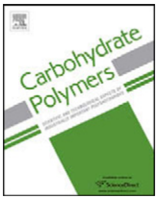
Carbohydrate Polymers 87 (2012) 1628–1636

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol



Durability of lignocellulosic fibers treated with vegetable oil–phenolic resin

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ARTICLE INFO

Article history:
Received 10 August 2011
Received in revised form 25 August 2011
Accepted 23 September 2011
Available online 29 September 2011

Keywords:
Lignocellulosic
Transesterification
Biodegradation
Tensile strength
Vegetable oil

ABSTRACT

Jute and sisal fibers were treated with an aqueous emulsion of neem oil and phenolic resin at elevated temperature for enhancing their tensile strength, hydrophobicity and resistance against biological and chemical degradations. The process was found to lead to the transesterification of cellulose chain hydroxyl groups and increased crystallinity. Treatment efficacy was evaluated by characterizing fibers by exposing them to biological and chemical degradations. The results indicate that the short-term tensile strength increased by 61–75% following treatment. After biodegradation, treated fibers were found to retain 63–70% of their initial tensile strength, while untreated fibers retained 28–32%. Treated fibers retained 52–60% of tensile strength after 90-day exposure to 3% salinity and 48–55% of tensile strength after similar exposure to pH between 3 and 10. For untreated fibers the corresponding figures were 9–13% and 10–12% respectively.

1. Introduction

The major impediments in high performance industrial applications of lignocellulosic fibers (LCFs) are that they are mechanically weak and are highly susceptible to chemical and biological degradations vis-à-vis many man-made fibers. LCFs are composites of cellulose, hemicelluose and lignin with small amounts of pectin and other chemical constituents. Crystalline cellulose mainly imparts mechanical strength and ductility to the LCFs. Hemicellulose molecules are attached to crystalline cellulose through hydrogen bonding forming an amorphous matrix (Jayaraman, 2003). Although lignin and pectin enhance primary dimensional stability of the LCFs, they are brittle and often prevent efficient transfer of mechanical load. The free hydroxyl and other oxygen-containing groups of the LCFs exhibit a tendency to attract water molecules through hydrogen-bond formation causing the fibers to swell. As a result, the cellulose molecules are exposed to microbial attacks, which degrade the cellulose and cause strength loss. Exposure to chemical environment similarly results in loss of tensile strength because of hydrolysis, oxidation or dehydration reactions. Thus, one of the possible strategies to minimize microbial degradation and increase long term mechanical strength would be to make the LCFs less hydrophilic by blocking the free hydroxyl groups.

Chemical modification of hydroxyl groups of LCFs by graft copolymerization with methyl methacrylate, saturated fatty acid, subtilisin Carlsberg solvent and silane coupling (Montazer & Salehi, 2008; Pickering, Abdalla, McDonald, & Franich, 2003; Vaca-García, Thiebaud, Borredon, & Gozzelino, 1998; Zhang & Fan, 2010) have also been reported to enhance hydrophobicity and mechanical strength. Resistance of LCFs against biodegradation could be increased by UV acrylamide photografting or boric acid or acetic anhydride treatment (Hassan, Islam, & Khan, 2002; Lyon et al., 2007; Teramoto, Urata, Ozawa, & Shibata, 2004). Transesterification of LCF hydroxyl groups with *n*-butylacrylate and pyridine led to the development of a greater resistance against biological and chemical degradations (Samal, Acharya, Mohanty, & Ray, 2001). Hydrophilicity of LCFs has been reduced by applying natural rubber (Jacob, Varughese, & Thomas, 2005), phenolic resin (Medeiros de, Agnelli, Joseph, Carvalho, & Mattoso, 2005), fatty acid derivative such as oleoyl chloride (Corrales et al., 2007), and pentafluorobenzoyl chloride (Cunha et al., 2007) on fiber surface. Similar application of vegetable oil and phenolic cross-linking agents reportedly increased the mechanical strength of LCFs and dimensional stability of LCF-based particle boards (Wang, Wasylciw, & Guoliang, 2007). Surface application of chitosan (Lim & Hudson, 2004), and neem (*Azadirachta indica*) seed extract with cross linking agents on cotton–polyester fabric (Joshi, Ali, & Rajendran, 2007) has led to an enhanced resistance against microbial degradation. Enhancement of hydrophobicity, durability and tensile strength of LCFs in all the reported literature was based on the chemical modification such as coating with phenolic resin, grafting with methyl methacrylate, esterification and transesterification with synthetic or toxic chemicals.

In this study an alternative, non-hazardous and inexpensive process has been developed for treating LCFs to enhance

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doi:10.1016/j.carbpol.2011.09.070

their hydrophobicity, mechanical strength and resistance against biological and chemical degradations using a water-based emulsion of vegetable oil and phenolic resin (resol). As demonstrated later, vegetable oil treatment transesterified the fibers, while application of plant-based resol coated the fiber surface and increased process efficacy. It should be noted that the fatty acid triglycerides present in vegetable oil utilized here for durability enhancement are completely different from those in the process based on neem seed extracts described by others. Further, vegetable oils have not been used in a chemical process involving solvent-free transesterification of LCFs as has been accomplished in this research.

2. Experimental

2.1. Materials and chemicals

This study pertains to the treatment of jute (*Corchorus olitorius*) and sisal (*Agave sisalana*) fibers. Sodium hydroxide (NaOH) pellets (assay > 97%), resorcinol (assay > 99%), formaldehyde (37%), commercially available 40% oil extracted from neem seed (*A. indica*) and kernel, Neem oil (NO) or 20% rice bran oil (RBO) extracted from inner husk of rice (*Oryza sativa*), cashew nut shell liquid (CNSL) and commercial grade condensed black wattle plant tannin were used to treat the fibers as discussed below.

2.2. Chemical treatment

The LCFs washed with distilled water were oven dried at 85 ± 2 °C until obtaining a constant weight. These fibers were dipped in 0.5% (w/v) NaOH solution for 24 h at 30 ± 2 °C according to the procedure described earlier by our group (Saha et al., 2010). The alkali-treated fibers were then cooled, washed and neutralized at pH 7 ± 0.5 with distilled water.

