

Effect of Crosslinker and Nanoclay on Jute Fabric Reinforced Soy Flour Green Composite

Murshid Iman, Tarun K. Maji

Department of Chemical Sciences, Tezpur University, Assam 784028, India

Correspondence to: T. K. Maji (E-mail: tkm@tezu.ernet.in)

ABSTRACT: Bio-based composites were prepared by using soy flour, jute, glutaraldehyde (GA), nanoclay, and glycerol. An optimum concentration of glycerol was used as a plasticizer. The synthesized composites were characterized by various techniques such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffractometry (XRD), Fourier transform infrared spectroscopy (FTIR), and thermogravimetric analysis (TGA). The exfoliation of clay layers was detected both by XRD and TEM study. FTIR study showed an interaction between clay, jute, and soy flour. The percentage content of GA and nanoclay was found to have profound influence on various physical properties of the composites. The increase in the concentration of GA and nanoclay improved the thermal stability, flame retardancy, dimensional stability, and most importantly the mechanical properties of the prepared composite. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: biofibers; crosslinking; flame retardance; mechanical properties; nanocomposites

Received 12 December 2011; accepted 16 March 2012; published online 00 Month 2012

DOI: 10.1002/app.37713

INTRODUCTION

Conventional polymers which are obtained from petrochemicals are non-renewable and environment unfriendly.^{1,2} The environmental impact of polymeric waste is increasing global concern, and alternative disposal methods are limited. Besides this, the earth has finite resources in terms of fossil originated fuel. So, there is a need to reduce the use of such conventional polymers by using bio-degradable composite materials which are produced from renewable resources such as agricultural and biological origin. Various bio-degradable polymers such as starch, soy protein, whey protein, wheat gluten, zein, polyhydroxy butyrate-*co*-valerate (PHBV), etc., have been used with bio-fibres (like jute, hemp, flax, ramie, etc.) as matrix and reinforcing materials to form eco-friendly product, with minimum impact on the environment.¹ Moreover, the use of natural fibres to reinforce thermoplastics such as polypropylene and polyethylene as an alternative to synthetic or glass fibres has been and continues to be the subject of research and development.^{3,4} The fibre reinforcement of biopolymers such as PLA can produce composites with suitable mechanical properties for light weight construction materials. Plackett et al. have found that the tensile strength and stiffness of PLA can be approximately doubled when jute fibre as reinforcement is used.⁵

Bio-fibres offer several advantages such as low cost, easy availability, low density, high specific strength, and renewability. Apart from these advantages, bio-fibres have some disadvantages like variation in mechanical properties which depend on several factors such as moisture content, cultivation area, processing methods, and poor thermal stability. These fibres in combination with the bio-degradable matrices can produce environmentally friendly “green” products with improved properties.^{6–10} Jute, a kind of natural fibre, is widely available and can be used for making composites. Surface modification like dewaxing and mercerization of jute fabrics are essential before their use for composite preparation. Surface modification will not only decrease the moisture absorption property but also concomitantly increase the wettability of fabrics with matrix polymer and the interfacial bond strength. Both are critical factors for obtaining better mechanical properties of the composites.

Soy protein is one of the less expensive bio-polymers abundant worldwide. It was first introduced by Henry Ford in automobile manufacturing as alternating source for plastics and fibers.¹¹ Its purification process is benign and environment friendly. This protein can also be used as resin due to its ability to form ductile and viscous polymers. Out of different varieties available commercially, defatted soy flour (SF) is the least expensive one. SF contains approximately 55% protein and 32% carbohydrate.

© 2012 Wiley Periodicals, Inc.

Soy protein consists of different polar and nonpolar amino acids. These amino acids present as cystine, arginine, lysine, histidine, etc., may be capable of reacting with a crosslinking agent to form a composite with improved properties.¹² Out of the various crosslinking agents glutaraldehyde is found to interact strongly with soy flour resulting in an improved tensile, thermal properties and water resistance over uncrosslinked soy flour composites.^{1,13–15}

Nanotechnology deals with material in sub micron level. It has been successfully applied in many fields. Nanomaterials can provide better reinforcing efficiency because of their large aspect ratio. The incorporation of the nanoparticles can play a vital role in improving the properties of composite based on natural polymer and plant fibre. Among all the potential nanocomposites precursors, montmorillonite (MMT) is widely used. Few reports¹⁶ are available regarding natural polymer/natural fibre based nanocomposites. It is envisaged that a systematic and thorough investigation of such type of composite may provide some valuable information for the development of green nanocomposites in future.¹⁷

In this report, we have studied the impact of nanoclay on the various properties of the composite formed by a mixture of jute fabric, soy flour, nanoclay, and glutaraldehyde. Furthermore, the effect of glutaraldehyde on different properties of the composite has also been studied.

EXPERIMENTAL

Materials

Soy flour (SF) was provided by Raja Soya, Tezpur (Assam, India). Jute fabrics (0.400 g/cm²) were purchased from local market (Tezpur, Assam). GA (25%, w/v), benzene (purity >99%), and NaOH (purity >97%) pellets used for this study were obtained from Merck Private Limited (Mumbai, India). Glycerol (AR grade) and montmorillonite K-10 clay powder (purity 99.99%) were obtained from Qualigens Fine Chemicals (Mumbai) and Sigma Aldrich, respectively. All other chemicals received as such were used without any further treatment.

Methods

Surface Modification of Jute. Jute fabrics (J) were treated with 2% soap solution at 70°C for 1 h followed by washing with distilled water and finally drying in a vacuum oven at 100°C for 12 h. The washed fabrics were dewaxed by treatment with a mixture of alcohol and benzene (1 : 2) for 72 h at 50°C. It was washed with distilled water and dried for 12 h. The fabrics were then treated with 5% (w/v) NaOH solution for 30 min at 30°C, and washed with distilled water for several times to leach out the absorbed alkali. The fabrics were finally kept immersed in distilled water overnight and were washed repeatedly to avoid the presence of any trace amount of alkali. The alkali treated fabrics were dried in a vacuum oven at 70°C for 12 h, and stored at ambient temperature in a desiccator.

Preparation of the Slurry. “Green” composites were synthesized from suitable resin prepared by using SF powder which was first mixed thoroughly with deionized water at 1 : 10 ratio (by w/w) and stirred continuously. Then glycerol was added as a plasticizer. SF was found to be brittle, weak and difficult to

process into useful films in absence of plasticizer. The slurry containing SF and glycerol was transferred to a 500 mL round bottom flask and stirred with a mechanical stirrer maintaining the temperature at 55°C ± 5°C for 4 h. The temperature of the slurry was then brought down to 35°C ± 5°C. After that GA was added and stirred for another 5 min at that temperature. The amount of GA was varied from 30 to 70% (w/w of SF). This stage is referred to as pre-cured resin. To prepare clay filled resin, desired amount of clay [1–5% (w/w) of SF] was first taken in a beaker containing water, stirred for 6 h using magnetic stirrer followed by sonication for 30 min under 0.5 cycle and a wave amplitude of 140 μm using a sonicator (model Heilscher UP200S, Germany) and finally added to the pre-cured resin.

