earlier methods resulted in up to 90% nitration of the available hydroxyl groups [15]. The complexation of explosive molecules in the CD cavities also reduces the sensitivity of the explosive to external stimuli [8].

Here we report the synthesis of a βCXCD system and its nitrated derivative βNCXCD using TEGDGE and PEGDGE cross-linkers. The two cross-linkers were chosen as soft segments for their low glass transition temperatures of −80 and −68 °C, respectively [16, 17]. We selected βCD for the initial tests because it is less expensive than γCD. However, the γCD cavity would encapsulate larger energetic molecules and more tests using γCD will be published in the future. All βCXCDs were subsequently nitrated to determine the impact of the βNCXCD systems on degradation energies and the glass transition temperature. We also carried out preliminary studies to determine the degree of compatibility between the inert and nitrated products and energetic fillers.

2 Experimental Section

2.1 Materials

The βCD ($\geq$ 97%, Sigma-Aldrich) was used from stock (TGA, 13% water content). Polyethylene glycol diglycidyl ether (PEGDGE 500 Mw, Sigma-Aldrich), sodium hydroxide (Fisher Chemicals), acetylated dialysis membrane (2000 MWCO, Sigma-Aldrich), tetra-n-butylammonium bromide (TBAB, Sigma-Aldrich), and triethylene glycol (TEG, Sigma-Aldrich) were obtained from commercial sources and used without further purification. Triethylene glycol diglycidyl ether (TEGDGE, 262.0 g/mol) was synthesised as previously described [14]. The βCXCD cross-linking ratio was determined by ^{1}H NMR.

2.2 Characterisation

NMR spectra were recorded on a Bruker Ascend (400 MHz) with a BBFO probe in deuterated dimethyl sulfoxide (DMSO-d_6) solution using tetramethylsilane (TMS) as an internal reference. Spectra were also recorded in deuterated water (D_2O) with 3-(trimethylsilyl)-1-propane-sulfonic acid sodium salt as an internal reference. Peak multiplicities were described as follows: singlet (s), doublet (d), triplet (t), multiplet (m), doublet of doublet (dd), and broad (br). Thermal properties were determined by DSC using a Mettler Toledo DSC822 or DSC30 with heating and cooling rates of $10 °C \, min^{-1}$ and a flow of dry nitrogen. The reported values were the measurements performed on samples with a mean weight of 10 mg for inert materials and low temperature, whereas 1 mg was used to assess the decomposition temperature of energetic materials. Yields were measured as mass of products over mass of reactants. Gel Permeation Chromatography (GPC) measurements were performed in tetrahydrofuran (THF) at 35 °C, using Agilent PLgel 10 μm mixed B columns and Agilent polystyrene calibration kit (M_w 500–6.9 × 10^6).

2.3 Synthesis of βCXCDs

The βCD (5–5.6 g, 3.8–4.4 mmol) was dissolved in 5.6–50% w/w NaOH (21.0 mL) and stirred mechanically for 0–16 h. Diepoxide (TEGDGE n = 3 or PEGDGE n = 9) (17.4–5.8 mL, 13.2–36.9 mmol) was then added dropwise in 20 min with vigorous stirring. The reaction mixture was heated to 30–70 °C for 30 min with vigorous stirring. After cooling for 20 min, the mixture was neutralised with 6 M HCl. The purification method depended on the solubility of the product in water. The volume of solvent for soluble products was reduced and the crude solute was precipitated in acetone three times. The solid was then collected and dissolved in distilled water and dialysed against water using a cellulose membrane (2000 MWCO) for 5 days. The insoluble products

were filtered from the crude reaction mixture and washed with acetone. The insoluble solid was then collected and suspended in distilled water and dialysed against water using a cellulose membrane (2000 MWCO) for 5 days. The dialysis water was replaced every day. The dialysed solid was collected and the water was evaporated under reduced pressure. The final product was characterised by ^{1}H NMR and DSC. ^{1}H NMR (400 MHz, DMSO-d$_6$, ppm): $\delta = 5.9$–5.6 (br m, O$\underline{H}$–C$_2$, O$\underline{H}$–C$_3$, 5.1–4.8 (m, $\underline{H}$-1), 4.7-4.5 (br m, O$\underline{H}_A$, O$\underline{H}_B$ and O$\underline{H}_C$), 4.4 (br m, O$\underline{H}$–C$_6$), 4.0-3.2 (br m, βCD–OC$\underline{H}_2$–(C$\underline{H}$–O$\underline{H}$)–C$\underline{H}_2$–O–C$\underline{H}_2$–C$\underline{H}_2$). DSC (10 °C min^{-1}, N$_2$) 240–250 °C (dec) (See Supporting Information).

2.4 Synthesis of βNCXCDs

Nitric acid (95–100 % 0.5–1 mL) or 100 % nitric acid/100 % sulfuric acid mixture (50:50 v/v, 1 mL) was poured into a round-bottomed flask and cooled to below 10 °C in ice water. Dichloromethane (DCM) (1.8 mL) was added when route 2 reported later in the paper (Figure 2) was followed. The bath was removed and βCXCD (X = P and T, 200.0 mg) was added in small fractions over 5 min, ensuring that the temperature remained below 10 °C. The crude slurry or solution was then left stirring at room temperature for 1 h. The reaction mixture was poured into ice/water (10 mL) and the solid was dissolved in acetone (5 mL) and precipitated in water (100 mL). The clean product was collected, dissolved in acetone and dried under vacuum. Small portions necessary for characterisation were taken and the rest was stored under DCM. The ^{1}H NMR analysis was performed in acetone-d$_6$ and DMSO-d$_6$. DSC (10 °C min^{-1}, N$_2$) 197–210 °C (dec) (See Supporting Information).

3 Results and Discussion

3.1 Synthesis of βCXCDs

Several βCXCDs were synthesised at 70 °C to determine the effect of different parameters on the yield of the reaction and the physicochemical properties of the products. The cross-linked compounds were recovered after cooling the reaction mixture followed by neutralisation with 6 M HCl. The final products were obtained by precipitation from water in acetone followed by dialysis against water using a cellulose membrane with a molecular weight cut-off (MWCO) of 2000 for 5 days.

The cross-linking reaction involved the alkoxidation of βCD combined with diglycidyl ethers of two different lengths: PEGDGE with n = 9 repeating ethylene glycol units and TEGDGE with n = 3 ethylene glycol units. The hydroxide (OH$^-$) ions from the basic medium (NaOH) reacted first with the hydroxyl groups of the βCDs to form alkoxides, and the latter then reacted with the epoxide ring of the diglycidyl ether molecule. The hydroxyl groups of the βCDs would not

react at room temperature with the epoxides. Heating the reaction mixture (up to 70 °C) under variable basic conditions (5.6 % w/w, 40 % w/w and 50 % w/w) led to the partial substitution of all three hydroxyl groups attached to C-2, C-3 and C-6 atoms of βCD units in βCXCDs as from ^{1}H-NMR characterisation in dimethylsulfoxide (DMSO); this is discussed later in this paper. As a general rule for the reactivity of βCD hydroxyl groups, the primary hydroxyl groups attached to C-6 atom (Figure 1), are considered the most reactive [18–20]. The difference of reactivity of the primary and secondary hydroxyl groups of βCD cannot be assessed by the authors in these earlier studies due to the overlap of the hydroxyl proton signals in the NMR analyses. The number of unreacted hydroxyl groups attached to C-2 and C-3 atoms was evaluated by ^{1}H-NMR spectroscopy in dimethylsulfoxide (DMSO) and was found to depend on the concentration of NaOH. The least concentrated NaOH solution (5.6 % w/w) promoted more cross-linkages whereas stronger NaOH solutions (40–50 % w/w) inhibited the formation of the cross-linked product (Table 1) because of i) the higher amount of degraded cross-linker by the reaction conditions discussed in the following paragraph and ii) the supressed formation of βCD-alkoxide in the very viscous reaction mixtures.

Under the basic cross-linking conditions we used, a competitive side reaction occurs and the degradation of the diepoxide cross-linker produces a tetra-hydroxyl by-prod-
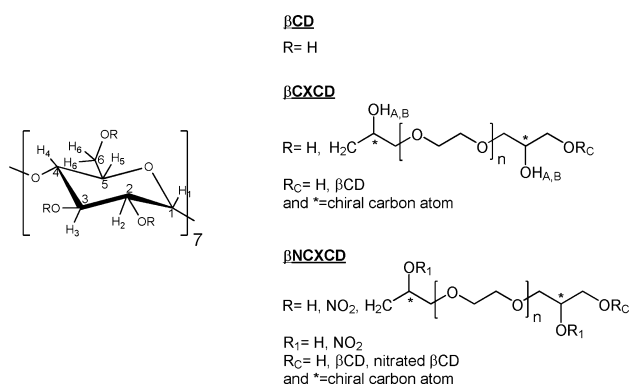
Figure 1. Proposed chemical structure of βCD, βCXCD and βNCXCD (X=T,P) with numbered H and C atoms.

Table 1. Effect of NaOH concentration on the properties of βCPCDs.

Sample[1]	NaOH[2] (% w/w)	Reaction time (h)	Yield[3] (%)	T_g (°C)	Water solubility
βCPCD1	50.0	1.00	<1	–	Y
βCPCD2	40.0	1.00	<1	–	Y
βCPCD3	5.6	0.66	88	−30	N

[1] PEGDGE:βCD ratio = 9:1, [2] Reaction temperature = 70 °C, [3] Yield measured as mass of products/mass of reactants.

uct, thus affecting the yield of the reaction and physical properties of the final product. The effect of the NaOH concentration was investigated at 70 °C for short reaction times ($\leq$ 1 h) (Table 1) and this had a significant influence on the reaction. When the NaOH concentration was low, the reaction become more efficient and reached the gelation point accompanied by the appearance of a solid product and the increasing of the viscosity of the reaction mixture, whereas strong NaOH solutions delayed the formation of gels and affected the yield of the reaction due to faster cross-linker degradation.