A mixture of phenolic compounds was prepared by mixing resorcinol, CNSL and condensed tannin proportioned 1:4:5 by weight. Base catalyzed phenol–formaldehyde resin (resol type) was prepared following Singh and Gupta (2005) by mixing the above phenolic composition with formaldehyde in 1:1.3 ratio (by weight) at 28 ± 2 °C. Solid content of this resol was adjusted to 1 ± 0.2% (w/v). The diluted resol resin was found to be stable up to 12 h without any agglomeration. An aqueous emulsion was prepared by mechanically mixing 4–7% (by volume) of NO or RBO and 0.01% (by weight) of sodium dodecyl sulfate (SDS) surfactant. Stability of this emulsion was also evaluated via emulsification index (Kodali, Das, & Sen, 2009) and found to be satisfactory. The vegetable oil emulsion was mixed with the resin solution in 1:1 proportion (by volume) to get a final reagent within 12 h from resin preparation. Amount of vegetable oil in the final reagent was 2–3.5% (by weight) and subsequently the solid content of the resol was 0.5 ± 0.1% (by weight). The final reagent was found to be stable for several days. Finally the reagent mixture was sprayed over the alkali-treated fibers maintaining a fiber to liquid ratio of 2:1 (by weight). Subsequently, the fibers were mechanically squeezed to recover excess reagent. Finally, the fibers were cured in an air circulating oven at 105 ± 5 C for 1 h.

2.3. Testing and characterization

Untreated and treated fibers were characterized for their mechanical strength and flexibility, hydrophilicity, surface characteristics, chemical composition, crystallinity, and susceptibility to biological and chemical degradations as described below.

2.3.1. Mechanical strength and flexibility

Single fibers were manually separated from fiber bundles for assessing their uniaxial tensile strength. To ensure fiber separation and measure fiber diameter Leica DMLM microscope (at 10×) was used. For tensile strength measurement of each fiber, a maximum load of 100 N with the crosshead speed of 3 mm/min was applied and a gage length of 25 mm was maintained. Tensile strength of 50 fiber samples was measured following ASTM D 3822-01 (ASTM, 2001) using Hounsfield H10KS universal testing machine maintaining 25 ± 2 mm gage length and 3 mm/min crosshead speed. For each batch tested, the average and standard deviation of these measurements were used as the estimates of the uniaxial tensile strength and its variability, respectively.

2.3.2. Hydrophilicity estimation

Steady state water absorption, equilibrium moisture content (EMC), and contact angle were measured to estimate the hydrophilicity of LCFs before and after treatment. These parameters were determined on triplicate samples of bundle of 10 fibers and the average is reported in this study.

The steady state water absorption was obtained after immersing oven dry LCF specimens in distilled water at 30 ± 2 °C following Alvarez and Vázquez (2006). A portion of the specimens was taken out from the distilled water bath after fixed time periods. It was carefully wiped with an absorbent paper to remove surface water and weighed to determine the steady state water absorption. The exercise was continued for longer immersion periods until obtaining a constant value of water absorption.

The EMC was determined according to ASTM D 4442-07 (ASTM, 2007). Before testing, the LCF specimens were oven dried until obtaining a constant weight.

A fiber bundle washed with ethyl alcohol was placed on a glass slide and a drop (1–2 μl) of Millipore water was carefully placed on the fiber bundle using a micro syringe. The contact angle between the drop and the fiber bundle was estimated at 30 ± 2 °C from digital photographs following Alix et al. (2009).

To evaluate the swelling property and the effect of charge density on the hydrophilicity of LCFs, apparent zeta potential (ζ) was measured using Zetasizer ZS90, Malvern Instrument System at 30 ± 2 °C following Pothan, Simon, Spange, and Thomas (2006). For this, samples were prepared by manually cutting LCFs maintaining 1–2 mm length, dispersing 10 ± 2 mg of the LCF sample in 1×10^{-3} M NaCl solution and sonicating the liquid for 15 min. Zeta potential was determined for 5 fiber powder samples and their average is reported in this study.

2.3.3. Surface characteristic

Surface characteristic of the LCF specimens was investigated through scanning electron and atomic force microscopy.

LCF powder samples for scanning electron microscopy (SEM) were prepared by washing LCFs with ethyl alcohol and manually cutting 5 ± 1 mm long pieces of LCFs. 1–2 mg of sample was coated with a thin layer of gold by a plasma sputtering apparatus and examined with TESCAN VEGA$_{LSV}$ scanning electron microscope operated in the high vacuum mode with secondary electron detector and with accelerating voltage between 5 and 10 kV.

The surface topography of LCF samples was examined with Nanonics Multiview 1000 atomic force microscope at 70 ± 5% relative humidity and at 30 ± 2 °C following Pietak, Korte, Tan, Downard, and Striger (2007). The microscope was equipped with a silicon nitride tip and was operated in the contact mode. LCFs, prewashed with ethyl alcohol, were cut into 1–2 mm long pieces and 2 ± 0.5 mg of these pieces was dispersed in 50 ml distilled water by sonicating the liquid for 30 min. About 1.5 μl of the suspension was extracted with a micro tip and placed on a glass slide for examination with the microscope.

Table 1
Mechanical properties and hydrophilicity of untreated and treated fibers.