Impregnation of Jute Fabrics and Fabrication of Composites. The whole resin was then poured in a bowl and the surface modified jute fabric was dipped into the resin slurry for 24 h at ambient temperature (25°C). The impregnated jute fabrics were placed in Teflon coated glass plate and dried over a heating plate at 60–70°C. The weight of the jute fabrics was noted before impregnation (W_1).

Composite laminates were prepared by the method of film stacking. The layers of impregnated jute fabric were placed on one another on 15 levels in a metal mould of thickness 3 mm. The laminates were then compression moulded in a compression moulding press (Santec, New Delhi) at 80°C under a pressure of 100 MPa. The laminates were 3 mm in thickness. The final weight of the composite was noted (W_2). The calculations were made as per the following equations:

$$\text{Percentage of Jute in the Composite} = (W_1/W_2) \times 100 \quad (1)$$

$$\text{Percentage of Resin in the Composite} = [(W_2 - W_1)/W_2] \times 100 \quad (2)$$

We have prepared the samples as coded in Table I. The wt (%) of the components viz. SF, glycerol, and Jute were kept constant in all the samples where as the wt (%) of GA and nanoclay were varied. The wt (%) of the various components used for the synthesis of the composite are provided in Table I.

MEASUREMENTS

X-Ray Diffractometry (XRD)

The XRD measurements were carried out in a Rigaku X-ray diffractometer (Miniflex, UK) using Cu K α ($\lambda = 0.154$ nm) radiation at a scanning rate of 2°/min with an angle ranging from 2° to 30° to know the degrees of clay intercalation in soy flour composite.

Transmission Electron Microscopy (TEM)

The study of the dispersion of silicate layers of nanoclay particles in jute reinforced SF composite was carried out by using Transmission Electron Microscope (JEOL JEM 2100) at an accelerating voltage of 200 kV.

Scanning Electron Microscopy (SEM)

The surface morphology of some of the as such samples and fracture flexural test samples were studied by using a JEOL

Table I. Composition of Plasticized Soy Flour Based Composite

Sample	Starch (wt %) ^a	Glycerol (wt %)	GA ^b (wt %)	Jute (wt %)	MMT (wt %)
S/J	100	5	-	75	-
S/J/G30	100	5	30 (6)	75	-
S/J/G40	100	5	40 (8)	75	-
S/J/G50	100	5	50 (10)	75	-
S/J/G60	100	5	60 (12)	75	-
S/J/G70	100	5	70 (14)	75	-
S/J/G50/M1	100	5	50	75	1
S/J/G50/M3	100	5	50	75	3
S/J/G50/M5	100	5	50	75	5

^aTwenty gram of soy flour is assumed to be 100., ^bThe percentage of GA with respect to Soy flour. The values in the parenthesis indicate the amount of GA in gram.

scanning electron microscope (model JSM-6390LV) at an accelerating voltage of 5–15 kV. All of the samples were platinum coated before observation.

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra of the post cured composite samples were recorded in FTIR Nicolet, Impact 410 spectrophotometer. Small quantities of finely powder composite samples were dispersed in KBr and further ground to a fine mixture in a mortar before pressing to form transparent KBr pellets for analysis.

Mechanical Property

The flexural properties of the composite specimens were measured by using Universal Testing Machine-HOUNSEFIELD, England (model H100K-S) at a crosshead speed of 2 mm/min at room temperature according to ASTM D-790. Ten samples were tested for each set and the mean value was reported.

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis of the composite samples were done by using Shimadzu TGA 50, thermal analyser under the nitrogen flow rate of 30 mL/min at the heating rate of 10°C/min from 0° to 600°C.

Limiting Oxygen Index (LOI)

LOI values were measured by flammability tester (S.C. Dey, Kolkata) according to ASTM D-2863 method. The ratio of nitrogen and oxygen was recorded at which the sample continued to burn for at least 30 s.

Limiting oxygen index (LOI) =

$$\left[\frac{\text{Volume of O}_2}{\text{Volume of (O}_2 + \text{N}_2)} \right] \times 100. \quad (3)$$

Dimensional Stability

Dimensions of oven dried samples were measured and conditioned at room temperature (30°C) and 30% relative humidity. The samples were then kept in humidity chamber at room temperature maintaining relative humidity of 65% for a defined time period (0–72 h). The specimens were taken out from the humidity chamber after stipulated time period and volume were measured with the help of slide callipers. Swelling is considered

as a change in volume and expressed as percentage of volume increase compared to oven dried samples. The percentage of swelling in water vapor was calculated as formula given below:

$$\% \text{ Swelling} = \left[\frac{(V_t - V_0)}{V_0} \right] \times 100$$

where “ V_t ” is volume of the sample after time “ t .” “ V_0 ” is initial volume of composite sample before water vapor absorption.

RESULTS AND DISCUSSION

X-Ray Diffractometry Results

Figure 1(a–c) represents the XRD pattern of pure clay, jute, and SF, respectively. A broader peak at $2\theta = 19^\circ$ was found to appear in SF diffractograms.¹⁸ Figure 1(d,e) represents the XRD pattern of mixture of S/J and S/J/G50, respectively. It could be seen from the XRD pattern that the mixing of the polymer components along with the crosslinker did not modify the crystallinity of either of the components. However, on incorporation of nanoclay in the synthesized composite (prepared by SF, Jute,

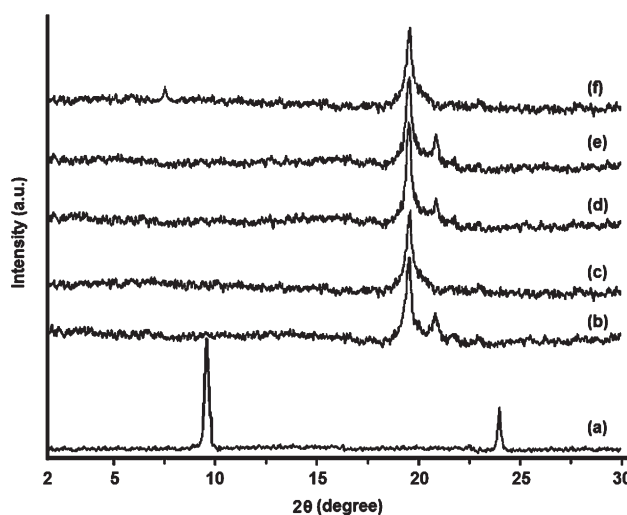


Figure 1. XRD patterns of (a) clay, (b) Jute, (c) soy flour, (d) S/J, (e) S/J/G50, and (f) S/J/G50/M5.

