Durability Study of Nanophased Jute-Based Green Composites

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ABSTRACT

The current study was carried out to investigate the effect of chemical treatment and nanoclay on durability of jute fabric reinforced poly (3-hydroxybutyrate-co-3-hydroxyvalerate-12%), commercially known as Biopol, composites (JBC) fabricated by compression molding process. The surface modification of jute fibers are accomplished by performing subsequent chemical treatments such as detergent washing, dewaxing, alkali treatment, and acetic acid treatment to improve fiber/matrix interface adhesion and moisture induced degradation. Durability study was done using moisture absorption and biodegradability test. The effect of moisture absorption on flexural properties and biodegradability on the dynamic mechanical properties were also studied. Moisture absorption resulted in significant decrease in the flexural properties of the UTJBC and TJBC compared to the composites with nanoclay. Nanoclay infused TJBC showed better storage modulus for the better adhesion between fiber and matrix even after degradation.

Keywords: surface treatment, compression molding, green composites, biodegradability, moisture absorption.

1. INTRODUCTION

Manufacturing of synthetic fiber composites not only consume huge energy but also their disposal at the end of the life cycle is very difficult since there is virtually no recycling option. Hence, the biocomposite industry is developing at a significant pace to meet growing consumer awareness and follow new environmental regulations [1]. Natural fibers composites possess good thermal and acoustic insulating properties, light weight, higher specific properties, and higher resistance to fracture [2,3]. Lignocellulosic bio-fiber derived from various origins such as leaf, bast, fruit, grass or cane contribute to the strength of bio as well as synthetic polymer composites in various applications [4]. Jute fiber is known to have excellent tensile strength and a high modulus among other lignocellulosic fiber [5]. Jute-based green composites can be used in consumer goods, low-cost housing, and interior of cars, civil structures, and biomedical applications due to their ease of availability, echo-friendliness, low cost, and good specific properties that are comparable to synthetic fibers. To improve interfacial strength, silane treatment [6], alkali treatment [7], acetylation [8], coupling agents [1], are used. Alkali treatment is the easiest and most widely investigated surface treatment techniques for natural fibers. The effects of alkali treatment on mechanical and thermal properties of composites have been studied by different researchers [9,10]. Biodegradable polymers can be obtained from renewable resources, synthesizing petroleum based chemical or microbially synthesizing in laboratory [11]. Various research groups have worked on biodegradable polymeric materials, such as bionolle, biopol, poly (3-hydroxybutyrate) (PHB) and polylactic acid (PLA), to use in natural fiber reinforced composites. However, PHB and biopol can be considered as true biopolymers because they are synthesized by bacteria as macromolecules [12]. PHB and its copolymers (biopol) are highly crystalline and have a melting point, strength, and modulus comparable to those of isotactic polypropylene [13]. It has been established that the addition of small amounts of nanoparticles to a matrix system can increase thermal and mechanical properties without compromising the weight or process-ability of the composite [14]. Moisture barrier, flammability resistance, thermal, and mechanical properties of polymeric composites can be improved by infusing nanoclay at a very low filler loading [15]. In this study, jute fibers were chemically treated with a modified 4-step process for better interfacial adhesion with matrix and evaluated the treated fibers by analyzing SEM micrographs. 2%, 3% and 4% nanoclay was infused by solution intercalation techniques and treated/untreated jute fiber-biopol biocomposites with/without nanoclay were manufactured using compression molding process and their performance was studied through moisture absorption, flexure test, degradation, and dynamic mechanical analysis (DMA).

2. EXPERIEMNTAL

2.1 Materials Selection

The bacterial copolyester, poly(3-hydroxybutyrate-co-3-hydroxyvalerate-12%) commercially known as Biopol (pellet size 5 mm) and obtained from Goodfellow (UK),

was used as matrix without additional purification. Commercially available hessian jute fabric was supplied by Online Fabricstore.net (USA) having average thickness 0.80 mm, was used as reinforcement after chemically surface modification. Montmorillonite K10 nanoclay, supplied by Sigma-Aldrich, was used as filler in this study. For chemical treatment, Alcojet detergent, ethanol (50% solution), NaOH (50% solution), acetic acid (99% solution) and to dissolve the biopol chloroform (99% solution) were used. All chemicals were supplied by Sigma–Aldrich and were used without further purification.