We also investigated the effect of the number of ethylene glycol units in the cross-linker when the cross-linker:βCD ratio was maintained at 9:1, and 40 % w/w NaOH was used for all the reactions. The trend of the reactions suggested that TEGDGE produces gels more quickly than PEGDGE. Given this result and the insoluble nature of the gels produced with TEGDGE, we decided to focus on the longer cross-linker (PEGDGE), which was expected to confer better mechanical properties upon the cross-linked products.

Another parameter that affects the cross-linking of βCD is the time needed to prepare its alkoxide. Initial trials suggested that leaving the βCD stirring in basic conditions for 16 h leads to better yields of soluble products (Table 2). It is therefore necessary to allow the cyclodextrin to form the alkoxidic groups prior to the addition of the cross-linker as discussed below. Indeed, the alkoxide promoted successful ether linkage formation between cyclodextrin and PEGDGE (see the Supporting Information).

Table 2. Role of the temperature on the yield of βCPCDs.

Sample	T (°C)	Yield (%)	T_g (°C)	Water solubility
βCPCD4[1]	70	1	–	Y
βCPCD5[1]	50	13	+6	Y
βCPCD6[2]	50	30	−18	Y
βCPCD7[2]	30	34	−22	Y

[1] Cross-linker:βCD = 5:1, 0 h alkoxide formation, 5 h reaction time,
[2] Cross-linker:βCD = 5:1, 16 h alkoxide formation, 5 h reaction time.

Higher temperatures affect the kinetics of cross-linking by increasing the rate of cross-linking and also by accelerating the degradation of the cross-linker. Two sets of trials were carried out using the following conditions: a low concentration of NaOH (5.6 % w/w), a cross-linker:βCD ratio of 5:1, 0 or 16 h for the formation of the alkoxide and 5 h for the cross-linking reaction itself. The longer time for alkoxide formation was set at 16 h based on the results discussed above. The cross-linker:βCD ratio was set to 5:1 to prevent gelation, which occurred at the higher ratio of 9:1. The data summarised in Table 2 suggest that the cross-linker is more stable at 30 °C, but higher temperatures such as 50 °C and

70 °C reduce the yield due to the loss of cross-linker in the competitive degradation reaction.

The effect of the cross-linker:βCD ratio was investigated under the optimal conditions determined thus far, i.e. 5.6 % w/w NaOH, 30 °C, 16 h for the formation of the alkoxide and 5 h for the completed cross-linking reaction (Table 3). The thermal properties of the cross-linked products at low temperatures were affected, i.e. lower amounts of cross-linker resulted in products with higher degree of crystallinity and higher T_g. The ratio of cross-linker:βCD in the cross-linked product is lower than in the initial feed of the reaction. The difference is caused by the degradation of the cross-linker as mentioned above and the NMR analysis of the compounds is discussed in detail later, in the section dealing with characterisation.

Table 3. Effect of cross-linker:βCD ratio on the properties of βCPCDs.

Sample[1]	Cross-linker:βCD ratio feed	Cross-linker:βCD ratio by NMR	Yield (%)	T_g (°C)	Water solubility
βCPCD7	5:1	3.75:1	34	−22	Y
βCPCD8	4:1	3:1	36	−13	Y
βCPCD9	3:1	2.25:1	68	−3	Y
βCPCD10	2:1	1.5:1	44	+8	Y

[1] 5.6 % (w/w) NaOH, 30 °C, 16 h alkoxide formation, 5 h reaction time.

A final investigation demonstrated that the duration of the addition of the cross-linker to the reaction mixture also influenced the reaction yield. If prolonged addition times were used, a small proportion of cross-linker was lost in the competing degradation reaction. Further studies are needed to determine the optimal conditions to improve the yield of water-soluble samples ($\leq$ 68 % at present). Higher yields were achieved only for insoluble gels. The cross-linking of βCPCDs therefore requires further optimisation. The samples obtained in these early experiments were used for the nitration reactions described in the following section.

The images of βCPCD7 and its precursor βCD were compared by scanning electron microscopy (SEM) and the corresponding images are provided in the Supporting Information. The images show the homogeneity of the surface of the βCPCDs, whereas the βCDs have a crystalline appearance.

3.2 Synthesis of βNCXCDs

The βCXCDs were functionalised with nitro groups to form energetic derivatives that can contribute energy to explosive formulations. The nitration of a set of water-soluble βCPCDs and insoluble βCTCD precursors with variable phys-

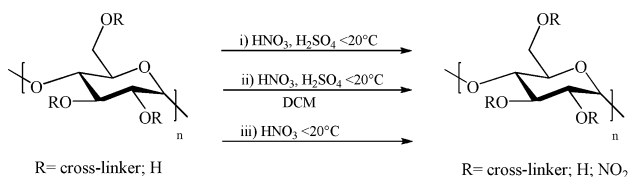ical properties was carried out using the reaction conditions shown in Figure 2.

R= cross-linker; H   R= cross-linker; H; NO$_2$

Figure 2. Overview of the synthesis of βNCXCDs.

In initial tests we evaluated the following nitration methods: (i) using 1:1 98% sulfuric acid/100% nitric acid; (ii) two-phase nitration, using 1:1 98% sulfuric acid/100% nitric acid followed by dichloromethane (DCM); and (iii) using 100% fuming nitric acid as the nitrating phase. DCM did not improve the control and/or efficiency of the nitration reaction because the βNCXCDs were insoluble in DCM and were not extracted from the acidic water phase during the reaction. Therefore, DCM was not included in subsequent experiments. Attempts to nitrate insoluble gel compounds also achieved no control of the nitration reaction, and thus the physicochemical and hazard properties of the products were unpredictable, so these precursors were also abandoned.

The βCXCDs were difficult to dissolve in the mixed acids and their conversion to analogous nitrated products was compromised. The sulfate esters [21,22] of βCXCDs formed in these nitration conditions are expected to affect their solubility and consequently the efficiency of the nitration reaction. In contrast, the βCXCDs dissolved efficiently in the fuming nitric acid within the 1 h duration of the nitration reaction. Table 4 summarises the data obtained when 100% fuming nitric acid was used as the nitrating agent. All βNCPCDs were soluble in organic solvents such as acetone and THF, suggesting good processability, which is important in energetic formulations because the different components must be mixed thoroughly. The βNCPCDs were purified by re-precipitation from acetone in water and their thermal stability was satisfactory, as shown by their high decomposition energy and negative T$_g$ values. A nitrated sample βNCPCD1 was examined by gel permeation chromatog-

raphy (GPC) in THF and compared with poly(styrene) standards. The results Mn = 7350 Da and Mw = 15140 Da, confirmed the polymeric nature of the sample (see Supporting Information).

Like the βCPCDs precursors, the T$_g$ of the nitrated products was dependent on the number of soft ethylene glycol units in the cross-linker. The T$_g$ increased when less PEGDGE was used (Table 4) and we speculate from very preliminary modelling [23] investigation on nitrated CDs that the polar nitro groups could inhibit the mobility of the polymeric chains. On the other hand, the large number of OH to ONO$_2$ (nitrato) transformations contributed to the overall energy of the system. The decomposition temperature (T$_{dec}$) stabilised at 196 °C, which is similar to nitrocellulose samples with a 12.5% nitrogen content [24]. As expected, the energy of the system was also affected, with higher decomposition energies (ΔH$_{dec}$) such as 1750 J g^{-1} for sample βNCPCD3. The thermal properties of the βNCPCDs can be tuned to give the desired product for specific applications. A very small, second-order transition was observed in all thermograms at ~80 °C, which was attributed to the glass transition of the rigid βCD units in the cross-linked systems.

When TEGDGE was used as the cross-linker, both the βCTCD precursors and the βNCTCDs derivatives were insoluble gels. The βNCTCDs were characterised by low T$_g$ values, thermal stability and relatively low decomposition energies compared to the analogous βNCPCDs (Table 4). Although the cross-linker:βCD ratio was 9:1 to guarantee low transition temperatures, the degree of nitration was lower in these materials due to the inability of the acids to penetrate the polymer structure and efficiently nitrate the hydroxyl groups of the βCD units. The nitration of the same βCTCD resulted in the synthesis of βNCTCDs with variable properties. This highlights the lack of control over the nitration of insoluble products. Also, it was difficult to purify the insoluble βNCTCDs from the acid traces. The stability of these products and their hazard properties is strongly affected by the efficiency of the purification process.

3.3 Chemical Characterisation

The cross-linked products we synthesised were characterised by ^{1}H NMR spectroscopy in deuterated dimethylsulf-

Table 4. Thermal properties of βNCXCD oligomers.

