CHEMICALLY MODIFIED RANDOMLY ORIENTED ISORA FIBRE REINFORCED POLYESTER COMPOSITES

Abstract

Short isora fibre surface was modified chemically to bring about improved interfacial interaction between the fibre and the polyester matrix. The fibre surface was chemically modified by acetylation, benzoylation, silane and triton treatments. Modified surfaces were characterized by IR Spectroscopy and SEM. Chemical modification was found to have a positive effect on the fibre/matrix interactions. The improved fibre/matrix interaction is evident from the enhanced tensile and flexural properties. The lower impact properties of the composites, except triton treated fibre composite, further point to the improved fibre/matrix adhesion, compared to the untreated fibre composites.
Chapter-5

5.1. Introduction

Cellulose based natural fibres are a potential resource for making low cost composite materials, where high strength and stiffness are not of first priority[1]. Although plant fibres are generally considered to be viable for use in composites, the problem of compatibility of the fibre with the matrix is to be solved. Plant fibres, due to the abundance of hydroxyl groups, are incompatible with hydrophobic polyester resin. This incompatibility leads to a poor interfacial adhesion between the fibre and matrix, poor wetting of the fibres by the resin and a reduction in mechanical performance when the composite is exposed to moisture. Thus, in order to develop composites with good properties, it is necessary to improve the interface between the matrix and the lignocellulosic materials used as fillers. In order to improve interfacial bonding, modification of the fibre surface is essential [2-5].

When two materials are incompatible, it is often possible to bring about compatibility by introducing a third material that has properties intermediate between those of the other two by forming weak boundary layers, deformable layers or restrained layers. Coupling agents can improve the wettability between polymer and substrate or can form covalent bonds with both materials [1]. Chemical or irradiation induced removal of some hydroxyl groups has been used to improve hydrophobicity and chemical bonding at the interface [6-8]. Silane interfacial coupling agents widely used on glass fibre to form stable covalent bonds to both the mineral fibre surface and the resin are potentially suitable for use on cellulosic fibres. Acetylation is an effective method of modifying the surface of natural fibres and making it more hydrophobic. In addition, acetylation is one of the most studied reactions of lignocellulosic materials [9]. Hill and Khalil [10] studied the effects of chemical modification of coir and oil palm fibres by acetylation, silane treatment and titanate coupling agent, on the mechanical properties of the polyester composites. They found that interfacial strength between the fibre and matrix was increased by acetylation.
Rout et al. [11] observed that fibre surface modification by chemical treatment significantly increased the mechanical performance of coir-polyester composites. To improve the moisture resistance, Chand et al. acetylated sisal fibre and studied its tensile strength [12]. It was shown that acetylation could reduce the moisture content, but the tensile strength of the acetylated fibre was reduced due to the loss of hemi cellulose in the fibre during acetylation. Zafeiropoulos et al. [9] studied the effect of acetylation on flax fibres and found that the presence of moisture is beneficial for the reaction and also acetylation increased the weight percent gain (WPG) of fibres at high levels. This implied that the treatment is affecting the bulk and not just the surface of the fibres. Uma Devi et al. [13] investigated the effect of silane A-172 treatment on the mechanical properties of pine apple leaf fibre (PALF) reinforced polyester composites and observed significant improvement in the tensile strength for the treated fibre-composite.

In this Chapter, the effect of various fibre surface modifications on the mechanical properties of short isora fibre reinforced polyester composites is proposed to be evaluated. The surface modification is proposed to be effected by treatment with acetic anhydride, benzoyl chloride, vinyl triethoxy silane and triton X-100 (iso octyl phenoxy poly ethoxy ethanol). The physical changes induced by these treatments will be analyzed by Scanning electron microscopy (SEM). The effects of these modifications on the tensile, flexural and impact properties of the composites are also proposed to be evaluated.

5.2. Results and Discussion
5.2.1. Physical changes: SEM studies

The SEM photographs of the chemically treated isora fibre surface are given in the Figure 5.1. SEM gives strong evidence for the physical and micro structural changes occurred on the fibre surface during chemical treatment, compared to the SEM of untreated fibre given in Figure 3.5. On modification, the pores became clearer and the fibres became thinner. This may be due to the dissolution and leaching out of fatty acids and lignin components of the fibre.
This roughened the fibres, enhancing the mechanical interlocking at the interface. As a result of the introduction of functional groups by chemical treatment, the fibre surface became irregular and rough as shown in the Figure 5.1. Similar changes have been reported in grafted natural fibres such as cotton and jute [14].

Figure 5.1 (a-d): SEM photographs of (a) acetylated (b) benzoylated (c) silane treated and (d) triton X-100 treated isora fibre.

