Effect of Chemical Treatments on the Physical Properties of Non-woven Jute/PLA Biocomposites

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Biocomposites based on poly(L-lactic acid) (PLA) and non-woven jute fabrics (NWJF) were fabricated by sandwiching non-woven jute mat between PLA sheets. First, composites were fabricated with various weight proportions of jute fabric (5, 10, 20, and 30 wt.%) with the PLA matrix, and the effect of fabric loading on their mechanical properties was investigated. Higher mechanical properties were found at 10 wt.% fabric-loaded composite. The results show that the tensile, flexural, and impact strengths were increased by 61.7, 52.3, and 47.2%, respectively, as compared with neat PLA. In the second part, the jute fabrics were chemically treated with NaOH, $NaClO_2$, acrylonitrile, acetic anhydride, $KMnO_4$, diphenylmethane diisocyanate, and benzoyl chloride. The effect of chemical treatment on the mechanical and water absorption properties of NWJF/PLA biocomposites was studied. The mechanical properties of these biocomposites were found to be higher than those of untreated biocomposites. Among all the treatments, the combined alkali-benzoylated-treated fabric composite showed higher mechanical properties. The water absorption properties of these composites were found to be remarkably lower than those of untreated fibers. The interfacial adhesion between the fiber and the matrix was shown to increase with surface modification as revealed by SEM analysis.

Keywords: Non-woven jute fabric; Chemical treatments; Biocomposites; Mechanical properties; Water absorption

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INTRODUCTION

Because of their renewable origins, jute fiber and polylactic acid (PLA)-based biocomposites have attracted growing interest in recent years in various fields, including biomedical applications (Rasidi *et al*. 2014; Hamad *et al.* 2015). PLA is the most promising bio-based thermoplastic and offers a potential alternative to petro-based plastics because of its relatively high strength and stiffness (Rasal *et al*. 2010; Shi *et al*. 2015). Currently, PLA composites with natural fibers have been extensively studied (Qu *et al*. 2010; Tawakkal *et al*. 2012; Rasidi *et al*. 2014; Boubekeur *et al.* 2015). In addition to their light weight, natural fibers generally result in increased modulus of PLA biocomposites. The effectiveness of natural fibers to enhance the mechanical properties of biocomposites depends on the fabrication method, interfacial adhesion, types of fibers, and chemical and physical characteristics of the fiber, including fiber length, arrangement, and fabric pattern (Bledzki *et al*. 2009).

Jute fiber has a high aspect ratio, high strength to weight ratio, and good insulation properties. It also has a hydroscopic, porous, non-abrasive, viscoelastic, biodegradable, and reactive nature, which makes it a versatile filler for the fabrication of various biocomposites (Behera *et al*. 2012). Jute fibers are primarily comprised of cellulose, hemicellulose, and lignin. These constituents play a vital role in the properties of the fiber; for example, cellulose gives the fiber stiffness, strength, and stability. However, the hydrophilic nature of cellulose makes it incompatible with the hydrophobic polymer matrix in composite fabrication. Thus, surface modification of the fiber is needed to improve the interfacial adhesion between the fiber and polymer matrix.

Various physical and chemical methods have been used for surface modification of jute fiber to improve its adhesion with the PLA matrix (Sikdar *et al*. 1995; Mishra *et al*. 2001; Aziz and Ansell 2004; Bledzki *et al*. 2004; Mohanty *et al*. 2004). Gibeop *et al.* (2013) studied the effect of plasma treatment with various exposure timings on the mechanical properties of jute fiber/PLA biocomposites. The results were compared with alkali-treated composites. They observed superior interfacial shear strength (IFSS) and mechanical and hardness properties for plasma-treated fiber composite compared with alkali-treated PLA biocomposites. The tensile strength, Young's modulus, and flexural strength were found to increase by 28, 17, and 20%, respectively, for plasma-treated jute fiber biocomposites.

Similarly, Rajesh and Prasad (2014) studied short jute fiber/PLA composites with different concentrations of NaOH and H_2O_2 treatments on jute fibers. The effect of fiber loading and alkali concentrations used for fiber treatment on the mechanical properties of the composites were investigated. It was reported that the tensile properties of composites with treated fiber at higher fiber loadings were better than those of untreated fiber. The composite with successively treated jute fiber at 10% NaOH and H_2O_2 with 20 wt.% fiber loading showed a 7.5% increase in tensile strength. The tensile modulus of composites with treated fibers at higher fiber loadings was shown to be improved by 125% and 40% over that of neat PLA.

The effect of alkali, permanganate, peroxide, and silane treatments on the jute fiber surface was studied to analyse the mechanical and abrasive wear performance of polylactide/jute biocomposites. It has been reported that surface treatments improved the tensile and flexural properties of these composites (Bhanu *et al.* 2012).

The strength improvement of injection-molded jute fiber-reinforced polylactide composites was carried out using long and short jute fiber pellets. This pellet was compounded with different screw configurations of a twin-screw extruder. A considerable enhancement in the dispersion of the jute yarn to jute bundle and the decohesion of the jute bundle to elementary fibers was observed. This fiber separation was shown to be caused by high-intensity mixing, which led to an efficient load transfer from matrix to fiber, thereby improving the interfacial strength of these composites (Arao *et al.* 2015).

In the present work, PLA-based biocomposites were fabricated with various weight proportions of nonwoven jute mats, and their effect on mechanical properties was studied. The jute fiber was chemically treated with various modifiers. An effort was also made to establish the possible reaction mechanism between PLA and the treated fibers. The mechanical and water absorption capacities and morphological analysis of these composites were also studied.

EXPERIMENTAL

Materials

The PLA polymer used in this study was synthesized using the polycondensation methods described in our previous study (Khan *et al.* 2013a), and its properties are given in Table 1. The jute fiber was collected from a local market in the Jhenidha district, Bangladesh, and 60 cm from the middle portion of the stem was taken. Sodium carbonate, acetic acid, sodium acetate, sodium chlorite, sodium metabisulfite, chloroform, benzyl alcohol, toluene, acrylonitrile, benzoyl chloride, diphenylmethane diisocyanate (DPMIC), and acetic anhydride were purchased from Merck (Germany) and used as received.

Table 1. Properties of PLA

Molecular weight (mol/L)	110000
Tensile strength (MPa)	34±5.2
Young's modulus (MPa)	365±11
Elongation (%)	4.4±0.4

Methods

Preparation of jute sample

Approximately 20 g jute fiber was shocked into a solution containing 3.5 g/L Na_2CO_3 and 6.5 g/L detergents at 70 °C in a beaker in order to remove any adhering dirt. After 30 min the fiber was washed with distilled water, dried and kept in a poly bag for further treatments.