Fibers	Treatment	Water absorption (wt% increase) ± COV[a]					EMC[b] (wt%)	TS[c] ± COV[a]	EB (%)[d] ± COV[a]
		6 h	12 h	24 h	48 h	72 h			
Jute	Untreated	186 ± 23	216 ± 20	256 ± 23	252 ± 21	255 ± 18	14 ± 06	370 ± 68	1.4 ± 0.48
	Resin	130 ± 30	103 ± 21	106 ± 17	98 ± 10	95 ± 07	09 ± 02	518 ± 55	1.2 ± 0.30
	6% NO	127 ± 12	141 ± 14	145 ± 05	147 ± 10	146 ± 15	11 ± 04	594 ± 84	1.5 ± 0.52
	5% RBO	105 ± 19	128 ± 12	131 ± 09	133 ± 12	134 ± 06	10 ± 04	528 ± 68	1.6 ± 0.22
	NO–resin	62 ± 09	76 ± 10	78 ± 10	78 ± 12	79 ± 16	07 ± 02	648 ± 94	1.5 ± 0.46
	RBO–resin	82 ± 11	101 ± 13	103 ± 07	102 ± 03	103 ± 04	9 ± 02	606 ± 70	1.5 ± 0.15
Sisal	Untreated	156 ± 17	176 ± 12	182 ± 13	186 ± 9	185 ± 11	12 ± 03	471 ± 49	1.5 ± 0.26
	Resin	120 ± 14	111 ± 16	102 ± 19	101 ± 03	98 ± 13	07 ± 02	564 ± 72	1.3 ± 0.34
	5% NO	90 ± 11	103 ± 12	113 ± 08	112 ± 16	115 ± 13	06 ± 03	796 ± 91	1.7 ± 0.56
	5% RBO	130 ± 08	127 ± 17	136 ± 15	135 ± 11	135 ± 10	10 ± 02	752 ± 64	1.6 ± 0.35
	NO–resin	56 ± 09	63 ± 08	62 ± 11	61 ± 10	62 ± 08	05 ± 02	759 ± 78	1.5 ± 0.33
	RBO–resin	70 ± 21	77 ± 13	75 ± 06	78 ± 07	78 ± 06	08 ± 01	708 ± 58	1.4 ± 0.24

[a] COV: standard deviation/mean, was calculated based on 50 observations.
[b] Equilibrium moisture content expressed in wt% increase.
[c] TS: tensile strength in MPa unit.
[d] EB: elongation at break.

2.3.4. Fourier transform infrared (FTIR) spectroscopy

Changes in fiber chemistry were assessed from FTIR spectra of LCFs obtained using a Thermo Nicolet, Nexus 870 spectrophotometer operated at 35 ± 2 °C. Samples for FTIR spectroscopy were prepared by cutting LCFs, pre-washed with ethyl alcohol, into powder form and oven drying them at 105 ± 2 °C for 1 h. The spectra were recorded for wave numbers ranging between 4000 cm^{-1} and 400 cm^{-1} using 32 scans for each sample comprised of 10 ± 2 mg of LCFs mixed with 100 ± 10 mg of potassium bromide (KBr) pellets.

2.3.5. Quantitative elemental analysis

Elemental analysis was carried out to investigate the chemical changes of LCFs after chemical modification. The mass percentages of carbon, hydrogen, oxygen and nitrogen of LCFs were analyzed following the method described elsewhere (Phan et al., 2006). LCFs, pre-washed with ethyl alcohol, were cut into small pieces and 3 ± 0.5 mg of them was tested with EURO EA Elemental Analyzer in triplicate.

2.3.6. X-ray diffraction (XRD)

RIGAKU X-ray diffractometer (ULTIMA III) operated at room temperature was used to characterize the crystallinity of LCFs as changes in crystallinity partly affect the tensile strength and hydrophilicity of the fibers. LCFs were cut into 5 ± 1 mm long pieces, 1 ± 0.5 g of which was subjected to XRD. The diffractogram was obtained using Cu-Kα radiation source for 2θ range between 10° and 50° and at a scanning speed of 2° min^{-1}. According to Buschle-Diller and Zeronian (1992), the degree of crystallinity is given by the equation, $Cr = (I_{22.5} - I_{18.5})/I_{22.5}$, where $I_{22.5}$ and $I_{18.5}$ are the intensities at 2θ values of 22.5° and 18.5°, respectively.

2.3.7. Durability assessment

Resistance to biodegradation of LCFs was assessed from soil burial test by exposing LCFs to a composting environment. The susceptibility to chemical degradation was evaluated by exposing LCFs to elevated (3% by weight) saline solutions and alkaline–acidic pH conditions.

The compost for soil burial tests was prepared by mixing organic (black) garden soil, sand and cow dung in 2:1:1 ratio (by weight) as specified in BIS (BIS, 1992). The compost was changed once every seven days for simulating the fiber degradation in an open environment. Further, the fibers were exposed to biodegradation up to 90 days instead of the 21 days duration specified by BIS. Three specimens of LCF bundle were tested for each category. The ratio of LCF fiber bundles to soil was kept 1:100 (by weight) as suggested by other researchers (Di Franco, Cyras, Busalmen, Ruseckaite, & Vàzquez, 2004). Soil pH was maintained within 6 and 7 by adding dilute hydrochloric acid or dilute sodium hydroxide as needed and the moisture content of the soil was kept at 65 ± 5% over the entire duration of biodegradation. The compost-LCF system was kept in a vented glass enclosure, which, in turn, was stored within an incubator at 35 ± 5 °C and 85 ± 5% relative humidity during the test. Fiber samples were periodically recovered, washed and tested for tensile strength.

The chemical stability of LCFs was investigated by immersing them within an aqueous solution of 3% sodium chloride (by weight) and aqueous solutions of hydrochloric acid and sodium hydroxide with pH ranging between 3 and 10 for 90 days duration. These tests were conducted at 35 ± 5 °C maintaining fiber to liquid ratio as 1:100. LCF specimens were periodically recovered, oven-dried and tested for tensile strength.

3. Results and discussions

3.1. Tensile strength and elongation at break

Maximum increase in uniaxial tensile strength of jute and sisal fibers was observed when they were treated with 5–6% of NO or RBO in the absence of phenolic resin. Upon treatment with NO the tensile strength was found to increase by 69%, while for the RBO treatment the increase was 60% (Table 1). For treatment with phenolic resin without vegetable oil, on the other hand, uniaxial tensile strength increased up to 40% and 20%, respectively, for jute and sisal fibers when the fibers were treated with a resin with 1% solid content. Tensile strength was found to increase up to 75% and 64% when jute fibers were treated with NO and RBO, respectively, in the presence of resin emulsion. For sisal fibers, corresponding increases were 61% % and 50%, respectively.

The covariance (standard deviation divided by sample mean) of tensile strength and elongation at break for vegetable oil–phenolic resin treated LCFs was found to be less compared to corresponding values of untreated fibers (Table 1). This demonstrates a reasonable repeatability of treatment outcome.

