

Manufacturing and Characterization of Sustainable Hybrid Composites using Sisal and Hemp fibres as Reinforcement in Poly (lactic acid) via Injection Moulding

Asokan Pappu¹, Kim L Pickering² and Vijay Kumar Thakur^{3*}

¹CSIR- Advanced Materials and Processes Research Institute, Bhopal, India

²School of Engineering, University of Waikato, Hamilton, New Zealand

³Enhanced Composites and Structures Center, School of Aerospace, Transport and Manufacturing, Cranfield University, Bedfordshire MK43 0AL, UK

Corresponding Author:

Vijay Kumar Thakur

Email ID: Vijay.Kumar@cranfield.ac.uk

Abstract

Natural polymers based composites offers significant advantages over synthetic fibre reinforced petroleum matrix based composites with regard to biodegradability, biocompatibility, design flexibility and sustainability. This work reports for the first time manufacturing of hybrid fibre reinforced biodegradable composites using sisal and hemp fibre with polylactic acid employing melt processing and injection moulding techniques. Granulated sisal and hemp fibres were blended and hybrid composites were manufactured

using aliphatic polyester made up of lactic acid (PLA) through extrusion and injection moulding and their performance was evaluated. Experimental results revealed that density, elongation at break and water absorption capacity of hybrid composites were 1.14 ± 0.07 g/cm³, $0.93 \pm 0.35\%$ and $1.06 \pm 0.18\%$ respectively. The achieved mean tensile strength (46.25 ± 6.75 MPa), Young's modulus (6.1 ± 0.58 GPa) and specific tensile strength (38.86 ± 5) of hybrid fibre reinforced PLA composites were improved compared to neat PLA. The flexural strength (94.83 ± 11.21 MPa), flexural modulus (6.04 ± 0.55 GPA) and specific flexural strength (79.76 ± 8.8) of hybrid fibre composites also showed better performance than those of neat PLA. Incorporation of sisal and hemp fibre with polylactide remarkably increased the impact strength of composites. Overall, the hybrid composites demonstrated good performance suggesting that they have great potential for use as an environmentally friendly alternative material in automotive, packaging, electronics, interiors and agricultural applications.

Keywords: Sisal fibre; Hemp fibre; Poly(lactic acid); Biodegradable hybrid composites; Extrusion; Injection moulding; Thermal degradation; Mechanical properties

1. Introduction

There is an enormous variety of natural fibres including flax, *grewia optiva*, *hibiscus sabdariffa*, jute, hemp, coir, *Saccharum cilliare*, ramie, sisal, banana, pine needles and pineapple to name a few which mainly consist of cellulose, hemicelluloses and lignin (Bleuze et al., 2018; de Oliveira et al., 2017; Goudenhooff et al., 2018; Kaschuk and Frollini, 2018). The physico-chemical and mechanical characteristics of these natural fibres

are generally found to be dependent on the source and age of plants as well as cellulose content. These properties are influenced by alkali treatment which removes hemicelluloses, lignin and other impurities including wax from the fibre (Requile et al., 2018) (Pappu et al., 2015; Singha et al., 2008). Natural fibres are used as replacement for glass fibre in composites attributed to their enormous advantages such as low density and environmental friendliness in terms of low energy consumption and renewability (Ochoa et al., 2017; Singha and Kumar Thakur, 2008; Thakur et al., 2012). However, compared to glass fibre they have higher heterogeneity, poor crimp properties which hamper yarn making, more limited processing temperatures as well as being hydrophilic and thus inherently incompatible with many matrix materials (Pappu and Thakur, 2017; Singha and Thakur, 2009; Thakur and Singha, 2010). However, increased consciousness of global climate change has attracted researchers' and technocrats' attention to the use of natural cellulose fibres for a number of applications. Among many natural fibres, hemp and sisal are two potential natural fibres that are being explored for a number of applications (Thakur and Singha, 2010). Hemp fibre is mainly of two types (i) industrial hemp fibre, derived from the bast material and (ii) Manila hemp fibre, derived from the leaves (Liu et al., 2017). Russia is the largest producer of hemp fibre in the world accounting for about 33% of the annual world production of 255,000 tonnes. Other countries such as France, Germany, Italy, Yugoslavia, Chile, China, Japan and Peru also produce considerable quantities of hemp fibre. However, India is the main producer and exporter of oil from hemp seed (Bodros et al., 2007). The chemical properties of hemp fibre have been studied by several researchers and the major chemical compositions in hemp fibre are: cellulose (55-75 %), hemicellulose (10-24 %), lignin (4-13 %) and wax (0.7-3%) (Pickering et al., 2016).

On the other hand, sisal fibre belongs to the *Agave* family. Sisal fibre exhibits relatively high mechanical properties in comparison to other natural fibres such as coir, jute, cotton, palm, and bamboo(Pappu et al., 2016; Senthilkumar et al., 2018). Annually, about 4.5 million tonnes of sisal fibres are produced globally and Tanzania, Brazil, China, South Africa are major sisal fibre producing countries(Pappu et al., 2015). Sisal fibre consists about 55-78% cellulose, 8-19% hemicellulose and 2-11% lignin, about 1% pectin with 6-10% moisture content(Pappu et al., 2016). It is an emerging reinforcing material for use in polymer composites for several industrial engineering applications. Amongst all natural fibre composites, those containing sisal exhibit the highest impact strength besides moderate tensile and flexural strength(Sarasini and Fiore, 2018). However, hemp fibre exhibits better tensile strength and proves to be a good reinforcement in various polymer matrices(Liu et al., 2017; Saradava et al., 2016). It is also recorded that natural fibre-based thermoset composites result in better mechanical properties than for thermoplastic composites, but thermoplastic composites have advantage for design flexibility and recycling potential. The fibre used in polymer composites is broadly classified as synthetic fibre (glass, aramid, carbon, etc.) and natural fibre (jute, hemp, flex, sisal etc.). However, it is reported that specific properties of natural fibre reinforced composites are as good as those of the glass fibre reinforced thermoplastics(Thakur and Thakur, 2014). Much research has been carried out by researchers and considerable improvement on interfacial bonding between fibre and matrix through modification of matrix hydrophobicity and fibre surface treatments has resulted(Thakur et al., 2014).

Currently bio-plastics are becoming increasingly attractive polymers for different industrial applications due to various environmental threats as replacement for traditionally used

synthetic polymers such as polyester, polyurethane and phenolic resins(Zhang et al., 2018b, 2018a). Many different polymers have been developed from renewable resources and have potential as composite matrices, but their low toughness, easy commercial availability, processability, high cost, low moisture resistance and thermal stability are some of major concern. Considerable research has been conducted on the use of biopolymers such as polylactic acid (PLA), modified cellulose, soya oil based epoxy, polycaprolactone (PCL), polyhydroxybutyrate (PHB), lignin and starch(Dubey et al., 2017; Miculescu et al., 2017) (Gan and Chow, 2018; Panaitescu et al., 2016) (Saradava et al., 2016).

Though, so far, polylactic acid (PLA) has only been used in biomedical applications, the discovery of a new polymerisation technique has resulted in cost-effective production of polylactic acid (PLA), supporting its use for consumer products and packaging materials (Dubey et al., 2017). In hybrid fibre composites, although several types of fibre can be used in the same matrix, a combination of two types of fibres has been found to be the most desirable to enable a balanced performance of properties. However, no work has been reported yet on hybrid fibre reinforced biodegradable composites using sisal and hemp fibre with polylactic acid using melt processing and injection moulding.

In the present study, equal parts of micronized sisal and hemp fibres were blended homogeneously and hybrid green composites were made using polylactic acid (PLA) through extrusion and injection moulding and assessed regarding their physical, mechanical, thermal and crystallinity characteristics. This paper describes a process for manufacturing of hybrid natural fibre (sisal–hemp fibre) poly-lactic acid composites and their characteristics for possible use as an auto component and as interiors/architectural materials in automotive and construction industries (**Scheme 1**).

2. Materials and Methods

2.1 Raw Materials: Natural Fibres and Polylactic Acid

Hemp fibre was obtained from Hemcore, UK and sisal fibre was brought from CSIR-AMPRI, Bhopal, India (**Figure 1**). Hemp (*Cannabis sativa* L.) is a plant in the Cannabaceae family which has been used historically as a source of fibre. The cultivation propagation of hemp for fibre production is mostly done through seedlings. Hemp fibre has been reported to have a tensile strength of 514-690 MPa and Young Modulus of about 24-60 GPa (Liu et al., 2017; Pappu and Thakur, 2017). Sisal fibre has a diameter of around 200µm, tensile strength about 600MPa, Young's modulus approximately 15 GPa with elongation about 5%. In the present study, granulated hemp fibres and sisal fibres were used in making hybrid green composites with polylactic acid. These fibres have relatively high fibre strength and long fibre when compared with other natural fibres (Pappu et al., 2016). Commercial grade polylactic acid (PLA) 4042D was obtained from Nature Works LLC, USA was used. The density of the PLA was 1.25 g/c³.

2.2 Fibres Processing

Sisal fibres were dried at 80± 2° C for 24 hrs. Hemp fibres were soaked in hot water (85± 2° C) for 10 minutes and unwanted impurities were removed by manual cleaning (**Figure 1**). The cleaned wet hemp fibres were oven dried at 80± 2° C for 12 hrs. The dried hemp and sisal fibre were aligned as a mat using a hand carding machine during which any further unwanted impurities in the stack of fibre were removed (**Figure 1**).

2.3 Preparation of Hybrid Fibres

The cleaned and carded fibres (**Figure 2A-B**) were cut into at 4 mm lengths using a granulator with a tri-blade cutting system, designed especially for natural fibres. For composite fabrication, PLA pellets were ground into powder (**Figure 2C**) using a microniser (Model 15 A, Eriez manufacturing Co. Erie PA, USA). Granulated sisal and hemp fibres were mixed homogenously in a 1:1 ratio (**Figure 2D**) and oven dried at $80 \pm 2^\circ$ C for 12 hrs prior to composite manufacturing.