The fibrils are well exposed on chemical treatment. On triton treatment, the fibre fibrillation occurred to a great extent, thus reducing the fibre diameter and resulting in considerable increase in fibre aspect ratio (Figure 5d). Indeed, with the use of solvents, these chemical treatments lead to a swelling effect, leaching
out of the waxes, gums and partial removal of lignin and hemi-cellulose, which are the cementing materials in vegetable fibres [15-17].

5.3. Chemical modifications: IR spectroscopy

The IR spectra of the raw and treated isora fibres are given in Figure 5.2. The IR peaks of the untreated fibre are already explained (4.2.1). On chemical modification of the fibre by acetylation, benzylation and silane treatment, the peaks corresponding to the functional groups were observed in the IR spectra. For acetylated fibre a peak at 1700 cm\(^{-1}\) indicates the introduction of an acetyl group. As a result of esterification of the hydroxyl groups, the hydroxyl vibrational absorption at 3300 cm\(^{-1}\) decreased.

![IR spectra of untreated and chemically modified isora fibre.](image)

**Figure 5.2.** IR spectra of untreated and chemically modified isora fibre.

IR spectra of benzyalted fibre indicates an absorption in the range 1400-1600 cm\(^{-1}\) due to the C=C stretching of aromatic rings and a carbonyl group absorption in the range 1700 cm\(^{-1}\) is also observed. In the case of silane
treated fibres, an additional peak at 3500 cm$^{-1}$ indicates intermolecular hydrogen bonding between the silanol -OH and cellulosic -OH of the fibre.

5.4. Reaction scheme of chemical treatments

a) Benzoylation

The reaction between the fibre surface and benzoyl chloride can be represented as:

$$\text{Fibre-OH} + \text{NaOH} \rightarrow \text{Fibre-O' Na}^+$$

$$\text{Fibre-O' Na}^+ + \text{Cl-C} \rightarrow \text{Fibre-O-C}$$

b) Acetylation

During acetylation, the typical reaction taking place on the fibre surface can be represented as:

$$\text{Fibre-OH} + \text{(acetic anhydride)} \rightarrow \text{Fibre-O-C-CH}_3 + \text{CH}_3\text{COOH}$$

(fibre) + (acetic anhydride) → (modified fibre) + (acetic acid)

c) Silane (vinyl triethoxy) treatment

The organo functional group in the silane coupling agent (here CH$_2$=CH-) causes the reaction with the polymer. This could be a co-polymerization, and/or the formation of an interpenetrating network. The curing reaction of a silane treated substrate enhances the wetting by the resin.

The general mechanism of formation of bonds of alkoxy silanes with the fibre surface [16], which contains hydroxyl groups, is as follows:
Alkoxy silanes undergo hydrolysis, condensation and the bond formation stage, under base as well as acid catalyzed mechanisms. In addition to these reactions of silanols with hydroxyls of the fibre surface, the formation of polysiloxane structures can take place.

d) **Triton X 100 treatment**

Chemically triton X 100 is iso octyl phenoxy poly ethoxy ethanol, with structure shown below.

![Triton X 100 structure](image)

R = iso octyl, n=10.

It is a non ionic synthetic surfactant and has a hydrophilic head and hydrophobic tail. The main function of a surfactant is cleansing action.
Non ionic surfactants are the most widely used for surface cleaning and have no charge in aqueous solutions. They are resistant to water hardness. The advantages of triton X 100 are:

1. Excellent detergent and oil in water emulsifier for many applications
2. Excellent wetting agent and
3. Effective performance across a broad temperature range.

5.5. Mechanical properties of the composite
5.5.1. Tensile properties

The effects of various chemical treatments on tensile strength, Young's modulus and elongation at break values of the chemically modified, randomly oriented isora-polyester composites are given in the Figures 5.3, 5.4 and 5.5 respectively.

The effect of chemical treatments, on the tensile strength of the composites is given in Figure 5.3. It is observed that fibre modification improved the tensile strength of all composites and the improvement followed the order: triton treated (TT) > acetylated (Ac) > Silane treated (Si) > Benzoylated (Bz) > Untreated
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(UT). The maximum improvement in tensile strength was observed for triton treated fibre composite. Compared to the untreated fibre composite, the percentage increase in tensile strength of treated fibre composites are TT-39%, Ac-27.8%, Si-16.7% and Bz-11%. The improvement in tensile strength can be attributed to the improved adhesion between the fibre and the matrix on chemical modification of the fibre.