GA, and nanoclay), a change in the XRD pattern was observed. In the absence of the nanoclay, the composite shows sharp peaks at $2\theta = 22^\circ$ (002 plane of cellulose I) and 19° (101 plane of cellulose II).¹⁰ However, after its modification with nanoclay the intensity of the peak at $2\theta = 22^\circ$ corresponding to 002 plane of cellulose I get diminished and a low intense peak at $2\theta = 7.5^\circ$ was newly emerged. This indicated that the clay particles were partially exfoliated and dispersed into the composite. The lowering of intensity of the peak at $2\theta = 9^\circ$ indicated the breakdown of the layered structure of nanoclay in the treated composite.¹⁹

There were no characteristic changes in the XRD patterns recorded for various samples prepared by treating with different concentrations of glycerol (not shown in Figure 1).

Transmission Electron Microscopy Study

TEM analysis was carried out to verify the extent of exfoliation of nanoclay particles in the prepared composites and was presented in Figure 2. Figure 2(a) represents the TEM micrographs without clay composite in 200 nm range whereas Figure 2(b,c) are taken within a range of 200 and 600 nm, respectively. The dispersion of clay layers as dark lines (shown by arrow mark) was observed in both the images. A closer look at Figure 2(a,b) revealed the successful incorporation of nanoclay into the composite which was clearly evident in Figure 2(b) but not in Figure 2(a). Moreover, it was evident from Figure 2(b,c) that the clay layers were delaminated into thin lamellas by soy protein with a dimension of about 10–15 nm in thickness. This suggested that the nanoclay layers were dispersed and partially exfoliated into soy protein matrix. Similar type of delaminated structure of MMT was also reported in various articles and had been considered as a successful intercalation of the nanocomposites.^{20,21} These transmission electron microscopic analysis are in accordance with the XRD findings. So, it could be concluded that jute reinforced soy flour clay nanocomposites with a delaminated structure could be prepared by solution induced intercalation method in neutral aqueous medium.

Scanning Electron Microscopy Study

The SEM micrograph of SF as shown in Figure 3(a) indicated that the particles were irregular compact disc shape,¹³ whereas the SEM micrographs of the jute fibers were smooth and regular as observed from Figure 3(b). Figure 3(c,d) showed micrographs of composites without and with GA. From the micrographs, it was observed that composites with GA crosslinks showed better adhesion of the SF matrix onto the jute surface compared to the composites without GA. The surface of the composite having GA was less smoother compared to that of composite without GA. This was due to the less adherence of the resin to the fibre surface. On addition of GA into the composite, less fiber was seen to protrude out of the composite [Figure 3(e)]. From Figure 3(d), it was also found that the surface of glutaraldehyde crosslinked S/J composite was rough.²² However, on addition of the clay nanoparticles, the brittleness along with the roughness of the composites was increased [Figure 3(f–i)]. This might be due to the fact that the clay particles enhanced the interaction between resin and jute surface through its hydroxyl groups. This resulted in enhancement of

adhesion and consequently less pull out of fibres from the fracture surface.¹⁶ The brittleness and roughness of the composite surface was found to increase with the increase in concentration of nanoclay particles from 1 to 5% [Figure 3(f,h)]. The increase in roughness and brittleness might be due to the adherence of either the soy flour or the soy flour/clay to the jute surface.

Fourier Transform Infrared Spectroscopy Study

FTIR spectra for soy flour, jute, clay, S/J, S/J/G50, and S/J/G50/M are presented in Figure 4. The FTIR spectra for all the samples except clay and jute showed the peaks in the region $3400\text{--}3000\text{ cm}^{-1}$, which could be attributed to the --OH and --NH stretching vibrations, respectively. The spectrum of SF [Figure 4(a)] shows peaks in the region 1648, 1544, and 1248 cm^{-1} for C=O stretching of amide – I, --NH bending of amide – II and C--N stretching of amide – III.²³ A peak was observed in the region 1738 cm^{-1} in the jute spectrum which might be due to the C=O stretching vibration of ester groups of hemicelluloses. Similarly, the peaks appeared in the FTIR spectrum of jute at 1640, 1254, and $1057\text{--}1116\text{ cm}^{-1}$ were for C=O stretching, --C--O--C-- bond in cellulose chain, and C--O stretching.²⁴ The peak observed in the region 1619 cm^{-1} was due to --OH bending vibration [Figure 4(b)]. The peaks shown in the range $1030\text{--}460\text{ cm}^{-1}$ were the characteristic peaks of oxide bonds of metals (M--O) like Si, Al, Mg, etc., present in the nanoclay [Figure 4(c)].

Characteristics peaks of soy flour and jute were apparent in all the spectra of the prepared composite [Figure 4(d–f)]. However, on addition of GA into the S/J composite [Figure 4(e)], the peak intensities in the region $3400\text{--}3000\text{ cm}^{-1}$ assigned for --OH and --NH stretching vibrations were found to decrease. Further, two peaks corresponding to 2230 and 1167 cm^{-1} assigned for --N--C=O and C--N stretching vibration were appeared [Figure 4(e,f)]. This might be attributed to the interaction of --OH and --NH_2 groups present in jute and SF with the GA. It was reported in the literature that GA could exist in different form in the solution and could able to crosslink proteins, leading to formation of a broad range of conjugates.²⁵ The probable interaction of soy protein and jute with GA is discussed below. On addition of MMT, the peak intensity in the region $3400\text{--}3000\text{ cm}^{-1}$ corresponding to --OH and --NH stretching vibration was reduced and sharpened. The peak intensities in the region $1030\text{--}460\text{ cm}^{-1}$ and 1620 cm^{-1} were also found to enhance. These results further confirmed the interaction of clay particles with GA and S/J composite.²⁶

The FTIR spectrum (not shown in Figure) taken for samples with different concentrations of glycerol did not exhibit any significant change in the peak intensity except the broadening of the --OH peak.