2.4 Manufacturing of Composites

It is known from several reported works that incorporation of natural fibre from 25-35 wt% in polymer composites ((Liu et al., 2017; Saradava et al., 2016) is found to be the most appropriate to achieve optimum technical and economic benefits and addition of more than 30 wt% fibre has not resulted in any significant enhancement in the mechanical properties of PLA fibre composites(Islam et al., 2010) (Singha and Thakur, 2009). Hence, in the present study, attempts were made to use 30 wt % natural fibres with PLA using optimised conditions. Though it is only one composition, the impact of hemp fibres with PLA and sisal fibre with PLA system have been studied by several researchers and the impact of each fibres as a separate entity with PLA were reported and discussed elsewhere (Liu et al., 2017; Saradava et al., 2016). The present study deals with hybridization of sisal and hemp fibres in making composite in PLA system. In hybrid fibre composites, although several types of fibres can be used in the same matrix, a combination of two types of fibres has been found to be the most desirable to enable a balanced performance of properties. No work has been reported yet on hybrid fibre reinforced biodegradable composites using

sisal and hemp fibre with polylactic acid using melt processing and injection moulding. Compounds were prepared using 15 wt% each of oven dried and granulated sisal and hemp fibre (1:1 ratio) with 70 wt% polylactic acid in a twin screw extruder (Thermo Prism). Though composites were prepared by using several compositions, the reported composition (30% in this article) is the optimized input parameters achieved to attain a workable condition. Otherwise, it would be very large data and difficult to present. The operating condition of the extruder was 175°C at the feeding zone; 190 °C in the mixing zone; 190 °C in the reacting zone, and 180 °C at the die exit. In the extrusion process a 75 rpm ram speed and 28-32 % torque was maintained. Extruded compound was granulated to a size of 4 mm using granulator. **Figure 3** (A) and 3(B) shows the extruded and granulated compound respectively. Composite specimens were made in an injection moulding machine and the operating temperature was 160 °C at the feeding zone; 180 °C at mixing zone; 190 °C at the reacting zone and 200 °C at the die exit zone and maintaining a ram pressure of 30kN. For comparison, micronized PLA was oven dried and injection moulded to obtain test specimens under the above conditions. Injection moulded tensile specimens are shown in **Figure 3** (C, D).

2.5 Materials Characterisation

2.5.1 Fibre Diameter and Strength Measurement

Fibre diameters of both hemp and sisal were measured employing an optical microscope (Olympus BX 60) at X10 magnification in a horizontal direction. For measuring fibre diameter, processed sisal and hemp fibres were cut into 25 mm length and fixed to a cardboard window frame as described in ASTM C 1557-03 (Standard Test Method for

Tensile Strength and Young's Modulus of Fibres). Further, tensile testing was performed compliance with the above standard. Twenty five samples were tested for each fibre type.

2.5.2 Thermal Analysis of Composites

In addition, thermal gravimetric analysis was carried out employing a simultaneous DTA-TGA (SDT 2960) analyser. A heating rate of 5° C/min was applied for both techniques from room temperature to a maximum temperature of 600°C with a static air flow of 150 ml/ min. A hybrid composite sample of approximately 10 mg was used for both tests.

2.5.3 XRD Analysis and SEM Microstructure of Composites

XRD analysis was performed between 2θ angles of 12 to 45° at a scanning speed 0.02°/ second to study cellulose crystallinity. Composite fracture surfaces were analysed employing a scanning electron microscope (Hitachi S 4700) under operating condition of 10 kV. SEM micrographs of hybrid composite (HBC- R1) shows: fibre fracture, fibre pull-out and adhesion at the fibre matrix interface.

2.5.4 Tensile Testing of Composites / PLA

Tensile testing of injection moulded composite/PLA specimens was performed in compliance with ASTM D 638-03 (Standard Test Method for Tensile Properties of Plastics). Samples were analysed using an Instron tensile testing machine (Instron 4042) using a 5 KN load cell and a 50 mm gauge length with 0.5 mm/min cross-head speed. Five hybrid composite specimens were tested to check the reproducibility of the results.

2.5.5 Flexural Testing of Composites

For flexural testing, injection moulded rectangular-type specimens were used. Three point bending was performed to comply with ASTM D 790-03, applicable for testing reinforced and un-reinforced plastics, using a Lloyd 100 KN machine with a 5 KN load cell with a span of 60 mm and a cross-head speed of 1.5 mm/min.

2.5.6 Impact Strength Testing of Composites

For impact testing, injection moulded rectangular specimens were cut into a specimen size of 80x8x3.5 mm (**Figure 3** (E, F)) using a laser cutting machine. The Charpy impact test was performed on the hybrid composites as per the method prescribed in the International Standard Organisation (ISO 179-1:2000) for determination of Charpy Impact Properties of Plastics using a Polytest impact tester with a universal pendulum with a hammer weight 0.475 kg at an impact velocity of 2.9m/s at 21° C wherein test specimen rested over two supports on either side of the test notch. Six replicate specimens were tested to confirm the reproducibility of the results.

2.5.7 Dynamic Mechanical Analysis of Composites

The mechanical response of hybrid composites was tested using a Perkin Elmer DMA 8000, to monitor the effect of frequency, temperature and time under an oscillating force where in the sinusoidal stress/ strain curves were recorded as a function of time. Hybrid composite specimens of dimensions 30mm x7.08 mm x 3.64 mm with a free length of 12.5 mm (**Fig.3**) were scanned at frequencies of 10 Hz with 0.5 mm dynamic displacement at a temperature ramp rate of 2° C per minute from room temperature to 120° C under single

cantilever bending. Parameters obtained were: (i) storage modulus (E') (ii) loss modulus (E'') and (iii) the mechanical damping factor ($\tan \delta$).

2.5.8 Density and Water Absorption Studies of Composites

Density of hybrid natural fibre PLA composites was determined using a high precision micro balance as prescribed in ASTM D 792-08 (Density and Specific Gravity of Plastics by Displacement). Samples stored in air and immersed in water were studied. Water immersion was studied as per ASTM D 570-98 (Standard Test Method for Water Absorption of Plastics). Initially fibres were dried until a constant weight was attained. Then, each sample was submerged in distilled water separately at $20 \pm 2^\circ\text{C}$ for 24 hours during which they were taken out periodically and subsequently weighed, after wiping the water from the specimen surface. The percentage water absorption was calculated from the weight of the hybrid composite specimens prior to and after immersion in water.

3. Results and Discussions

3.1 Characteristics of Sisal and Hemp Fibre

The unprocessed sisal fibre was observed to be white and bright in colour in contrast to hemp fibre which is brown. **Figure 4** shows the microscopic view of (A) sisal fibre and (B) hemp fibre. The average diameter of single sisal and hemp fibres was found to be $268.79 \pm 77.89.1 \mu\text{m}$ and $105.08 \pm 48.84 \mu\text{m}$ respectively. Density of hemp fibre was found to be 1.48 g/cm^3 whereas the density of sisal fibre was recorded as 1.42 g/cm^3 . The average tensile strength of sisal fibre was $294 \pm 113.2 \text{ MPa}$ and hemp fibre was $423 \pm 186 \text{ MPa}$. The tensile modulus of sisal fibre was $9.77 \pm 0.88 \text{ GPa}$ which was less than that for the hemp

fibre (14 ± 3.8 GPa). Overall, compared to sisal fibre, the tensile strength/ tensile modulus of hemp fibre was found to be higher.

3.2 TGA

TGA is an important study that provides the significant information about the thermal stability of the manufactured materials. Result from TGA analysis of hybrid composites are shown in **Figure 5**. In this figure, HBC-R1; HBC-R2 and HBC-R3 represents the replicate samples and have been reported to represent the reproducibility of the results. All samples underwent two-step decomposition comprising of one major step weight loss starting around 300 °C followed by a relatively much smaller weight loss starting at around 410°C that concludes rapidly by 425°C. It should be noted that PLA usually starts decomposing after 300 °C under Nitrogen atmosphere (Dubey et al., 2017) attributed mainly to the loss of ester. Natural fibre reinforced PLA composites are known to be sensitive to heat absorption and thermally degrade which leads to changes into polymer chain integrity and thus overall performance. In the present case, the three thermogram for the composite sample showed nearly identical profile although the third specimen underwent slightly higher weight loss (~ 8 % more) during the first decomposition range. Almost no residue remained after the second decomposition stage. The similarity in the thermal decomposition of the composites with that of pure PLA indicates no change in heat resistance. Indeed, natural fibre PLA composites are known to be sensitive to heat absorption and thermally degrade which leads to changes in the molecular structure. In summary, few differences were found between the different specimens from the point of view of processing. The mentioned changes indicate that degradation phenomena occur

and mostly they may regard the type of natural fibers (Dubey et al., 2017). Further, addition of hybrid fibre enhanced the elongation and impact properties and reduced the brittle behaviour of PLA composite.

3.3 XRD Analysis

The XRD diffractograms of the hybrid fibres composites are shown in Figure 6. In the figure 6 the HBC-R1 and HBC-R2 codes represent the (explicative) test samples in the previous sections (section 3.1-3.3). It is imperative to note that, for XRD analysis usually few replicate tests are sufficient to represent the samples' results, as such test results are authenticated by the respective machine, moreover, such test involves more time and other requirement. In the figure 6, both specimens exhibited identical spectra comprising of two amorphous halos. The first one ($2\theta = 12-27$) contained two small peaks ($2\theta = 15$; $2\theta = 22$) indicating the presence of certain amount of semi-crystalline phases in the composites. While, in case of neat PLA, two main diffraction peaks at 16.6 and 18.9 have been reported that correspond to the (110/200) and (203) plane of α -form orthorhombic crystal lattice respectively (Dubey et al., 2017; Requile et al. 2018). While no crystalline peak for PLA could be observed in the XRD, the appearance of two small peaks mentioned above can be attributed to the semi-crystalline sisal fibres present in the composite. This implies that the amorphous content of PLA remained largely unaffected by the inclusion of semi-crystalline fibres. In case of neat PLA while the processing conditions and the composition nature can greatly influence the amorphous content and induce small crystalline phase, the amorphous region usually ends around $2\theta = 45$. In the present case, this amorphous region further shifts

till 60 indicating large disordered regions or phases. It is evident that the hemp and sisal fibers are composed of cellulose and hemicelluloses, which presents crystalline domains that generate peaks in the diffractogram. Also, it is non-surprising fact that at high fibres loading levels coupled with shorter cooling impeded the formation of crystalline regions.

3.4 Characteristics of Hybrid Composites

The physical and mechanical properties of hybrid natural fibre reinforced PLA composites and neat PLA are shown in **Table 1** and **Table 2** respectively.

3.5 Tensile Testing of Composites

Figures 7(A) and **(B)** show the stress versus strain graphs for PLA and hybrid fibre reinforced composites respectively. In the figure, the R1-R5 represents five replicative test samples. For tensile testing, it is always recommended to perform more samples to validate the results and to check the reproducibility of the results. Hence, in the present study, for testing tensile properties, five replicate test specimens have been evaluated and is quite good selection. Since, PLA is commercially supplied materials and its specifications and test data were already reported by the manufacturer and thus only three samples (R1-R3) were selected for tensile testing. But, application of hemp and sisal fibres with PLA is a new class of study and thus to check the reproducibility five test samples were selected (R1-R5). PLA showed a tensile strength of 35 MPa and a modulus of 3.5 GPa (**Table 1**). In the table 1, sample ID No. 1-5 refers to tests specimens R1, R2, R3, R4, R5, with the mean and standard deviation reported. The specimen 1 represent the R1, the specimen 2

represent the R2, likewise the specimen 5 represent the R5. Addition of sisal and hemp fibres contributed to an increase in tensile strength of composites about 20%. The tensile modulus of hybrid fibre reinforced PLA composites was 6.1 ± 0.58 GPa which was 42.9% higher in comparison to the pristine PLA.