Nitrated sample[1]	Precursor Name	cross-linker:βCD	Reaction time (h)	T$_g$ (°C)	T$_{dec}$ (°C)	ΔH$_{dec}$ (J g^{-1})
βNCPCD1	βCPCD7	5:1	1.0	−20	202	1500
βNCPCD2	βCPCD8	4:1	1.0	14[2]	197	1640
βNCPCD3	βCPCD9	3:1	1.0	19	199	1750
βNCTCD1	βCTCD1	9:1	1.0	−21	210	530
βNCTCD2	βCTCD1	9:1	1.0	−20	208	650

[1] Using 200 mg of precursor and 1 mL 100% HNO$_3$, [2] Very broad transition; more investigation needed.

oxide (DMSO-d_6) and deuterated water (D$_2$O) as solvents. DMSO-d_6 was used to investigate the reactivity of the hydroxyl groups of the βCDs at 4.4–5.5 ppm (Figure 3 and 4).
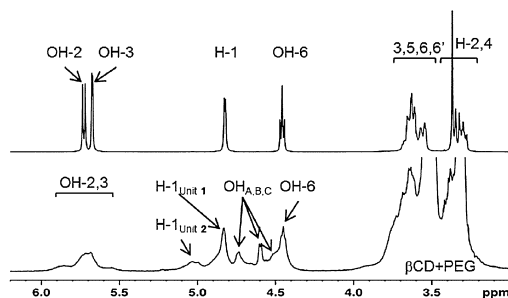

Figure 3. ^{1}H NMR spectrum of βCD and βCPCD8 in DMSO-d_6, suggesting the assignment of the proton of the OR groups when no substitution occurs. The OH$_C$ assignment is expected when R$_1$=H.
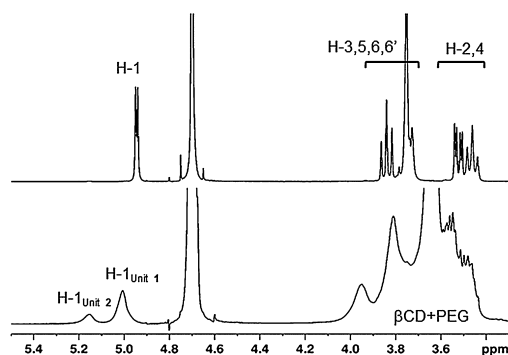

Figure 4. ^{1}H-NMR spectra of βCD (top) and βCPCD8 (bottom) in D$_2$O.

The spectrum of the βCPCDs shows broadened peaks due to the larger cross-linked molecules, when compared to the spectrum of pure βCD [2]. New peaks appear in the spectrum (Figure 4) and are attributed to the three hydroxyl groups (OH$_A$, OH$_B$ and OH$_C$ when R$_C$=H) on the cross-linking units. Due to the similar environments in the compound, many signals overlap. The water peak which overlaps the signals of the product at 3.3–3.4 ppm in DMSO-d_6 moves in the hydrogen-deuterium oxide (HDO) when D$_2$O is used, allowing us to determine the cross-linking ratio as reported below.

The cross-linker:βCD ratio in βCPCDs was calculated [11] from the ^{1}H NMR in D$_2$O (Figure 4).

- Integral 1 at 4.8–5.1 ppm = $n_{\beta CD}$ H-1 protons

- Integral 2 at 3.2–4.0 ppm = $6n_{\beta CD}$ H-2 to H-6 protons + $44n_{cross-linker}$ protons

The results show that the cross-linker is not consumed in the competing degradation reaction at 30 °C, allowing the reactants to react in a quasi-stoichiometric manner (25 % lower than the anticipated theoretical value, Table 3).

The βNCTCDs and βNCPCDs were characterised by ^{1}H NMR in acetone-d_6 and DMSO-d_6. The spectra recorded in DMSO-d_6 were compared with those of the starting oligomers and with a sample of nitrated βCD (βNCD) synthesised under the same conditions [15]. Figure 5 shows the ^{1}H NMR spectra of βNCD and βNCXCD in DMSO-d_6.
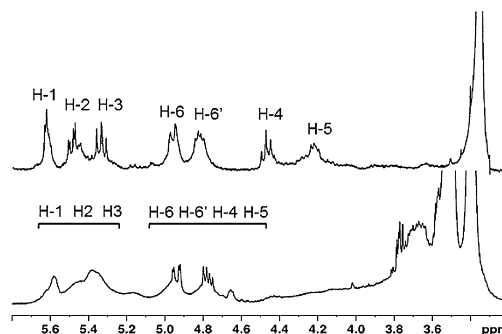

Figure 5. ^{1}H NMR spectra of βNCD (top) and βNCPCD1 (bottom) in DMSO-d_6. In the βNCPCD1 spectrum (bottom), the signals near the water peak are assigned to protons that are not near the nitrato groups.

The βNCPCD1 signals were broader due to the polymeric nature of this product. The broadness of the peaks and the down field shift of the signals compared to βCPCD reflect the complex chemical environment present in this energetic polymer. The different degrees of nitration on the cyclodextrin units result in overlapping signals representing protons close to the nitrato groups. The reference peak of proton H-1 close to the glycoside bond is present at 5.60 ppm. The broad signals at 5.55–5.10 ppm can be assigned to protons H-2 and H-3 attached to asymmetric carbon atoms 2 and 3, whereas the signals at 5.10–4.60 ppm can be assigned to CH$_2$, which is adjacent to nitrato groups in both βCD and the cross-linker units. Finally, the signals at 4.6–4.0 ppm can be assigned to CH$_2$ protons belonging to both βCD and the cross-linker units that are not adjacent to a nitrato group, but close enough to be influenced by them. The signals between 3.8 ppm and 3.2 ppm can be assigned to the methylene of the ethylene glycol units which are farthest from and least affected by the nitrato groups.

The degree of nitration in βNCD was determined using a previously described analytical method [15] and was nearly 90 %. The degree of nitration in the βNCPCDs will be assessed in future studies based on iron sulfate titration and comparison with ion chromatography data.

3.4 Thermal Characterisation

The T_g of the βCXCDs and βNCXCDs was determined by differential scanning calorimetry (DSC) within the temperature range $-100\,°C$ to $100\,°C$ at $10\,°C\,min^{-1}$ and the results are reported in Tables 1–4. The T_g of the βCXCDs ranged between $-22\,°C$ and $+8\,°C$ and increased in line with the proportion of βCD because the cross-linker introduces more mobility into the system. The glass transitions reported for a similar cross-linked system based on a carboxylic acid PEG linker ranged from $-20\,°C$ to $-16\,°C$ [11]. These values are consistent with the properties gained by the cross-linked system studied herein.

The low T_g of the βCXCD precursors was transferred to the βNCXCD derivatives and ranged from $-20\,°C$ to $+19\,°C$ (Table 4). This transition is particularly wide compared to the non-nitrated precursor (Figure 6) and the material begins to soften at very low temperatures. The T_g midpoint is difficult to determine in the nitrated product due to the broadness of the transition, which may reflect the sum of different arrangements of the entangled cross-linker chains in the compound. Dynamic mechanical analysis (DMA) of βCXCD and βNCXCD samples is currently underway and the results will be published in a separate article.
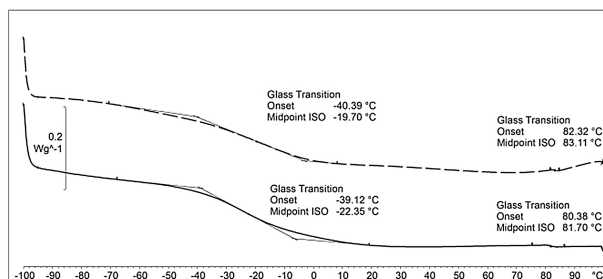

Figure 6. DSC thermogram of the glass transition of βCPCD8 (solid line) and βNCPCD1 (dashed line) between $-100\,°C$ and $100\,°C$.

All βNCPCDs derived from water-soluble βCPCD precursors showed similar thermal stabilities, with decomposition occurring at $\sim200\,°C$. This is comparable with the decomposition of nitrocellulose [24]. The decomposition energy fell within the range 1500–1750 J g^{-1} (Figure 7).

The energy released by the βNCXCDs was similar to that released by nitrocellulose samples with a nitrogen content of 12.5% measured using the same method [24]. As expected, cross-linking affected the maximum nitrogen content of the βNCXCDs, which declined with the increasing content of inert ethylene glycol chains. DSC revealed that the βNCXCD systems displayed lower decomposition energies than the βNCD sample with 90% nitration (1880 J g^{-1}). Micro-calorimetry measurements will be performed in the future to measure the decomposition energy of the βNCXCDs and the effective release of energy from these systems.
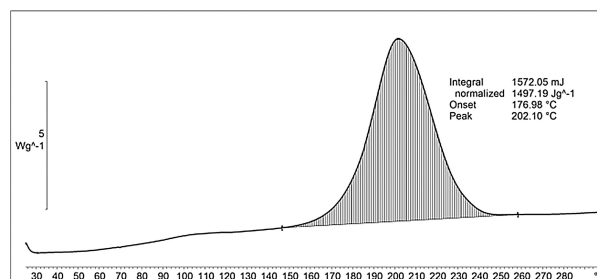

Figure 7. DSC thermogram of the decomposition of βNCPCD1.

The attempted nitration of insoluble βCXCD products also yielded compounds with a decomposition event at $\sim200\,°C$, but the decomposition energy was 500–800 J g^{-1}. This reduction in energy probably reflects the presence of fewer nitrato groups after nitration given the less accessibility to the hydroxyl groups of βCXCDs and a higher proportion of cross-linker in the system.

3.5 Compatibility Assessments

Initial compatibility tests based on DSC were carried out to determine whether contact between the βNCPCDs and energetic ingredients in a formulation could lead to undesirable or unexpected hazards. Sample βNCPCD1 was mixed with energetic fillers such as oxidisers, pyrotechnics and high explosives, and preliminary DSC compatibility tests were carried out according to STANAG 4147 Test 4 [25]. Any chemical interaction between the ingredients should lead to a change in the decomposition profile of the formulation. The thermal decomposition of the single ingredients and their mixture was compared (Table 5). The compounds were mixed in a 1:1 w/w ratio (total amount 1.0 mg) and heated from 30 to 500 °C at a rate of 2 °C min^{-1}.

Sample βNCPCD1 was tested with oxidisers such as ammonium dinitramide (ADN), potassium chlorate (KClO$_3$), ammonium perchlorate (NH$_4$ClO$_4$) and ammonium nitrate

Table 5. Summary of compatibility tests using βNCPCD1.