Mechanical Property Study

The flexural properties of composites with varying percentage of glutaraldehyde and clay are shown in Figure 5. The values shown in the Figure 5 are the mean value of 10 readings. It was observed that both the flexural modulus and strength increased with the increase in the concentration of glutaraldehyde. The increase in flexural values could be ascribed to the formation of crosslinking between the polar groups of soy flour and jute by glutaraldehyde as shown in Figure 6. The crosslinking between

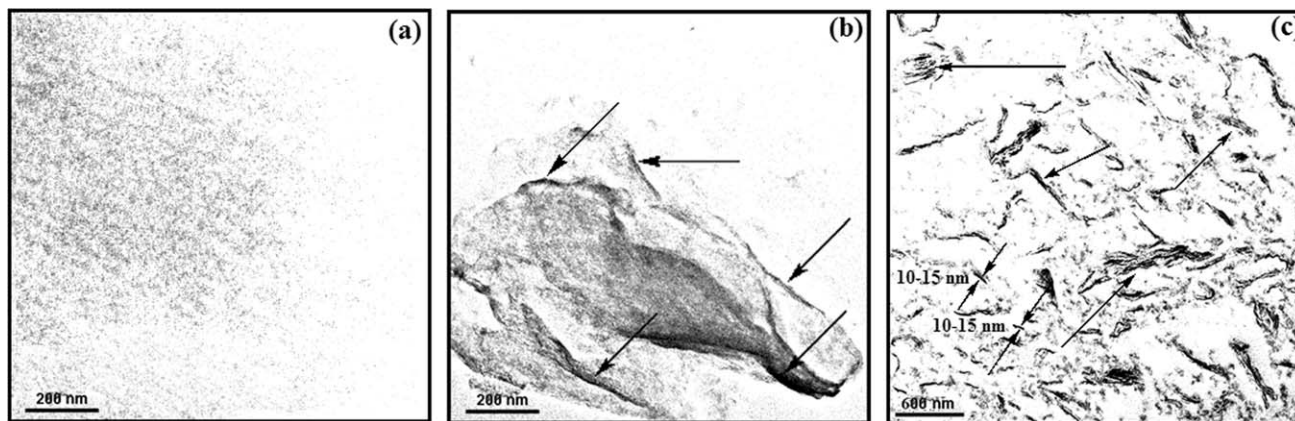


Figure 2. TEM micrographs of soy flour/jute composite (a) without clay taken within 200 nm range and (b) and (c) with clay composite at 200 nm and 600 nm scale.

soy protein and cellulose fibres was reported in the literature.²⁷ Although the mechanical properties of composites were found to increase with the concentration of GA, however, the increase in strength was significant up to 50%. Beyond that we did not

observe much improvement in the flexural properties, which may be the case that the crosslinking sites of SF and jute surface became saturated. Hence, considering the 50% concentration of the crosslinker as optimum, we modified the composite (S/J/

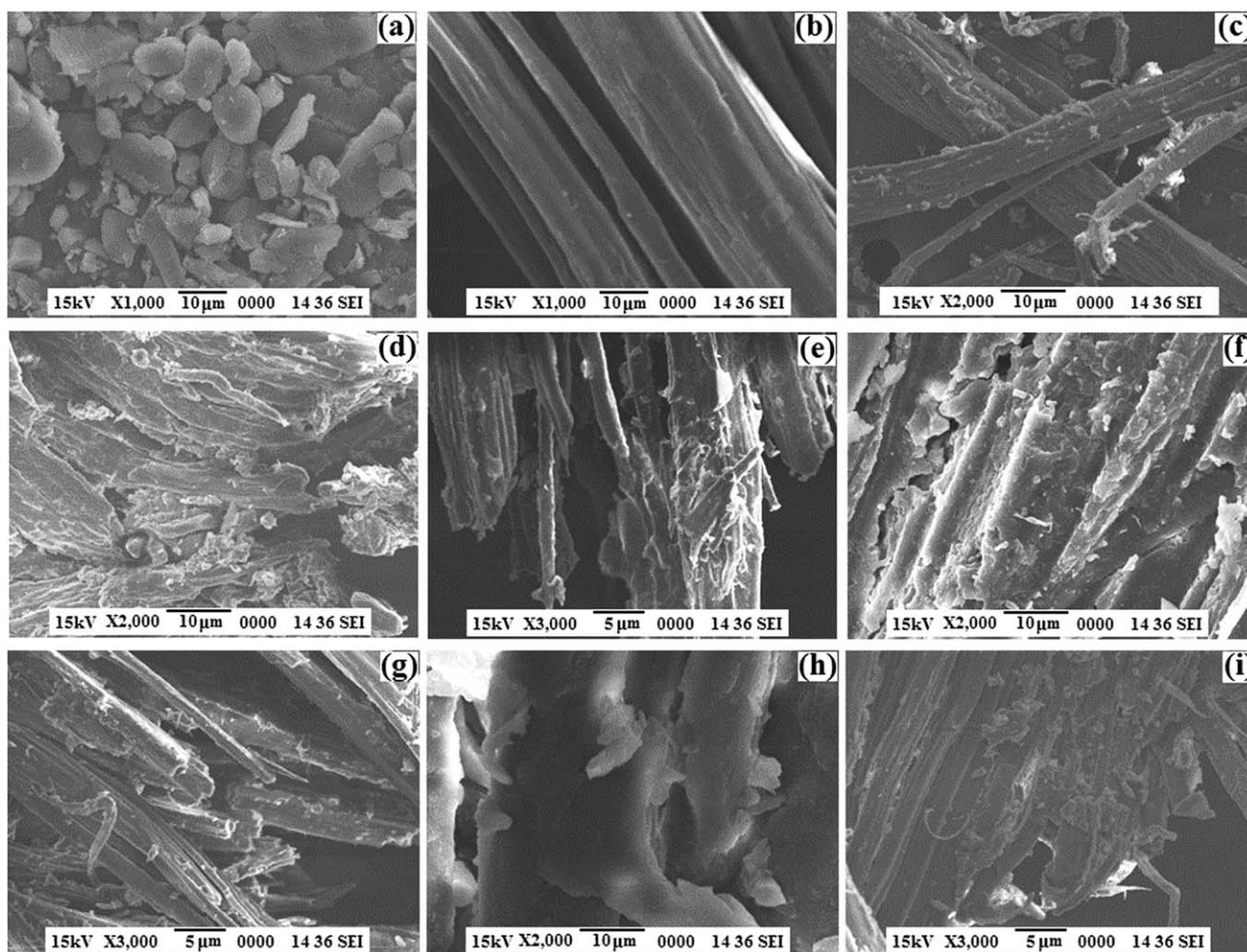


Figure 3. SEM micrographs of (a) soy flour, (b) jute, (c) S/J surface, (d) S/J/G50 surface, (e) S/J/G50 fracture surface, (f) S/J/G50/M1 surface, (g) S/J/G50/M1 fracture surface, (h) S/J/G50/M5 surface, and (i) S/J/G50/M5 fracture surface.