![Graph showing Young's modulus of different treated fibre composites](image)

**Figure 5.4.** The effect of different chemical treatments on the Young’s modulus of randomly oriented isora-polyester composites

The Young’s modulus of the composites (Figure 5.4) also improved on chemical modification of fibre and followed the order: TT > Ac > Bz > Si > UT. Compared to the untreated fibre composite, the percentage increase in Young’s modulus of treated fibre composites are TT-113, Ac-78, Bz-52.6, Si-37.8. The improvement in Young’s modulus also is due to the improvement in adhesion between the fibre and the matrix, on chemical modification of the fibre.
The percentage elongation at break values of short isora-polyester composite varied with fibre treatment as shown in the Figure 5.5. It is observed that on chemical modification of the fibre, elongation at break values of the composites decreased and followed the order: UT > Si > Ac > Bz > TT. As expected from the modulus values, TT fibre composite has the lowest and silane treated fibre composite has the highest elongation at break values. When the fibre-matrix adhesion is higher, the composite will fail at a lower elongation. The reduced elongation at break values of the composites confirms the improved adhesion between the fibre and resin.

Now, we can examine the mechanism involved in the improvement of adhesion in each case. The improvement in tensile properties of benzoylated fibre composite is attributed to the presence of phenyl groups in the treated fibre which interacts with the benzene rings and methyl groups present on polyester, which improves the thermodynamic compatibility between the fibre and polyester. Also the reduction in hydrophilicity of the fibre on benzoylation makes the fibre more compatible with the hydrophobic polyester.
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Figure 5.6. A hypothetical model of interface of benzoylated isora-polyester composite

In addition to this, benzoylation makes the surface of the fibre very rough and provides better mechanical interlocking with the polyester matrix. A hypothetical model of interface of benzoylated isora fibre-polyester composite is shown in Figure 5.6.

Acetylated fibre composites show improvement in properties, next to triton treated fibre composites. Rong et al. [17] have reported such results for acetylated jute fibre reinforced epoxy composites. They concluded that the improvement in interfacial bonding is due to the H-bonds between acetyl groups of the acetylated fibre and hydroxyl or amine groups in epoxy resin and mechanical interlocking between epoxy and the caved fibre surface due to alkali pretreatment. Since there is no possibility of H-bond formation between acetyl groups of the acetylated fibre and the unsaturated polyester resin, the improvement in tensile properties can be attributed to the second factor, which is the mechanical interlocking between the polyester resin and the fibre surface. This is supported by the rough surface morphology of the acetylated fibre evident from the SEM micrograph (Figure 5.1.a). Also the hydrophobic methyl groups attached to the fibre interacts with the methyl and benzene rings present in the polyester, thereby increasing the compatibility with the hydrophobic polyester matrix. A hypothetical model of the interface of acetylated isora fibre-polyester composite is shown in Figure 5.7. Another important contributing
factor is the reduction in the hydrophilicity of the fibre as a result of acetylation, which makes the fibre more compatible with hydrophobic polyester.

![Figure 5.7. A hypothetical model of interface of acetylated isora-polyester composite](image)

Vinyl triethoxy silane has two functional groups, a hydrolysable group which can condense with the hydroxyls of the fibre and an organo functional group (CH₂=CH⁻) capable of interacting with the matrix. The hydrolysed silanol forms strong covalent bonds or hydrogen bonds with-OH group of cellulose.

![Figure 5.8. A hypothetical model of interface of silane treated isora-polyester composite](image)

The individual coupling agent molecules attached to cellulose forms a continuous link. The long hydrophobic polymer chain can adhere to the matrix mainly because of Van der waals type attractive force. As a result, silane-coupling agents form a bridge at the interface. The hydrophobic alkyl groups (R = CH₂=CH⁻) attached to the fibre as a result of silane treatment increases the compatibility with the hydrophobic polyester matrix and improves the mechanical properties of the composite. A hypothetical model of the interface of silane treated fibre-polyester composite is shown in Figure 5.8.
On triton treatment of the alkali pre-treated fibre, which has less dense interfibrillar region and more oriented fibrils, become more dispersable and well exposed as evident from the SEM photograph in Figure 5.1. (d). The aspect ratio of the fibre is also enhanced. The increased dispersability results in a larger area of contact and improved wetting of the fibre. This leads to greater mechanical interlocking between fibre and matrix, making the interfacial adhesion stronger and the mechanical properties higher. This explains the maximum values of tensile strength and Young’s modulus for triton treated fibre composite. Similar result was reported by D. Ray et al. [18] for alkali treated jute fibre-vinylester resin composite. They found that alkali-treated fibres were dispersed more readily and uniformly in the resin than the untreated ones. Treated fibres were seen to be finely separated from one another whereas the untreated fibres remained mostly in clusters (Figure 5.9).