Energetic Name	Mixture			
	T_{deg} (°C)	T_{deg} (°C)	ΔT (°C)	Change in shape
ADN	174	161	−13	Significant
KNO$_3$[1]	–	–	–	Minor
NH$_4$ClO$_4$	300	242	−58	Significant
NH$_4$NO$_3$[1]	–	–	–	Significant
KClO$_3$[1]	–	–	–	–
Red Phosphorous	400	404	+4	Minor
PETN	185	187	−2	None
HMX	279	279	0	Minor
RDX	225	210	−15	Minor

[1] No degradation observed.

(NH_4NO_3). No changes in either the decomposition temperature (T_{dec}) or the curve shape were observed for mixture βNCPCD1/$KClO_3$ compared to the thermogram of the pure oxidiser (Table 5). We found that βNCPCD1 is not compatible with NH_4ClO_4 or NH_4NO_3 and that ADN shifted the T_{dec} by −13 °C and changed the shape of the curve. Further vacuum stability tests are needed to confirm compatibility with ADN. Sample βNCPCD1 showed good compatibility with pyrotechnics such as red phosphorous. All thermograms are provided in the Supporting Information.

Sample βNCPCD1 also showed good compatibility with symmetric nitro-esters such as pentaerythritol tetranitrate (Figure 8) suggesting that βNCPCDs could potentially be combined with nitroglycerine in double-based and triple-based propellants [26].
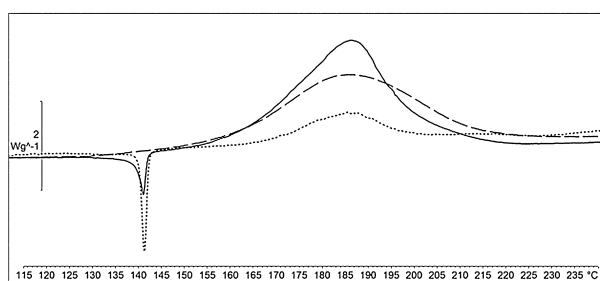

Figure 8. Thermograms of pentaerythritol tetranitrate (dotted line), βNCPCD1 (dashed line) and the mixture (solid line) at 2 °C min⁻¹.

Nitramines such as RDX and HMX were also tested for compatibility with βNCPCD1. Although the T_{deg} of RDX was 15 °C lower when mixed with βNCPCD1, the degradation of HMX was not affected (Figure 9).
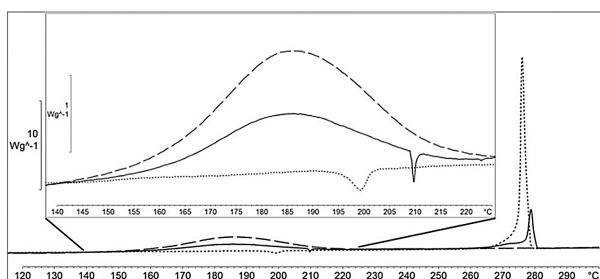

Figure 9. Thermograms of HMX (dotted line), βNCPCD1 (dashed line) and the mixture (solid line) at 2 °C min⁻¹.

The small amount of HMX used in the test underwent degassing within the degradation temperature range of βNCPCD1. The phenomenon was detected by DSC as an endothermic peak at 210 °C. The measurement was repeated several times and the endothermic peak shifted at different temperatures every time, supporting the degassing hypothesis.

4 Conclusions

The synthesis of βCXCD systems from βCD and diglycidyl ethers yielded cross-linked insoluble or water-soluble derivatives with low T_g values down to −30 °C, the first such observation for this type of product. The physicochemical properties of the products were affected by several reaction parameters, including the temperature, cross-linker:βCD ratio, concentration of NaOH, time allowed for the formation of βCD alkoxide, and the duration of reaction with the cross-linker. The cross-linking reaction parameters were tuned to obtain soft, soluble precursors to make the subsequent nitration reaction safer and more consistent. The polymers were water soluble if prepared with a PEGDGE:βCD ratio of up to 5:1 at 30 °C. The T_g of the cross-linked materials was primarily affected by the quantity and length of PEG spacer present in the system.

The βNCPCDs retained some of the mechanical properties of the precursor systems. The T_g was maintained below 0 °C after the nitration of βCPCD derivatives made of high βCD:cross-linker ratio. The presence of polar nitrato groups on the cross-linked molecules increased the packing density of the molecules and thus reduced their freedom, increasing the T_g. Thermal analysis revealed that the nitrated products soften from −60 °C in a linear manner. The thermal stability and energy released by the βNCPCDs is similar to that observed for nitrocellulose samples with a nitrogen content of 12.5–13.5 % making them promising nitrocellulose substitutes in energetic compositions. The further processing of βNCXCDs using the same purification methods applied to nitrocellulose would improve the thermal stability even more.

Initial compatibility tests indicated that βNCPCDs may be suitable binders in formulation with selected energetics. The reaction will need to be scaled up for proper compatibility and Energetic Materials Testing and Assessment Policy (EMTAP) tests to determine the sensitivity of the new nitrated cross-linked compounds to ESD.

5 Recommendations/Future work

The assessment of the properties of the new nitrated cross-linked β-cyclodextrins developed in this work is in progress. Investigation of the change of properties with time and overall ageing of the nitrated binder as well as their compatibility with stabilisers/plasticisers is recommended. The cross-linking reaction of βCD with TEGDGE and other ethylene glycol diglycidyl ethers is currently investigated.

Supporting Information

The following files are available free of charge.

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Material Properties

Thermomechanical characterisation of cross-linked β-cyclodextrin polyether binders

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ABSTRACT

Cyclodextrins are promising building blocks for the synthesis of industrial binders. A new binder was prepared by cross-linking β-cyclodextrin with variable amounts of polyethylene glycol diglycidyl ether (40–60% w/w) to produce a soft polyether network that was soluble in water and alcohol, and the thermomechanical properties of the binder were determined. Increasing the amount of cross-linker reduced the glass transition temperature of the binder, as determined by differential scanning calorimetry and dynamic mechanical analysis. Cooling experiments revealed sudden stress relief below the glass transition temperature, reflecting the de-bonding of the polymer from the metallic supports. This was prevented by contact with polytetrafluoroethylene tape. Optical microscopy confirmed the stress relief in the form of cracking, and revealed self-healing by reptation, promoted by a higher cross-linker content and temperature. The information gained on the influence of the support medium on the thermomechanical properties of the cross-linked β-cyclodextrins can be used by industry for optimising manufacture and storage methods for new binders.

1. Introduction

Binders are typically large molecules that are used to bond the particulate components in formulations and improve the physicochemical properties of the mixture. The paint manufacturing industry is historically one of the major investors in the development of new polymeric binders in order to improve the cohesion of pigment particles and adhesion to the coated substrate following evaporation of the solvent [1–3]. The electronics industry uses binders to improve the conductivity and mechanical strength of electrodes in batteries [4–6]. Binders are also used in rocket manufacturing to improve the safety and ballistic performance of propellants [7,8]. Finally, medical researchers seek biocompatible binders that facilitate controlled drug release [9]. Most current binders are derived from petrochemical resources and there is a strong demand for more sustainable alternatives [4,10–12].

Cyclodextrins (CDs) are polysaccharides derived from starch that provide a promising set of sustainable building blocks for the synthesis of new binders, particularly in the pharmaceutical industry [14]. As shown in Fig. 1, these toroidal macrocycles comprise six, seven or eight glucopyranose units to form α, β and γ CDs, respectively [14]. CDs have the ability to complex small molecules and alter their physicochemical properties, allowing the controlled release of drugs [15,16] or the entrapment and inactivation of toxins [17]. The many hydroxyl groups

carried by CDs are easily derivatised to yield binders that can be used to manufacture electrodes [18–20] or drug products [21–24]. Polymeric derivatives of all three types of CDs can respond to external stimuli such as pH or temperature, and safely deliver their cargoes of drugs to target organs [25–27]. In order to process the encapsulated drugs, crystalline CDs have been chemically modified to allow the incorporation of drugs during extrusion [26–28]. CDs were cross-linked with either multifunctional isocyanate or ethylene glycol diepoxides to form insoluble hydrogels, which can easily be formulated into pills or capsules [15,29–32]. These hydrogels are thermoresponsive and some of them self-heal following physical damage [31,33]. The self-healing mechanism relies on the supramolecular interactions in the hydrogel, such as hydrogen bonding promoted by the hydroxyl groups in the polymer [34] and interactions between CD macrocycles and the polyether chains [35–37]. Furthermore, the soft hydrogel matrix allows the polymer chains to diffuse and re-bond in a damaged area [38–40]. The self-repair of damaged synthetic materials typically involves physical flow of the material at or near the damaged area followed by reversible covalent bonding or supramolecular chemistry, which also includes metal-ligand coordination, π-π stacking and ionic interactions [41].

Most self-repairing CD systems show a high degree of cross-linking and are insoluble in water and common organic solvents. This limits their use as binders because post-synthesis reactions cannot be achieved
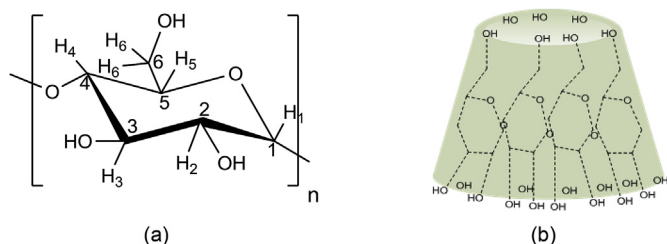

Fig. 1. a) Chemical structure of α (n = 6), β (n = 7) and γ (n = 8) cyclodextrins. b) Toroid structure of a cyclodextrin molecule [13].

without modifying the chemical structure, and the hydrogel becomes brittle because it cannot dissipate mechanical stress when swollen [42]. To address these drawbacks, we recently synthesised water and alcohol soluble cross-linked βCDs using polyethylene glycol diglycidyl ether (βCPCDs) [13]. Here, the thermomechanical properties of the cross-linked βCPCD system are characterized and the thermosensitive, self-healing and adhesive behaviour of the synthetic materials investigated by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). These experiments provide more information about these new binders and will facilitate the development of appropriate manufacturing and storage methods.

