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Effect of fibre treatments on interfacial shear strength of hemp fibre reinforced polylactide and unsaturated polyester composites

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Abstract

Surface treatment of hemp fibres was investigated as a means of improving interfacial shear strength (IFSS) of hemp fibre reinforced polylactide (PLA) and unsaturated polyester (UPE) composites. Fibres were treated with sodium hydroxide, acetic anhydride, maleic anhydride and silane. A combined treatment using sodium hydroxide and silane was also carried out. IFSS of PLA/hemp fibre samples increased after treatment, except in the case of maleic anhydride treatment. Increased IFSS could be explained by better bonding of PLA with treated fibres and increased PLA transcrystallinity. The highest IFSS was 11.4 MPa which was obtained for the PLA/alkali treated fibre samples. IFSS of UPE/hemp fibre samples increased for all treated fibres. This is believed to be due to the improvement of chemical bonding between the treated fibres and the UPE as supported by FT-IR results. The highest IFSS (20.3 MPa) was found for the combined sodium hydroxide and silane treatment fibre/UPE samples.

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1 Introduction

The interface between reinforcing fibre and the matrix plays a critical role in the mechanical performance of composites. A weak interface generally results in low strength and stiffness but high resistance to fracture, whereas a strong interface produces high strength and stiffness, but often low resistance to fracture [1, 2]. Several test methods (e.g. single fibre pull-out, fragmentation, microindentation, and push out) have been developed to characterise the interface

and improve understanding of the interfacial bonding between fibre and matrix. The single fibre pull-out test has been used for measuring the interfacial strength between reinforcing fibres and polymer matrices for more than four decades and has become the most popular technique for interface characterisation [3]. The test is involved with pulling a single fibre out of a block of resin and the maximum pull-out force is used to assess the interfacial shear strength (IFSS) according to the following equation [3, 4]:

$$\tau = F / \pi d\, l_e \qquad (1)$$

where F is the maximum force, d is the fibre diameter and l_e is the embedded length.

In recent years, natural fibre reinforced polymer composites have been the focus of academic and industrial research (e.g. automotive, construction and packaging) interest due to several advantages, such as low cost, high strength-to-weight ratios, low densities and recyclability compared to the synthetic fibre composites [5]. The properties of fibre reinforced composites mainly depend upon the nature of fibre, matrix and fibre/matrix adhesion. Natural fibres such as hemp, sisal, flax, kenaf and jute are highly hydrophilic due to the presence of hydroxyl groups (OH). However, these fibres are covered with pectin and waxy materials, thus hindering the hydroxyl groups from reacting with polymer matrices. This can lead to the formation of ineffective interfaces between the fibres and matrices, with consequent problems such as debonding and voids in resulting composites. Chemical treatments provide an important and effective means to remove non-cellulosic components in cellulose fibres and add functional groups to enable better bonding in polymer composites. Many chemicals have been screened in laboratory experiments for potential to enhance fibre/matrix interface of polymer composites, such as sodium hydroxide, peroxide, organic and inorganic acids, silane, anhydrides and acrylic monomers [6-15]. Due to the commercial potential for natural fibre reinforced polymer composites in automotive applications and building construction as well as demands for environmentally friendly materials, the development of PLA and UPE based composites for many applications is an interesting area of research. This study focuses on the influence of hemp fibre surface treatments (e.g. sodium hydroxide, acetic anhydride, maleic anhydride and silane) in interfacial bonding and IFSS of PLA and UPE matrices.

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2 Materials and methods

2.1 Materials

NatureWorks® PLA (polylactide) polymer 4042D, from NatureWorks LLC, USA was used as a thermoplastic matrix. A standard unsaturated polyester resin (Crystic P489 from Nuplex, New Zealand) of 60% styrene content was used as thermoset matrix. The industrial hemp fibres were supplied by Hemcore Ltd, UK.

2.2 Methods

2.2.1 Fibre treatment

Hemp fibres were treated with sodium hydroxide, acetic anhydride, maleic anhydride and silane. A combined treatment using sodium hydroxide and silane was also carried out. In the case of alkali treatment, pre-dried fibres were soaked in 5 wt% sodium hydroxide aqueous solution at ambient temperature for 30 min. In silane treatment process, first the fibres were immersed in a solution of 0.5 wt% silane coupling agent [3-(2-aminoethyl amino)propyl trimethoxy silane] in acetone for 45 min. Then the treated fibres were removed from the solution and dried in an oven at 65 °C for 12 h. Similar silane treatment procedures also employed for fibres that were previously alkali treated. Maleic anhydride treatment of hemp fibres was carried out by using a solution of 5 wt% maleic anhydride in acetone at 65 °C for 3 h. In acetylation, hemp fibres were immersed in acetic anhydride for 15 min and then the fibres were placed in a pre-heated (120 °C) oven for 2 h to encourage esterification. In all the cases, fibres were copiously washed with water after treatment to remove any traces of chemical on the fibre surface and then dried in an oven at 80 °C for 48 h. Further details of the treatments are given elsewhere [16, 17].