Treatment of LCFs with phenolic resin led to a reduction in the elongation at break for the LCF specimens. Other treatments resulted in marginal increase in this parameter. Enhancement of uniaxial tensile strength and marginal reduction of brittleness of vegetable oil–resin treated LCFs shows that the effectiveness of this treatment is more than that of others.

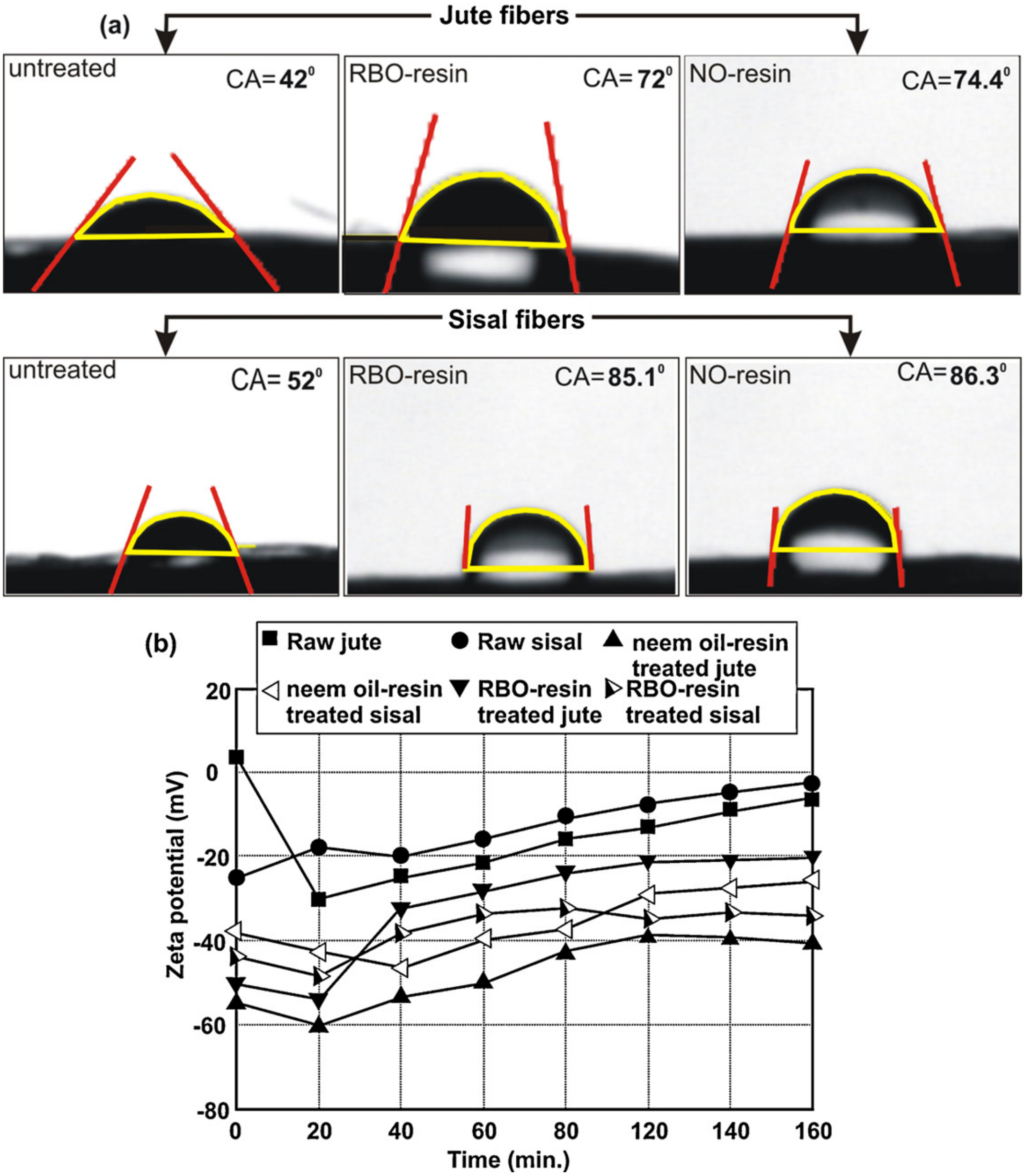

Fig. 1. (a) Measured contact angle (CA) values for untreated and treated LCFs (RBO: rice bran oil and NO: neem oil); (b) variation of Zeta potential (ζ) of untreated and treated LCFs with time.

3.2. Hydrophilicity

Water absorption and EMC of the treated LCFs with vegetable oil only, phenolic resin only and combination of oil and resin were measured and the results have been presented again in Table 1. It was observed that the hydrophilicity for the combined treatment with vegetable oil (NO and RBO) and resin was reduced to the maximum extent. NO–phenolic resin treatment was found to reduce water absorption on an average from 255% to 79% for jute fibers and 185–62% for sisal fibers. While the contact angles for untreated jute and sisal fibers were found to be 42° and 52°, respectively. The corresponding values following NO–resin treatment were 74.4° and 86.3° and RBO–resin treatment were 72° and 85.1° (Fig. 1a).

The covariance of water absorption and EMC for vegetable oil–phenolic resin treated LCFs was found to be less compared to corresponding values of untreated fibers demonstrating a reasonable repeatability of treatment efficacy.

Continuous reduction of the ζ-potential with time for untreated LCFs was observed as shown in Fig. 1b. In comparison, for treated LCFs the ζ-potential was found to decrease up to about 60 min and remained relatively unchanged thereafter, also shown in Fig. 1b. It has been suggested by others (Bismarck, Springer, Mohanty, Hinrichsen, & Khan, 2000) that such reductions in ζ-potential is due to moisture absorption and consequent swelling of dissociable groups, e.g., uronic acid in hemicelluloses, other weaker acids in lignin and free hydroxyl groups in cellulose, and removal of water soluble constituents such as hemicelluloses and pectin. Thus the results obtained in this research appears to indicate that while untreated LCFs continued to swell over the 160 min exposure to NaCl solution, treated LCFs did not swell appreciably beyond the initial 60 min of exposure. For treated fibers the water soluble constituents and lignin were substantially removed and dissociable groups were partially blocked by vegetable oil treatment leading to a reduction in swelling tendencies.