2. Materials

The βCPCD samples were synthesised from βCD (≥97% purity, Sigma-Aldrich) prepared as a stock (13% water content, determined by thermogravimetric analysis) and polyethylene glycol diglycidyl ether (PEGDGE, Sigma-Aldrich, Mw = 500 Da, polydispersity index = 1.7), as previously described [13]. The chemical structure and purity of all precursors and products were assessed by proton nuclear magnetic resonance (^{1}H NMR) spectroscopy and DSC. The PEGDGE/βCD ratios used are reported in Table 1, and the PEG/βCD ratio in the cross-linked products was determined by ^{1}H NMR, as previously described [35]. The physical appearance of the cross-linked products was influenced by the proportion of PEGDGE: cross-linked malleable products were generated when the PEGDGE content exceeded 50% w/w (Fig. 2a, sample βCPCD1), whereas powdery products were generated when less PEGDGE was present (Fig. 2b, sample βCPCD3).

3. Experimental

3.1. Dynamic mechanical analysis

The thermomechanical properties of the βCPCD products were determined by DMA using a Perkin Elmer DMA8000 device. The samples underwent a controlled sinusoidal displacement of 0.05 mm at frequencies of 1, 5 and 10 Hz in the single cantilever clamping bending
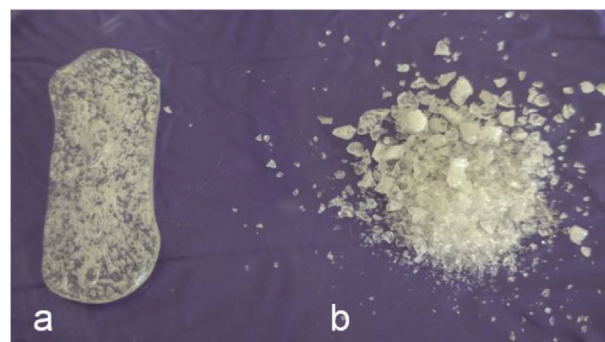

Fig. 2. Physical characteristics of βCPCD: a) malleable βCPCD1, and b) powdery βCPCD3.

configuration. The storage modulus (E′), loss modulus (E″) and damping factor (tanδ) were monitored as a function of temperature and time. The free sample length between the vibrating and fixed cantilever clamps was ~15 mm. The test temperature was cycled three times between −100 and 140 °C at a rate of either 2 or 10 °C min^{-1}. Each material was tested in triplicate under each condition.

The cross-linked βCPCD samples were incapable of self-support and were, therefore, tested in aluminium pockets (Fig. 3a), a stainless steel mesh (Fig. 3b), or aluminium pockets with polytetrafluoroethylene (PTFE) tape (Fig. 3c) with the aim of assessing the debonding effect of the polymer on the support. The aluminium pockets recommended by Perkin Elmer consisted of rectangular shims (30 × 14 mm) cut from a 0.1 mm thick aluminium strip (supplied by RS) and then folded lengthwise to form the pockets. Approximately 25 mg of the cross-linked βCPCD sample was placed in the centre of each pocket. PTFE tape (30 × 15 mm) was used to fold the sample in the pocket and assess the bonding interaction between the sample and the metallic support during cooling. Rectangular strips of type 18 mesh (30 × 15 mm) were cut from a 0.65 mm thick sheet (supplied by RS). Approximately 30 mg of the crosslinked βCPCD material was spread around and in the centre of the mesh strips.

3.2. Differential scanning calorimetry

Thermal analysis of the βCPCD samples and their precursors was carried out using a Mettler Toledo DSC3+ device. 10 mg of the material was placed in a 40 μl aluminium pan with a pierced lid. The DSC chamber was continuously purged with N₂ gas at a flow rate of 50 ml min^{-1}. The test temperature was cycled three times between −100 and 140 °C. The variation of the heat flow in the samples was recorded as a function of temperature and time.

3.3. Optical microscopy

The dynamic physical properties of the βCPCD materials under the influence of temperature were investigated by optical microscopy using a Leica DM microscope fitted with a temperature-controlled stage (Linkam THMS 600). The temperature was changed using a T95 controller and an automated LNP95 liquid N₂ pump (both from Linkam). The material was placed on a 0.5 mm thick quartz microscopy cover slip. The slide was placed in a carrier within the stage to allow visual scanning. The stage was cooled to −100 °C and then heated to 100 °C at either 2 or 10 °C min^{-1}. To prevent condensation forming on the windows of the cold stage, the interior was purged with dry N₂ gas prior to cooling. A digital Qicam Fast 1394 CCD camera (QImaging) was used to continuously record any changes in the samples during the temperature cycle. The sample was illuminated by a white light source set in transmission mode.

Table 1
Dynamic mechanical analysis and differential scanning calorimetry data for βCPCD samples and their precursors.

Sample	PEGDGE:βCD (% w/w)	Cracking temperature[a] (°C)	E′ drop (%)	T_g (°C)	
				DMA[b]	DSC[c]
βCD	–	–	–	–	83
PEGDGE	100/0	−70	23	−60/-25	−73/-41/-20[d]
βCPCD1	60–40	−42	33	41	−17
βCPCD2	55–45	−31	21	75	−8
βCPCD3	40–60	+42	11	93	+96

[a] The third cooling cycle at 1 Hz.
[b] The tanδ peak.
[c] Midpoint.
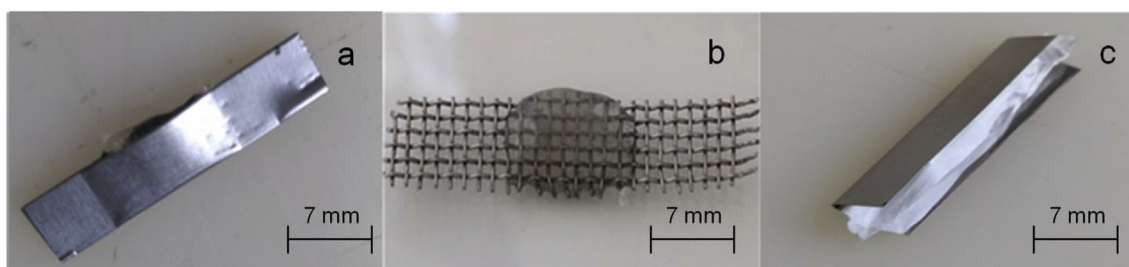[d] The tanδ peaks of the three major transitions of PEGDGE.

Fig. 3. Photographs of βCPCD samples supported by a) an aluminium pocket, b) a stainless-steel mesh, and c) an aluminium pocket wrapped in PTFE tape.
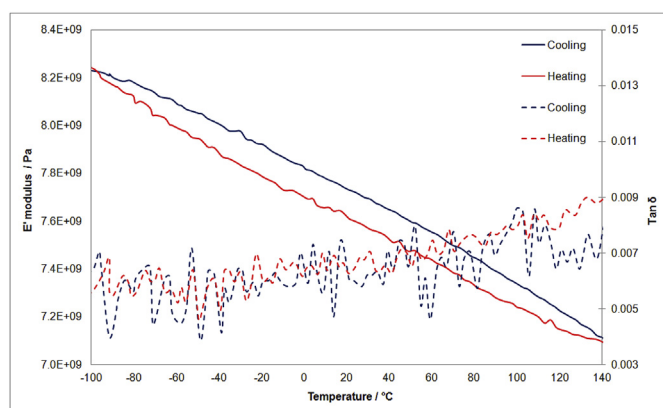

Fig. 4. Dynamic mechanical analysis showing the variation of the storage modulus (E′) (solid lines) and tanδ (dashed lines) of βCD (10 °C min^{-1}, 1 Hz, third temperature cycle from −100 °C to 140 °C, aluminium pocket).

Fig. 5. Differential scanning calorimetry thermogram of βCD (10 °C min^{-1}, third temperature cycle from −100 °C to 100 °C).

Fig. 6. Dynamic mechanical analysis showing the variation of the storage modulus (E′) (solid lines) and tanδ (dashed lines) of PEGDGE (10 °C min^{-1}, 1 Hz, third temperature cycle from −100 °C to 100 °C, aluminium pocket).

4. Results and discussion

4.1. Precursor analysis – βCD

DMA was used to determine the storage modulus (E′) and damping factor (tanδ) of βCD over three heating/cooling cycles from −100 °C to 140 °C at 10 °C min^{-1}. The last cycle is shown in Fig. 4. The E′ value was slightly higher during the first thermal cycle compared to the second and third cycles, reflecting the presence of synthesis-dependent stresses. There were no significant differences between the second and third thermal cycles, which are shown in the Supporting Information (SI).

The E′ values of the pure βCD sample were inversely related to the temperature, whereas the tanδ values remained relatively constant during each temperature cycle, showing there was no phase transition. This is consistent with earlier experiments that defined βCD as a crystalline compound [14]. Minor hysteresis was observed between cooling and heating. The lower E′ value during heating reflects the higher degree of relaxation in the material at high temperatures. Therefore, the higher E′ value during cooling is due to the stress created by the high cooling rate.