2.2.2 Interfacial strength measurement by pull-out test

For pull-out specimen preparation, a hole of 6 mm diameter was made in a silicone rubber mould (18mm x 24mm x 3 mm) from the top side of mould using a punch. Along the 18 mm length side of the mould wall a slot was cut to a depth of 2.5 mm. The mould was flexed to open the cut to allow the introduction of a fibre and then released to grip the fibre. The desired embedded length was obtained by drawing the fibre through the cut under optical light microscope. Fibre diameters were measured using an optical light microscope with a calibrated eye-piece. The average diameter of untreated and treated hemp fibres was varied from 31.5 to 25.3 μm. The mould was

kept on a piece of Teflon sheet on a glass plate. PLA and fibres were dried overnight at 40°C in an oven prior to sample preparation. To prepare PLA/hemp fibre samples, two pieces of PLA pellet were placed into the mould cavity. The samples were obtained by placing the prepared moulds in a pre-heated oven (180 $^{\circ}$C) for 5 min and then allowing cooling in air at room temperature. In the case of UPE/hemp fibre samples, UPE resin was mixed with 1% (w/w) methylether ketone peroxide initiator and then poured into the mould cavity. The samples were cured at room temperature for 5 h followed by post-curing in a pre-heated (80 $^{\circ}$C) oven for 3 h. SEM micrographs of typical PLA/hemp fibre and UPE/hemp fibre pull-out test specimens are shown in Fig. 1. Both the PLA/hemp fibre and UPE/hemp fibre samples were prepared with a range of embedded lengths from 0.25 mm to 2 mm and a free-fibre length of approximately 5 mm. The free-fibre end was glued to a piece of cardboard. Nomenclature for all the samples used in this work is listed in Table 1.

Pull-out test was performed using an Instron 4204 machine at a cross-head speed of 0.5 mm/min. The sample was held on the upper cross-head and the cardboard was gripped with the stationary bottom part. The force was measured with an accuracy of ± 0.1 mN. From the maximum debonding forces, IFSS of the samples was calculated using Eq. (1). Five samples were assessed for each embedded length of each batch of samples.

2.2.3 Fabrication of composites

Composites consisting of PLA and hemp fibre (untreated and treated) were fabricated by extrusion and subsequent injection moulding. In the case of hemp fibre (untreated and treated) reinforced UPE composites, fabrication was carried out by compression moulding. Further details of the processing methods are available elsewhere [16, 18].

2.2.4 Preparation of micro-composites

Micro-composites of PLA and hemp fibres were prepared between two glass slides by embedding the fibre into molten PLA. The samples were isothermally crystallised at 110 $^{\circ}$C for 15 min and then cooled to room temperature. An optical light microscope was used to examine the transcrystallinity at the fibre/matrix interface in micro-composites.

2.2.5 Optical light microscope

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In this work, an Olympus BX60F5 optical light microscope was used (i) to measure fibre

embedded length and diameter for pull-out testing, and (ii) to investigate transcrystallinity of PLA

in micro-composites.

2.2.6 Fourier transform infrared spectroscopy (FT-IR)

FT-IR measurements were performed using a Digilab FTS-40 FT-IR spectrometer equipped with a

DTGS detector. A total of 30 scans were taken for each composite sample with a resolution of 4

cm^{-1}. Ground dried composites and KBr (2 mg sample per 150 mg KBr) were pressed into a disk

for FT-IR measurement.

2.2.7 Scanning electron microscope (SEM)

In this study, a Hitachi S-4000 and a S-4700 field emission scanning electron microscope were

used to observe the surface topography of pull-out samples. The Hitachi S-4000 was operated at 5

kV and the Hitachi S-4700 was operated between 5 to 20 kV. All samples were mounted with

carbon tape on aluminium stubs and then ion sputter coated with platinum and palladium to make

them conductive prior to SEM observation.

3 Results and discussion

3.1 FT-IR analysis of PLA and PLA/hemp fibre composites

Typical FT-IR spectra of the PLA and untreated fibre reinforced PLA composites (PLA/FB) are

presented in Fig. 2. The spectrum of untreated fibre (FB) is presented for comparison. The

principal absorbance peaks obtained for the PLA are as follows: (i) the peak around 3500 cm^{-1} was

attributed to the hydroxyl (OH) stretching, (ii) the strong peaks at 2998 and 2944 were assigned to

the asymmetric and symmetric mode of C-H stretching, respectively, (iii) the C=O stretching

(from ester linkage) was observed at 1756 cm^{-1}, (iv) the peak at 1456 cm^{-1} was characterised by the

CH_3 band, (v) the C-H deformation appeared at 1386 cm^{-1}, (vi) the O-C asymmetric mode of the

ester groups was observed at 1083 cm^{-1}, and (vii) the peaks appeared at 956 and 922 cm^{-1} could be

attributed to the rocking mode of CH_3 [19-21].

As can also be seen in Fig. 2, the OH stretching in the PLA/FB composite that appeared at 3437

cm^{-1}, was found to be different to that of the FB fibres (3410 cm^{-1}) and the PLA (3500 cm^{-1}). This

indicates that in the PLA/FB composites, the OH groups (from fibres) formed hydrogen bonds

with the carbonyl groups (C=O) of PLA. A similar observation has also been reported for the PLA/rice starch composites by other researchers [22]. In addition, it was also evident that the intensity of C=O (1756 cm^{-1}) stretching in the PLA/FB composites was significantly higher than that of the PLA. This was due to the esterification between OH groups of hemp fibres and terminal carboxylic acid groups (COOH) of PLA. This agrees with the work reported by Semba *et al.* [23] who showed that the peak intensity of the C=O group increased due to the chemical reaction between the dicumyl peroxide and the PLA in a blend of PLA/polycaprolactone.

FT-IR spectra of various treated hemp fibre reinforced PLA composites are shown in Fig. 3. In general, the spectra of all the treated hemp fibre reinforced PLA composites were similar to that of the untreated fibre reinforced composites (PLA/FB). However, the intensity at around 1756 cm^{-1} (C=O stretching) was found to depend on fibre treatment, which increased in the order: PLA/MA < PLA/FB < PLA/ACY < PLA/SIL < PLA/ALKSIL < PLA/ALK. The physical and chemical bonding of PLA with the untreated and various treated hemp fibres could be explained as follows. Since cellulose is the main component of hemp fibres, it could be speculated that most bonding interactions occurred between the OH groups of cellulose of hemp fibres with the carbonyl (C=O) and carboxylic acid (COOH) groups of PLA. Untreated hemp fibres contain pectin and waxy materials on their surfaces as discussed elsewhere [17] which indicates that only a limited number of OH groups (from fibres) are exposed for bonding with C=O and COOH groups of PLA. In contrast, for the alkali treated fibres (ALK), the number of available OH groups increased due to the removal of pectin and waxy materials from the surfaces. Thus, it could be believed that the increased exposure of the OH groups of fibres provided improved potential for hydrogen and covalent bonding with the carbonyl (C=O) and carboxyl (COOH) groups of PLA, respectively. The silane grafted hemp fibres (SIL and ALKSIL) possessed various functional groups namely hydroxyl (OH), primary amine (-NH2) and secondary amine (=NH), which would be able to form hydrogen bonds and covalent bonds with the carbonyl (C=O) and carboxyl (COOH) groups of PLA, respectively. It seems likely that a greater degree of bonding has occurred between the silane grafted hemp fibres and the PLA. Huda *et al.* [24, 25] suggested similar bonding interaction for the silane grafted kenaf and pineapple leaf fibre reinforced PLA composites. In another study, Zhang

