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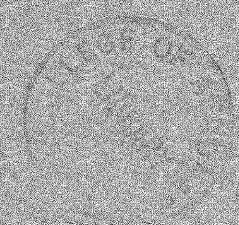
THE COLLEGE OF AERONAUTICS
CRANFIELD



A PRELIMINARY INVESTIGATION OF THE REACTION BETWEEN
PHENYL GLYCIDYL ETHER (2.3 EPOXY PROPYL, PHENYL ETHER)
AND PHENYL ISOCYANATE

- by -

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A preliminary investigation of the reaction between
phenyl glycidyl ether (2.3 epoxy propyl, phenyl ether)
and phenyl isocyanate

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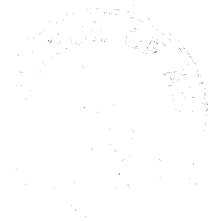
SUMMARY

Isocyanates have been in use for some time as cross-linking agents for polyester and polyether polymers. These form three-dimensional network polymers on cross-linking and are familiar commercial materials. This cross-linking system has the merit that it is possible to produce a wide range of materials from a given isocyanate or polyester by varying the reaction proportions, catalysts and so on. In addition, these materials possess a useful range of physical properties. In the present work the chemical basis of cross-linking epoxide resins with isocyanates has been investigated. Previous work on the subject has been largely empirical and though certain workers have produced cross-linked polymers by this means, the precise nature of the cross-linking process has not been established. As an initial step it was decided to investigate the nature of the link between the two types of compound, using mono-functional model compounds. These were phenyl glycidyl ether (2-3 epoxy propyl phenyl ether), and phenyl isocyanate. Phenyl glycidyl ether resembles in structure the active part of the epoxide resin molecule, and phenyl isocyanate is similar to toluene di-isocyanate, which is frequently used in isocyanate cross-linking mechanisms.

A reaction has been found to take place giving a crystalline material which is a one-to-one addition compound of the two reagents, together with a red oil, which may be a mixture of alkyl anilides. The structure of the crystalline material has not been fully proved, but is believed to be a 2-oxazolidone.

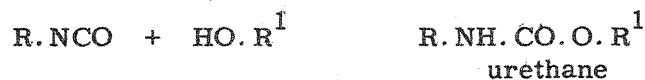
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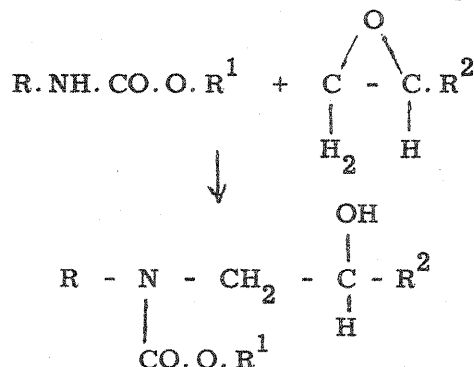


1. Introduction

This note represents the beginning of an attempt to investigate the mechanics of cross-linking of epoxide polymers with isocyanates. Normally epoxides are cross-linked using amines, amides or acid anhydrides, whereas isocyanates are used for cross-linking polyester or polyether materials. Most of the previous work on this subject is in the form of patents (Refs. 1, 2, 3, 4) and does not cover the fundamental chemical mechanism of the reaction. The subject has been discussed by Poswick and Dramais (Ref. 5). In their work it was assumed that the isocyanates do not react with epoxide groups but with hydroxyl groups present as phenols, according to the conventional scheme :-



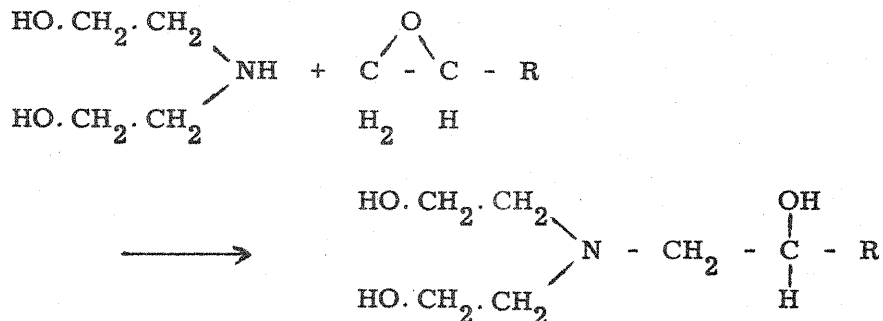
This urethane was assumed to react with an epoxide group



according to a conventional epoxide reaction mechanism.

As the work was done on resins it would be difficult to prove these contentions.