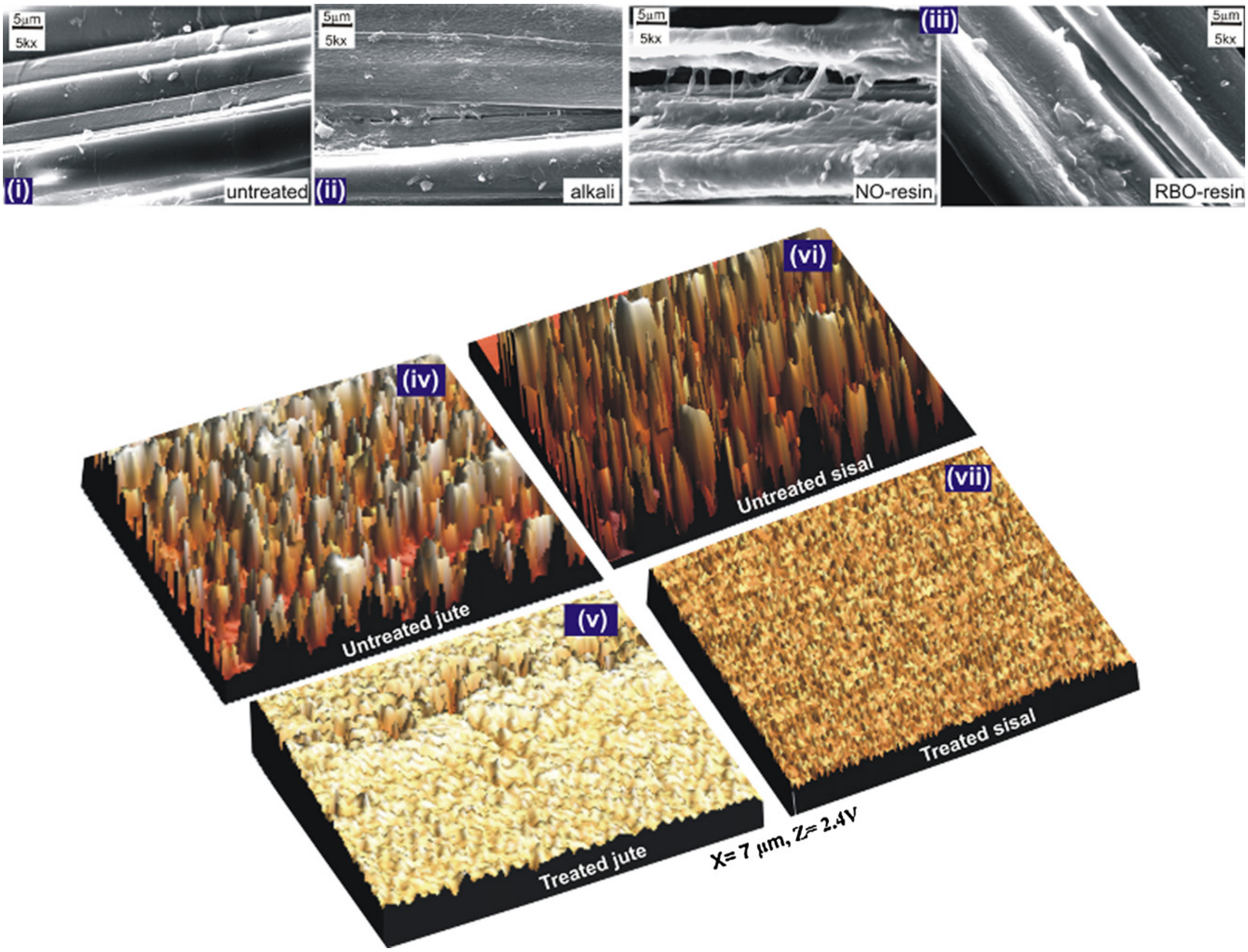

Fig. 2. SEM and AFM photomicrographs of untreated and treated LCFs. (i) untreated jute fibers, (ii) alkali treated jute fibers, (iii) neem oil (NO)–resin and rice bran oil (RBO)–resin treated jute fibers, in AFM topographic images, (iv) untreated jute, (v) neem oil–resin treated jute fibers, (vi) untreated sisal, and (vii) neem oil–resin treated sisal fibers.

From water absorption, EMC, contact angle and ζ-potential measurements it can be inferred that chemical treatments led to a reduction of hydrophilicity of LCFs and the maximum reduction of hydrophilicity was achieved with NO–resin treatment only.

3.3. *Surface morphology*

SEM photomicrographs of untreated and alkali-treated jute fibers, Fig. 2(i) and (ii), indicate that the surface roughness has increased and the fiber cross sectional area has become smaller following alkali treatment. The observed changes in the surface morphology and fiber cross section appears to be due to the partial removal of surface impurities, non-cellulosic materials, inorganic substances and waxes and fiber separation following alkali treatment. Vegetable oil–resin treatment was found to lead to the development of a smoother surface (Fig. 2(iii)). Surface smoothing in morphology for sisal fibers were also same as jute fibers (figures not given). Smoothening of surfaces of sisal fibers has been reported by Megiatto, Hoareau, Gardrat, Frollini, and Castellan (2007) after modification with furfuryl alcohol and polyfurfuryl alcohol. AFM topographic images, shown in Fig. 2(vi) and (vii), of jute and sisal fibers show similar smoothening in surface morphology following alkali and NO–resin treatment.

3.4. *FTIR spectroscopy*

Since the peak in the 3200–3450 cm^{-1} region in FTIR spectra of LCFs is often deemed to represent the OH stretching vibration of cellulose molecules or N–H stretching (Tornc et al., 2007), weakening of the intensity of the peak in this region following vegetable oil-resin treatment provides evidence of chemical alteration of some of the hydroxyl groups (Fig. 3). The corresponding reduction of intensity for resin-only and vegetable oil-only treatments was found to be less significant indicating relative inefficiencies of these treatments in hydroxyl group blocking.