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et al. [26] also indicated that the silane modified hydroxyapatite has the capability to form

hydrogen and covalent bonds with PLA. Acetylation of hemp fibres would be expected to replace

OH groups with CH_3CO groups to some extent [17]. This would decrease the number of available

OH groups in the acetylated fibres. Thus, it could reasonably be explained that a lower degree of

chemical bonding has occurred between the ACY fibres and the PLA, when compared with that of

ALK, SIL and ALKSIL fibres and PLA. Like the acetylated fibres (ACY), OH groups of hemp

fibres were replaced with HOOC-CHCH-CO-O- groups to some extent in the maleated hemp

fibres (MA) [17]. Thus, it could be believed that a limited number of OH groups from the MA

fibres were available to form covalent bond with the COOH groups of PLA. It is also possible that

hydrogen bonds were formed between the H of PLA and the C=O of MA fibres.

3.2 Interfacial shear strength (IFSS) PLA/hemp fibre samples

The IFSS of the PLA/hemp fibre samples as a function of fibre embedded length is depicted in

Fig. 4. As can be seen, the IFSS with respect to the embedded fibre length showed a non-linear

relationship, which indicated a brittle-like interface fracture as reported in literature [27]. Similar

behaviour has also been reported for flax fibre/high density polyethylene [27] and carbon

fibre/poly(phenylene sulfide) [28] samples.

The average IFSS of different embedded lengths of each batch of PLA/hemp fibre (untreated and

treated) samples is shown in Fig. 5. The average IFSS increased in the following order: PLA/MA

(5.33 MPa) < PLA/FB (5.55 MPa) < PLA/ACY (6.29 MPa) < PLA/SIL (8.22 MPa) <

PLA/ALKSIL (9.87 MPa) < PLA/ALK (11.41 MPa). This trend is similar to the trend in chemical

bonding as seen in the FT-IR results for composites. The IFSS values obtained in this work agree

well with the reported IFSS of PLA and other natural fibre samples. For instance, Tokoro *et al.*

[29] reported the IFSS (measured by micro-droplet test) of PLA and three different types of

bamboo fibre namely 'short fibre bundle' (SFB), 'alkali treated filament' (ATF) and 'steam-

exploded filament' (SEF). They found that the IFSS of PLA/SFB, PLA/ATF and PLA/SEF were

4.3, 9.8 and 12.6 MPa, respectively. In other work, Cho *et al.* [30] reported the average interfacial

strength (measured by microbond test) of PLA with jute and kenaf fibres. They found that the

average IFSS of jute/PLA and kenaf/PLA were approximately 5.5 and 10.5 MPa, respectively.

They also treated the fibres with water by static (STW) and dynamic (DTW) soaking. For treated jute fibres, the average IFSSs of STW/PLA and DTW/PLA were approximately 9.5 and 13 MPa (from graphs), respectively, and for the treated kenaf fibres, the average IFSSs of STW/PLA and DTW/PLA were approximately 11.5 and 11 MPa (from graphs), respectively. In contrast, Hubber *et al.* [31] observed a very weak interface (no data available) between flax fibres and PLA. They tested the samples by the single fibre fragmentation method, and did not see any fragmentation of flax fibres which was an indication of poor adhesion between the flax fibres and the PLA. From the aforesaid discussion, it could reasonably be said that the interfacial strength between the PLA and the natural fibres strongly depends on the type of fibre and surface treatment.

3.3 Transcrytallinity at the interface of PLA/hemp fibre samples

Natural fibres can induce crystallisation (transcrystallinity) from their surfaces in a semicrystalline polymer [32, 33]. The influence of fibre treatment on the PLA crystallinity at the fibre/matrix interface is presented in Fig. 6. As can be seen, a discontinuous transcrystalline layer of PLA was formed on the surface of untreated fibres (FB). This could be due to the presence of impurities (e.g. wax and pectin), acting as barriers to nucleation in PLA. However, a highly dense transcrystalline layer of PLA was formed in the case of ALK fibres. This could be because impurities were removed from the fibres by the alkali treatment, which in turn increased the number of nucleating sites (i.e. crystalline portion of cellulose [33]) of the fibres. The density of the nucleating sites of SIL, ALKSIL, ACY and MA fibres seemed not to be sufficiently high to form a highly dense transcrystalline layer of PLA. This was because crystalline cellulose of the SIL, ALKSIL, ACY and MA fibres decreased (presented in other report [17]) due to the destruction of hydrogen bonds in the crystalline cellulose structures (i.e. increase of amorphous cellulose portion [34, 35]). The degree of transcrystallinity of various treated hemp fibre/PLA samples was found to be similar with the trend in IFSS and chemical bonding as discussed previous sections.