A known amount of jute fiber was immersed in 1 L sodium hydroxide solution (10% w/v) for 3 h at room temperature with constant stirring. Then the fiber was washed with 0.05 M acetic acid and then with distilled water until it became neutral. The alkali treated fiber was stored after drying in oven at 80 °C for 6 h. The jute fiber (20 g) was bleached in 1 L of sodium chlorite ($NaClO_2$, 7g.L^{-1}) solution according to our previous study (Khan *et al.* 2009). For acetylation, alkali-treated jute fiber was soaked in glacial acetic acid for 1 h at 30 °C. Acetic anhydride containing 1 to 2 drops of concentrated H_2SO_4 was added and stirred for about 60 min (Mishra *et al.* 2003). Potassium permanganate solution of 0.5% concentration was used on alkali-treated fiber in the presence of 1 to 2 drops of concentrated H_2SO_4 and stirred for 10 min (Sreekumar *et al.* 2011). Again, alkali-treated jute fiber was suspended in 10% (w/v) benzoyl chloride using toluene as a solvent for benzoylation. The surface-treated jute fiber was then soaked in methanol for 1 h to remove the benzoyl chloride (Li *et al.* 2007). The bleached jute fiber was grafted by acrylonitrile monomer (50 wt.% of fiber) in the presence of $K_2S_2O_8$ as initiator (1 wt.% of fiber), and $FeSO_4$ as a catalyst. The reaction was carried out at 70 °C in a water bath for 90 min (Khan *et al.* 2009). The bleached fiber was also immersed on toluene solution containing diphenyl methanediisocyanate. This reaction mixture was stirred for 1 h at 70 °C (Khan *et al.* 2013b). All the treated fibers were finally washed thoroughly distilled water and dried in an oven at 105 °C for 2 h before composite preparation.

Composite fabrication

Poly L-lactic acid (PLA) film of 0.2 to 0.3 mm thickness was fabricated using a hot press-moulding machine. The temperature of two plates was set to 180 °C, and 50 KN pressure was applied to the stainless steel open mould. The mould was kept at 180 °C for 10 min, and thereafter it was cooled using tap water. A mould-releasing spray (BONEY-Mould release silicon spray, London Chemicals Inc., UK) was used for easy opening of the mould.

The jute fibers were cut into small pieces (length 2 to 3 cm) and mixed with 2 wt.% carboxymethylcellulose (CMC). The CMC was used as a binder. This was blended with a mechanical blender and then placed between two rubber belts. Compressing the rubber belt in the rolling mill made the non-woven jute mat. This prepared non-woven jute fabric was cut into a square shape with dimensions of about 15×15 cm^2. This jute fabric was then kept for drying in an oven at 60 °C for 24 h to remove moisture. The prepared PLA films also cut into the same dimension as the jute fabric, and the fabric was placed in between the PLA films. The PLA films were used in an equivalent manner to 0.95, 0.90, 0.80, and 0.70 weight reactions of the fabric. The specimens were then placed on a stainless steel closed mould and composites were fabricated using a technique similar to that of PLA film-making. The specimens for tensile [dimensions: 110×15× (0.5 to 1.0) mm^3] and flexural [dimensions: 79×10×(0.5 to 1.0) mm^3] tests were made using a cutting machine.

Mechanical test

The tensile tests were conducted according to ASTM D882 (2012) using a Universal Testing Machine (Hounsfield UTM 10KN, UK). The clamping length for each specimen on each jaw was 15 mm, and no extensometer was used for the tensile tests. The tests were performed at a crosshead speed of 5 mm/min. Three-point flexural tests of the composites were carried out using Hounsfield UTM 10KN according to the standard method used for flexural properties (ASTM D790-98 2003). The speed for the flexural test was set at 5 mm/min. Each value reported is the average of ten sample tests. A dynamic impact test was conducted on notched composite specimens according to ASTM D 6110-97 (2010) using a Universal Impact Testing Machine.

Moisture absorption test

The moisture absorption test was carried out in accordance with ASTM D570-98 (2010). The specimen for each composite system was cut into dimensions of (50×10) mm^2. The specimens were dried in an oven at 80 °C prior to testing. The weight of the samples was taken before immersion in the water. The specimens were taken out after 12 h, and all surface moisture was removed with a clean, dry cloth or tissue paper. The specimens were weighed regularly from 12 to 96 h with a 12-h gap of exposure. The moisture absorption was calculated by the weight difference (Khan *et al.* 2012).

FTIR spectroscopy

The FTIR spectroscopy of samples was taken using a Perkin Elmer (USA) Spectrum One spectrometer. A small amount of samples were mixed with KBr to make a transparent pellet. For each sample, five scans were taken at a resolution of 4 cm^{-1}.

Scanning Electron Microscopy

Scanning electron microscopes FEI QUANTA 200 3D (USA) and JEOL 6400 (USA) were used to analyze the surface morphology of biocomposite samples with an accelerating voltage of 10 kV. The surface was coated with 3-nm thick gold before analysis.

RESULTS AND DISCUSSION

Mechanical Properties of the Composites

Figure 1 shows the variation of the tensile stress-strain curve of the untreated jute fabric-reinforced PLA composites at different fabric loadings. The mechanical properties (tensile, flexural, and impact strengths) of neat PLA and untreated non-woven jute fabric/PLA composites as a function of fabric loading are also presented in Table 2. From the data, it is evident that the mechanical strength of the composites increased with increased fabric loading up to 10 wt.%. The percentage of tensile, flexural, and impact strengths were found to be increased by 61.7%, 52.3%, and 47.2%, respectively, as compared with neat PLA. This behavior is primarily attributed to the reinforcing effect of the fabric, which leads to a uniform stress distribution from the fabric phase to a continuous polymer matrix. However, with a further increase of the fiber loading from 20 to 30 wt.%, all the mechanical properties were found to decrease. This decrease in mechanical properties at higher fabric loadings was attributed to the lower wettability of fabric by the PLA matrix, which promotes non-uniform stress transfer due to void formation between the fiber and matrix (Khan *et al.* 2013c). Table 2 also shows the effect of fabric content on stiffness (tensile modulus). The stiffness values were positively correlated with increased fabric loading, and the highest value was observed for 20 wt.% of fabric-loaded biocomposite. Stiffness was found to increase by about 197% for this composite. However, a slight drop in stiffness was observed for 30 wt.% of the composite due to poor wetting of the matrix. The elongation percentage did not show prominent change with an increase in fabric content.