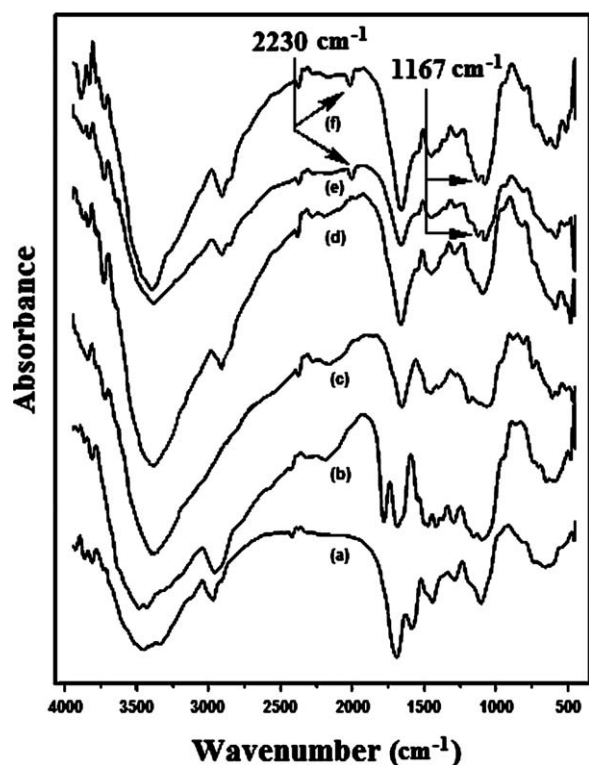


Figure 4. FTIR spectra of (a) soy flour, (b) Jute, (c) clay, (d) S/J, (e) S/J/G, and (f) S/J/G/M.

G50/M1, S/J/G50/M3, and S/J/G50/M5) with different percentage of nanoclay ranging from 1 to 5%. The flexural properties of the samples viz. S/J/G50/M1, S/J/G50/M3, and S/J/G50/M5 were found better compared to the clay untreated samples. The higher the percentage of clay, the higher was the flexural properties. The increase in flexural values was due to the restriction

in the mobility of the intercalated polymer chains present inside the silicate layers of clay.²⁸

Thermal Property Study

The initial decomposition temperature (T_i), maximum pyrolysis temperature (T_m), decomposition temperature (T_D) at different weight loss (%) and residual weight (RW) for soy flour, jute, S/J composites with or without crosslinker, and nanoclay treated S/J composite are shown in Table II. T_i values of S/J composites were found to enhance with the increase in the percentage of crosslinker. T_i values increased further due to incorporation of clay. T_m value for jute apparent at 368°C, was due to the decomposition of cellulose.²⁹ In the case of soy flour, T_m values for the first and second stages of pyrolysis were due to the dissociation of the quaternary structure of proteins and degradation of peptide bonds in the amino acid residues.³⁰ T_m values for both the stages of pyrolysis were found to increase as the percentage of crosslinker were increased. Nanoclay incorporation further increased the values. T_D values of the crosslinked S/J composite were higher than uncrosslinked S/J composite. The higher the crosslinker concentration, the higher was the T_D value. This might be due to the formation of crosslinking caused by the interaction between glutaraldehyde and different polar groups such as amine, carboxyl, and hydroxyl group present in soy flour and jute. The interaction is shown in Figure 6. The T_D values were improved further when clay were added to it. The increase of thermal stability is attributed to the hindered diffusion of volatile decomposition products within the nanocomposites.³¹ This might be also due to the physicochemical adsorption of the volatile degradation products on the silicates.³² The silicates delay the volatilization of the products originated by carbon-carbon bond scission in the composite.³³ Clay treated composite showed a marginal increase in RW values over clay untreated composite. These results provide evidence that the thermal stability of the S/J composites increased on addition of crosslinker and nanoclay.

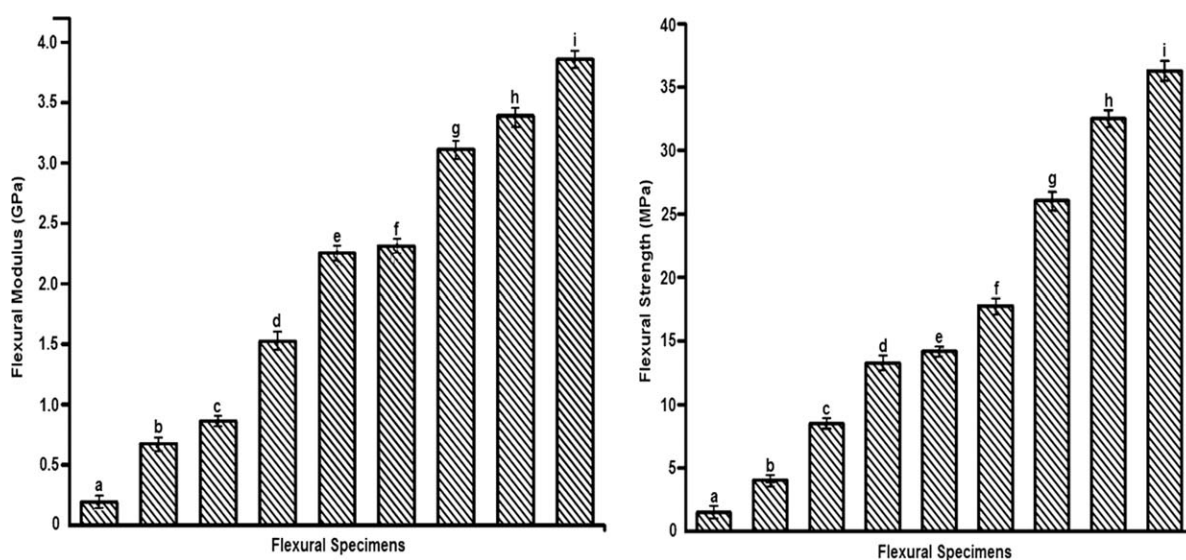


Figure 5. Mechanical properties of (a) S/J, (b) S/J/G30, (c) S/J/G40, (d) S/J/G50, (e) S/J/G60, (f) S/J/G70, (g) S/J/G50/M1, (h) S/J/G50/M3, and (i) S/J/G50/M5.