The peaks in the FTIR spectra in the 1734 cm^{-1} region for untreated jute fibers and that in the 1650 cm^{-1} region for untreated sisal fibers representing C=O stretching vibration for aryl ester of hemicellulose and lignin (Frisoni et al., 2001; Navarro et al., 2003) were found to disappear following alkali treatment indicating substantial removal of hemicellulose and lignin in the process (Abraham et al., 2011). Surface roughening due to removal of hemicellulose and lignin of LCFs was observed from photomicrographs obtained from SEM and AFM after alkali treatment. Reappearance of the peak following vegetable oil–resin treatment could be interpreted as indicators of a new ester bond formation due to transesterification of the hydroxyl groups in LCFs with triglycerides in vegetable oil. Similarly, the peaks in the 1230–1250 cm^{-1} and 1150–1160 cm^{-1} regions for both jute and

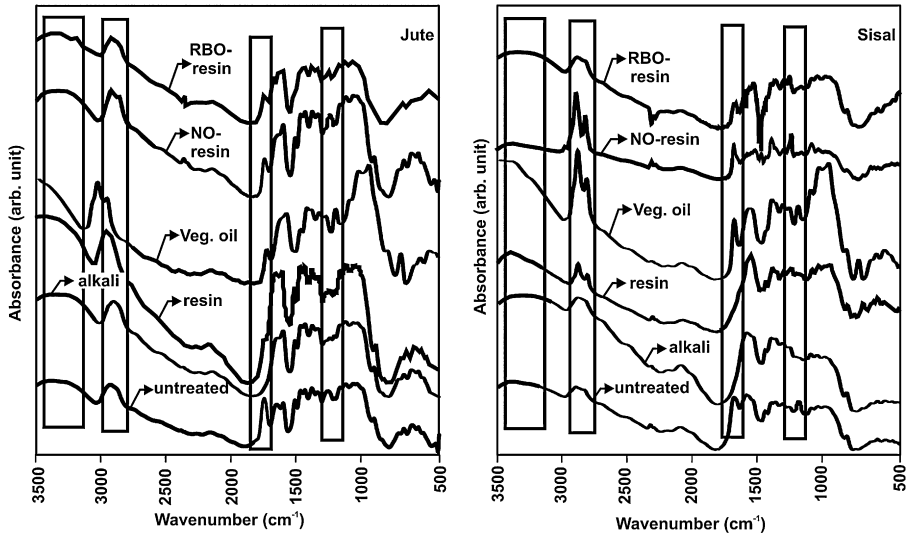

Fig. 3. FTIR spectra of LCFs (RBO: rice bran oil and NO: neem oil).

sisal fibers correspond to glycosidic C–O–C and C–O stretching of ester groups of lignin and hemicellulose (Peng et al., 2011; Bessadok et al., 2009) disappear after alkali treatment and reappear following vegetable oil-resin treatment. This observation also indicates transesterification of hydroxyl groups in LCFs.

FTIR response in the 2800–2950 cm^{-1} region representing C–H stretching vibration of LCFs (Ibrahim, Dufresne, Zawaway, & Agblevor, 2010) was found not to amplify or de-amplify significantly following alkali treatment. The response becomes more intense following vegetable oil and resin treatment due to the attachment of long aliphatic chain of vegetable oil triglyceride to cellulose (Pasquini, Belgacem, Gandini, & Curvelo, 2006) after transesterification.

The FTIR spectra of LCFs treated with vegetable oil only also indicate similar chemical transformation. In contrast, for the LCFs treated with phenolic resin only no transesterification could be inferred from FTIR spectroscopy. However, the FTIR response in the 2800–2950 cm^{-1} region was found to intensify in the resin-only treatment because of attachment of polymeric side chain of phenolic resin to the LCF cellulose.

3.5. Elemental analysis

The results of elemental analysis show the enhancement of the relative weight percentages of carbon, hydrogen, nitrogen and the lowering of relative weight of oxygen in LCFs following vegetable oil–resin treatment (Table 2). Increase of weight percentages of carbon and hydrogen could have resulted from the attachment of long hydrocarbon side chain of vegetable oil triglycerides to free hydroxyl group of cellulose or hemicellulose unit following transesterification. Mass percentage of nitrogen increases possibly because of nitrogenous impurities in vegetable oil. Similar improvement of weight % of carbon and hydrogen and reduction of oxygen was reported by Pasquini et al. (2006) in case of surface esterification reaction of microcrystalline cellulose with ethanol/water mixture in heterogeneous condition.

Table 2
Elemental composition of fibers.

Fibers	Treatment	Experimental values (wt%)				
		C	H	O	N	Residue
Jute	Untreated	45.00	6.20	46.30	0.20	2.30
	NO–resin	57.55	8.10	32.30	0.70	1.35
	RBO–resin	53.30	6.60	38.20	0.80	1.10
Sisal	Untreated	43.30	5.20	48.20	0.30	3.00
	NO–resin	53.40	8.10	36.00	0.60	1.9
	RBO–resin	52.10	7.30	38.40	0.80	1.40

Increase of weight percentages of carbon and hydrogen for NO–resin treatment was found to be more pronounced than that in RBO–resin treatment. This observation indicates that RBO–resin treatment was relatively ineffective in inducing chemical modification in LCFs. As has already been pointed out, enhancements in tensile strength and hydrophobicity were more pronounced in NO–resin treatment compared to RBO–resin treatment. The observations suggest transesterification of OH groups is a major cause for enhancements in tensile strength and hydrophobicity of LCFs.

3.6. Crystallinity

In x-ray diffractograms, all the diffraction peaks for LCFs were observed of the 2θ angles around 16.3°, 22°, and 35°, which represented the cellulose-I structure (Liu, Han, Huang, & Zhang, 2009). Apparent increase in inferred crystallinity of jute and sisal fibers following alkali treatment, Table 3, is possibly because of partial removal of amorphous hemicellulose, lignin and pectin. Inferred crystallinity was found to increase further following vegetable oil–resin treatment for jute fibers. In contrast, for sisal fibers inferred crystallinity reduced marginally after vegetable oil–resin treatment. The reduction is possibly due to the damage in fiber crystals induced by the attachment of long aliphatic chains. Other researchers observed similar reductions in crystallinity in chemical grafting of cellulose with isocyanates (Siqueira, Bras, & Dufresne, 2010). Improved crystallinity resulted from the ordered orientation of fiber crystal following alkali treatment partially imparts

Table 3
Crystallinity (%) of fibers.