It is worthy to note here that composites with a polypropylene matrix used currently in automotive applications exhibit tensile strength/ modulus of 28 MPa and 1.3GPa respectively (Islam et al., 2010). The present study demonstrates fully biodegradable composites without compromising its quality as a viable option for automotive applications. Decrease in tensile performance of hybrid fibre composites was observed to occur when test specimens failed near the grips (Saxena et al., 2008). Recent work in the literature reports bio- composites made using PLA reinforced with 25% flax fibre to have a specific Young's modulus of 6.5 GPa which was close to that achieved with glass polyester composites (7.8 GPa) (Saxena et al., 2008).

The specific tensile strength of hybrid fibre reinforced PLA composite was 38 MPa which is about 22% higher than that for neat PLA. The interface among the matrix and fibre is very important for load transfer and therefore load bearing. The properties of natural fibre reinforced PLA composite depends upon on fibre length/orientation, matrix properties (kinetics and crystallinity) and processing techniques. Roughness of fibre surfaces assists mechanical interlocking with matrices. Hemp fibre here was found to be have a rougher surface than the sisal fibre and so could be expected to have better interfacial bonding with the matrix. It is reported that exposed cellulose hydroxyl groups can lead to covalent and hydrogen bonding with matrices which enhances mechanical properties and thermal stability. Cellulosic fibres are rigid and brittle and hence they act as stress concentrators,

leading to reduction in the ultimate elongation of hybrid composites. The stress-strain curves of hybrid fibre composite are shown in **Figure 7**. The tensile fracture of hybrid fibre composite shows linear deformation at lower strains and nonlinear deformation at higher strains with lower failure strains generally than for PLA alone.

3.6 Flexural Testing of Composites

The graphs of flexural stress versus flexural extension obtained during three point bending of PLA and hybrid fibre composites are shown in **Figure 8 (a,b)** respectively. The average flexural strength of neat PLA was 82 MPa with a flexural modulus of 3.2 GPa. However, the flexural strength of polylactic acid reinforced with hemp and sisal fibre ranged from approximately 81 MPa to 104 MPa with flexural modulus of 6 GPa. The specific flexural strength of hybrid fibre reinforced PLA composites was 79 which is about 27% higher than that for PLA specimens without reinforcement. It is observed from the present study that sisal and hemp fibre incorporation resulted in a significant enhancement in the tensile and flexural properties followed by an excellent aroma (In the context of this article, aroma means a food fragrance realized during the processing of raw materials especially during extrusion and injection moulding) and better heat stability. Hybrid fibres contributed to the increment in the tensile and flexural modulus of composites. Tensile and flexural modulus of composites with cellulose fibre incorporation were found to exhibit mutually exclusive properties and the flexural strength values were consistent with tensile strength where in flexural strength was found to be proportionately increased the flexural modulus.

3.7 Impact Strength of Composites

The Charpy impact test of the hybrid composite specimens was performed with a universal pendulum at an impact velocity of 2.9 m/s wherein the test specimen rests over two supports on either side of the test notch. Results revealed that the impact strength of the hybrid composite developed using sisal-hemp fibre reinforced polylactic acid varied from 9.21 KJ/m² to 11.08 KJ/m² (**Table 1**). It is apparent that impact strength is expressed to measure the ability of materials to withstand fracture. Neat PLA exhibits low impact strength (6.4 KJ/m²) and was brittle in nature; however, the present study revealed that the incorporation of sisal and hemp fibre with polylactide remarkably increased the impact strength. Pappu et al., 2016 reported that bi-directional sisal textile fibre reinforced polyester composites (0.4 volume fraction) exhibited an impact strength of 21.803 ± 1.84 KJ/m² (Pappu et al., 2016). It is evident from all these studies that fibre incorporation enhances the impact strength of PLA composites. In the present study, extruded and injection moulded hybrid natural fibre composites might have reduced the aspect ratio of biofibres and thus improved fibre matrix adhesion better than long fibre, leading to improved mechanical properties. This has been substantiated with the results of percentage elongation at break and possibly the reduction in toughness as could be recorded from the area under the stress-strain curve.

3.8 Dynamic Mechanical Analysis of Composites

Results of properties from dynamic analysis for PLA and hybrid composites are shown in **Figure 9**. In this work, only two replicative test specimens have been tested for the dynamic mechanical analysis of composites and the results have been compared with PLA results. The changes in (a) storage modulus (E'), (b) loss modulus (E'') and (c) mechanical damping

factor ($\tan \delta$) demonstrates that there are significant variations relating to the degree of molecular mobility in hybrid natural fibre PLA composites. E' / E'' was found to be higher in comparison to the PLA across the entire spectrum of the studied temperature. The glass transition temperature (T_g) increased from 50°C for PLA to 80°C for composites. After a big drop in E' associated with T_g , it was found that it increases again to give a small peak at 80°C which is likely to be due to cold crystallisation. It is reported that crystallisation of PLA happens at 80-100 °C. The area under $\tan \delta$ verses temperature curve decreased with fibre addition suggesting increase in the damping ability of hybrid fibre PLA composite compared to pristine PLA. Fibre reinforced PLA composites were sensitive to the thermal degradation. The $\tan \delta$ verses temperature plot represent the molecular transition and the $\tan \delta$ peak shows the T_g which is also around 68°C and not much difference could be noticed between PLA and hybrid composites. Generally at room temperature, there is an increment in the storage modulus with fibres addition. Decrease in storage modulus was recorded with increase in temperature which indicates the softening of composites at 60°C in which the loss modulus was increased **Figure 9(a, b)**.

3.9 SEM Microstructure of Composites

Morphological images (SEM micrographs) of fracture surfaces of hybrid composites specimens are shown in **Figure 10**. It appears that there was reasonably good interfacial adhesion among the fibre and PLA and a moderate dispersion of fibre could be seen. However, some fibre pull-out was noticed in the fractured specimens, wherein sisal fibre which was mostly in bundle form was found to have de-bonded more than the hemp fibre (**Figure 10 A**). It is observed that the average cells size in PLA was found to be larger than

that of hybrid fibre PLA composites which may be due to the nucleation in the presence of fibre leading to reduction in the cell size. Earlier work done using pull-out tests showed that PLA flax fibre composites had poor adhesion between fibre and matrix when the flax fibres were in the single fibre form (Islam et al., 2010). It is apparent from the SEM microstructures that the non-linear deformation behaviour in the composites specifies plastic deformation and micro-crack initiation at the fibre matrix interphase leading to crack propagation along the fibre boundary (**Figure 10 B, C**). Moreover, there is evidence of here being few voids and good interfacial bonding giving only limited fibre pull-out resulting in enhanced mechanical properties. This is an improvement on earlier work on PLA composites with incorporation of agricultural residues where there was non-uniform adhesion between fibre and PLA, more porosity and insignificant improvement in the mechanical properties.

3.10 Density and Water Absorption of Composites

Lower density of natural fibres over synthetic fibres is one of their advantageous property. **Table 2** shows the physical and mechanical properties of hybrid natural fibre PLA composites fabricated under extrusion and injection moulding system. All specimens were analysed in detail. Density and water absorption of composites were tested for five replicative samples namely HBC-R1, HBC-R2, HBC-R3, HBC-R4, HBC-R5. In the present study, the density of hybrid composites was 1.2 g/cm^3 . Natural fibre density varied from $1.3 - 1.5 \text{ g/cm}^3$, however, measured density of hemp fibre and sisal fibre varied from $1.2 - 1.48 \text{ g/cm}^3$ which is about 43% lower than the density of E-glass (2.6 g/cm^3). Neat PLA showed about 1.25 g/cm^3 density. Application of such low density composites may

not only result in saving fuel in automotive applications but also introduce fully biodegradable composites for the environmental friendly and sustainable growth. The developed hybrid composite materials can be used in automobile applications, especially the interior parts including back safety cover, door panels. Application of these hybrid biodegradable composite materials will also reduce the persistent plastic waste leading to maintaining balanced CO₂ level/ emission in the atmosphere. For water absorption study, five injection moulded impact specimens were used. The submerged test specimens in distilled water were taken out periodically and subsequently weighed, after wiping out the water on the specimen surface. Water absorption of hybrid fibre PLA composites showed $1.08 \pm 0.21\%$ which is found to be very less than that of timber products(Saxena et al., 2008).

4. Conclusions

In the present study, PLA a thermoplastic polyester derived from corn starch was used as an ideal binding medium, which is 100 % biodegradable, about 8 times recyclable and compostable at the end of its service life and is a promising and sustainable materials leading to reduction in the societal solid waste disposal problem. From the analysis of the mechanical properties, water absorption studies, thermal analysis, crystallinity and microstructure properties, it is clear that high performance hybrid fibre reinforced composite can be manufactured using sisal and hemp fibre in combination with polylactic acid using extrusion (melt processing) and injection moulding. The hybrid composites resulted in good material properties in terms of tensile strength (46.25 ± 6.75 MPa), Young's modulus (6.1 ± 0.58 GPa), flexural strength (94.83 ± 11.21 MPa), low density

(1.14 ± 0.075 g/cm³) and low water absorption ($1.06 \pm 0.18\%$). The SEM microstructure revealed the improved interfacial adhesion between PLA matrix and fibre with hybridisation of natural fibre resulting in enhanced mechanical and thermal properties of composites. These hybrid biodegradable composite are renewable and avoid the dependence of diminishing fossil resources.

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References

- Bleuze, L., Lashermes, G., Alavoine, G., Recous, S., Chabbert, B., 2018. Tracking the dynamics of hemp dew retting under controlled environmental conditions. *Ind. Crops Prod.* 123, 55–63. <https://doi.org/10.1016/j.indcrop.2018.06.054>
- Bodros, E., Pillin, I., Montrelay, N., Baley, C., 2007. Could biopolymers reinforced by randomly scattered flax fibre be used in structural applications? *Compos. Sci. Technol.* 67, 462–470. <https://doi.org/10.1016/j.compscitech.2006.08.024>
- de Oliveira, F., da Silva, C.G., Ramos, L.A., Frollini, E., 2017. Phenolic and lignosulfonate-based matrices reinforced with untreated and lignosulfonate-