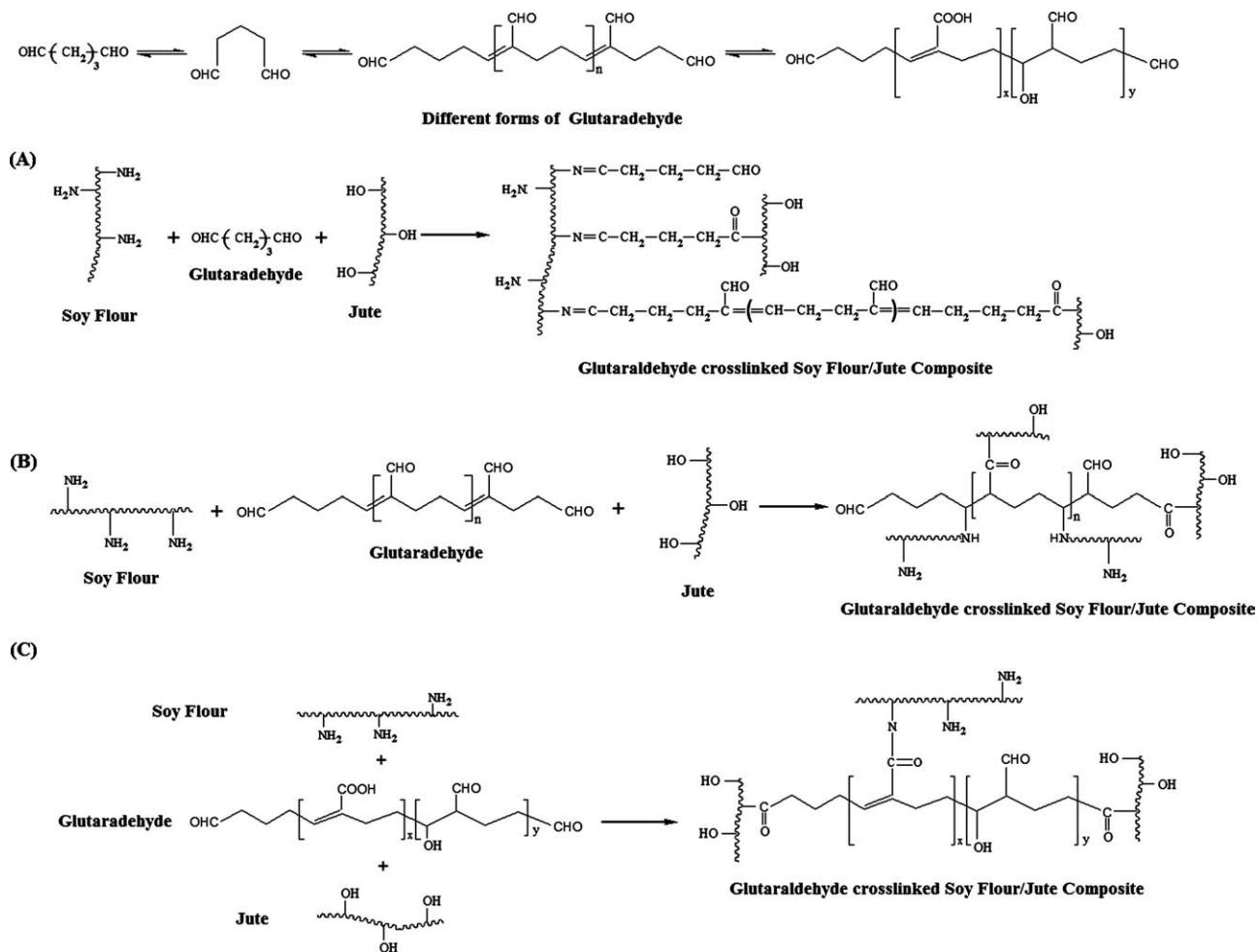


Figure 6. Schematic diagram of glutaraldehyde crosslinked soy flour/jute composite.

Limiting Oxygen Index study

The LOI values of the S/J composites with different percentage of crosslinker and clay are shown in Table III. From that table, it was observed that LOI value increased with the increase in crosslinker percentage. Since GA formed crosslinks between jute and soy flour and it increased with the increase in the concen-

tration of glutaraldehyde. The network structure would restrict the accessibility of oxygen for the production of degradable components from the composites and hence LOI value would be higher. LOI values were further improved with increasing concentration of nanoclay and were found more than the nanoclay untreated composite. Jute fabrics primarily composed of

Table II. Thermal Properties of Soy Flour, Jute, and S/J Glutaraldehyde and Nanoclay Composite

Sample particulars	T_i	T_m^a	T_m^b	Temperature of decomposition at different weight loss (%)						RW % at 600°C
				20	30	40	50	60	70	
Soy Flour	182	235	308	255	285	315	337	394	29	
Jute	195		368	326	347	360	364	368	7	
S/J	168	221	309	250	280	302	325	378	26	
S/J/G30	187	230	313	254	282	310	326	363	27	
S/J/G50	191	234	317	261	285	312	329	356	28	
S/J/G70	230	326	378	286	290	321	332	344	30	
S/J/G50/M1	200	250	322	250	292	322	330	382	30	
S/J/G50/M5	214	252	325	268	300	327	364	427	31	

^a T_m value for first step, ^b T_m value for second step.

Table III. Limiting Oxygen Indices and Flaming Characteristics of the Prepared Composites

Samples	LOI (%)	Flame description	Smoke & Fumes	Char
S/J	29 (\pm 1.0)	Candle like flame	Small and black smoke	Little
S/J/G30	29 (\pm 2.0)	Small localized flame	Small and black smoke	Little
S/J/G40	38 (\pm 1.0)	Small localized flame	Small and black smoke	Little
S/J/G50	38 (\pm 3.0)	Small localized flame	Small and black smoke	Little
S/J/G60	44 (\pm 1.0)	Small localized flame	Small and black smoke	Little
S/J/G70	47 (\pm 2.0)	Small localized flame	Small and black smoke	Little
S/J/G50/M1	50 (\pm 2.0)	Small localized flame	Small and black smoke	Higher
S/J/G50/M3	56 (\pm 1.0)	Small localized flame	Small and black smoke	Higher
S/J/G50/M5	56 (\pm 1.0)	Small localized flame	Small and black smoke	Higher

plant materials cellulose and lignin which require a very low amount of oxygen for the production of flammable volatiles and propagation of flame and hence showed very low LOI value. The addition of the clay particles produced a silicate char on the surface of the composites which increases their flame resistance property.³⁴ The silicate rich surface had better barrier property to heat and oxygen transport due to which ignition of the composite delayed. The higher the percentage of clay, better was the resistance of flame propagation and hence higher the values of LOI.