The variation in E′ and tanδ was also investigated as a function of the oscillation frequency. The increase in frequency during the temperature cycle had no significant influence on either value. The corresponding thermogram is shown in the SI. A phase transition indicated by DSC at 83 °C (Fig. 5) persisted at temperature cycles up to 140 °C. Earlier reports attributed this phenomenon to the dissolution of βCD crystals in the water present in the sample [43]. Molecular dynamics simulations predicted a glass transition temperature (T$_g$) for βCD of 61 °C [44] whereas others reported a measured T$_g$ value of 216 °C [45].

4.2. Precursor analysis – PEGDGE cross-linker

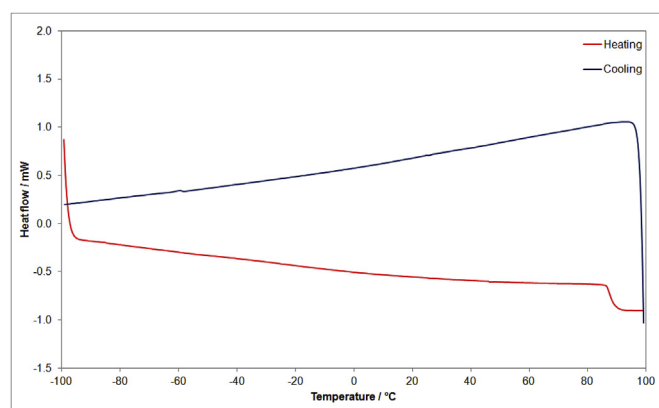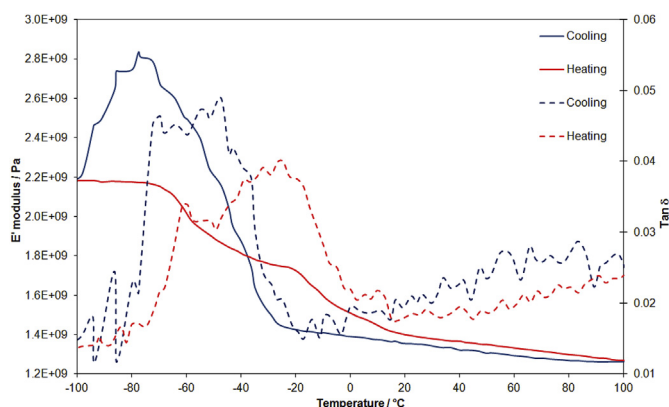DMA was also used to determine the thermomechanical properties

of the PEGDGE cross-linker, again with three heating/cooling cycles from −100 °C to 140 °C at 10 °C min^{-1}. There was no significant difference between the thermal cycles so only the third cycle is shown in Fig. 6. The E′ value fell during heating, with two main transitions at −70 °C and −22 °C, corresponding to the glass transitions of the PEGDGE sample. The broad and laddered decline in E′ reflects the specific properties of this commercial product, a blend of polyethylene glycol (PEG) chains with an average molecular weight of 500 Da and a polydispersity index of 1.7.

Previous studies have shown that the T$_g$ of PEGDGE is inversely related to its polydispersity because the shortest polymer chains act as a plasticiser, reducing the brittleness, lowering the tensile strength and increasing impact strength of the material overall [46,47]. During cooling, PEGDGE underwent a single glass transition event, increasing its stiffness. However, the rapid increase in E′ from about −30 °C was followed by a sudden drop at about −75 °C, the latter corresponding to

28% of the maximum E′ value. This phenomenon also occurred in tests conducted at the lower heating/cooling rate of 2 °C min⁻¹. DMA was used to test the aluminium support in order to eliminate artefacts caused by the machine and/or support matrix (SI). The E′ value of the support showed linear variation within the experimental temperature range, suggesting that the observed phenomenon is caused by the viscoelastic behaviour of the PEGDGE and its strong interaction with the supporting pocket. Hydroxyl, epoxy and carboxyl functionalities in a polymer allow the formation of hydrogen bonds with metal and glass [48]. The strong adhesive interactions and the change in the stiffness of the PEGDGE sample during the glass transition promote internal stress which is suddenly released, initiating cracking and de-bonding of the sample from the support, recorded as a sudden drop in the E′ value. The physical damage (such as cracking) that emerged during the cooling cycle provided an interesting initial assessment of the adhesive strength between the sample and different support matrices. The same thermal profile during the second and third cycles confirmed that PEGDGE recovers its initial mechanical properties when heated above the T_g in each cycle, and the process is, therefore, reversible.

The effect of the oscillation frequency on the mechanical properties of PEGDGE was tested at 1, 5 and 10 Hz. The E′ curves at 1 and 10 Hz are shown in Fig. 7. The cooling and heating curves at both frequencies diverge at the point of glass transition. During heating, the glass transition of the compound is complete at ~25 °C, as confirmed by the small decrease in E′ and the overlapping of the curves at different frequencies. The T_g is directly proportional to the frequency during both heating and cooling, and thus increases at higher frequencies [49,50]. The drop in the E′ values caused by cracking is also influenced by the oscillation frequency: the E′ peak at 1 and 5 Hz occurs at −78 °C whereas the 10 Hz peak occurs at −70 °C.

The cracking of the PEGDGE samples was analysed by DSC with a temperature cycle between −100 and 100 °C. The heat flow variation in the sample during the third temperature cycle is shown in Fig. 8. DSC revealed a thermal transition during the cooling interval from −23 to −50 °C reflecting both the crystallisation and vitrification of the blend. Therefore, the mechanical phenomenon observed by DMA is likely to occur when the PEGDGE becomes fragile following crystallisation of the longer chains (−34 °C) and vitrification of the shorter chains (−42 °C). The lower baseline heat flow adsorption after the crystallisation peak from −22 °C possibly indicates the presence of a glass transition due to the middle-length and shorter polymer chains that act as a plasticiser, as reported for PEG [51]. During heating, the heat flow adsorption of the PEGDGE increases between −70 and 10 °C in a multi-step transition that represents the combination of longer polymer chains melting (~1 °C) and the increased mobility of the middle length and shorter chains after the glass transition. Notably, the phase transformation

measured by DMA occurred at a higher temperature compared to that recorded by DSC (Table 1), probably reflecting the oscillation frequency applied to each sample and the different sample masses used in the two analytical techniques.

4.3. Analysis of the βCPCD product in aluminium pockets

The characteristics of the precursors allowed selection of suitable methods for the analysis of βCPCD product samples. First, DMA and DSC were used to determine how the amount of PEGDGE cross-linker (ranging from 40% to 60%) affected the thermomechanical properties of βCPCD, initially with the samples held in aluminium pockets as recommended for materials incapable of self-support. The DMA and DSC data for βCD, PEGDGE and βCPCD are compared in Table 1.

The E′ and tanδ values for βCPCD1 containing 60% PEG units during the third temperature cycle from −100 to 140 °C are shown in Fig. 9. There were no significant differences in either value when comparing the three temperature cycles, suggesting that the cross-linked system is not affected by the thermal history of the sample, as observed for PEGDGE (SI). The PEG chains dominated the behaviour of the cross-linked samples, with a notable shift in the transitions towards positive temperature values. During heating, DMA revealed a gradual stepwise decrease in E′ between the temperature extremes, with a major step at 55 °C coinciding with a tanδ peak. This broad transition was frequency dependent, suggesting it represented a glass transition event for βCPCD1 (SI). The softening of the βCPCD1 product was represented by a change in the slope of the E′ curve at −10 °C, matching with the onset of the tanδ peak, and this relates to the viscoelasticity of the PEG soft segments.

With an aluminium support in place, the DMA thermogram for βCPCD1 showed a similar profile to PEGDGE during the cooling phase, which can be attributed to the cracking of the sample. A sudden drop in E′ from its maximum value to 31% occurs at around −42 °C. The temperature at which cracks begin to appear in the βCPCD1 sample was not significantly dependent on the oscillation frequency, whereas cracking of the PEG chains shifted from −78 °C at 1 Hz in PEGDGE to −70 °C at 10 Hz. The lower mobility of the βCPCD1 samples reflects the existence of a cross-linked matrix compared to the viscous PEGDGE liquid, which has a higher adhesive surface area.

The DMA curves of samples βCPCD1 (60% w/w PEGDGE) and βCPCD3 (40% w/w PEGDGE) are compared in Fig. 10. When the PEG content was lower, the βCPCD cracked at a much higher temperature (35 °C) and the E′ value dropped to 10% of its maximum, far below the 30% of maximum observed for the sample with a higher PEG content. A low PEG content appears to increase the brittleness of the sample and reduces its viscoelastic behaviour, also reducing its binding strength given that the drop in E′ is related to the strength of adhesion to the metallic support. The glass transitions determined from the peak tanδ values shift to higher temperatures when the PEG content is low. The absence of first-order transitions in the βCPCD samples during cooling was confirmed by DSC (Fig. 11 and SI) suggesting that βCPCD products are completely amorphous at temperatures between −100 and 100 °C.