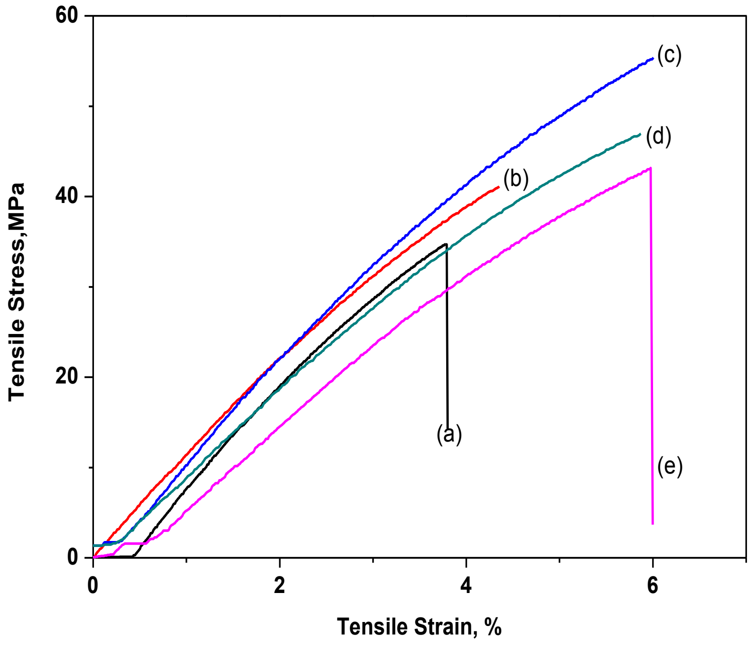

Fig. 1. Tensile stress-strain curves of (a) 0 wt.%, (b) 5 wt.%, (c) 10 wt.%, (d) 20 wt.%, and (e) 30 wt.% untreated jute fabric-loaded jute/PLA composites

The effect of fabric loading of alkali treated fabric and bleached fabric reinforced PLA composites on the mechanical properties (tensile, flexural, and impact strengths) are shown in Fig 2. It was observed that the mechanical strength of the alkali treated and bleached fabrics composites were increased with the increases of fabric loading up to 10 wt.%, similar to untreated fabric composite. Furthermore, the tensile and flexural modulus of the alkali treated and bleached fabrics composites showed similar trends to those of untreated fabric composites. Therefore on the basis of mechanical strength, the optimum fabric loading, *i.e.* 10 wt.%, was selected for further study.

Table 2. Mechanical Properties of PLA and Untreated Non-Woven Jute Fabric/PLA Composites with Different Fabric Loadings

PLA : Fabric	Tensile Strength (MPa)	Tensile Modulus (MPa)	Elongation (%)	Flexural Strength (MPa)	Flexural Modulus (GPa)	Impact Strength (KJ/m^2)
100:0	34±5.2	365±11	3.90±0.4	44±6.8	1.81±0.5	8.82±0.91
95:5	42±8.4	511±17	4.33±1.0	56±8.9	2.24±0.6	10.85±1.06
90:10	55±11.5	867±22	6.01±1.1	67±8.4	2.83±1.1	12.98±1.05
80:20	46±11.8	1086±25	5.93±1.7	62±9.6	3.26±0.8	12.02±1.40
70:30	41±11.6	1024±27	6.08±1.9	54±9.9	3.44±1.0	10.23±1.21

The tensile, flexural, and impact strengths, as well as the tensile and flexural modulus of 10 wt.% fabric-loaded composites of jute fabrics/PLA are shown in Table 3. It is evident that when the fabric was treated chemically, a huge improvement of the mechanical properties was observed compared with untreated fabric biocomposites. This increment may be attributed to the mechanical and chemical interactions between the fabric and the matrix (Murali *et al.* 2014). Greater enhancement of these fabrics was observed when fabrics were subjected to combined treatments such as alkali-acetylation, alkali-$KMnO_4$, alkali-benzoylation, bleaching-AN grafting, bleaching-DPMIC treatment, *etc.*

Among all the chemical treatments, the composites of alkali-treated jute fabrics were found to achieve better mechanical properties than untreated and bleached jute fabrics. This is because of the fact that alkali treatment removes most of the hemicelluloses from the fabric surface. When the hemicelluloses are removed, the interfibrillar region is likely to be less dense and less rigid, thereby making the fibrils more capable of rearranging themselves along the direction of tensile deformation. Similar observations have been reported for mercerized coir, flax, and bamboo fiber (Sharma *et al.* 1995; Sreenivasan *et al.* 1996; Das and Chakraborty 2006; Moryganov *et al.* 2008). During fabrication of the composites, the PLA penetrates the fabric surface pores as well as the pores inside the microfibrillar bundles, so that the composite failure cannot occur by simple interfacial failure. These may cause the improvement in the tensile strength and tensile modulus of the composites, which was improved by 13% and 40%, respectively. Similarly, the flexural strength is found to increase in alkali-treated jute fabric/PLA composite compared with untreated fabric/PLA composite.

The mechanical properties of the composite made from bleached jute fabric were found to be better than untreated fabric composite. It was observed that the tensile, flexural, and impact strengths were enhanced by 10.7%, 14.9%, and 11.9%, respectively, as compared with untreated fabric composite. The improvement in mechanical properties can be attributed to the fact that the bleaching reaction leads to the fibrillation of the fiber bundle, *i.e.*, breaking down of fiber bundles into smaller fibers, and thereby increases the effective surface area available for contact with the PLA matrix. Bleaching also improves the fiber surface adhesive characteristics by removing lignin and other impurities (Mukherjee *et al.* 1993).