Correlation Between Mechanical, Thermal, and LOI Study

From the above mechanical, thermal, and LOI studies it was found that all these properties were significantly improved on modification of the S/J composite with crosslinker, GA, as well

as with nanoclay. The plot of residual weight (%) at 600°C, i.e., the thermal properties against LOI values gave the regression value (R^2) to be 0.964, which indicated a good correlation between these two properties [Figure 7(a)]. Furthermore, the co-efficient value in the equation shown in the plot was found to be positive indicating an increase in thermal properties with the increase in the LOI values or vice versa. Similarly, the plot of thermal versus mechanical and LOI versus mechanical also showed the R^2 value as 0.9017 and 0.9541, respectively, and their respective equations also showed positive slope. According to regression analysis, a value of $R^2 > 0.8$ was considered to be significant.³⁵ From our analysis, the R^2 value was found to be highly significant hence we could conclude that there was an intrinsic link between these three properties, e.g., increases in the thermal property increased the mechanical as well as LOI

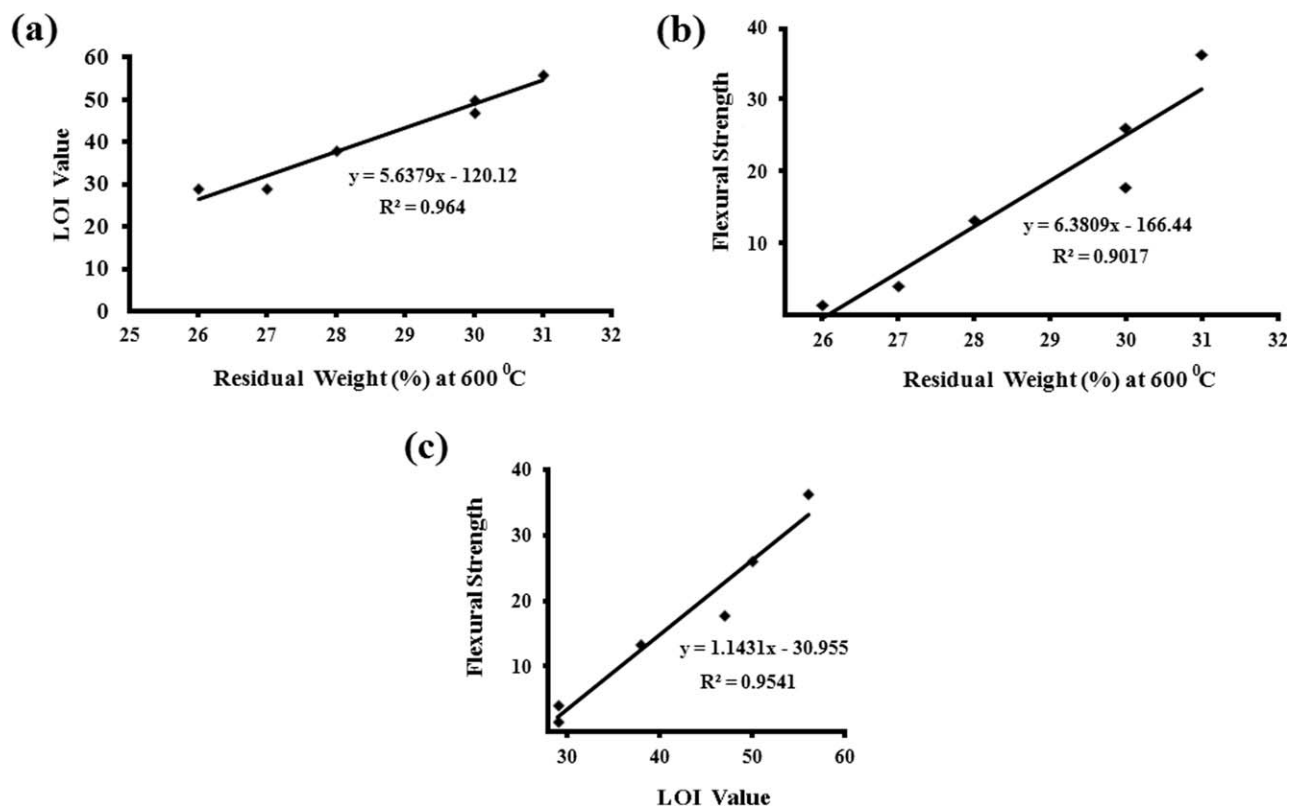


Figure 7. (a) Plot of residual weight (%) versus LOI value, (b) plot of residual weight (%) versus flexural strength, and (c) plot of LOI value versus flexural strength.

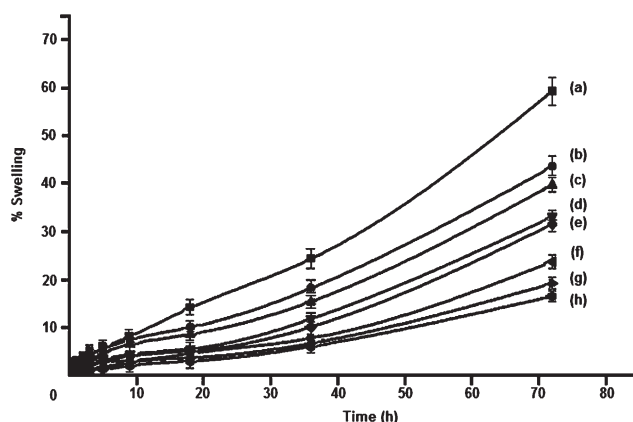


Figure 8. Swelling behavior of (a) S/J, (b) S/J/G30, (c) S/J/G40, (d) S/J/G50, (e) S/J/G70, (f) S/J/G50/M1, (g) S/J/G50/M3, and (h) S/J/G50/M5.

values. Moreover, the improvement in all the properties (e.g., mechanical, thermal, LOI) might be due to the crosslinks formed between SF and Jute by GA as shown in Figure 6.

Dimensional Stability Test

The effect of swelling in water vapor at room temperature and 65% relative humidity for the composite samples for different time periods is shown in Figure 8. From the Figure, it was found that the composites having higher percentage of GA showed less swelling than the composites containing lower percentage of glutaraldehyde. Composites containing higher percentage of glutaraldehyde swelled less due to higher crosslink densities and less availability of the polar groups.¹⁵ Clay treated composites swelled less than those of clay untreated samples. The higher the amount of clay, the lower was the swelling. The silicate layer of clay provided a tortuous path which hindered the diffusivity of water through the composites.³⁶

CONCLUSION

Composites prepared by using renewable resources such as soy flour and jute were characterized by various techniques. The effect of the crosslinking agent, GA and the nanoclay particles were studied. The incorporation of the crosslinking agent improved the physicochemical properties such as mechanical, thermal, dimensional stability, and flame retardancy via a covalent interaction of the aldehydic group of the crosslinker with the hydroxyl and amino group of the jute and SF. The optimum concentration of GA for such improvement on the physical properties of the synthesized composites was found to be 50%. The exfoliation of nanoclay was studied by XRD and TEM. SEM study showed that the surface of the composite became rough due to the presence of nanoclay and SF. The higher the percentage of clay, the higher was the roughness. The presence of the covalent interaction between the crosslinker and S/J composite was confirmed by FTIR analysis which clearly shows an additional peaks at 2230 and 1167 cm^{-1} due to -N-C=O and C-N stretching vibration. On addition of nanoclay to the resultant composites viz. S/J/G50/M1, S/J/G50/M3, and S/J/G50/M5, the mechanical properties, flame retardancy, and dimensional stability were found to be improved further. The intrinsic correlation among the three properties namely thermal, mechanical,

and LOI study was observed by the regression analysis. Such type of nanoclay modified composites obtained from renewable sources could be considered eco-friendly compared to the composites obtained from conventional plastics and fibers whose replacement is of global concern.