![Figure 5.9. Dispersability of jute fibres in vinylester resin: (a) raw jute; (b) 2 h. alkali-treated jute. [Ref: 18]](image)

The improvement in adhesion between the treated fibre and polyester resin can be understood from the SEM photographs of the fracture surface of untreated isora fibre-polyester composite (Figure 3.6) and that of treated fibre composites given in Figures 5.10 (a) to (d). While the fracture surface of untreated fibre composite shows holes and fibre ends indicating poor adhesion between the fibre and matrix, fracture surface of treated fibre composites shows fibre breakage rather than pull out, indicating better interfacial strength.
Figure 5.10. SEM photographs of the tensile fracture surface of
(a) triton treated (b) acetylated (c) silane treated and (d) benzoylated randomly oriented
isora-polyester composites (magnification × 200 and × 700)
5.5.2. Flexural properties

The effect of fibre modification on flexural strength, flexural modulus and flexural strain of short isora fibre reinforced polyester composites are shown in the Figures 5.11, 5.12 and 5.13 respectively. All fibre treatments resulted in improvement in flexural strength and flexural modulus of the composites. The improvement in flexural strength of the composites followed the order: TT > Ac > Si > Bz > UT. The percentage increase in flexural strength compared to untreated fibre composite is TT-50, Ac-27.3, Si-10.6, and Bz-4.5.

![Graph showing flexural strength of different treatments](image)

**Figure 5.11.** The effect of different chemical treatments on the flexural strength of randomly oriented isora-polyester composites

In the case of composites, the flexural properties are controlled by the resistance to interlaminar failure. Therefore, high flexural strength and modulus of treated fibre composite is due to better interfacial adhesion in the composite.
The improvement in flexural modulus followed the order TT > Ac > Bz > Si > UT. The percentage increase in flexural modulus compared to untreated fibre composite is TT-88.4, Ac-63.2, Bz-23 and Si-18.8.

The improved flexural properties of the treated fibre composite can be attributed to the physical and chemical changes on the fibre surface effected by the treatments, which enhanced the adhesion between the fibre and matrix as in the case of tensile properties.
Flexural strain values of all treated fibre composites are lower than that of untreated fibre composite, and followed the order: UT > Si > Ac > TT > Bz. This is due to improved bonding between the treated fibre and resin.

5.5.3. Impact properties

The impact strength of a composite is influenced by many factors such as the toughness properties of the reinforcement, the nature of interfacial region and the frictional work involved in pulling the fibres from the matrix [10]. The nature of interface region is of extreme importance in determining the toughness of the composite. The lowering of adhesion between fibre and matrix leads to improvement of toughness. However, very low adhesion efficiency may result in the lowering of toughness.

The variation of impact strength with different chemical treatments is given in the Figure 5.14. It is observed that the impact strength decreased as the interfacial bond strength increased except in the case of triton treated fibre composite. The impact strength followed the order: TT > UT > Bz > Ac > Si. While silane treatment, acetylation and benzoylation of the fibre resulted in
reduction in the impact strength of the composites, triton treatment of the fibre enhanced the impact strength of the composite, compared to untreated fibre composite. It is an established fact that a strong interface between the fibre and the matrix reduces the impact strength of the composites [19-21]. At high levels of adhesion, the failure mode is brittle and relatively little energy is absorbed. In the case of a weak interface the triaxial stresses at the tip of an advancing crack cause debonding to occur and a crack bunting mechanism takes place and improves the toughness of the material [22].

In the case of triton treated fibre, the treatment has improved the dispersion of the fibre in the resin. In addition, in this case the adhesion between the matrix and the fibre may be intermediate and leads to progressive delamination which require additional energy and hence an improved impact strength. Hill and Abdul Khalil [10] also got an improvement in impact strength for acetylated oil palm fibre reinforced polyester. In acetylated fibre the improved impact strength is assumed to be due to the improved toughness of the fibre. Similar results have been reported earlier [23]. When the fibre-matrix adhesion is strong, the mechanism of failure changes from fibre debonding and pull out to brittle failure and reduce the impact strength.

5.6. Conclusion

Isora fibre was modified chemically by acetylation, benzylation, silane treatment and triton treatment. All fibre modifications improved the tensile and flexural properties of the composite. The decrease in hydrophilicity and increase in thermodynamic compatibility of the treated fibre with the polymer matrix are responsible for the improvement in the mechanical properties. The maximum improvement in tensile properties was observed for triton treatment. SEM studies also suggest strong fibre-matrix adhesion in treated randomly oriented isora-polyester composites. In all cases except triton treatment, fibre modification decreases the impact strength of the composites.
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References