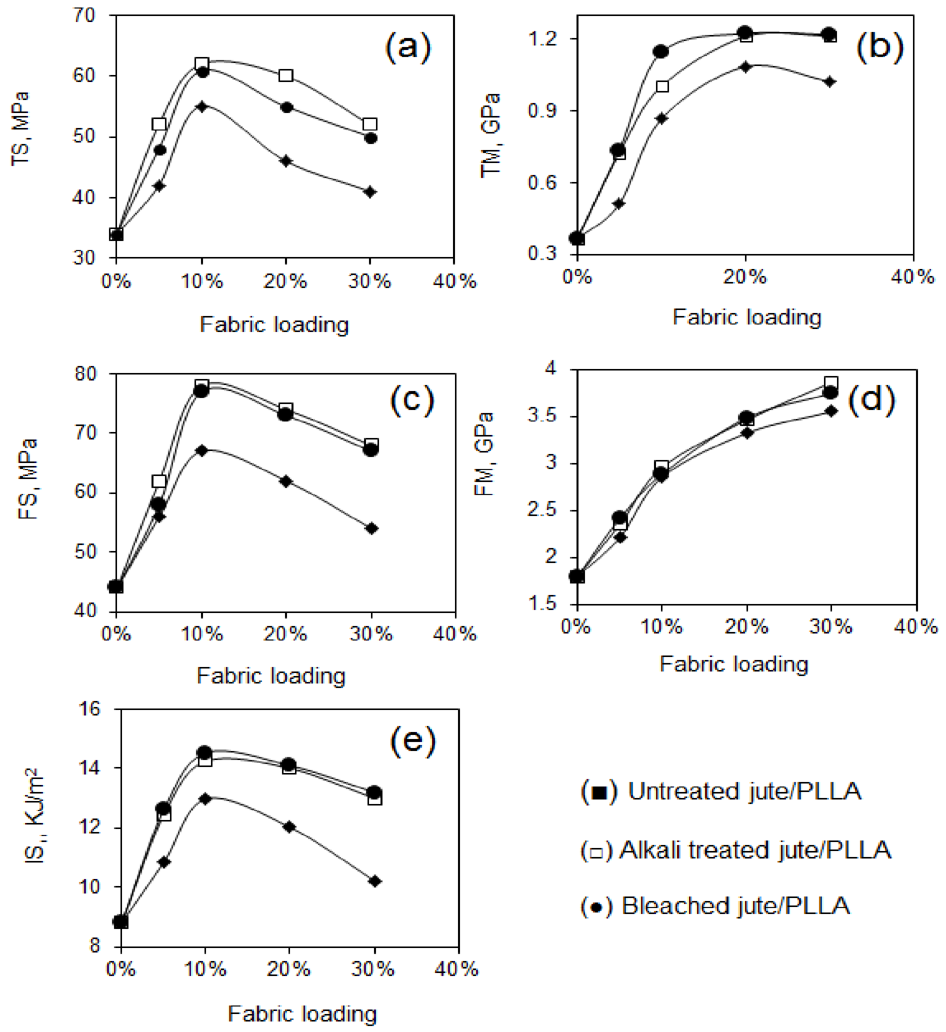

Fig. 2. Mechanical properties of non-woven jute fabric/PLLA composites with different fabric loading (a) tensile strength, (b) tensile modulus, (c) flexural strength, (d) flexural modulus, and (e) impact strength

Table 3. Mechanical Properties of Treated and Untreated Non-woven Jute Fabrics/PLA Composites with 10 wt.% Fabric Loading

Jute/PLA Composites	Tensile Strength (MPa)	Tensile Modulus (GPa)	Elongation (%)	Flexural Strength (MPa)	Flexural Modulus (GPa)	Impact Strength (KJ/m^2)
Untreated	55±11.5	0.867±0.022	6.21±1.1	67±8.4	3.550±0.05	12.98±1.05
Alkali-treated	62.1±9.3	1.211±0.051	6.01±1.0	78±6.6	3.861±0.06	14.25±1.3
Bleached	60.9±9.5	1.224±0.043	5.30±1.3	77±6.9	3.744±0.06	14.53±1.1
Acetylated	66.3±7.0	1.280±0.030	5.63±0.7	81±5.3	4.275±0.07	14.98±1.2
$KMnO_4$-treated	63.2±8.2	1.287±0.047	5.52±0.8	79±4.9	4.133±0.05	15.05±1.3
Benzoylated	71.2±6.5	1.292±0.012	6.66±0.5	88±5.2	4.668±0.04	16.44±1.8
AN-grafted	69.1±5.9	1.339±0.020	5.60±0.6	83±5.4	4.576±0.05	16.01±0.9
DMPIC-treated	70.0±6.1	1.305±0.031	7.30±0.7	85±5.9	4.542±0.05	15.99±1.0

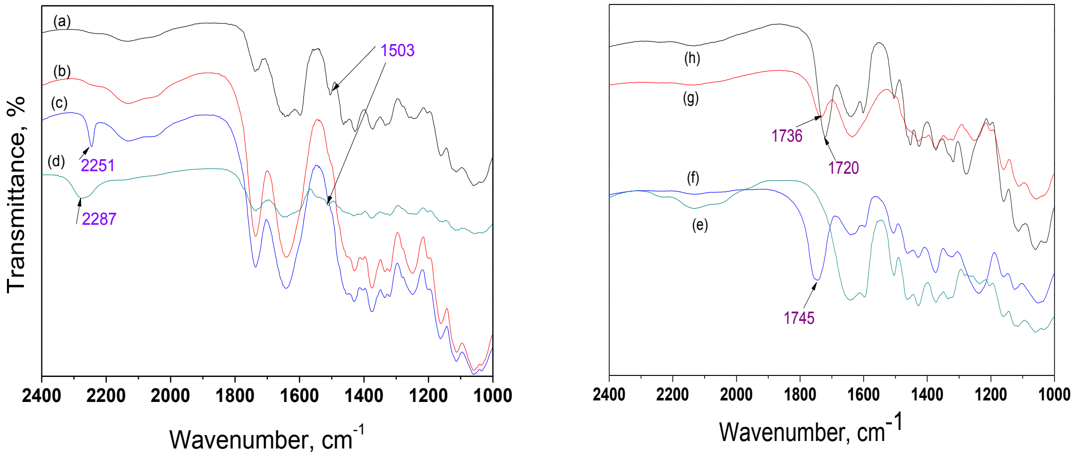

Fig. 3. FTIR spectra of (a) untreated jute, (b) bleached jute, (c) AN-grafted jute, (d) DPMIC-treated jute fiber, (e) alkali-treated jute, (f) acetylated jute, (g) $KMnO_4$-treated jute, and (h) benzoylated jute

The influence of the acetylation of jute fabrics on the mechanical properties of acetylated jute fabric/PLA composite is shown in Table 3. It appears that the tensile property of composites with acetylated jute was higher than those of untreated and alkali-treated jute composites. With the incorporation of acetylated jute, the composite improved by 6.7% in tensile strength, 3.8% in flexural strength, and 4.9% in impact strength over the alkali-treated jute fabric composite. The improvement in the tensile properties of acetylated jute fabric composite is attributed to the presence of $–CH_3$ groups in acetylated jute, which cause better interaction with PLA.

The change in chemical structure of acetylated jute was analyzed using FTIR spectra (Fig. 3f). The methyl groups in acetylated jute are less polar than the –OH groups in untreated and alkali-treated jute, and thus acetylated jute is more compatible with PLA. Moreover, the decrease in the polarity of jute on acetylation can cause a reduction in its hydrophobicity. It is clear that, even though there was no direct chemical bond binding acetylated jute fabric and PLA, the increased hydrophobicity of jute after treatment is responsible for the improvement in its mechanical properties (Bledzki *et al.* 2008).

Table 3 shows the effect of $KMnO_4$ treatment on the mechanical properties of treated jute fabric/PLA composites at 10 wt.% fabric loading. It can be seen that the tensile strength and flexural and impact strengths of permanganate-treated jute fabric/PLA composites were increased to 11.4%, 1.2%, and 5.9%, respectively, in comparison with alkali-treated jute fabric/PLA composites. The tensile modulus and flexural modulus of $KMnO_4$-treated jute/PLA composites increased with increased fabric loading, and these values were higher compared with alkali-treated and untreated jute fabrics/PLA composites.