3.4 FT-IR analysis of UPE and UPE/hemp fibre composites

Typical FT-IR spectra of the UPE and untreated fibre reinforced UPE composites (PLA/FB) are presented in Fig. 7. The spectrum of untreated fibre (FB) is presented for comparison. The principal absorption peaks obtained for the UPE are as follows: (i) the peak around 3436 cm^{-1}

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which can be attributed to the stretching vibrations of hydroxyl (OH) groups; (ii) strong peaks at 3083, 3060, 3027 and 2922, assigned to C-H stretching; (iii) the peak at 2854 cm^{-1} assigned to the symmetric stretching vibrations of the methylene group (CH$_2$); (iv) a very intense peak observed at 1727 cm^{-1} due to the carbonyl (C=O) stretching from the ester linkage; (v) peaks at 1585 and 1493 cm^{-1} attributed to the C=C stretching vibrations within the aromatic ring; (vi) a strong peak at 1238 cm^{-1} due to the twisting vibration of CH$_2$ groups; and (vii) peaks at 1160 and 1129 cm^{-1} assigned to the C-O stretching vibration [36-39].

As can also be seen in Fig. 7, the stretching vibration peak for OH group of the UPE/FB composites (3440 cm^{-1}) was much broader than that of the UPE (3436 cm^{-1}) and FB fibres (3410 cm^{-1}). This suggests that hydrogen bonding could have occurred between UPE and FB fibres. Other researchers have also reported similar observations for the polyester/glass fibre and polyester/carbon fibre composites [36]. For UPE, the peak intensity of the C=O group at 1727 cm^{-1} was relatively lower than that of the OH group at 3436 cm^{-1}, whilst for the composites, the peak intensity of the C=O group at 1727 cm^{-1} was observed to be significantly higher than that of the OH group at 3440 cm^{-1}. This indicates that covalent bonding has taken place through an esterification reaction between the fibre OH groups and polyester COOH groups.

FT-IR spectra for various treated hemp fibre reinforced UPE composites are presented in Fig. 8. In general, the spectra of all the treated hemp fibre reinforced UPE composites were fairly similar to that for untreated fibre reinforced composites. However, in the treated fibre composites, the peak for C=O groups at 1727 cm^{-1} was more intense than the untreated fibre composites suggesting more esterification reactions, increasing in the order: UPE/FB < UPE/ALK < UPE/ACY < UPE/MA < UPE/SIL < UPE/ALKSIL. It appears that due to the removal of pectin and waxy materials from the surface of untreated fibres, for alkali treated fibres, the number of available OH groups increased for greater esterification with UPE. For the acetic anhydride, maleic anhydride and silane fibres, the number of reactive sites was greater than the untreated and alkali treated fibres enabling increased esterification with UPE.

3.5 Interfacial shear strength (IFSS) of UPE/hemp fibre samples

IFSS as a function of fibre embedded length for the UPE/hemp fibre (untreated and treated) samples is depicted in Fig. 9. As can be observed, IFSS showed a non-linear relationship with the embedded fibre length, indicating a brittle interfacial fracture as reported in literature [27]. This was consistent with the PLA/hemp fibre samples as seen in Fig. 4. Similar observation has also been reported by other researchers for glass fibre/polyester composites [40].

The average IFSS of different embedded lengths of each batch of UPE/hemp fibre (untreated and treated) samples is shown in Fig. 10. As can be seen, IFSS increased in the order: UPE/FB2 (9.9 MPa) < UPE/ALK (11.7 MPa) < UPE/ACY (12.6 MPa) < UPE/MA (15.1 MPa) < UPE/SIL (16.3 MPa) < UPE/ALKSIL (20.3 MPa). This trend was consistent with the level of esterification between the treated fibres and the UPE as seen in the FT-IR results. The IFSS results of UPE/hemp fibre samples are reasonable when compared with other studies on natural fibre/polyester samples. For instance, the IFSS of untreated flax fibre/UPE and alkali-acetic anhydride treated flax fibre/UPE samples was found to be 14.2 and 16.1 MPa (measured by microbond test), respectively, as reported by Baley *et al.* [41]. In another work, Joffe *et al.* [42] found that the IFSS (measured by single fibre fragmentation test) of the silane treated flax fibre/polyester samples (22 MPa) improved by 22.2% compared with that for the untreated flax fibre/polyester samples (18 MPa).

The IFSS of all the UPE/hemp fibre samples appeared higher than that of the PLA/hemp fibre samples. This indicates that the number of functional groups in the UPE resin to bond with the fibres may be higher than the PLA matrix. In addition, viscosity of the UPE resin was possibly lower than the PLA matrix during sample preparation, which facilitated UPE resin for better bonding with fibres.

4 Conclusions

Spectroscopic analysis (FT-IR) of the untreated and treated hemp fibre reinforced PLA and UPE composites revealed that covalent and hydrogen bonding between fibres and matrices increased as the fibre treated with alkali, silane, acetic anhydride and maleic anhydride (except for the maleic anhydride/PLA sample). This could be due to the removal of non-cellulosic components (i.e. wax

and pectin) from the fibres surface and due to increased exposure of bonding sites (i.e. functional groups) of the treated fibres. In the case of maleic anhydride treated fibre reinforced PLA composites, it was found that covalent bonding between the treated fibre and PLA decreased compared to the untreated fibre and PLA sample, which was believed to be as a result of decreased available bonding sites of the treated fibres. The IFSS results of the untreated and treated hemp fibre reinforced PLA and UPE samples were found to be similar with the trend in chemical bonding as seen in the FT-IR results for composites. In addition, micrographs of the hemp fibre/PLA samples revealed that transcrystallinity significantly contributed to improve the IFSS of the samples. For PLA matrix, the highest IFSS was found for the alkali treated fibre and for UPE matrix, the highest IFSS was found for the combined alkali and silane treated fibre.

Acknowledgement

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Figure Captions:

Fig. 1. (a) Schematic diagram of pull-out test sample and SEM micrographs of (b) PLA/ALK and

(c) UPE/ALK samples.

Fig. 2. FT-IR spectra of PLA and untreated fibre reinforced PLA composite. Spectrum of the

untreated fibre is shown for comparison.