- treated sisal fibers. *Ind. Crops Prod.* 96, 30–41.
<https://doi.org/10.1016/j.indcrop.2016.11.027>
- Dubey, S.P., Thakur, V.K., Krishnaswamy, S., Abhyankar, H.A., Marchante, V., Brighton, J.L., 2017. Progress in environmental-friendly polymer nanocomposite material from PLA: Synthesis, processing and applications. *Vacuum* 146, 655–663. <https://doi.org/10.1016/j.vacuum.2017.07.009>
- Gan, I., Chow, W.S., 2018. Antimicrobial poly(lactic acid)/cellulose bionanocomposite for food packaging application: A review. *Food Packag. Shelf Life* 17, 150–161. <https://doi.org/10.1016/j.fpsl.2018.06.012>
- Goudenhooff, C., Bourmaud, A., Baley, C., 2018. Conventional or greenhouse cultivation of flax: What influence on the number and quality of flax fibers? *Ind. Crops Prod.* 123, 111–117. <https://doi.org/10.1016/j.indcrop.2018.06.066>
- Islam, M.S., Pickering, K.L., Foreman, N.J., 2010. Influence of alkali treatment on the interfacial and physico-mechanical properties of industrial hemp fibre reinforced polylactic acid composites. *Compos. Part Appl. Sci. Manuf.* 41, 596–603. <https://doi.org/10.1016/j.compositesa.2010.01.006>
- Kaschuk, J.J., Frollini, E., 2018. Effects of average molar weight, crystallinity, and hemicelluloses content on the enzymatic hydrolysis of sisal pulp, filter paper, and microcrystalline cellulose. *Ind. Crops Prod.* 115, 280–289. <https://doi.org/10.1016/j.indcrop.2018.02.011>
- Liu, M., Thygesen, A., Summerscales, J., Meyer, A.S., 2017. Targeted pre-treatment of hemp bast fibres for optimal performance in biocomposite materials: A review. *Ind. Crops Prod.* 108, 660–683. <https://doi.org/10.1016/j.indcrop.2017.07.027>

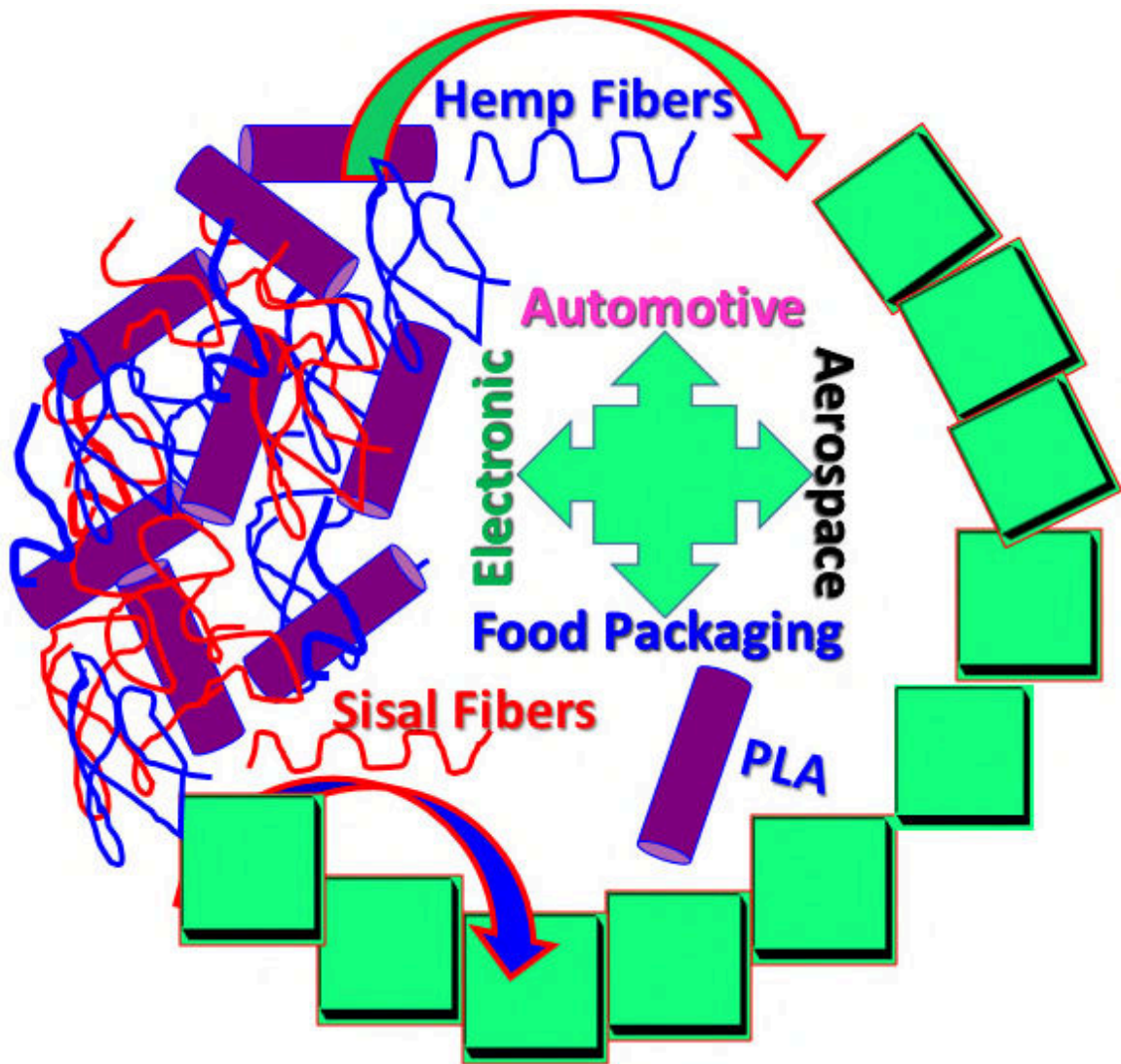
- Miculescu, F., Maidaniuc, A., Voicu, S.I., Thakur, V.K., Stan, G.E., Ciocan, L.T., 2017. Progress in Hydroxyapatite–Starch Based Sustainable Biomaterials for Biomedical Bone Substitution Applications. *ACS Sustain. Chem. Eng.* 5, 8491–8512. <https://doi.org/10.1021/acssuschemeng.7b02314>
- Ochoa, M., Collazos, N., Le, T., Subramaniam, R., Sanders, M., Singh, R.P., Depan, D., 2017. Nanocellulose-PE-b-PEG copolymer nanohybrid shish-kebab structure via interfacial crystallization. *Carbohydr. Polym.* 159, 116–124. <https://doi.org/10.1016/j.carbpol.2016.12.028>
- Panaitescu, D.M., Frone, A.N., Chiulan, I., 2016. Nanostructured biocomposites from aliphatic polyesters and bacterial cellulose. *Ind. Crops Prod.* 93, 251–266. <https://doi.org/10.1016/j.indcrop.2016.02.038>
- Pappu, A., Patil, V., Jain, S., Mahindrakar, A., Haque, R., Thakur, V.K., 2015. Advances in industrial prospective of cellulosic macromolecules enriched banana biofibre resources: A review. *Int. J. Biol. Macromol.* 79, 449–458. <https://doi.org/10.1016/j.ijbiomac.2015.05.013>
- Pappu, A., Saxena, M., Thakur, V.K., Sharma, A., Haque, R., 2016. Facile extraction, processing and characterization of biorenewable sisal fibers for multifunctional applications. *J. Macromol. Sci. Part A* 53, 424–432. <https://doi.org/10.1080/10601325.2016.1176443>
- Pappu, A., Thakur, V.K., 2017. Towards sustainable micro and nano composites from fly ash and natural fibers for multifunctional applications. *Vacuum* 146, 375–385. <https://doi.org/10.1016/j.vacuum.2017.05.026>

- Pickering, K.L., Efendy, M.G.A., Le, T.M., 2016. A review of recent developments in natural fibre composites and their mechanical performance. *Compos. Part Appl. Sci. Manuf.*, Special Issue on Biocomposites 83, 98–112.
<https://doi.org/10.1016/j.compositesa.2015.08.038>
- Requile, S., Goudenhooff, C., Bourmaud, A., Le Duigou, A., Baley, C., 2018. Exploring the link between flexural behaviour of hemp and flax stems and fibre stiffness. *Ind. Crops Prod.* 113, 179–186. <https://doi.org/10.1016/j.indcrop.2018.01.035>
- Saradava, B.J., Kathwadia, A.J., Gorviyala, A.D., Joshi, V.K., 2016. Mechanical Characterization of Hemp Fiber Reinforced Polyester Composites: A Review. *J. Polym. Compos.* 4, 1–3.
- Sarasini, E., Fiore, V., 2018. A systematic literature review on less common natural fibres and their biocomposites. *J. Clean. Prod.* 195, 240–267.
<https://doi.org/10.1016/j.jclepro.2018.05.197>
- Saxena, M., Morchhale, R.K., Asokan, P., Prasad, B.K., 2008. Plant fiber - Industrial waste reinforced polymer composites as a potential wood substitute material. *J. Compos. Mater.* 42, 367–384. <https://doi.org/10.1177/0021998307087014>
- Senthilkumar, K., Saba, N., Rajini, N., Chandrasekar, M., Jawaid, M., Siengchin, S., Alotman, O.Y., 2018. Mechanical properties evaluation of sisal fibre reinforced polymer composites: A review. *Constr. Build. Mater.* 174, 713–729.
<https://doi.org/10.1016/j.conbuildmat.2018.04.143>
- Singha, A.S., Kumar Thakur, V., 2008. Saccharum Cilliare Fiber Reinforced Polymer Composites [WWW Document]. *J. Chem.* <https://doi.org/10.1155/2008/941627>

- Singha, A.S., Shama, A., Thakur, V.K., 2008. X-Ray Diffraction, Morphological, and Thermal Studies on Methylmethacrylate Graft Copolymerized *Saccharum ciliare* Fiber. *Int. J. Polym. Anal. Charact.* 13, 447–462.
<https://doi.org/10.1080/10236660802399747>
- Singha, A.S., Thakur, V.K., 2009. Fabrication and Characterization of *H. sabdariffa* Fiber-Reinforced Green Polymer Composites. *Polym.-Plast. Technol. Eng.* 48, 482–487. <https://doi.org/10.1080/03602550902725498>
- Thakur, M.K., Gupta, R.K., Thakur, V.K., 2014. Surface modification of cellulose using silane coupling agent. *Carbohydr. Polym.* 111, 849–855.
<https://doi.org/10.1016/j.carbpol.2014.05.041>
- Thakur, V.K., Singha, A.S., 2010. Mechanical and Water Absorption Properties of Natural Fibers/Polymer Biocomposites. *Polym.-Plast. Technol. Eng.* 49, 694–700.
<https://doi.org/10.1080/03602551003682067>
- Thakur, V.K., Singha, A.S., Thakur, M.K., 2012. Biopolymers Based Green Composites: Mechanical, Thermal and Physico-chemical Characterization. *J. Polym. Environ.* 20, 412–421. <https://doi.org/10.1007/s10924-011-0389-y>
- Thakur, V.K., Thakur, M.K., 2014. Processing and characterization of natural cellulose fibers/thermoset polymer composites. *Carbohydr. Polym.* 109, 102–117.
- Zhang, Y., Li, Y., Thakur, V.K., Gao, Z., Gu, J., Kessler, M.R., 2018a. High-performance thermosets with tailored properties derived from methacrylated eugenol and epoxy-based vinyl ester. *Polym. Int.* 67, 544–549. <https://doi.org/10.1002/pi.5542>
- Zhang, Y., Thakur, V.K., Li, Y., Garrison, T.F., Gao, Z., Gu, J., Kessler, M.R., 2018b. Soybean-Oil-Based Thermosetting Resins with Methacrylated Vanillyl Alcohol as

Bio-Based, Low-Viscosity Comonomer. *Macromol. Mater. Eng.* 303, 1700278.