Unpublished work by the Shell Chemical Company uses the principle of reacting epoxide resins with diethanol amine :-



This reaction converts each epoxide group into three hydroxylic sites for diisocyanate cross-linking. This scheme evades the reaction of the epoxide group

with the isocyanate group.

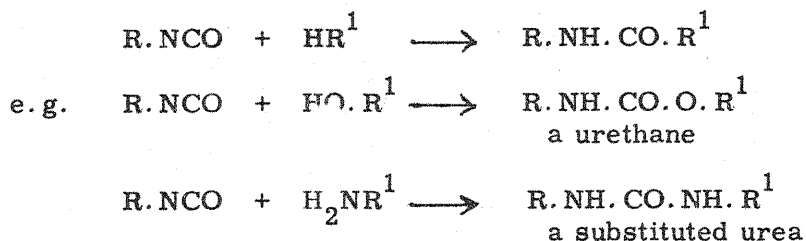
Senda and Oda (Ref. 6) discussed the problem in a more fundamental way. They obtained a number of useful surface-coating polymers from a variety of resins and diisocyanates, and thus showed that polymers can be formed without recourse to de-epoxidation, as in the Shell work. They assumed, however, that the reaction mechanism was the conventional reaction of the isocyanate group with the hydroxyl groups present on the epoxide resins, without investigating the matter in detail.

It was decided to undertake a study of the reaction of the epoxide group with the isocyanate group, using mono-functional model compounds to render the problem more amenable to normal chemical techniques. The models chosen were phenyl isocyanate and phenyl glycidyl ether.

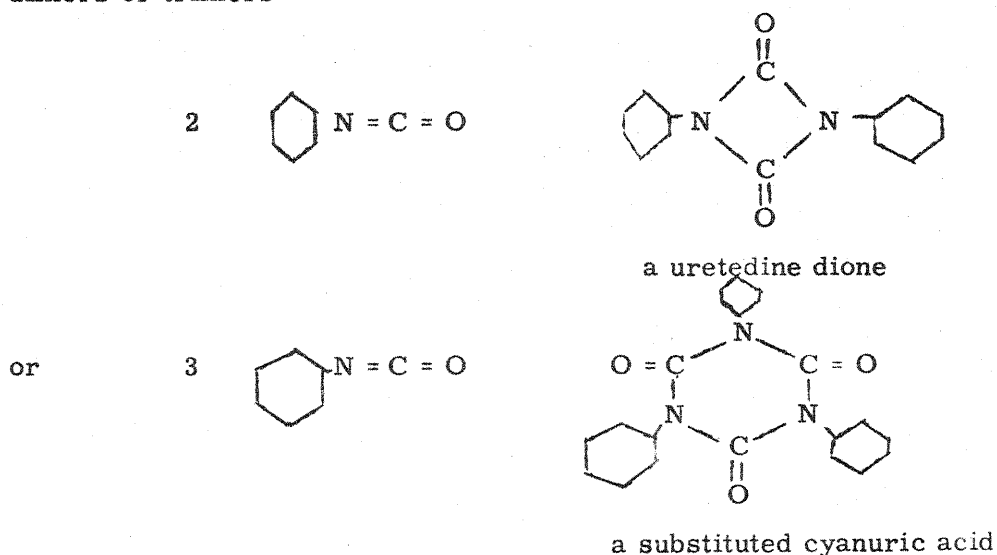
2. Experimental

2.1. In general the reactions of isocyanates are of two kinds :-

(a) with a very wide variety of compounds containing labile hydrogen the scheme is :-



(b) involving rupture of the carbon-nitrogen double bond as in the formation of dimers or trimers



It was the object of this work to determine whether this reaction occurs between isocyanates and epoxides and if it does, to discover into which category the reaction falls and the nature of the linkage formed.

2.2. Attempts were made to react phenyl glycidyl ether and phenyl isocyanate in chloroform at 60°C but no reaction took place under these conditions.