Fig. 3. FT-IR spectra of the various treated hemp fibre reinforced PLA composites.

Fig. 4. IFSS versus embedded fibre length of PLA/hemp fibre (untreated and treated) samples.

Fig. 5. Average IFSS of untreated and treated hemp fibre/PLA samples.

Fig. 6. Optical light micrographs showing transcrystalline layer of PLA from untreated and treated

hemp fibre surfaces (scale bar = 50 μm).

Fig. 7. FT-IR spectra of UPE and untreated fibre reinforced UPE composite. Spectrum of the

untreated fibre is shown for comparison.

Fig. 8. FT-IR spectra of the various treated hemp fibre reinforced UPE composites.

Fig. 9. IFSS as a function of embedded length for UPE/hemp fibre (untreated and treated) samples.

Fig. 10. Average IFSS of untreated and treated hemp fibre/UPE sample.
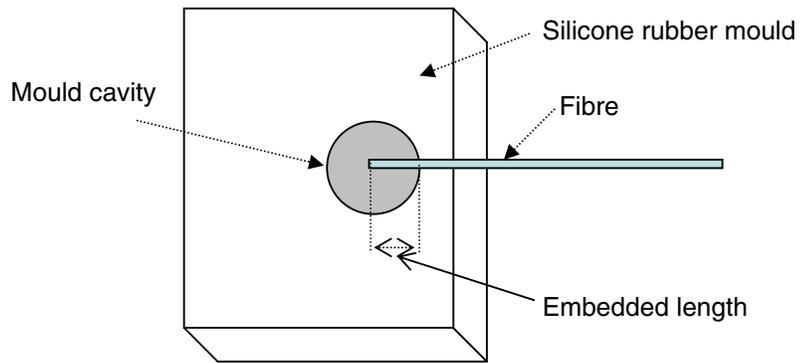
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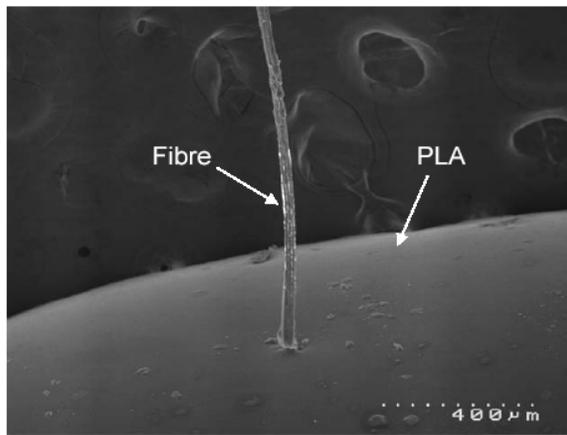
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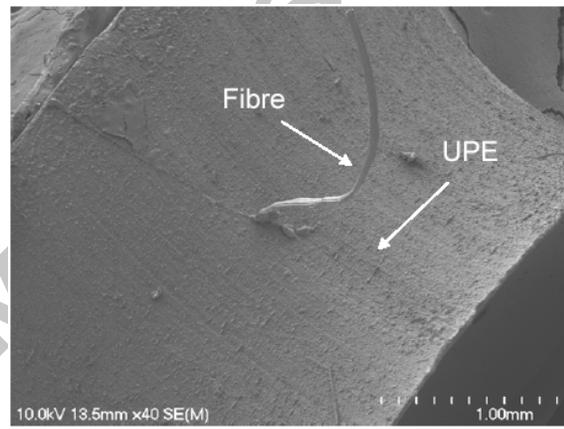
(c)