<https://doi.org/10.1002/mame.201700278>



Scheme 1: Schematic for synthesis and manufacturing of hybrid natural fibre (sisal–hemp fibre) reinforced poly-lactic acid based sustainable composites.



Figure 1. As received sisal fibre (A); as received hemp fibre (B); processing/ cleaning of hemp fibre in hot water (C) & carding of hemp fibres using hand carding machine (D)



Figure 2. Processed hemp fibre (A); processed sisal fibre (B); Micronised PLA powder (C) & granulated hybrid natural fibres (Sisal fibre to Hemp fibre ratio 1:1 ratio) (D)



Figure 3. Extruded compounded hybrid composite (A); Granulated extruded compound of hybrid natural fibre and matrix (B); Fabricated tensile test specimens of pristine PLA (C); Fabricated tensile test specimens of Hybrid fibre reinforced with PLA (D); 9 Composite impact test specimens (E) and hybrid composite DMA test specimens (F).

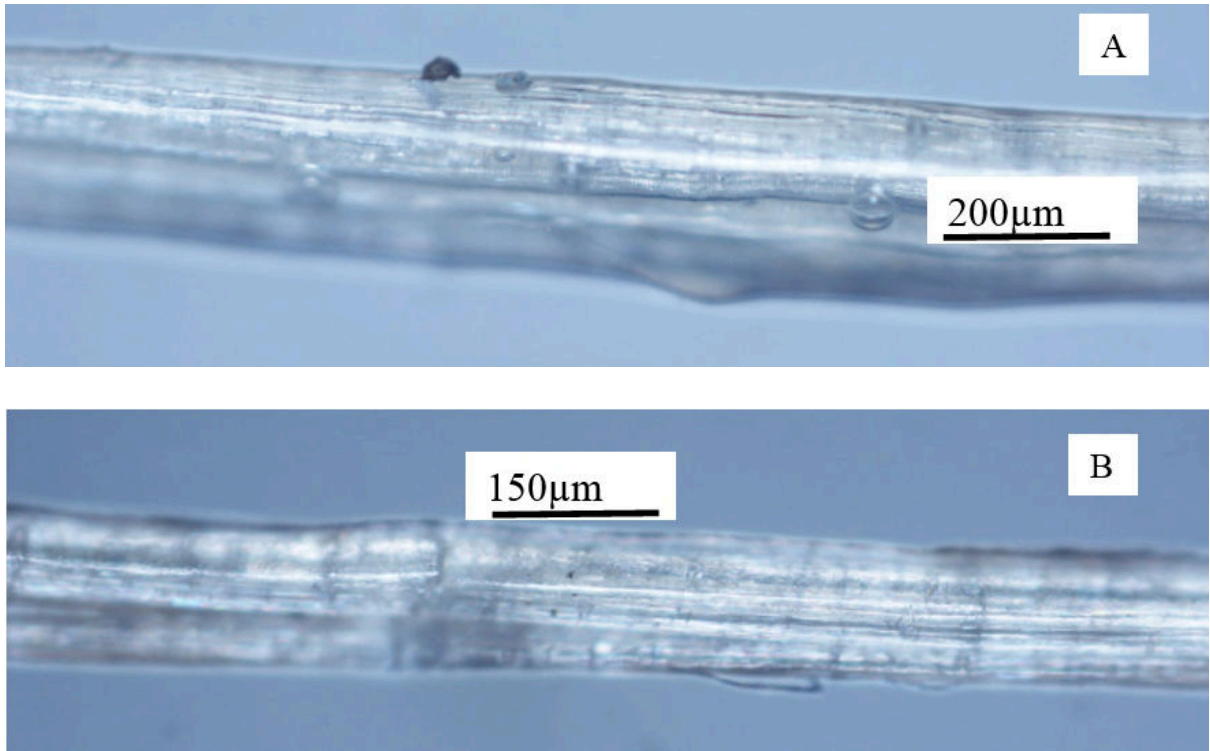


Figure 4. Microscopic view of (a) sisal fibre and (b) hemp fibre

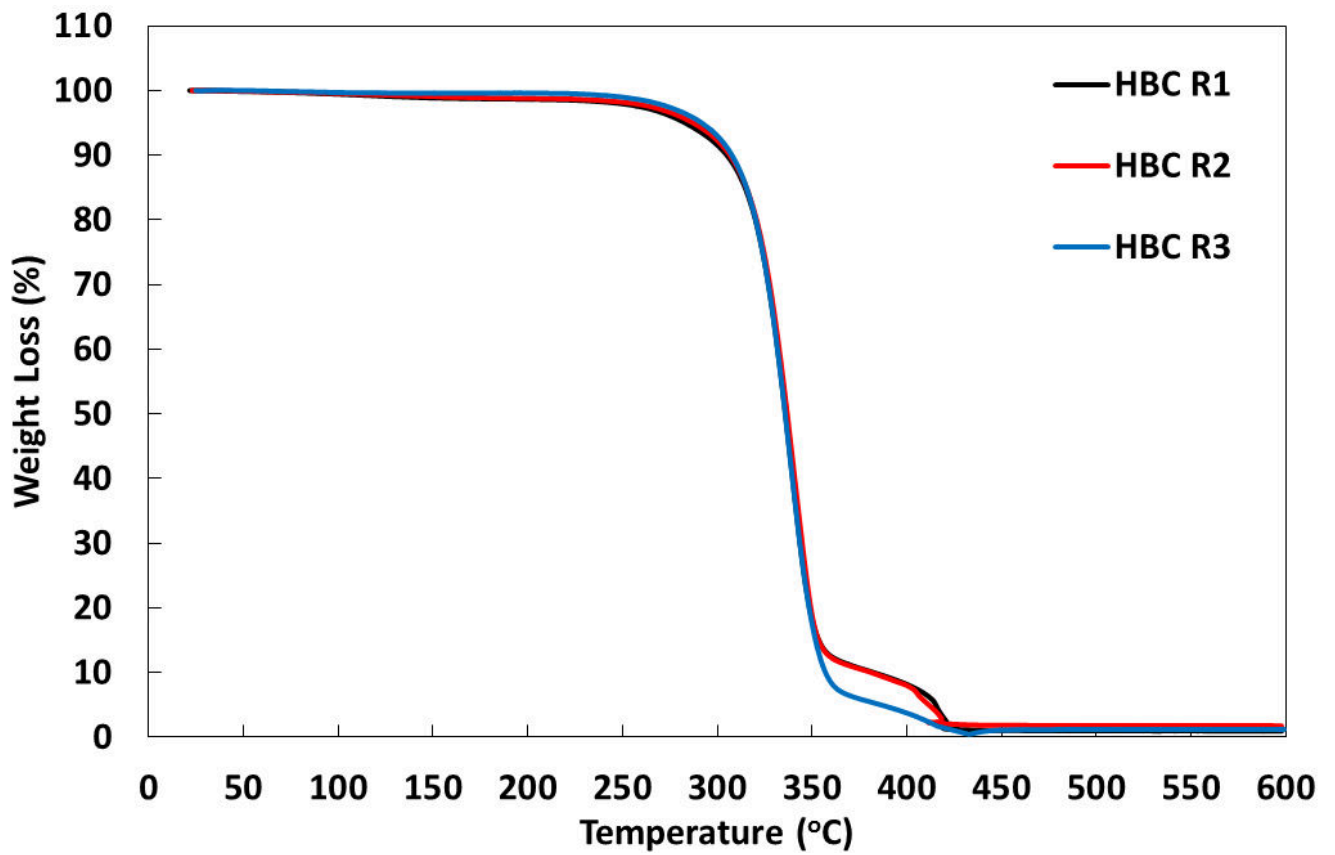


Figure 5 Thermal analysis (TGA) of hybrid composites

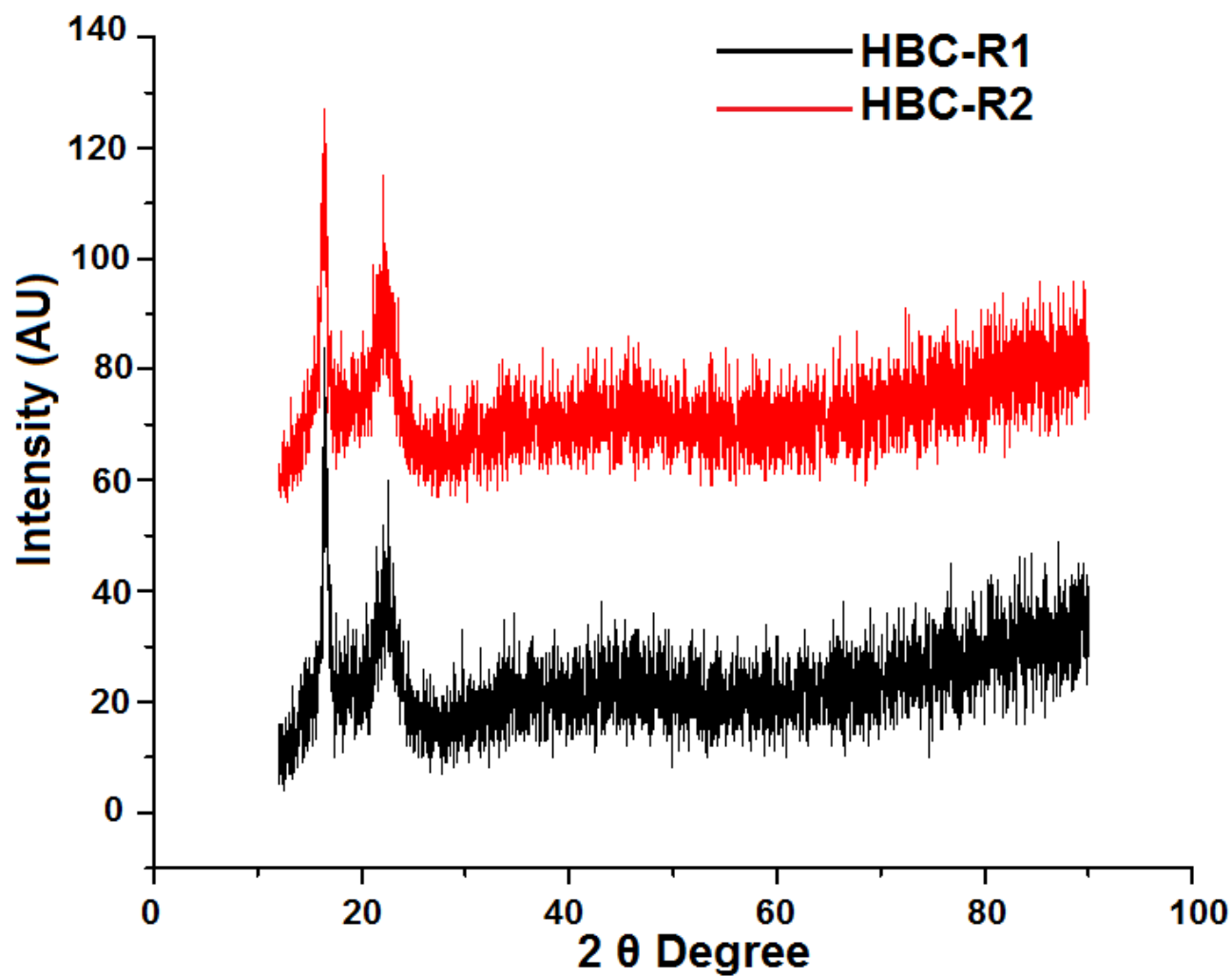
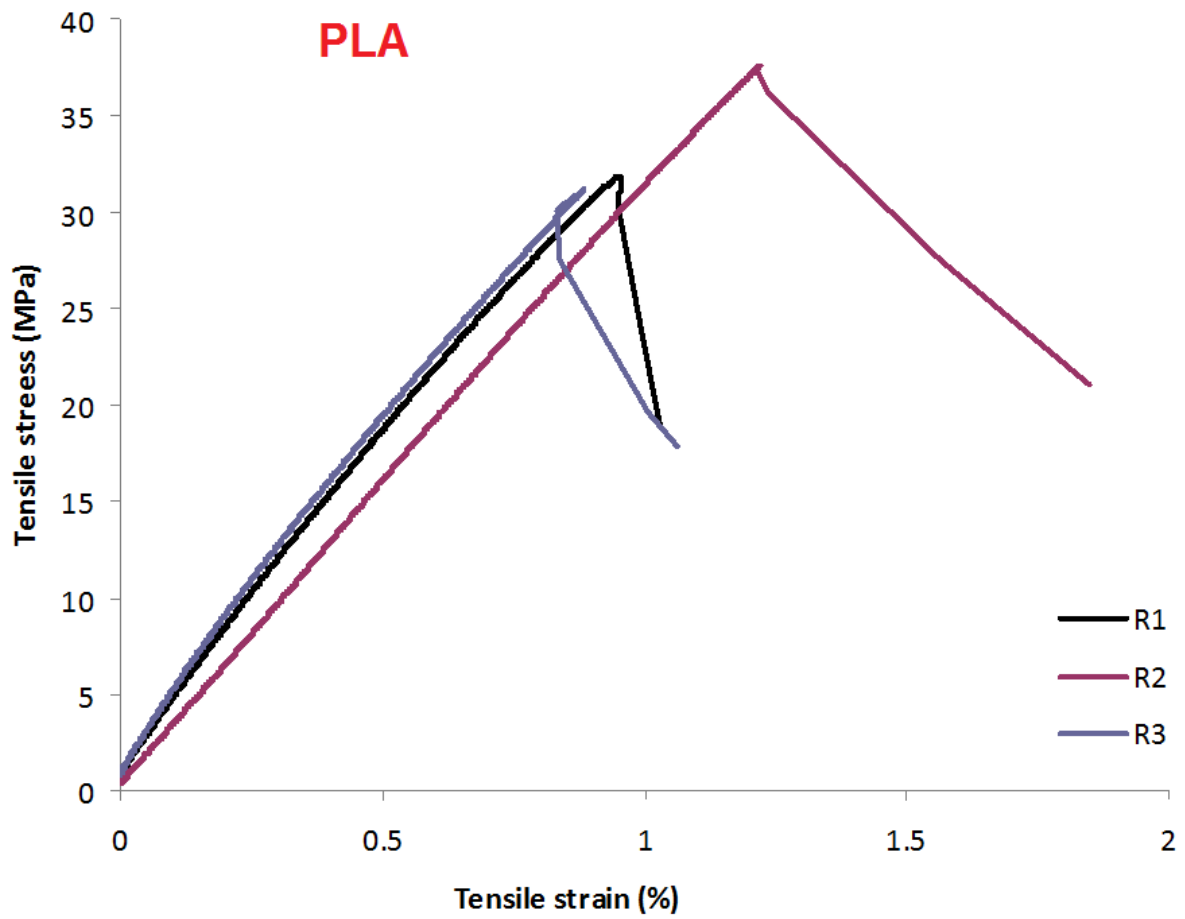
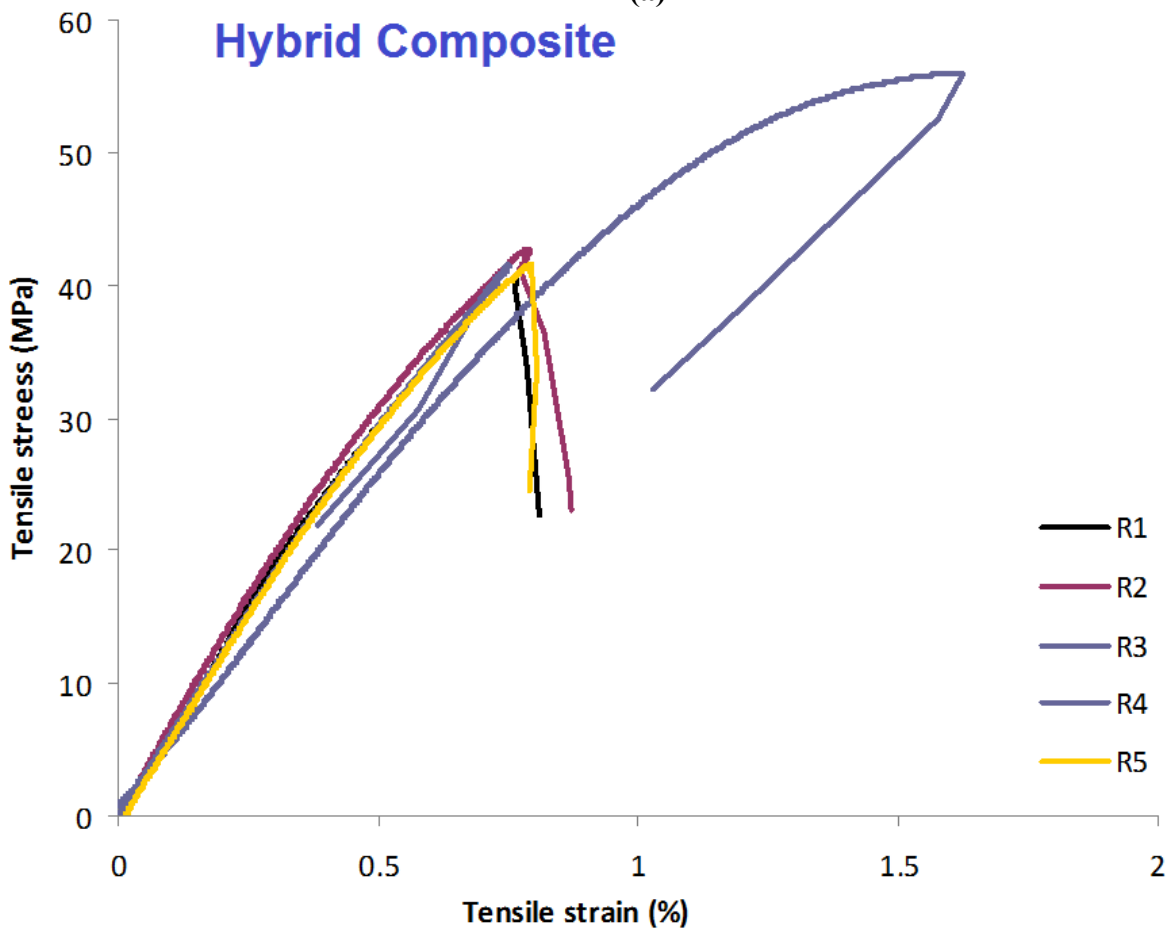


Figure 6 XRD trace of hybrid composites

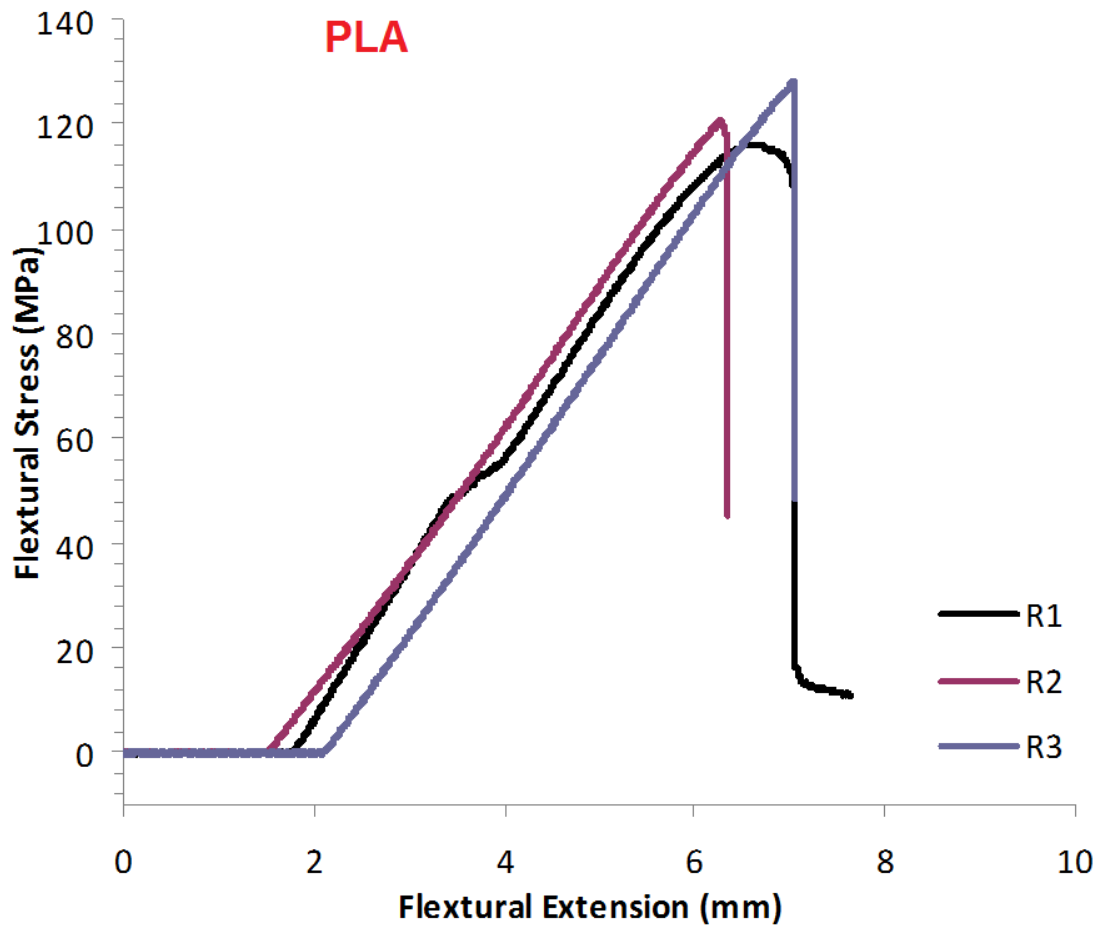


(a)