The increase in mechanical properties of permanganate-treated jute composites was caused by the fact that permanganate induces grafting on the jute surface. Permanganate treatment can also cause an increase in the porous nature of the jute fabric and can be seen in Fig. 4g. The highly reactive Mn(III)+ ions are responsible for initiating graft copolymerization (Joseph *et al.* 1996), as shown below:

$$\text{Cellulose-H} + \text{Mn(llI)} \rightarrow \text{Cellulose-H-Mn(III) complex} \qquad (1)$$

$$\text{Cellulose-H-Mn(III)} \rightarrow \text{Cellulose}\bullet + H^+ + \text{Mn(III)} \qquad (2)$$

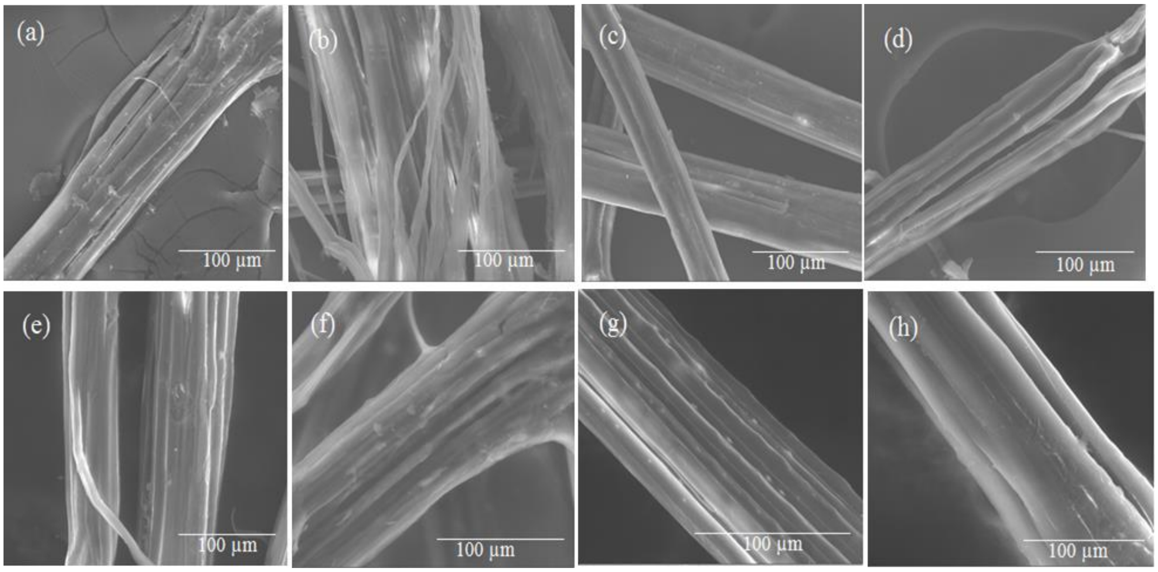

Fig. 4. SEM topography of (a) untreated jute, (b) bleached jute, (c) AN-grafted jute, (d) DPMIC-treated jute fiber, (e) alkali-treated jute, (f) acetylated jute, (g) $KMnO_4$-treated jute, and (h) benzoylated jute fiber

The effect of the benzoylation of jute fabric on the mechanical properties of composites can be assessed from Table 3. The benzoylated jute fabric/PLA composite showed an improvement in the tensile strength, flexural strength, impact strength, tensile modulus, and flexural modulus by 14.6%, 6.6%, 12.8%, 20.9%, and 15.1%, respectively, in comparison with alkali-treated jute fabric/PLA composites. Drastic enhancement of these properties was found when compared with untreated jute fabric. It is well known that the mechanical property of a composite mainly depends on the strength and modulus of the fabric, matrix, and the effectiveness of the interfacial adhesion. When fiber-reinforced composite is subjected to load, the fibers act as carriers of a load and stress is transferred from the matrix along with the fibers, which leads to effective and uniform stress distribution that result in a composite with good mechanical properties. The increment in the tensile properties could be caused by greater interfacial adhesion between the fiber and matrix. It is clear from SEM micrographs that the surface became rougher as a result of leaching out of alkali soluble fractions on benzoylation (Fig. 4h). The fiber surface also showed defibrillation, which can be attributed to the removal of hemicellulose and lignin (Paul *et al.* 2008). Moreover, benzoylation causes production of the hydrogen atoms that may react with the fabric (Nair *et al.* 1996). Moreover, there was an improvement in physical adhesion at the interface because of the benzoyl group attached to the fiber, which provides hydrophobic interaction with the PLA matrix (Fig. 5h).

Table 3 shows the effect of acrylonitrile (AN) grafting onto the jute surface on the mechanical properties of the resulting composites. In this case, to study the effect of grafting, bleached jute composite was taken as a standard material for comparison. It was observed that the tensile, flexural, and impact strengths were increased by 13.5%, 7.7%, and 10.2%, respectively in comparison with bleached jute fabric/PLA composites. The enhanced strength of these composites may be attributed to an improved compatibility between the polymer matrix and jute fabrics through vinyl moieties on the fabric surface during modification (Rout *et al.* 1999).

Table 3 also shows the mechanical properties of diphenylmethane diisocyanate (DPMIC)-treated jute fabric composite with 10 wt.% loading. The DPMIC-treated fabric composites showed superior strength and modulus compared with bleached treated and untreated composites. Moreover, the functional group -N=C-O in DPMIC is highly reactive with the -OH groups of cellulose and lignin (Maldas *et al.* 1989). This may lead to the formation of a urethane linkage. The presence of free-isocyanate groups in treated fabric can be confirmed by FTIR, which shows the intense peak around 2300 cm^{-1}, as shown in Fig. 3. Also, this free isocyanate group may react with either –OH or –COOH groups of PLA, thereby forming a bond between the jute and PLA. The possible reaction between the free isocyanate groups in cellulose and PLA is illustrated in Fig. 5d.