Fig. 1

Fig. 2

Fig. 3

Fig. 4


Fig. 5

(a) PLA/FB

(b) PLA/ALK

(c) PLA/SIL

(d) PLA/ALKSIL

(e) PLA/ACY

(f) PLA/MA
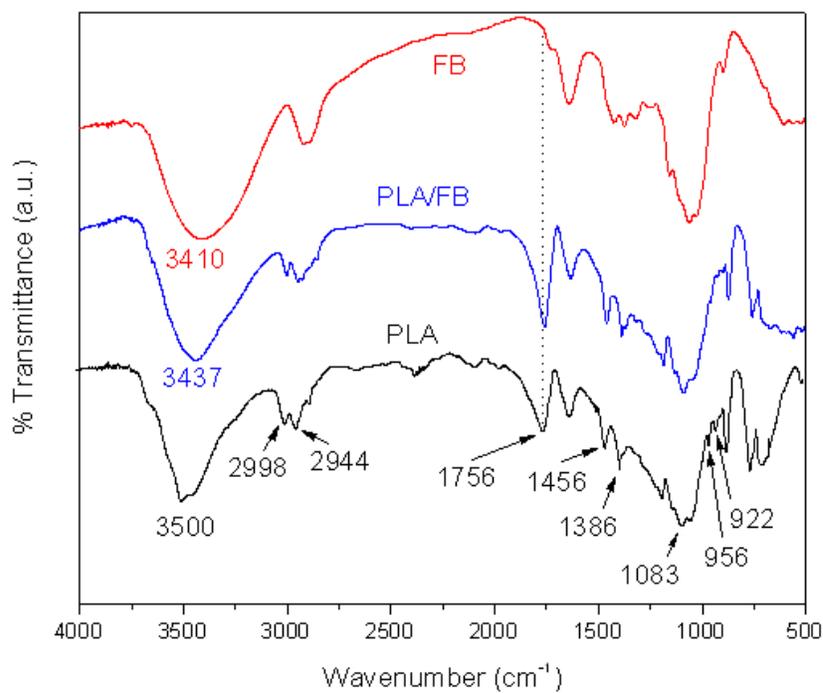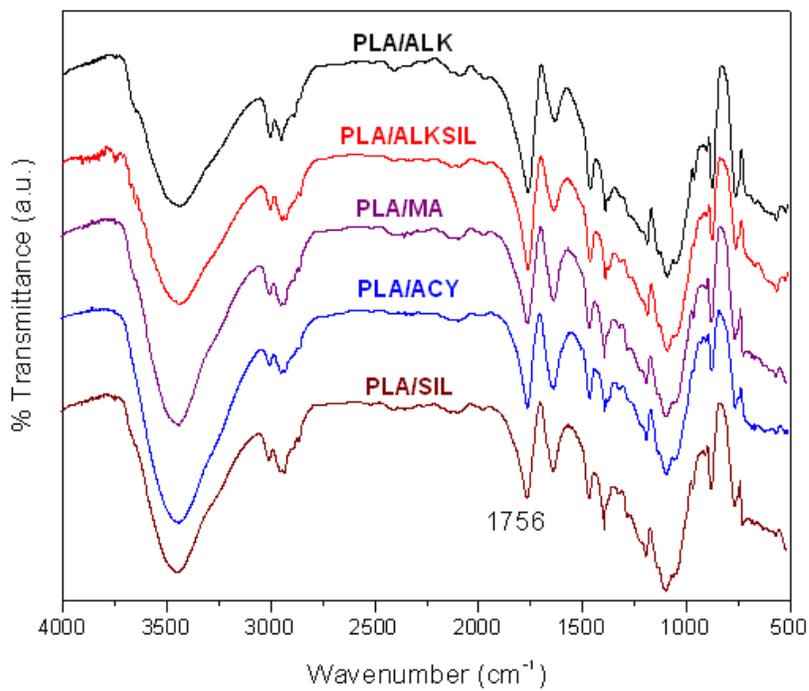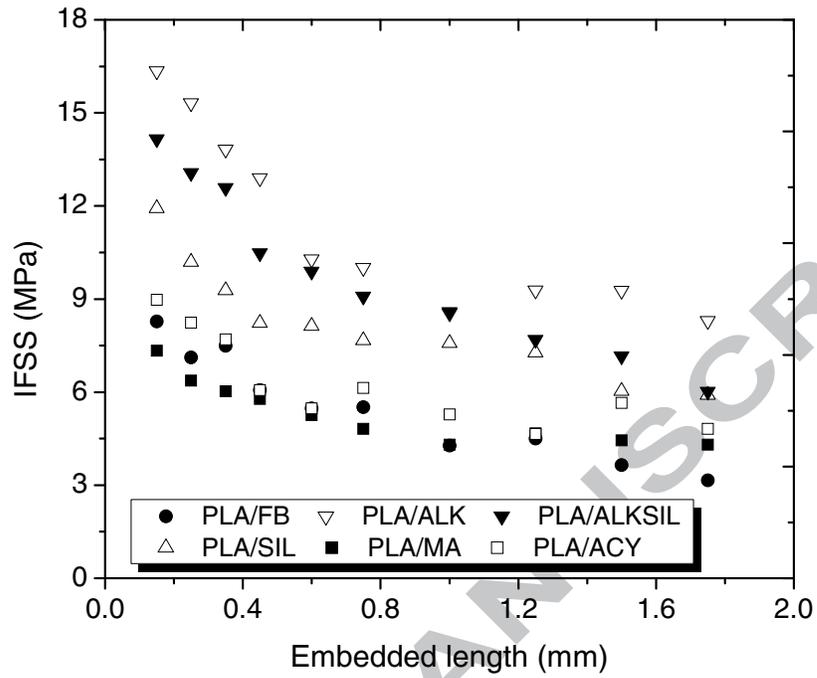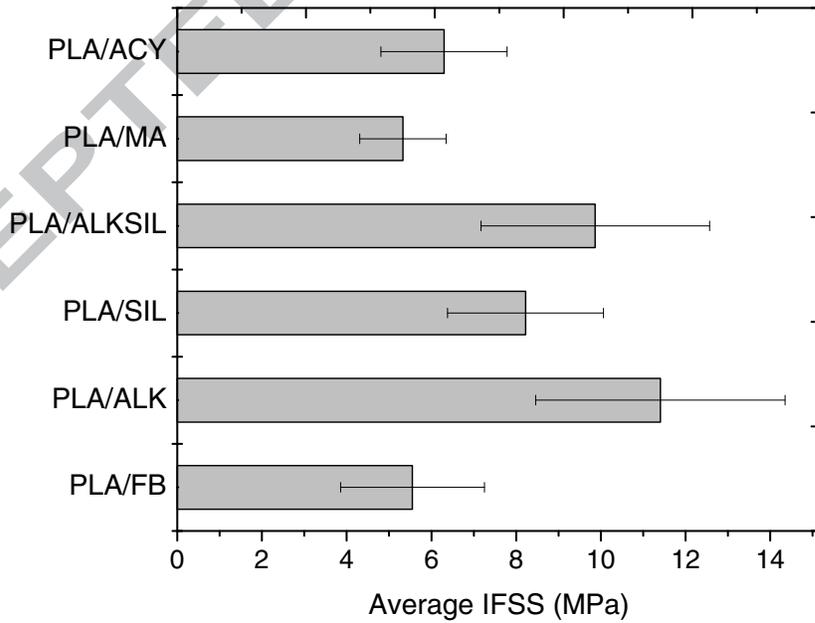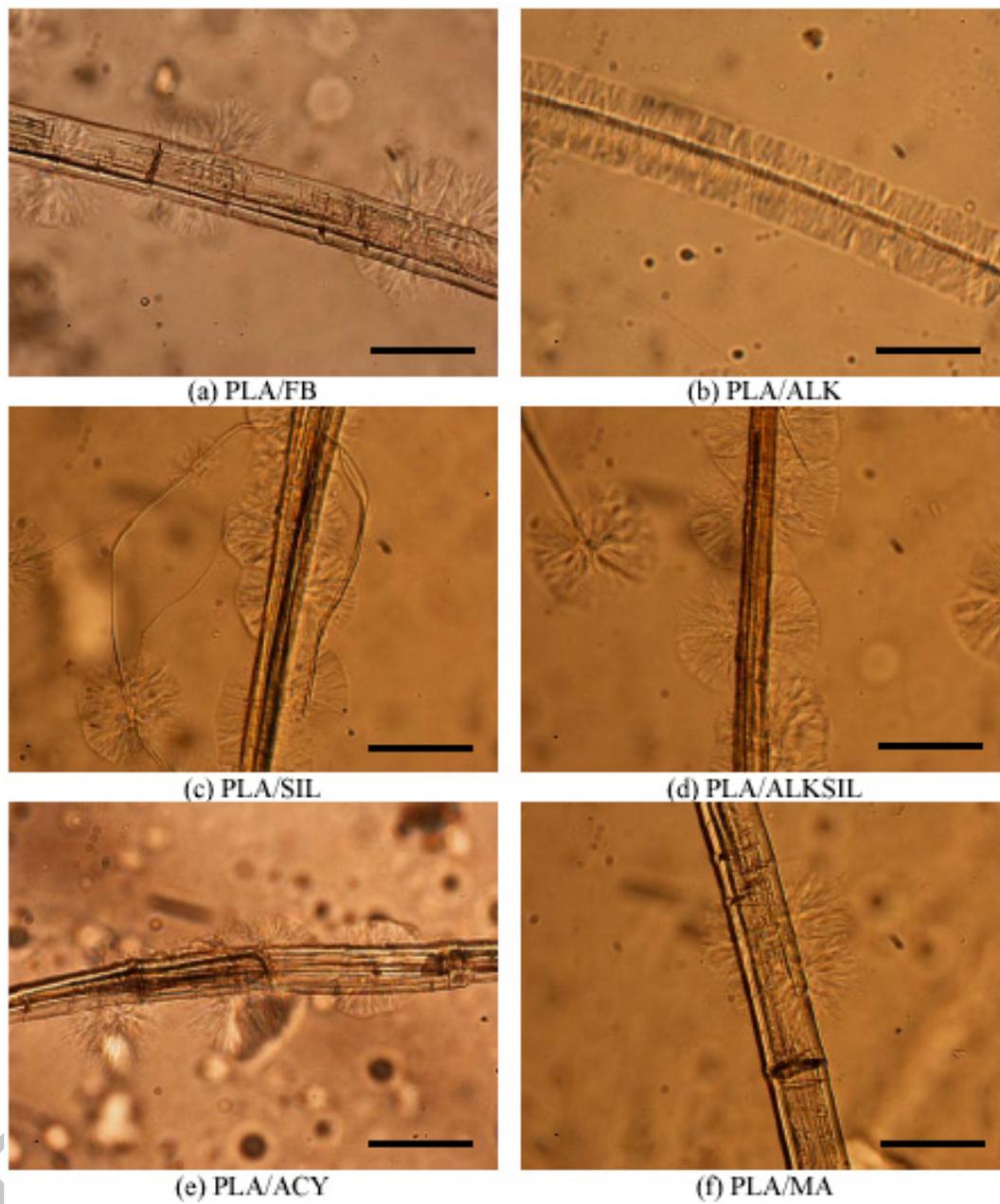
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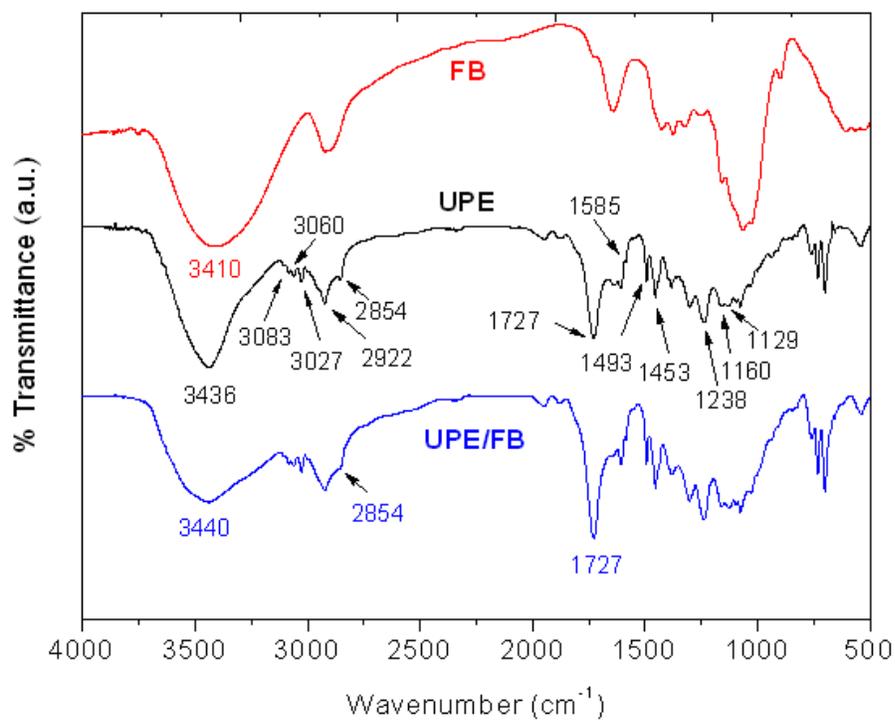
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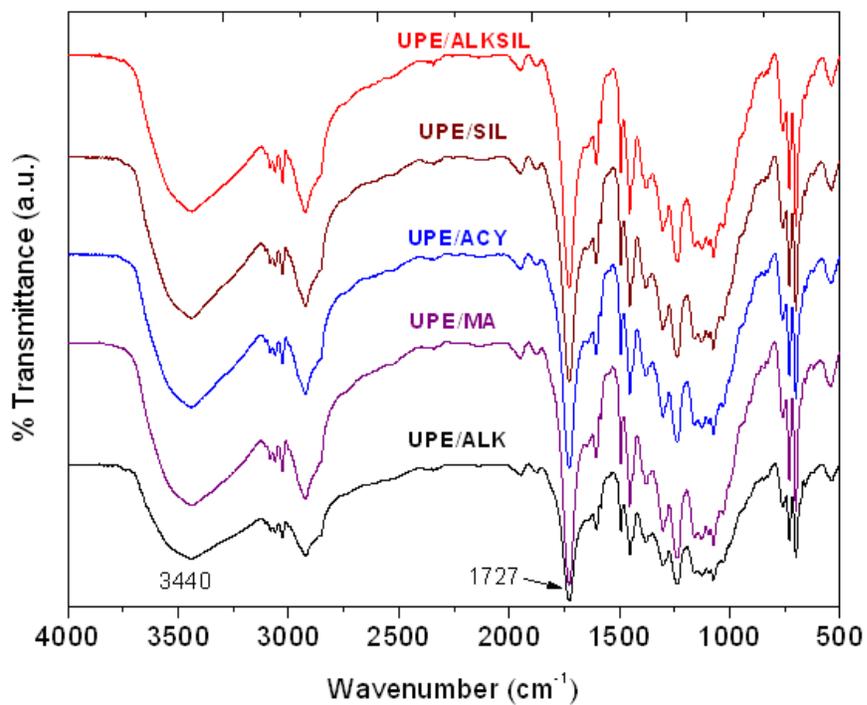
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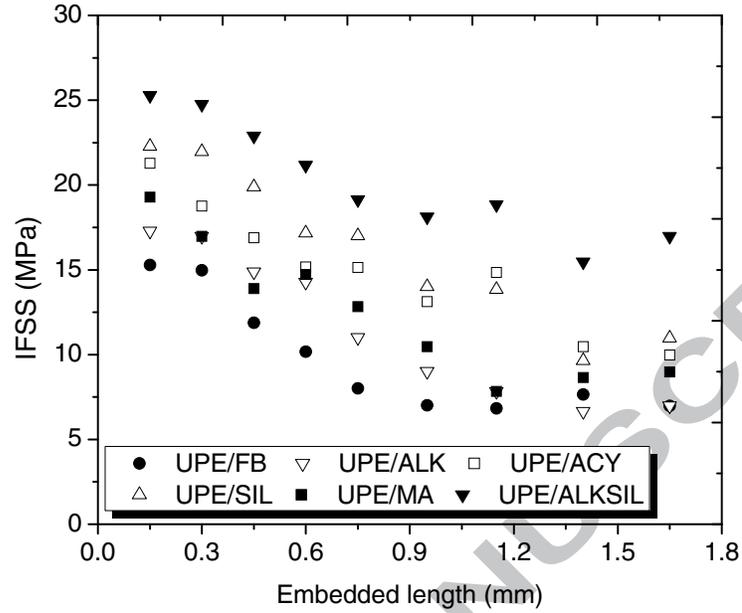