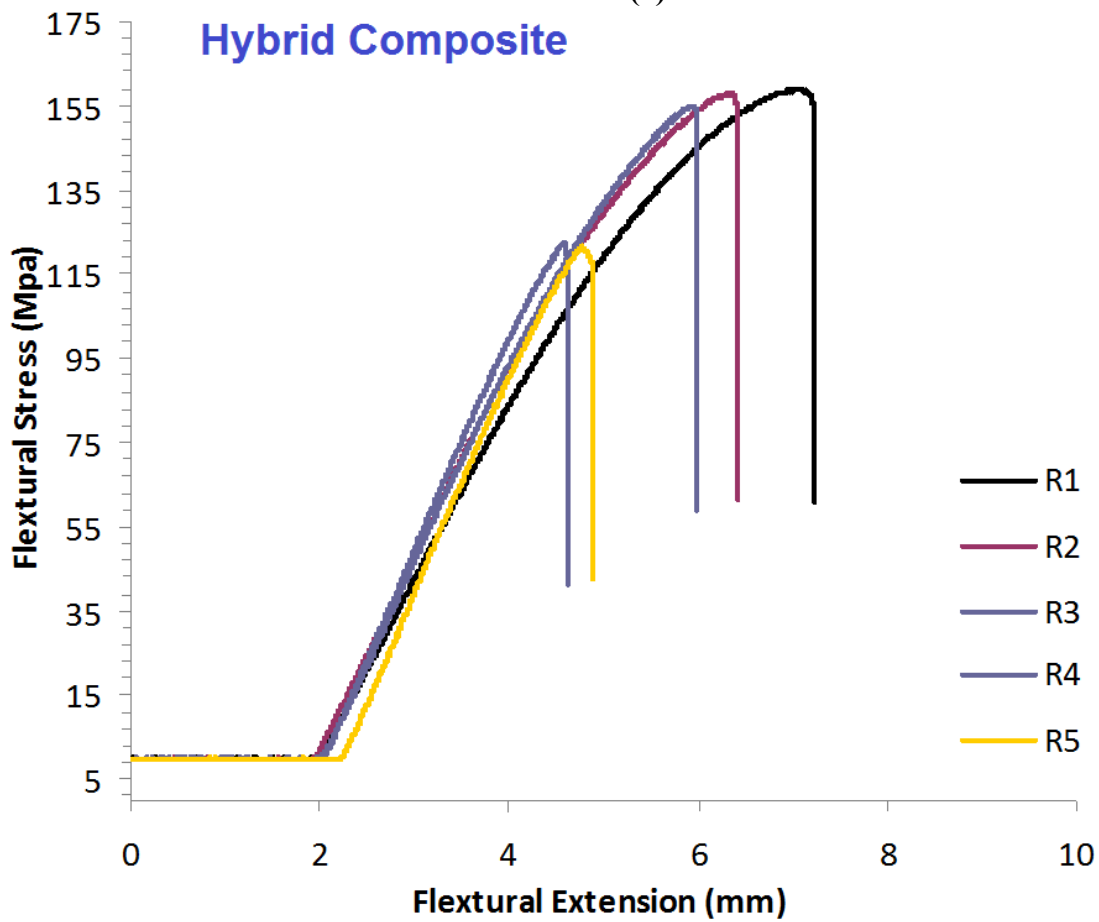


(b)

Figure 7 Tensile stress versus strain of (a) PLA, (b) hybrid composites

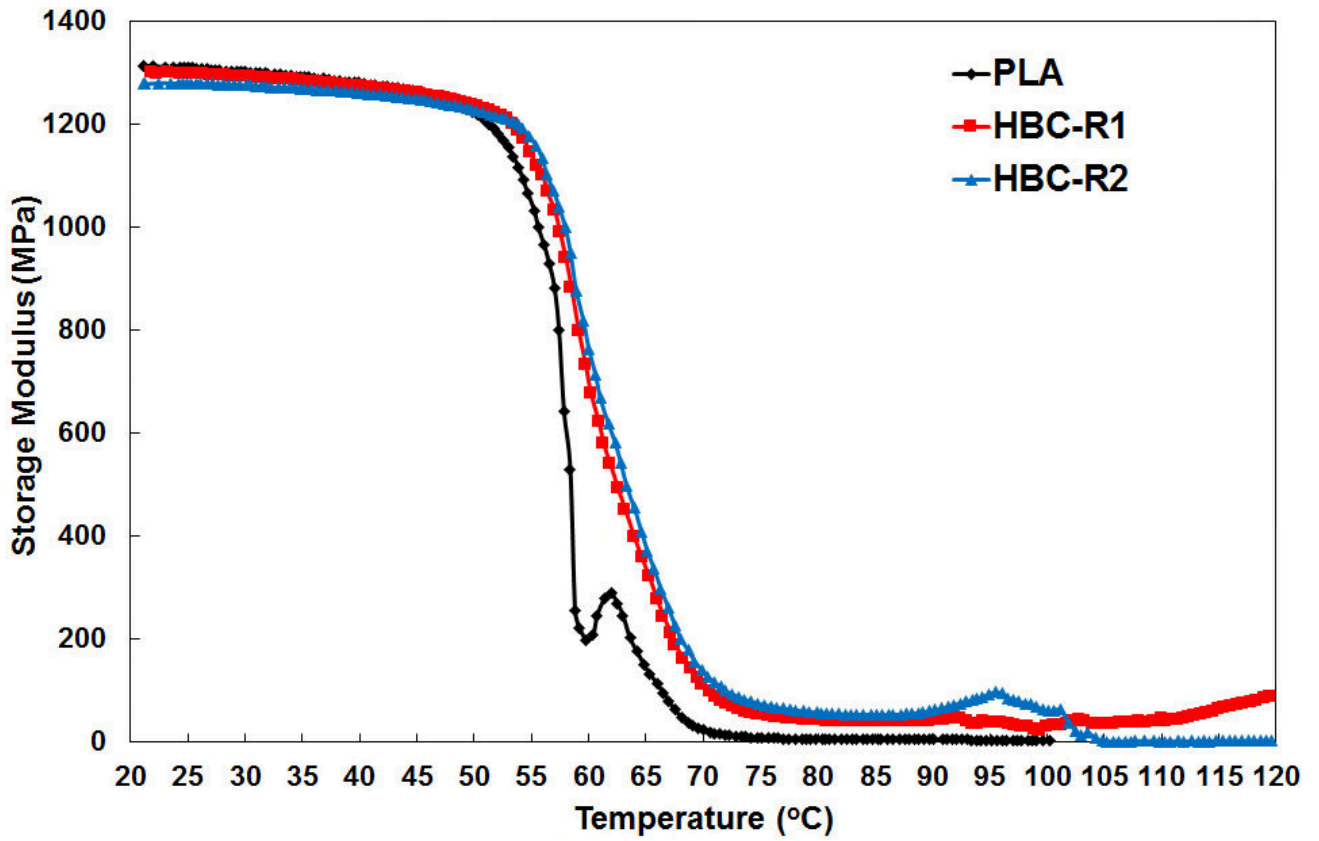


(a)

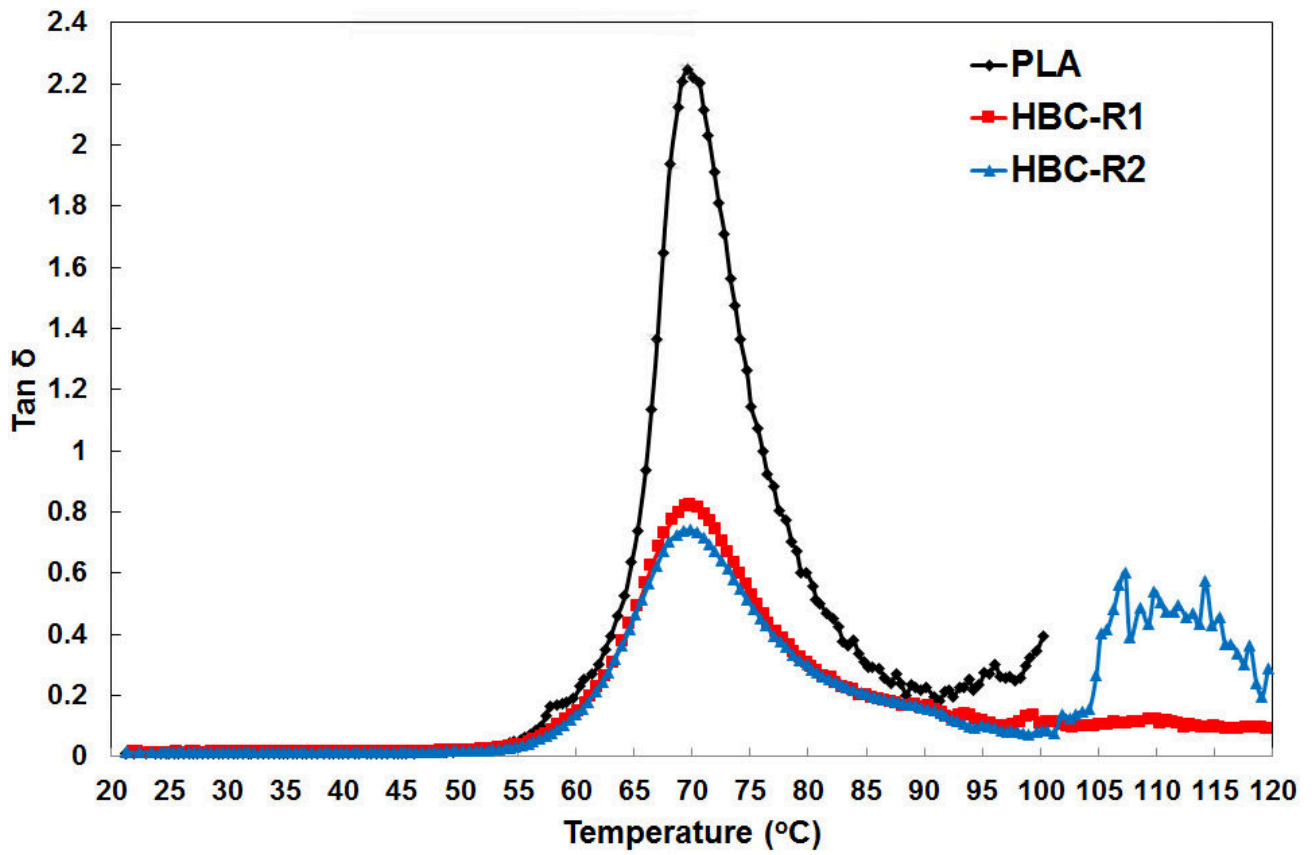


(b)