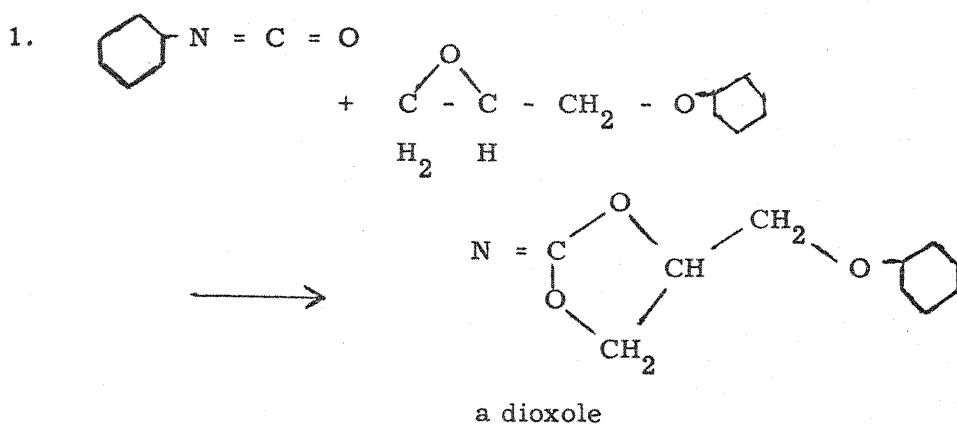
11.6g of phenyl isocyanate were refluxed with 15g of phenyl glycidyl ether for 6 hours at 170°C. On cooling a dark solid mass was obtained. This was dissolved in 300 ml of chloroform. After decolorisation, several crops of a white material were obtained, in total 10.1g. Complete evaporation of the chloroform left behind 6.2g of a dark red oil with a "phenolic" type smell. The white substance will be referred to as material A and the red oil as material B. A good deal of carbonisation also occurred. The yields thus were: material A, 38.0%, and material B, 23.3%. Material A was recrystallised from chloroform to give needles of m.p. 134-5°C.

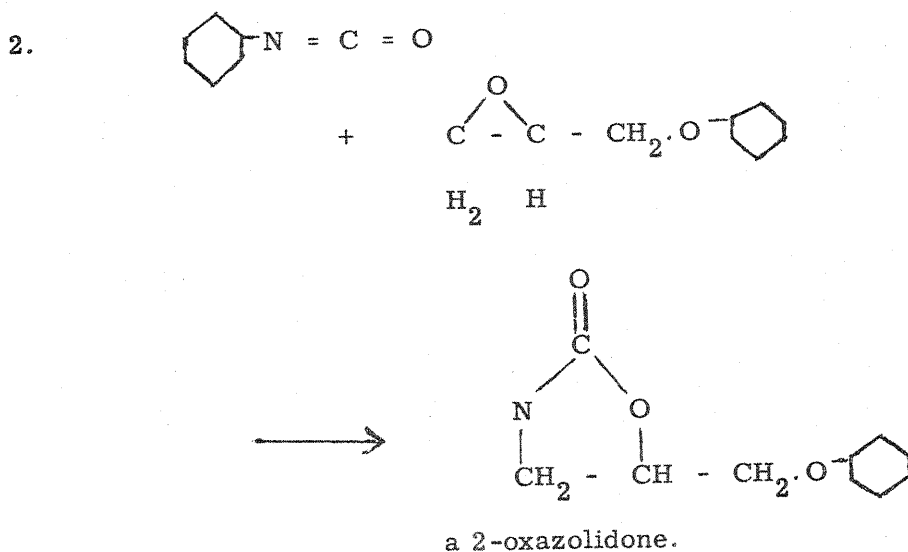
2.3. Analysis of material A for carbon, hydrogen and nitrogen agreed well with the idea of a one-to-one addition of the two compounds, without by-products, as is shown by the following table. The theoretical column indicates the analysis for a one-to-one addition compound.

Material A

%	Theoretical	Experimental		
%C	71.32%	71.69%	71.90%	71.44%
%H	5.61%	5.76%	5.84%	5.83%
%N	5.20%	5.16%	4.95%	5.37%

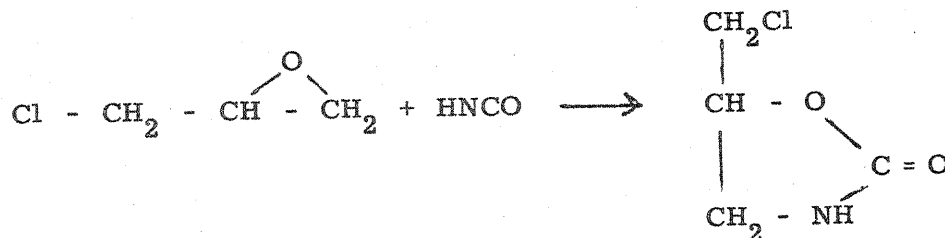
There are two possible mechanisms by which one-to-one addition might occur :-