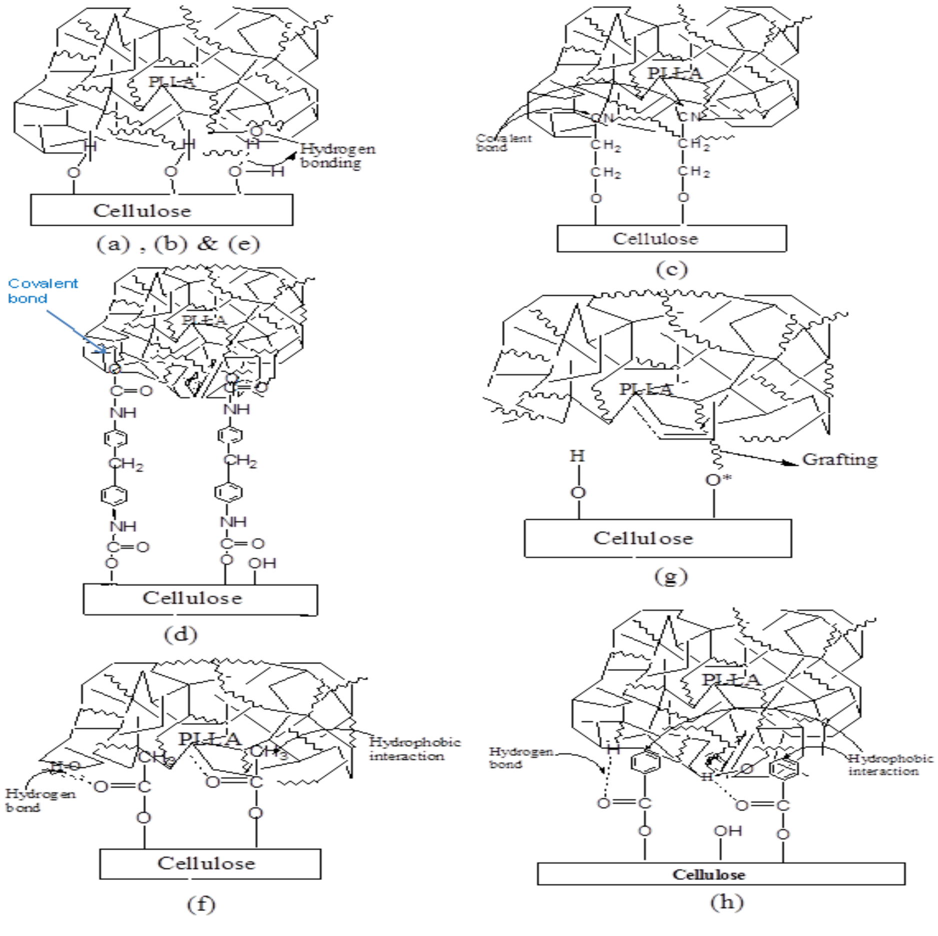

Fig. 5. Possible interaction mechanism of PLLA with (a) untreated jute, (b) bleached jute, (c) AN-grafted jute, (d) DPMIC-treated jute fiber, (e) alkali-treated jute, (f) acetylated jute, (g) KMnO$_4$-treated jute, and (h) benzoylated jute fiber

The impact failure of a composite occurs by factors such as fiber/matrix debonding, fiber and/or matrix fracture, and fiber pull-out. The fiber fracture dissipates less energy compared with fiber pull-out. Ray *et al.* (2001) observed that in composites with weak interfacial bonding, a crack propagated along the fabric/matrix interface and caused debonding. Table 3 represents the variation of the impact strength of treated and untreated jute fabric-reinforced PLA composites. The impact strength of treated jute fabric-reinforced composites was higher than that of untreated fabric. It was found that treated fabric composites exhibited the impact strength in order of benzoylated > AN-grafted > DPMIC-treated > $KMnO_4$-treated > acetylated > bleached > alkali-treated jute fabric.

Morphological Analysis

The interfacial properties of non-woven jute fabric/PLA composites were investigated using SEM analysis. Figure 6 shows SEM micrographs of the fracture surfaces of all the composite samples subjected to tensile stress. It was observed that the surfaces of the untreated fabrics were completely devoid of matrix material. This is a clear indication of fabric-matrix interfacial failure followed by extensive fiber pull-out. Furthermore, the matrix also shows considerable tearing. The alkali-treated fabric and bleached fabric also showed interfacial failure, but in this case, very small fiber pull-out was observed. These composites showed considerable failure of both the fabrics and the matrix. The failure mode observed on the fabrics indicates that fibers were splitting and tearing, which can be attributed to a better interaction with the matrix. The micrographs of acetylated and $KMnO_4$-treated jute fabrics/PLA composites are shown in Fig. 6g-h. These figures show that fiber pull-out occurred with the existence of cracks at the broken fiber ends/sites. This indicates the adherence of the PLA at a broken fiber fragment. This could be caused by strong bonding between the fabric and matrix.

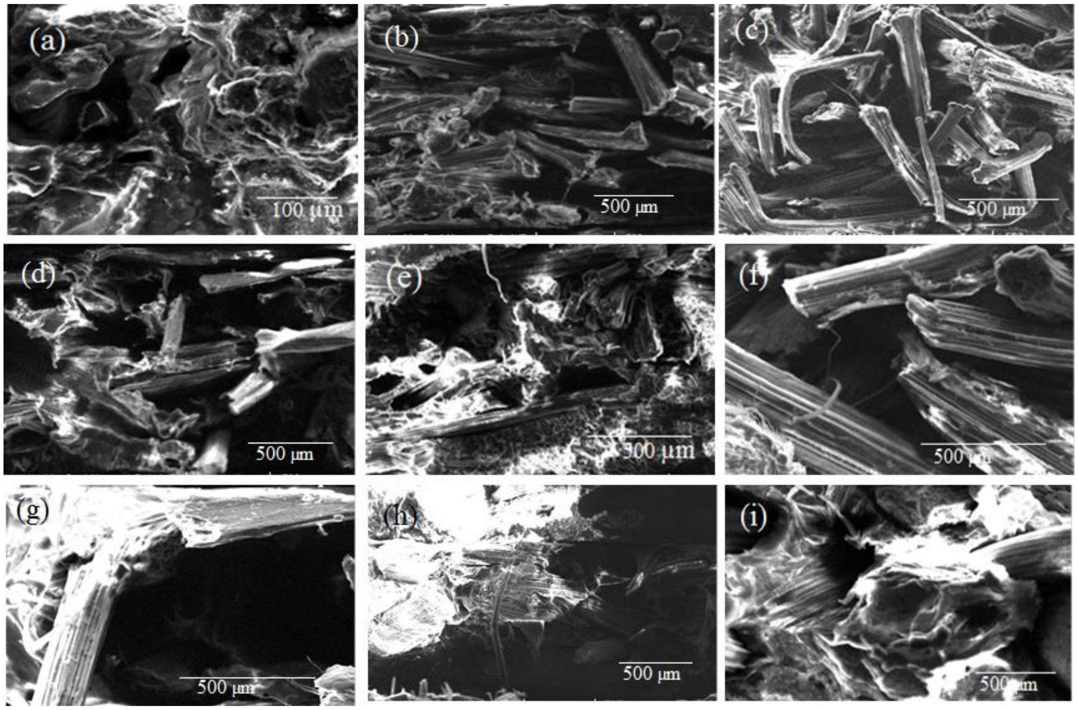

Fig. 6. Scanning electron micrographs (SEM) of tensile fractured non-woven fabric composites (10 wt.% fabric loading): (a) PLA, (b) Untreated jute/PLA, (c) Bleached jute/PLA, (d) AN-grafted jute/PLA, (e) DPMIC-treated jute/PLA, (f) Alkali-treated jute/PLA, (g) Acetylated jute/PLA, (h) $KMnO_4$-treated jute/PLA, and (i) Benzoylated jute/PLA.