4.4. Analysis of the βCPCD product on a steel mesh support

The way in which βCPCD1 (60% w/w PEGDGE) and βCPCD3 (40% w/w PEGDGE) interacted with a stainless-steel mesh in lieu of the aluminium pocket was also investigated. The samples were spread over the mesh prior to analysis (Fig. 1b). The glass transition of βCPCD1 as determined by DMA was interrupted by stress relaxation at 15 °C (Fig. 12). The relaxation declined between the thermal cycles but was still present during the third cycle (SI). Cracking was still observed during cooling, but the phenomenon was less severe when compared to the sample held in an aluminium pocket (Fig. 12). The cracking also manifested itself over a wider temperature range (−14 °C to −70 °C) compared to the sudden drop observed with the aluminium pocket. The
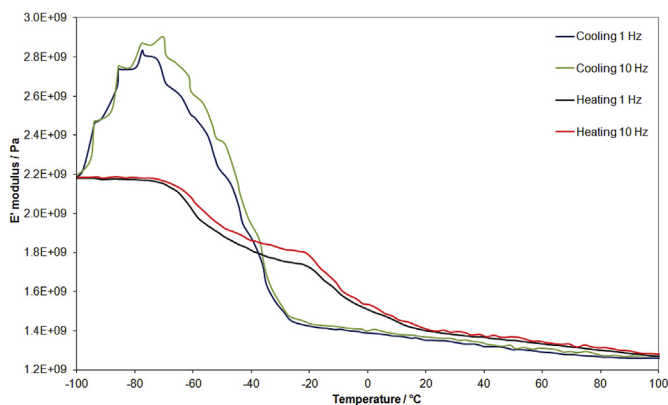

Fig. 7. Dynamic mechanical analysis showing the variation of the storage modulus (E′) of PEGDGE with frequency (1 and 10 Hz) during cooling (blue and green lines) and heating (black and red lines) (10 °C min⁻¹, third temperature cycle from −100 °C to 100 °C, aluminium pocket).
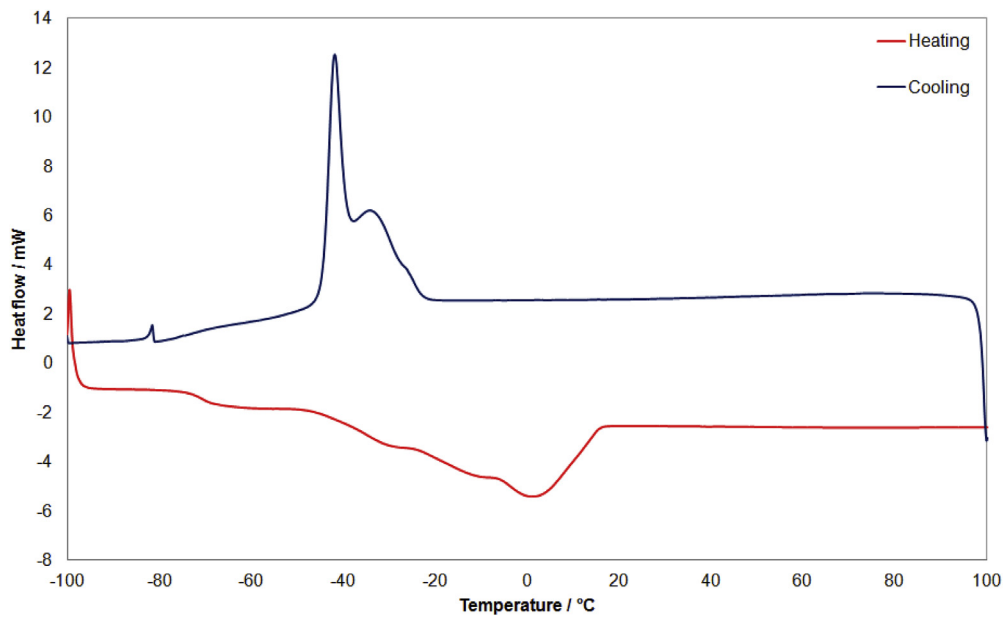
Fig. 8. Differential scanning calorimetry thermogram of PEGDGE from −100° to 100 °C (10 °C min^{-1}, third temperature cycle, aluminium crucible).
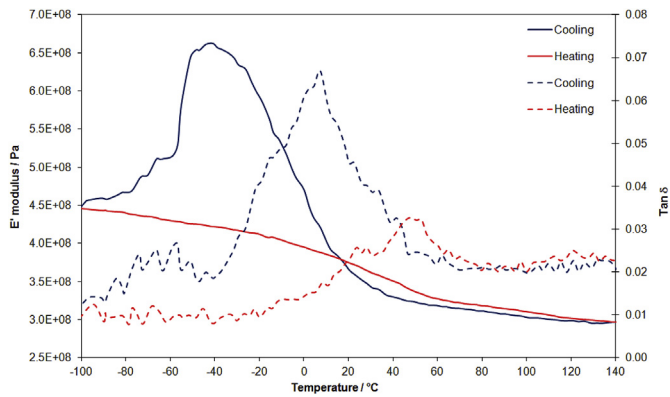

Fig. 9. Dynamic mechanical analysis showing the variation of the storage modulus (E′) (solid lines) and tanδ (dashed lines) of βCPCD1 (10 °C min^{-1}, 1 Hz, third temperature cycle from −100 °C to 140 °C, aluminium pocket).
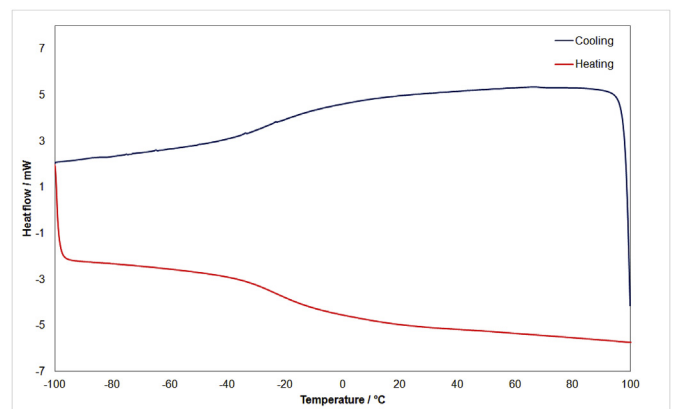

Fig. 11. Differential scanning calorimetry thermogram of βCPCD1 from −100° to 100 °C (10 °C min^{-1}, third temperature cycle, aluminium crucible).
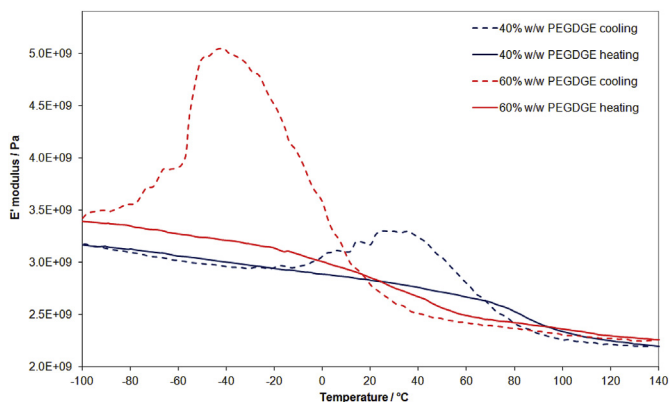

Fig. 10. Dynamic mechanical analysis showing the variation of the storage modulus (E′) and tanδ of βCPCD1 (60% w/w PEGDGE, solid and dotted red lines) and βCPCD3 (40% w/w PEGDGE, solid and dotted blue lines) (10 °C min^{-1}, 1 Hz, third temperature cycle from −100 °C to 140 °C, aluminium pocket).

Fig. 12. Dynamic mechanical analysis showing the variation of the storage modulus (E′) (solid lines) and tanδ (dashed lines) of βCPCD1 (10 °C min^{-1}, 1 Hz, third temperature cycle from −100 °C to 140 °C, stainless-steel mesh).

characteristic drop in E′ began at about −17 °C and reached 3% of the maximum value. The drop was visible during each cycle, confirming the stress relaxation effect that occurs with each round of heating. The metallic mesh changes the manner in which the stress introduced
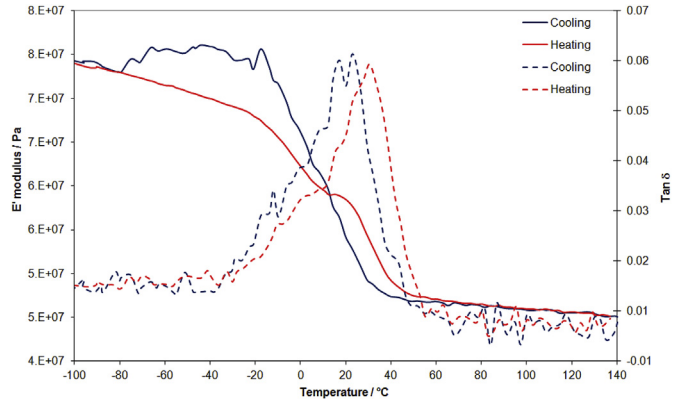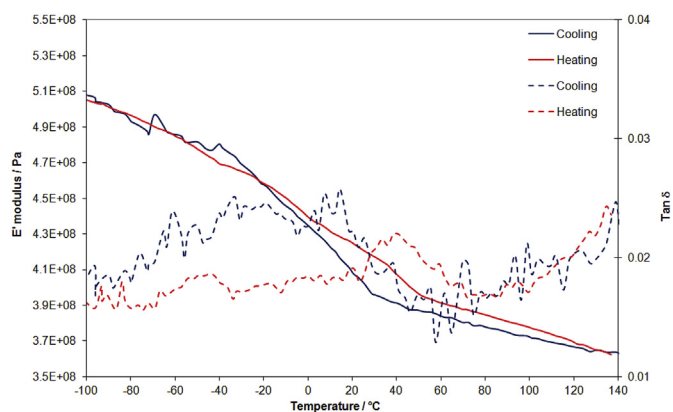
Fig. 13. Dynamic mechanical analysis showing the variation of the storage modulus (E′) (solid lines) and tanδ (dashed lines) of βCPCD1 (10 °C min^{-1}, 1 Hz, third temperature cycle from −100 °C to 140 °C, aluminium pocket and PTFE tape).

during each cooling cycle is dissipated. The mesh has a greater surface area to which the βCPCD1 can bind (362 mm^2) compared to the aluminium pocket (180 mm^2) but, nevertheless, allows stress to be dissipated within the bulk sample much more effectively.