Fiber	Treatment	Crystallinity index (%)
Jute	Untreated	67.90
	Alkali	71.30
	NO–resin	73.00
	RBO–resin	72.20
Sisal	Untreated	49.70
	Alkali	69.00
	NO–resin	68.10
	RBO–resin	66.80

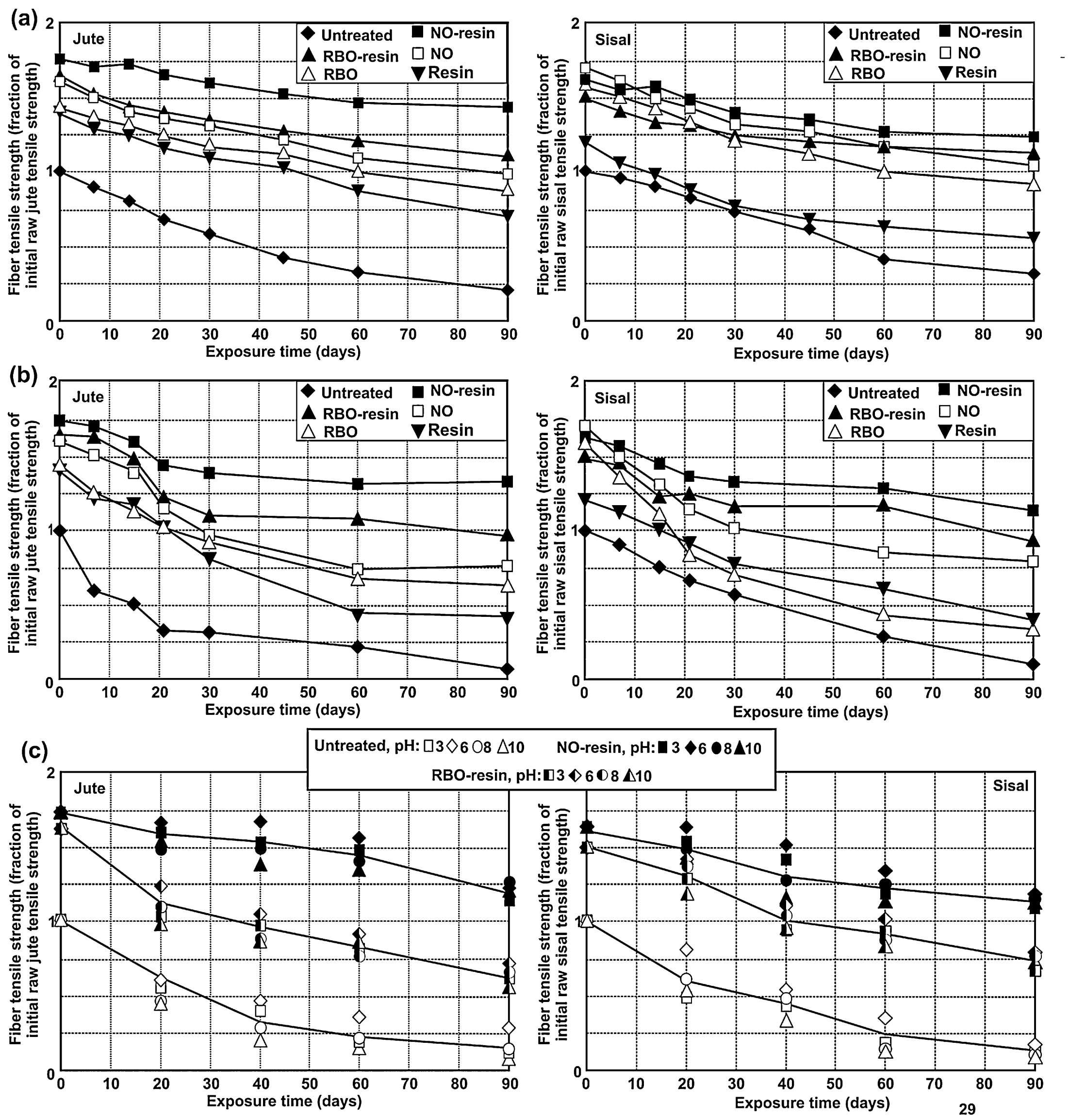

Fig. 4. (a) Degradation of tensile strength upon exposure to composting environment in soil; (b) degradation of tensile strength of LCFs upon exposure to elevated salinity of 3% (by wt) sodium chloride solution; (c) degradation of tensile strength of LCFs upon exposure to different pH environment (pH 3–10).

enhanced tensile strength and hydrophobicity in LCFs (Jacob, Thomas, & Varughese, 2004).

3.7. Durability

Durability of the transesterified fibers was investigated both by exposing the fibers to a composting environment, elevated salinity levels and alkaline and acidic pH conditions. Tensile strength degradation resulting from 90-d exposure to a composting environment is presented in Fig. 4a. These results indicate that vegetable oil–resin treated fibers retain between 70% (for jute) and 63% % (for sisal) of their initial tensile strengths. The corresponding tensile strength retention for untreated fibers was only 28% or less. In fact, the residual tensile strengths for vegetable oil and resin treated fibers exceeded the corresponding initial tensile strengths of untreated fibers by 43% (for jute) to 25% (for sisal).

Tensile strength degradation resulting from 90-d exposure to elevated salinity level is presented in Fig. 4b. These results indicate vegetable oil–resin treated fibers retain between 60% (for jute) and 52% (for sisal) of their initial tensile strengths. The corresponding tensile strength retention for untreated fibers was only 13% % or less. In fact, the residual tensile strengths for vegetable oil and resin treated fibers exceeded the corresponding initial tensile strengths of untreated fibers by 31% (for jute) to 19% (for sisal). Strength loss of LCFs upon saline exposure was resulted from the penetration of NaCl into the void space of fibers (Rowell, 2005).