In the case of the benzoylated fabrics, the failure surface indicates a high matrix failure, and the fabrics were completely covered with the matrix with no fiber pull-out. Similarly, the micrographs of acrylonitrile-grafted (Fig. 6d) and DPMIC-treated (Fig. 6e) jute composites also showed better fabric-matrix interaction as observed from the reduction of fiber pull-out, as well as from the good dispersion of the fabric. As expected, the surface modification altered the properties of the resulting composites. From the SEM images and mechanical properties of different surface-modified composites, an enhanced fabric-matrix interaction was observed. It can be concluded that the increase of the tensile strength of the composite is an effect of the improvement of the fabric-matrix interface.

Water Absorption Properties

Figures 7(a) and 7(b) show the water absorption curves for untreated and treated jute fabric-reinforced PLA composites at 30 °C and 90 °C, respectively. It was observed that the jute fabric-reinforced composites absorbed water very rapidly at the initial stage, and later a saturation level was attained without any further increase in water sorption. It is known that factors such as porosity content and fabric-matrix adhesion are responsible for the moisture absorption behavior of natural fabric composites (Stevulova *et al.* 2015). In these cases, the hydrophilicity of jute fabric, voids contents, and fabric-matrix adhesion might affect the moisture uptake of the composites.

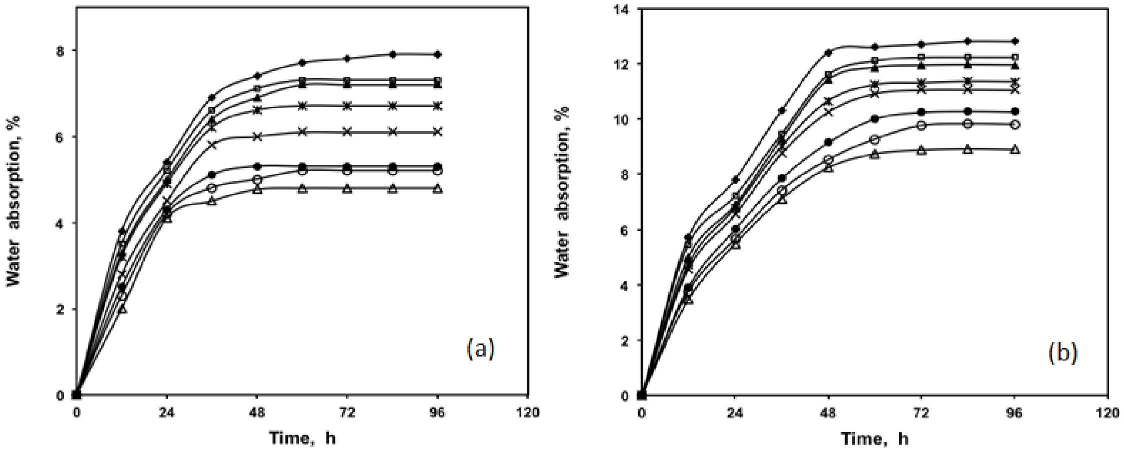

Fig. 7. Water absorption curves of non-woven jute fabric/PLA composites (10 wt.% fabric loading) at (a) 30 °C and (b) 90 °C [♦ - Untreated jute/PLA; ■ - Alkali-treated jute/PLA; ▲- Bleached jute/PLA; × - Acetylated jute/PLA; * - $KMnO_4$-treated jute/PLA; ○- Benzoylated jute/PLA; ● - AN-grafted jute/PLA; and □ - DMPIC-treated jute/PLA]

It was seen that untreated, fabric-reinforced composites showed greater water absorption because of the presence of high amounts of hemicellulose, which is hygroscopic in nature. It is also due to the large number of porous tubular structures and low compatibility with the PLA matrix. The water uptake nature of composites for different treatments also varies. It was observed that the moisture absorption behavior of the chemically treated fabric-reinforced PLA composites was lower than that of the untreated fabric composites when exposed to different temperatures. It is clear from observed data that changes in the surface chemistry of the fabric reduced the affinity of fabrics with the moisture. The fabrics get masked with the PLA with a stronger adhesion, resulting in greater hydrophobicity and less moisture absorption. The benzoylated and DPMIC-treated fabric-reinforced composites showed lesser water absorption because of the presence of aromatic rings in the fabric surface, which increase the hydrophobic nature of the composites (Sreekumar *et al.* 2011). Other treatments such as alkali, bleaching, permanganate, acetylation, and acrylonitrile grafting also decrease the equilibrium moisture absorption (M_e) values, indicating an increase in the fabric/matrix adhesion. It was observed that the water uptake of non-woven fabric/PLA composites were in the order of untreated > alkali-treated > bleached > $KMnO_4$-treated > acetylated > AN-grafted > DPMIC-treated > benzoylated fibers.

Table 4 represents the variation of the equilibrium moisture absorption (M_e) value for the composites at 30 °C and 90 °C. The water uptake was found to increase as a function of temperature, which was caused by the increase in the activity of the water molecules. Similar trends of moisture absorption were observed previously. As expected, the moisture absorption increased with immersion time and reached saturation after a certain time period. The time required to reach the saturation point is different for each environment. The time to reach the saturation limit was found to be 60 h for 30 °C and 72 h for 90 °C for most of the treated fabric-reinforced composites. It can be concluded that higher temperature and longer treatment duration accelerates the moisture uptake behavior in these composites.