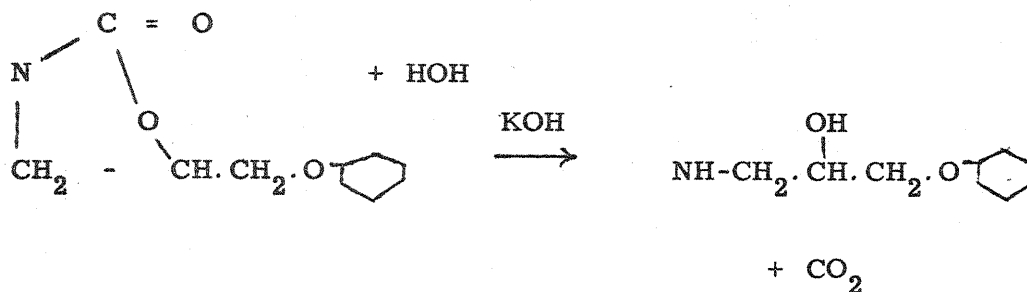
Of the two hypotheses, (2) is more probable for the following reasons :-

- (a) rupture of the ring by hydrolysis would give an imine in case (1) but a secondary amine in case (2). Nitrous acid on the hydrolysis product derived from A gave the yellow coloration characteristic of a secondary amine.
- (b) Thompson (Ref. 7) reacted cyanic acid (derived from potassium cyanate) with epichlorhydrin and believed he obtained a 2-oxazolidone compound.



This reaction would appear to be analogous to our own. The most reasonable hypothesis seemed thus to be that material A is 3 phenyl 5 phenoxyethyl 2-oxazolidone as shown above.

2.4. Any attempt to establish the structure of material A must depend on reducing it to a known compound or compounds. Aqueous caustic potash has no effect on the material but boiling for 2 hours in a 20% ethanolic solution of caustic potash produced a yellow oil which was extracted with ether. It could not be recrystallised, but on removing all the ether the oil was recovered. On cooling and standing for several days it changed to a yellow solid of m. p. 46-48° C. The yield was 52%. Following Thompson's work the following is a possible scheme of reaction.



giving 1 phenoxy 2 hydroxy propyl anilide and carbon dioxide which would be absorbed by the caustic potash. The substance we obtained will be referred to as material C and the following table gives its analysis compared with the theoretical one for 1 phenoxy 2 hydroxy propyl anilide.

Material C

%	Theoretical	Experimental
%C	74.11%	72.73%
%H	7.03%	7.14%
%N	5.75%	6.06%

The agreement is fair considering the non-crystalline nature of the material.

Material C was reacted with p-toluene sulphonyl chloride in ether, using triethylamine as catalyst, and a crystalline material D was obtained. On heating, this decomposed at 180°C, one resultant sublimed to a crystalline sublimate and the residue melted at 243 - 4°C. Analysis figures for D are quoted below and contrasted with the theoretical figures for the mono and di-p-toluene sulphonyl chloride derivatives of 1-phenoxy 2-hydroxy propyl anilide.

Material D

%	Theory Mono tosyl	Theory Di-tosyl	Experimental	
%C	66.46%	63.14%	52.58%	51.67%
%H	5.83%	5.30%	11.70%	11.86%
%N	3.52%	2.54%	9.94%	9.98%
%S	8.06%	11.62%	8.80%	9.05%

There is in fact no agreement here, but in view of the decomposition of the original substance at 180°C and the tendency to sublimation, it may be doubted whether the analysis is that of the original product.

1 phenoxy 2 hydroxy propyl anilide is reported by Fourneau and Poulenc in a patent application (Ref. 8). They prepared their material by reacting aniline and phenyl glycidyl ether for 2 hours at 130°C, obtaining, after recrystallisation from 60% ethanol, a crystalline solid of m. p. 57°C. This gave colour reactions with gold chloride and potassium mercuri-iodide. As substance C did not have the same melting point, nor yield the same colour reactions with gold chloride and potassium mercuri-iodide, it was decided to repeat their work. In spite of varying the reaction temperature, and even attempting to catalyse the reaction using chloro-dinitro-benzene it was found impossible to obtain any crystalline material at all. In view of this, and of the fact that no analysis figures are quoted in their paper, there is considerable doubt regarding the acceptability of the work of Fourneau and Poulenc. It cannot, therefore, be said that material C is a known compound. The action of nitrous acid on material C yielded a yellow oil, which suggests the material is a secondary amine.

2.5. Material A was reacted with concentrated hydrochloric acid in a sealed tube at 190 - 200°C for 2 hours. This yielded a dark oily material. Owing to the physical difficulties of the experiment only small quantities of end-product were obtained, too small for quantitative analysis. Qualitative analysis by Lassaigne's method showed that the oil was a chlorine-containing compound. The tube was under pressure at room temperature after the reaction, and this may have been due to the evolution of a gas during the reaction. This experiment is in harmony with the breaking of the oxazolidone ring by concentrated hydrochloric acid, as reported by Elderfield in his book "Hetero-cyclic Compounds".