The LCFs were exposed to series of aqueous solution of different pH ranges from 3 to 10 for 90-d. Degradation was accelerated for LCFs in higher and lower ranges of pH solution (Fig. 4c). Reduction of tensile strength was found to be less prominent for vegetable oil–resin treated LCFs compared to untreated and other treatments. Susceptibility to degradation of LCFs treated with vegetable oil–resin was maximum in solution higher than pH 9. High alkaline pH hydrolyses the ester bond formed in transesterification reaction and results reduction of uniaxial tensile strength. Enhanced degradation in lower pH environment (pH lower than 3) may be due to the presence of higher number of carboxyl groups present on the LCFs surface as stated by Park, Furuno, and Uehara (1996) for wood composites.

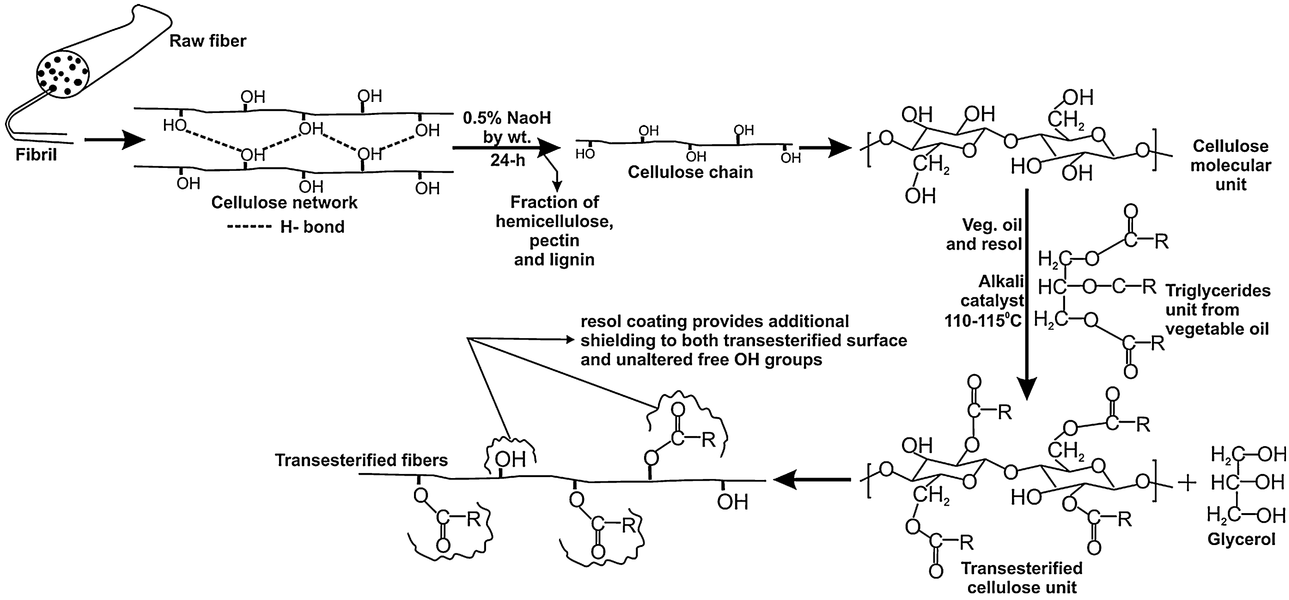

Fig. 5. Schematic representation of probable chemical alteration (transesterification) of fibers during chemical process.

3.8. Inferred chemical changes in LCFs

A schematic mechanism of probable transesterification reaction of LCFs has been shown in Fig. 5. Results obtained from ζ-potential measurement, FTIR-spectroscopy, and elemental analysis were found to point consistently towards possible transesterification of hydroxyl groups in LCFs with triglycerides fatty acid of vegetable oil. The presence of phenolic resin serves its purpose as a coating agent as well a potential antimicrobial agent when used with vegetable oil. Resol coating provides an additional protection to the transesterified fiber surface against the exposure to biological and chemical environments. Hence the durability of the LCFs shows maximum improvement when both vegetable oil along with phenolic resol were used. Less improvement of tensile strength, hydrophobicity and durability of LCFs following phenolic resin treatment only indicates the non-occurrence of the transesterification. It can therefore be proposed from the underlying evidences that transesterification would be the reason for enhanced tensile strength, hydrophobicity and durability for LCFs.

4. Conclusions

A process for transesterifying jute and sisal by treating them with a combination of rice bran oil and neem oil with resorcinol–tannin–cashew nut shell liquid based phenolic resin (resol type) at elevated temperature has been developed for enhancing their hydrophobicity, tensile strength and durability. The treatment involving neem oil and resol caused water absorption to decrease from 255% to 79% for jute fibers and from 185% to 62% for sisal fibers. Correspondingly, short term tensile strength increased by 75% and 61% for jute and sisal fibers. Treatments with combinations of rice bran oil and resol, neem oil or rice bran oil without resol, and resol without neem oil or rice bran oil were found to be relatively less effective.

Neem oil and resol treated jute and sisal fibers were, on an average, found to retain 70% and 63% of their initial tensile strengths, respectively, upon being exposed to biological degradation in a composting condition over 90 days duration. The corresponding tensile strength retention for untreated jute and sisal fibers were only 28% and 32%, respectively.

After 90-day exposure to 3% aqueous saline solution of NaCl, neem oil and resol treated jute and sisal fibers retained 60% and 52% of their initial tensile strength, while untreated jute fibers retained only 9% and sisal fibers 13%. Tensile strength retention for neem oil and resol treated jute and sisal fibers were 48% and 55%, respectively, after 90-day exposure to pH between 3 and 10. In comparison, untreated jute fibers only retained 12% and sisal fibers 10% of their initial tensile strengths.

Acknowledgements

We thank National Jute Board (NJB), India for funding this investigation. The first author (PS) is thankful to CSIR, India for his fellowship. We acknowledge the support of Dr. A.K. Ganguly, Professor, Department of Chemistry, Indian Institute of Technology, Delhi, India for providing the experimental facility for measuring zeta potential of the fibers.

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