Table 4. Variations of M_e, k, n, D_x, and P for Jute Fabric/PLA Composites (10 wt.% Fabric Loading) at 30 and 90 °C

Jute/PLA Composites	M_e (mol.%)	Log *k*	*k*	*n*	Diffusivity (mm²/s) $D_x \times 10^{-5}$	Permeability Coefficient, $P \times 10^{-6}$
At 30 °C						
Untreated	0.433333	−0.84	0.694376	0.48	1.85022	1.46168
Alkali-treated	0.405556	−0.96	0.659121	0.51	1.65257	1.20637
Bleached	0.400000	−0.98	0.653422	0.60	1.50553	1.08398
Acetylated	0.338889	−1.04	0.636618	0.68	1.69977	1.03686
$KMnO_4$-treated	0.372222	−0.99	0.650591	0.62	1.17346	0.786219
Benzoylated	0.266667	−1.46	0.530489	1.02	0.824942	0.395972
AN-grafted	0.294444	−1.18	0.599071	0.79	1.21021	0.641411
DPMIC-treated	0.288889	−1.31	0.566191	0.88	1.06356	0.553052
At 90 °C						
Untreated	0.711111	−0.84	0.694376	0.45	2.618	3.32486
Alkali-treated	0.680000	−0.80	0.706542	0.42	2.40625	2.94284
Bleached	0.663333	−0.90	0.676519	0.48	2.07272	2.47483
Acetylated	0.613889	−0.94	0.66487	0.51	2.01743	2.22926
$KMnO_4$-treated	0.630556	−0.92	0.670669	0.51	1.83098	2.06901
Benzoylated	0.494444	−1.13	0.61222	0.67	1.32739	1.17872
AN-grafted	0.571111	−1.07	0.628379	0.60	1.54075	1.57773
DPMIC-treated	0.545556	−1.08	0.625657	0.62	1.46962	1.43288

The water sorption kinetics in jute fabric-reinforced PLA composites were studied through the diffusion constants *k* and *n*. The behavior of moisture sorption in the composite was studied by the shape of the sorption curve represented by the following equation (Eq. 3),

$$\frac{M_t}{M_n} = kt^n \qquad (3)$$

where M_t is the moisture content at a specific time (t), M_e is the equilibrium moisture content, and k and n are constants. The values of k and n are determined from the slope and the intercept of M_t/M_e *versus* t in the log plot, which was drawn from experimental data of moisture absorption with time t.

Figures 8(a) and 8(b) show the typical curves of log(M_t/M_e) as a function of log t for both treated and untreated jute fabric-reinforced PLA composites. An example of the fitting of the experimental data for jute fabric/PLA composites at 30 °C is given in Fig. 8(a) and the values of k and n resulting from the fitting of all formulations are shown in Table 4. It was observed that the value of n was between 0.5 and 1 for all composites. A higher value of n and k indicates that the composite needs a shorter time to attain equilibrium water absorption. The value of k for untreated fabric composite was found to be higher than that of treated fabric composite at both temperatures. The benzoylated jute fabric composite shows lower k values than those of other treated fabric composites.

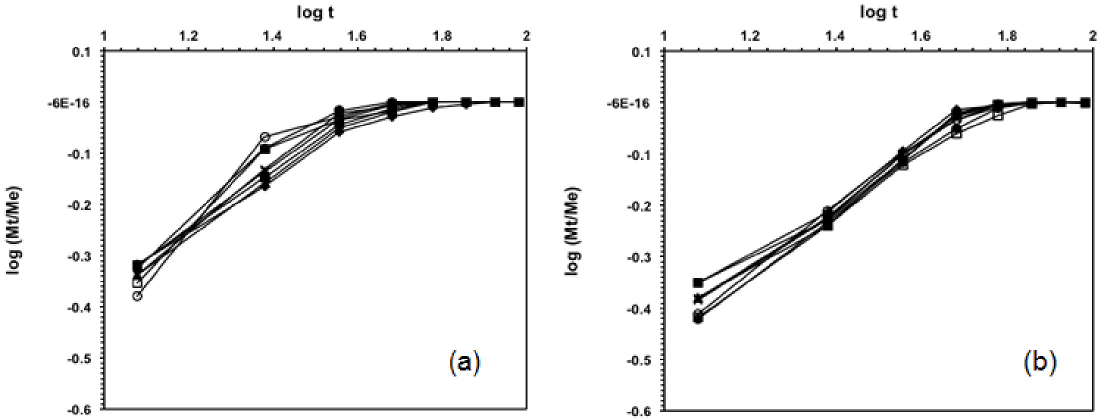

Fig. 8. log(M_t/M_e) vs log t for non-woven jute fabrics/PLA composites (10 wt.% fabric loading) at (a) 30 °C and (b) 90 °C [♦ - Untreated jute/PLA; ■ - Alkali-treated jute/PLA; ▲- Bleached jute/PLA; × - Acetylated jute/PLA; * - $KMnO_4$-treated jute/PLA; ○- Benzoylated jute/PLA; ● - AN-grafted jute/PLA; and □ - DMPIC-treated jute/PLA]

Similarly, the diffusion coefficient characterizes the ability of the penetrant to diffuse through a polymer. The diffusion coefficient, or diffusivity (D_x) of moisture absorption was calculated using the following equation (Eq. 4),

$$D_x = \pi \frac{h}{4M_m}\left(\frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}}\right)^2 \qquad (4)$$

where M_m is the maximum percentage of moisture content, h is the sample thickness, t_1 and t_2 are the selected points in the initial linear portion of the plot of M_t *versus* t (Fig. 8), and M_1 and M_2 are the respective moisture contents.

From the plot of M_t *versus* t (Figs. 8a, b), the value of D_x was evaluated and is summarized in Table 4. It can be observed that the surface modification of fabric decreases the diffusion coefficient (D_x). The benzoylated jute fabric composite exhibits a lower diffusion coefficient at both temperatures. The variation of the diffusion and permeability coefficients for treated non-woven jute fabric-reinforced composites is given in Table 4. The permeability (P) can be calculated by the following expression (Eq. 5),

$$P = DS, \tag{5}$$

where the sorption coefficient S was calculated using the following formula (Eq. 6),

$$S = M_\infty / M_p \tag{6}$$

where M_p is the initial mass of the polymer sample and M_∞ is the mass of the solvent taken up at equilibrium swelling. It was found that the diffusion and permeability coefficients varied with the treatments, and their values were lower for the benzoylated fabric-reinforced composites. Also, temperature plays a major role in the nature of the diffusion coefficient which increases with increased temperature.

CONCLUSIONS

In the present work, biocomposites of non-woven jute fabrics (NWJF) and poly-(lactic acid) were fabricated successfully by sandwiching non-woven jute mat between PLA sheets. Mechanical performance was studied as a function of fiber loading concentrations and various chemical treatments. FTIR spectroscopic studies revealed that surface modification of the fiber occurred after every fiber treatment. The surface treatments resulted in improvement of tensile properties. This can be attributed to an increase in interfacial adhesion as confirmed by morphological studies. Overall, following conclusions were drawn from this study:

1. The tensile modulus and flexural modulus of jute fabric composite increased proportionally with the fabric loading.
2. The change in mechanical properties of jute fabric-reinforced PLA composites under various loadings was nonlinear. The 10 wt.% fabric-loaded composite exhibited higher tensile, flexural, and impact strengths.
3. The chemically treated non-woven fabric composites showed better mechanical properties than untreated non-woven fabric and neat PLA.
4. The benzoylated jute fabric composite exhibited the highest tensile, flexural, and impact strength among all non-woven treated fabric composites.
5. Chemical treatment decreased the water absorption properties of the non-woven fabric/PLA composites.

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