4.5. Analysis of the βCPCD product in aluminium pockets with PTFE tape

Finally, to confirm that the drop in the E′ values during cooling was due to the de-bonding of the sample from its support, PTFE tape was used to hold βCPCD1 samples within an aluminium pocket, thus allowing the samples to contract freely with the decreasing temperature. Preliminary DMA characterisation of the PTFE tape (blank) showed a softening at the onset temperature of 18 °C (SI). The absence of adhesion between βCPCD1 and the support when enclosed by PTFE tape was confirmed by the drop in E′ during cooling as shown in Fig. 13. The hysteresis between the heating and cooling curves during the same temperature cycle diminished with each cycle. Therefore, the PTFE tape almost completely eliminated the de-bonding phenomenon and the formation of thermal stress in the sample during the cooling phase. The T$_g$ of βCPCD1 under these conditions was 41 °C, identical to the value recorded in the aluminium pocket without tape, confirming that the experimental setup does not affect the T$_g$.

4.6. Analysis of the βCPCD product by optical microscopy

Optical microscopy was used to characterise in more detail the cracking that occurred in the βCPCD1 product during cooling (Fig. 14). A glass support was considered adequate as a transparent substitute for

the metallic support used to investigate the adhesion of the compound. The sample was cooled from 25 °C (Fig. 14a) and began to crack at about −55 °C (Fig. 14b), with the cracks propagating further as the temperature was reduced to −100 °C (Fig. 14c and d). The same sample was then heated to 100 °C and the cracks began to self-repair, starting at 0 °C (Fig. 14e) until complete healing was observed at about 80 °C (Fig. 14h).

During a second thermal cycle on the same sample, cracking began at −58 °C and initiated at a different location (Fig. 15c). This confirms the evidence provided by the similar E′ value profiles in each thermal cycle, i.e. the thermal history of the sample is erased by heating, as previously reported for a hydrogel CD/PEG system [33]. In the second cycle, sample healing occurred at about 80 °C as in the first run (Fig. 15h). Furthermore, βCPCD1 placed on PTFE tape showed no evidence of cracking during the cooling phase, confirming that stress relief by cracking was due to the bonding of βCPCD1 to the glass support (SI).

This experiment confirmed the self-healing of the compound and explained why the E′ curves are identical during multiple temperature cycles. The self-healing behaviour is thought to reflect the reformation of hydrogen bonds and host–guest interactions, as seen in CD hydrogel systems due to the reduction of the viscosity of the cross-linked system when heated above T$_g$ [33,52–54]. The physical transformation occurs at the onset of material flow behaviour, allowing the crack to be filled in, and probably involves a rheological model involving the snake-like displacement of the polymeric chains, described as reptation [55].

The rupture strength of sample βCPCD1 was qualitatively assessed by intentionally cutting the sample (Fig. 16b). Both parts were subsequently re-joined and annealed in the oven at 70 °C for 30 min (Fig. 16c). The joined parts were found to be cohesive after this qualitative test (Fig. 16d). The sample was gripped at its extremities and pulled gently. The sample showed considerable elongation. Diffusion of the polymeric chains by reptation and the reforming of hydrogen bonds in the fracture allowed the material to qualitatively self-repair and self-heal. In future work, the self-healing capabilities of this compound will be assessed in more detail.

5. Conclusions

The thermomechanical properties of a new cross-linked binder based on βCD and PEG segments were assessed by DSC and DMA. The cross-linking improved the processability of the material compared to crystalline βCD, which has unsuitable physical properties for a binder. All cross-linked βCPCD products showed viscoelastic responses similar to those observed for the pure cross-linker. The viscoelasticity was directly related to the proportion of cross-linker in the βCPCD system, with T$_g$ values as low as −17 °C (determined by DSC) when cross-linker content was > 50% w/w. DMA revealed a sudden drop in E′ during the
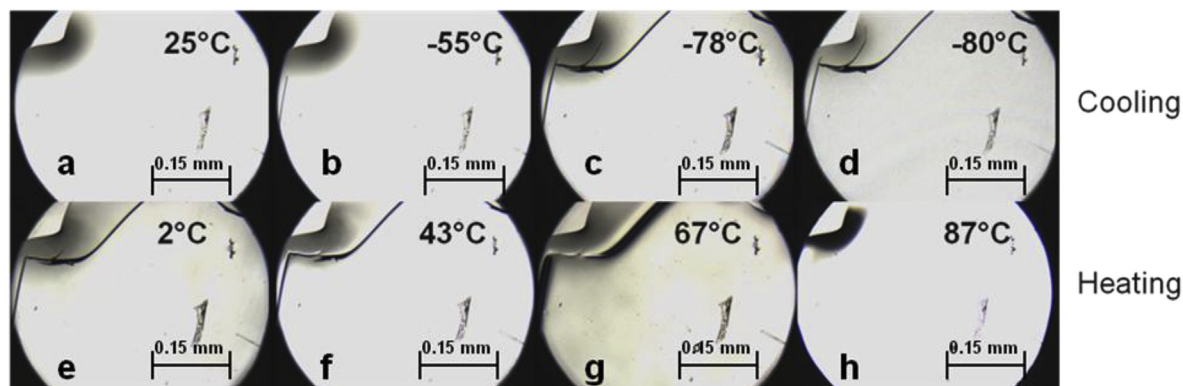

Fig. 14. Optical microscope images of βCPCD1 (60% w/w PEGDGE) during the first temperature cycle from −100 to 100 °C. The top row (a–d) shows the cooling phase captured at 25, −55, −78 and −80 °C, and the bottom row (e–h) shows the heating phase captured at 2, 43, 67 and 87 °C.
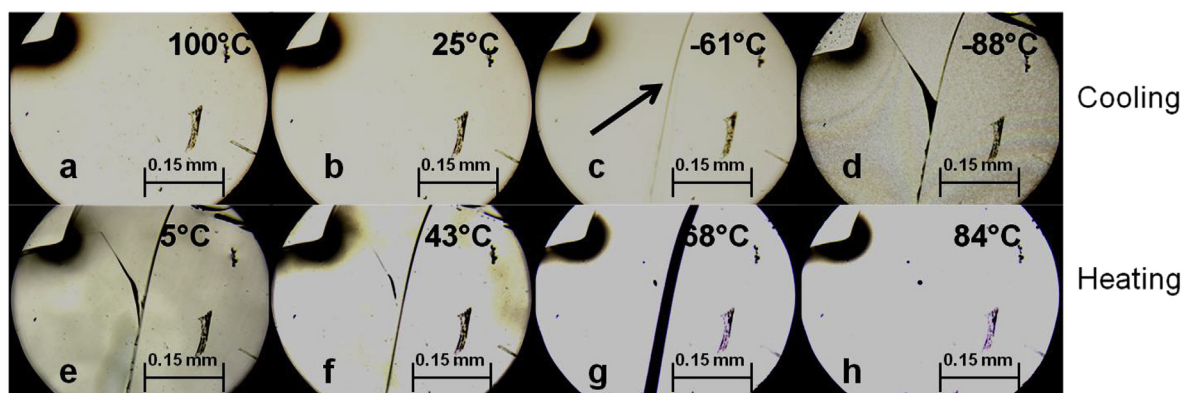
Fig. 15. Optical microscope images of βCPCD1 (60% w/w PEGDGE) during the second temperature cycle from −100 to 100 °C. The top row (a–d) shows the cooling phase captured at 100, 25, −61 and −88 °C, and the bottom row (e–h) shows the heating phase captured at 5, 43, 68 and 84 °C.
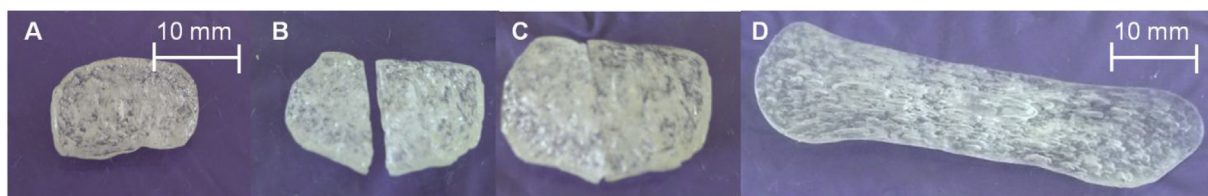

Fig. 16. Self-healing of βCPCD1 (60% w/w PEGDGE). a) Sample after solvent evaporation. b) Sample after cutting. c) The parts are placed in contact. d) The sample is heated to 70 °C for 30 min and pulled by the extremities.

cooling sequence, and the amplitude of the drop was directly proportional to the amount of cross-linker present. This phenomenon is thought to reflect the de-bonding of βCPCD from the metallic support when the sample was cooled below T_g. The adhesiveness of the material was drastically reduced when folded in PTFE film, indicating that the adhesive strength is due to the ability to form hydrogen bonds with the metallic support. Optical microscopy confirmed that the adhesiveness between the samples and the support, combined with the changes in viscoelasticity of the PEG and βCPCD segments at temperatures below T_g, produced mechanical stress that resulted in the propagation of cracks in the cross-linked material. Interestingly, the damaged βCPCD structure was able to restore its integrity by self-healing, which began at 0 °C and achieved complete self-repair at about 80 °C. The results show that the thermomechanical properties of the βCPCD system are superior to those of pure βCD. The influence of the support matrix on the thermomechanical properties of βCPCD could facilitate the development of optimal manufacturing and storage methods for new binders.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymertesting.2018.11.034.

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