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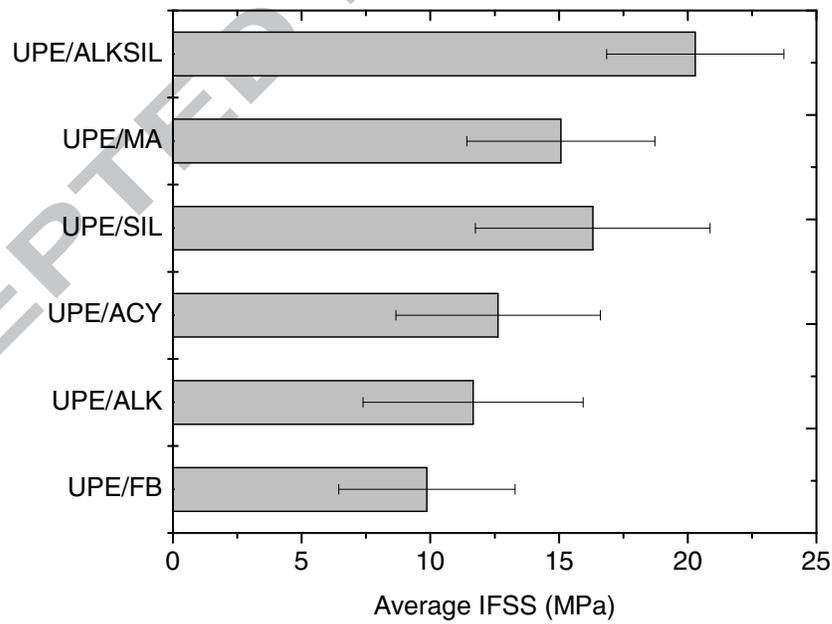
Fig. 10

Table 1

Nomenclature used for various treated and untreated hemp fibre reinforced polylactide and unsaturated polyester samples.

Abbreviation	Samples
PLA/FB	Untreated fibre reinforced polylactide sample
PLA/ALK	Alkali treated fibre reinforced polylactide sample
PLA/SIL	Silane treated fibre reinforced polylactide sample
PLA/MA	Maleic anhydride treated fibre reinforced polylactide sample
PLA/ACY	Acetic anhydride treated fibre reinforced polylactide sample
PLA/ALKSIL	Combined alkali and silane treated fibre reinforced polylactide sample
UPE/FB	Untreated fibre reinforced unsaturated polyester sample
UPE/ALK	Alkali treated fibre reinforced unsaturated polyester sample
UPE/SIL	Silane treated fibre reinforced unsaturated polyester sample
UPE/MA	Maleic anhydride treated fibre unsaturated polyester sample
UPE/ACY	Acetic anhydride treated unsaturated polyester sample
UPE/ALKSIL	Combined alkali and silane treated fibre reinforced unsaturated polyester sample