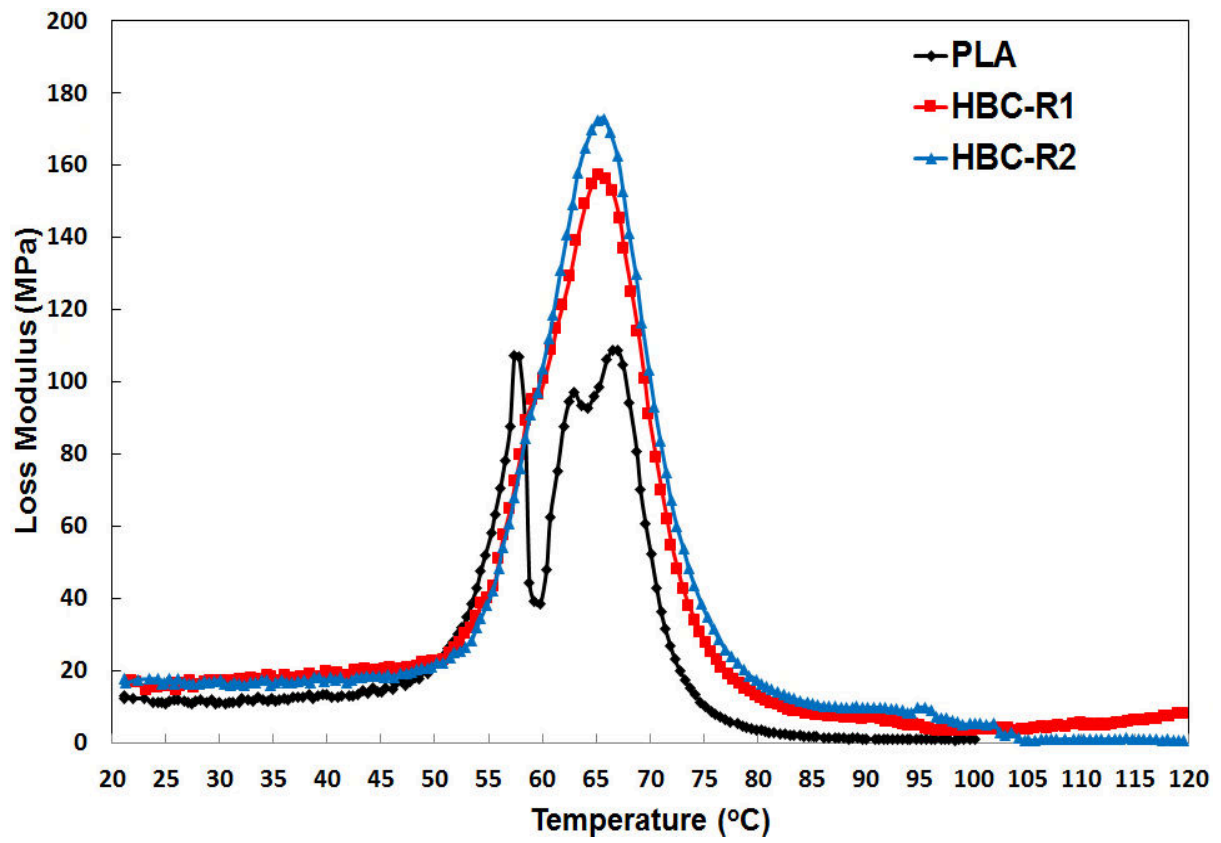
Figure 8 Flexural stress versus extension (a) PLA, (b) hybrid composites



(a)

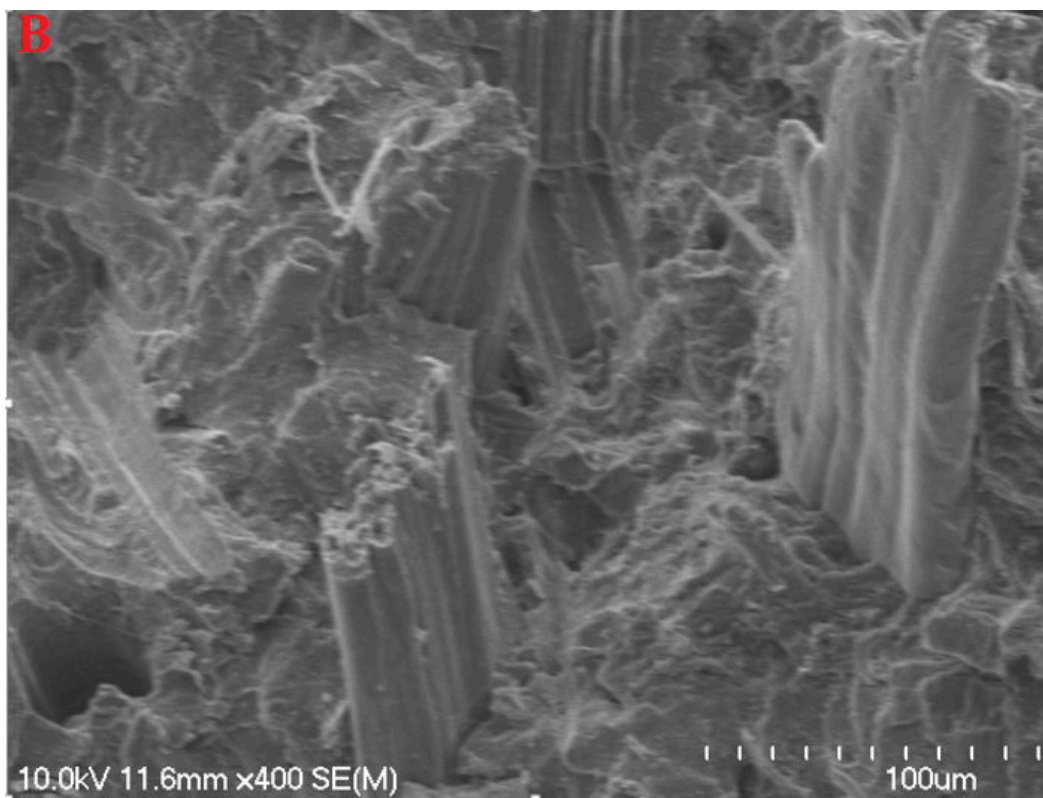


(b)



(c)

Figure 9 Dynamic mechanical analysis data: (a) storage Modulus, (b) loss Modulus, (c) tan delta at frequencies of 10 Hz



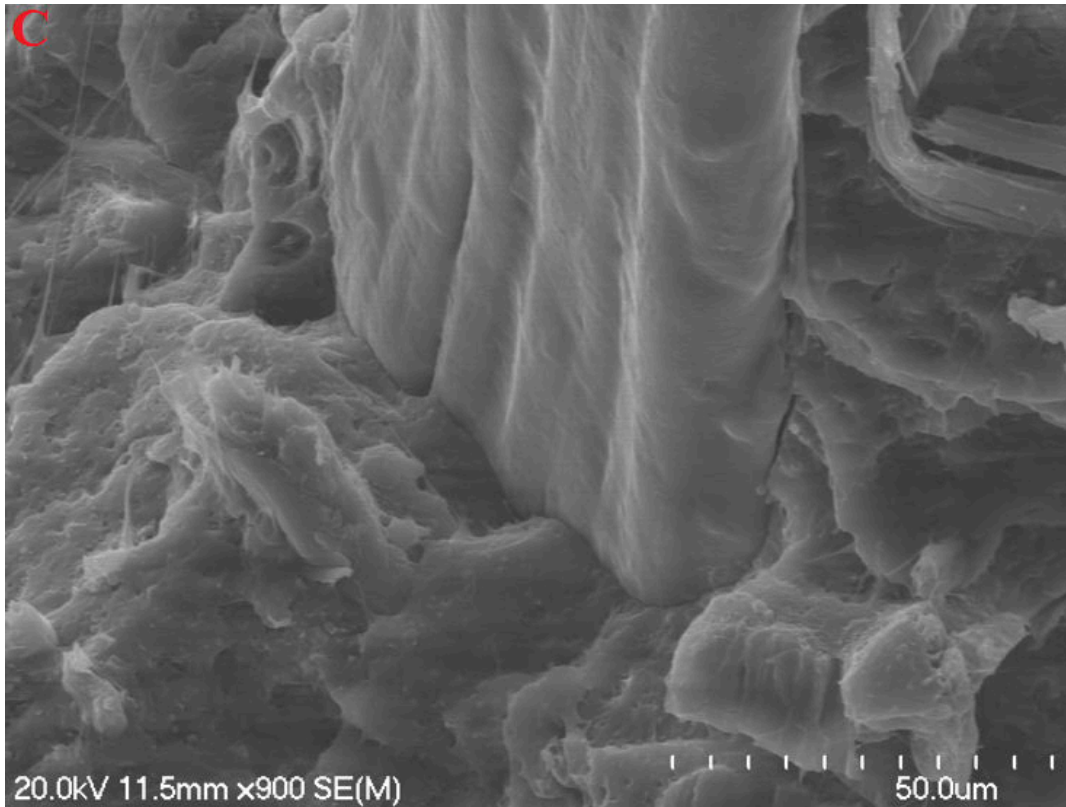


Figure10 SEM micrographs of hybrid composite (HBC- R1) showing: (a) fibre fracture, (b) fibre pull-out, (c) adhesion at the fibre matrix interface.

Table 1 Physical and mechanical properties of the hybrid composites

Sample ID	Density (g/cm ³)	Tensile strength (MPa)	Tensile Modulus (MPa)	Flexural strength (MPa)	Flexural modulus (MPa)	Specific Tensile Strength	Specific Flexural Strength	Maximum Elongation (%)	Impact Strength (kJ/m ²)	Water Absorption (Wt %)
R1	1.16	39.82	6626.06	104.88	5153.66	34.27	90.26	0.67	10.04	1.13426
R2	1.21	43.36	6281.00	104.29	5804.85	35.86	86.24	0.77	10.04	0.94205
R3	1.17	45.66	6392.18	81.03	6487.15	39.05	69.30	0.78	9.21	1.42826
R4	1.22	59.23	4967.74	102.74	6030.19	48.39	83.93	1.63	11.08	0.9961
R5	1.18	43.19	6238.57	81.21	6728.08	36.73	69.05	0.79	11.08	0.91489
Mean	1.19	46.25	6101.11	94.83	6040.79	38.86	79.76	0.93	10.29	1.08311
SD	0.024	6.751	582.422	11.217	550.343	5.009	8.874	0.354	0.797	0.21066

Table 2 Physical and mechanical properties of PLA

Sample ID	Density(g/cm ³)	Tensile Strength (MPa)	Tensile Modulus (MPa)	Flexural Strength (MPa)	Flexural Modulus (MPa)	Specific Tensile Strength	Specific Flexural Strength	Maximum Elongation (wt %)	Impact Strength (kJ/m ²)
R1	1.258	33.40	3522.81	81.97	3138.41	26.72	65.57	0.96	6.2
R2	1.23	38.49	3245.77	79.50	3332.67	30.79	63.60	1.22	6.8
R3	1.26	32.74	3690.40	81.97	3138.41	26.19	65.57	0.87	6.3
Mean	1.25	34.88	3486.33	81.15	3203.16	27.90	64.92	1.02	6.43
SD	0.02	3.147	224.549	1.421	112.158	2.517	1.137	0.182	0.32

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Manufacturing and characterization of sustainable hybrid composites using sisal and hemp fibres as reinforcement of poly (lactic acid) via injection moulding

Pappu, Asokan

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