2.6. Substance A did not react with nitrous acid, suggesting that there is no labile hydrogen attached to the nitrogen atom, when the formation of either diazo-compounds or nitroso-compounds might have been expected.

2.7. An attempt was made to prepare an oxime from substance A using hydroxylamine hydrochloride, but no reaction took place. If a carbonyl group is present, it is inhibited from normal ketone-aldehyde behaviour, but this might be expected in an oxazolidone ring due to the neighbouring nitrogen atom.

2.8. An attempt was made to reduce material A using the following method:- 2g of the material were dissolved in 15g of ethanol and benzene added until solution was complete. The solution was then added to 1g of metallic sodium. When the reaction had finished water was added and the two layers were separated. The benzene layer yielded crystals of material A but the aqueous layer, on cooling, was found to contain oily drops. An ether extraction was performed, and as the material would not crystallise out, the ether was totally removed leaving a yellowish oil. On standing for 2 days this yielded a solid of m. p. 55-57°C. Though the melting point is

close to that of the supposed 1 phenoxy 2 hydroxy propyl anilide prepared by Poulenc and Fourneau it gave different colour reactions with gold chloride and potassium mercuri-iodide. It also reacted differently to substance C with these reagents.

On reaction with nitrous acid the material gave a yellow coloration, which gave a brilliant green colour on standing. This suggested the nitroso reaction of a secondary amine. Analysis of the material is not yet complete.

2.9. On repeating the reaction between phenyl glycidyl ether and phenyl isocyanate on the scale of 75g of phenyl glycidyl ether to 58g of phenyl isocyanate, small quantities of two other materials were obtained. One of these melted at 273°C and was believed to be the trimer of phenyl isocyanate, the other melted at 221°C . Both were obtained in 10 mg. yield, and were considered to be side reactions of too little importance to merit further investigation.

2.10. The red oil, material B, which was prepared in the original reaction of phenyl glycidyl ether, was submitted to preliminary tests. It was found to be soluble in ethanol, acetic acid, sulphuric acid and hydrochloric acids, but insoluble in water and caustic soda solution. There was a colour reaction with ferric chloride, which turned olive green. This reaction is found in a fair number of amines and phenols. There was no reaction with phosphorus pentachloride however, suggesting that the material does not contain hydroxyl, carboxyl or phenol groups. Lassaigne's test indicated the presence of nitrogen and by reaction with nitrous acid a yellow coloration was obtained, suggesting the presence of a secondary amine group. A negative carbylamine reaction suggests that primary amine groups are not present. Bromination in acetic acid gave a brown precipitate, which may indicate that the material is aromatic. A possible hypothesis concerning this material is that it is an alkyl anilide, possibly formed due to the rupture of an oxazolidone compound.

3. Conclusions

1. There is a reaction between phenyl isocyanate and phenyl glycidyl ether yielding a crystalline material, which is a one-to-one addition of the two reagents, and an oil, which is probably an anilide. Thus in cross-linking such a reaction might also be expected in addition to the more conventional ones.

2. The one-to-one addition compound is probably 3 phenyl 5 phenoxy-methyl 2 oxazolidone and most of the evidence is in sympathy with this, but so far it has not been possible to reduce it to a known compound or compounds, and thus test the hypothesis. Owing to a paucity of information in the literature on the oxazolidone system, this may prove difficult.

3. Future work should be directed to the proof or disproof of the oxazolidone hypothesis, the elucidation of the nature of the red oil, and the part to be played by such catalyst as tertiary amines in the reaction. An attempt should then be made to assess the importance of the reaction in cross-linking processes.

4. References

1. Phillips, L. N. B. P. 758, 433
2. Barthel, E. U. S. P. 2, 788, 335
3. Johnson, S. C. B. P. 802, 127
4. Kazys, Sekmakas. U. S. P. 2, 906, 717
5. Poswick & Dramais "Polyurethane resins based on de-epoxidised epoxy resins".
Official Digest, Dec. 1958, pp 1431
6. Senda & Oda "Studies in the cross-linking of epoxy resins by means of di-isocyanates"
J. Chem. Soc. of Japan (Ind. Chem. Sec.) 57, p 753 (1954)
7. Thompson "Concerning the reaction of potassium cyanate and epichlorhydrin"
Berichte 11, p 2136 (1878)
8. Poulenc & Fourneau "Verfahren zur Darstellung von sekundären Amino alkoholen"
Friedlanders Fortschritte der Teerfabrikation 10, p 1173 (1910)