ACKNOWLEDGMENTS

The authors are thankful to Department of Science and Technology (SR/S5/GC-13/2008), New Delhi for financial support.

REFERENCES

1. Chabba, S.; Matthews, G. F.; Netravali, A. N. *Green. Chem.* **2005**, *7*, 576.
2. Mohanty, A. K.; Misra, M.; Hinrichsen, G. *Macromol. Mater. Eng.* **2000**, *276/277*, 1.
3. Eichhorn, S. J.; Baillie, C. A.; Zafeiropoulos, N.; Mwaikambo, L. Y.; Ansell, M. P.; Dufresne, A.; Entwistle, K. M.; Herrera-Franco, P. J.; Escamilla, G. C.; Groom, L.; Hughes, M.; Hill, C.; Rials, T. G.; Wild, P. M. *J. Mater. Sci.* **2001**, *36*, 2107.
4. Mohanty, A. K.; Khan, A.; Hinrichsen, G. *Compos. Part A.* **2000**, *31*, 143.
5. Plackett, D.; Andersen, T. L.; Pedersen, W. B.; Nielsen, L. *Compos. Sci. Technol.* **2003**, *63*, 1287.
6. Romhany, G.; Kocsis, J. K.; Czigan, T. *Macromol. Mater. Eng.* **2003**, *288*, 699.
7. Alvarez, V.; Vazquez, A.; Bernal, C. *Polym. Compos.* **2005**, *26*, 316.
8. Nishino, T.; Hirao, K.; Kotera, M.; Nakamae, K.; Inagaki, H. *Compos. Sci. Technol.* **2003**, *63*, 1281.
9. Wollerdorfer, M.; Bader, H. *Ind. Crops. Prod.* **1998**, *8*, 105.
10. Das, K.; Ray, D.; Banerjee, C.; Bandyopadhyay, N. R.; Sahoo, S.; Mohanty, A. K.; Misra, M. *Ind. Eng. Chem. Res.* **2010**, *49*, 2775.
11. Johnson, L. A.; Myers, D. J. In *Industrial Uses for Soybeans in Practical Handbook of Soybean Processing and Utilization*; David R. Erickson, Ed.; AOCS Press: Champaign, IL: **1995**; 565–584.
12. Tummala, P.; Liu, W.; Drzal, L. T.; Mohanty, A. K.; Misra, M. *Ind. Eng. Chem. Res.* **2006**, *45*, 7491.
13. Wang, Y.; Mo, X.; Sun, X. S.; Wang, D. *J. Appl. Polym. Sci.* **2007**, *104*, 130.
14. Park, S. K.; Bae, D. H.; Rhee, K. C. *J. Am. Oil Chem. Soc.* **2000**, *77*, 879.
15. Chabba, S.; Netravali, A. N. *J. Mater. Sci.* **2005**, *40*, 6263.
16. Ray, D.; Sengupta, S.; Sengupta, S. P.; Mohanty, A. K.; Misra, M. *Macromol. Mater. Eng.* **2007**, *292*, 1075.
17. Ray, S. S.; Okamoto, M. *Prog. Polym. Sci.* **2003**, *28*, 1539.
18. Kaith, B. S.; Jindal, R.; Bhatia, J. K. *J. Macromol. Sci. Part A: Pure Appl. Chem.* **2011**, *48*, 299.
19. Huang, X.; Netravali, A. N. *Biomacromolecules* **2006**, *7*, 2783.
20. Chen, P.; Zhang, L. *Biomacromolecules* **2006**, *7*, 1700.
21. Yoonessi, M.; Toghiani, H.; Kingery, W. L.; Pittman, C. U., Jr. *Macromolecules* **2004**, *37*, 2511.

22. Hillberg, A. L.; Holmes, C. A.; Tabrizian, M. *Biomaterials* **2009**, *30*, 4463.
23. Schmidt, V.; Giacomelli, C.; Soldi, V. *Polym. Degrad. Stab.* **2005**, *87*, 25.
24. Ray, D.; Sarkar, B. K. *J. Appl. Polym. Sci.* **2001**, *80*, 1013.
25. Migneault, I.; Dartiguenave, C.; Bertrand, M. J.; Waldron, K. C. *BioTechniques* **2004**, *37*, 790.
26. Darder, M.; Colilla, M.; Hitzky, E. R. *Chem. Mater.* **2003**, *15*, 3774.
27. Nam, S.; Netravali, A. N. *J. Adhes. Sci. Technol.* **2004**, *18*, 1063.
28. Deka, B. K.; Maji, T. K. *Compos. Sci. Technol.* **2010**, *70*, 1755.
29. Saha, A. K.; Das, S.; Basak, R. K.; Bhatta, D.; Mitra, B. C. *J. Appl. Polym. Sci.* **2000**, *78*, 495.
30. Swain, S. N.; Rao, K. K.; Nayak, P. L. *Polym. Int.* **2005**, *54*, 739.
31. Gilman, J. W.; Jackson, C. L.; Morgan, A. B.; Harris, R.; Manias, E.; Gannelis, E. P.; Wuthenow, M.; Hilton, D.; Phillips, S. H. *Chem. Mater.* **2000**, *12*, 1866.
32. Zanetti, M.; Camino, G.; Reichert, P.; Mulhaupt, R. *Macromol. Rapid. Commun.* **2001**, *13*, 176.
33. Qin, H.; Zhang, S.; Zhao, C.; Feng, M.; Yang, M.; Shu, Z.; Yang, S. *Polym. Degrad. Stab.* **2004**, *85*, 807.
34. Urbanczyk, L.; Bourbigot, S.; Calberg, C.; Detrembleur, C.; Jerome, C.; Boschini, F.; Alexandre, M. *J. Mater. Chem.* **2010**, *20*, 1567.
35. Sun, J.; Cai, S.; Mei, H.; Li, J.; Yan, N.; Wang, Y. *J. Mol. Model.* **2010**, *16*, 1809.
36. Rana, H. T.; Gupta, R. K.; Rao, H. V. S. G.; Sridhar, L. N. *AIChE J.* **2005**, *51*, 3249.