2.2 Surface Modification

To improve the interfacial adhesion between the non polar matrices and hydrophilic fibres, fibres should be modified chemically. Surface treatment decrease moisture absorption, increase the tensile strength [16] and also increases wettability of the fibers by the matrix. In this study subsequently detergent washing, dewaxing, alkali treatment and soaking with acetic acid were performed on jute jute fabrics to increase the interfacial bonding with hydrophilic polymer Biopol. For detergent washing, jute fabrics were kept into 5% detergent solutions at 30^0C for 1h and then it was washed with water and dried. Dewaxing is performed to remove pectin (waxes) from the jute fabrics. Detergent washed jute fabrics kept into 5% ethanol solution at 30^0C for 1 hour followed by washing with water and drying. Dewaxed jute fabrics were kept into 5% NaOH solution for 2 hours at 30^0C and washed with distilled water. Alkali treatment removes lignins and hemicelluloses and results major number of hydroxyl group (O-H) accessible on the surface of the fiber. Alkali treatment also breakdown the fiber bundles into single fibers and increase the effective surface area available for contacting with the polymer matrix. Alkali treated jute fabrics were soaked with distilled water-acetic acid (2%) solution for 1 hour followed by washing with distilled water and drying. Acetic acid neutralizes sodium ions which come with fiber during alkali treatment and react with O-H group on the fiber surface to convert hydrophilic surface of jute fibers into hydrophobic which is important for the better adhesion with hydrophobic matrix.

2.3 Composite Fabrication

Jute biopol composites were fabricated using treated and untreated fibers and biopol by compression molding process. Biopol was dissolved into chloroform at a ratio of 1:8 at room temperature and stirred by magnetic stirrer for 4 hours to prepare a homogeneous solution. In case of nanophased composites, nanoclay were infused into biopol using solution intercalation techniques. Measured amount of nanoclay was dissolved into chloroform and solution was then poured to biopol chloroform solution and again stirred for 2 hours to prepare a homogeneous mixture. Final solution with/without nanoclay was poured into a mold to prepare a 1.5 mm thick film and dried in a vacuum oven at 60 °C to evaporate all choloroform. Dried thick films were then placed in the hot press and 13.34 kN force was applied at 166 °C for 10 minutes to prepare 0.50 mm thin films. Jute-biopol composites were manufactured by stacking prepared films with/without nanoclay and treated/untreated fibers like a sandwich using compression molding process applying 13.34 kN force at 166 °C for 15 minutes.

2.4. Experimental Procedures

Morphological characterization of the treated and untreated fibers was conducted using a JEOL JSM-5800 scanning electron microscope (SEM). The fibers were coated with silver using sputtering machine to prevent charging. Moisture absorption tests of JBC were conducted according to ASTM D2495-07. Five rectangular samples from each category (dimension: $100 \times 13 \times 3$ mm) were dried in a vacuum oven at 105 °C for five hours and dry weight (W_0) was taken after cooling. To make a humid environment, some distilled water was placed into a desiccator and after 12 hours the inside humidity was found to be 98%. Dry samples were then kept on a platform above water in the desiccator. The weights (W_t) of the samples were measured after 7, 14, 20, 30, and 60 days conditioning using a precision balance having an accuracy of 0.0001 gm. Moisture content was calculated eq. (1).

$$M_t (\%) = [(W_t - W_0)/W_0] \times 100. \qquad (1)$$

Flexural properties of JBC before and after moisture absorption test were evaluated using Zwick Roell testing unit according to ASTM D790-02 standard under displacement control mode at a crosshead speed of 2.0 mm/min. Five samples from each category were tested to determine the average result.

The composites panels were cut into 55mm $\times$ 13mm $\times$ 3.5mm for biodegradability testing. Biodegradability was determined by measuring weight loss of the specimens buried into natural soil at Tuskegee University campus. Soil was taken from the surface layer. All inert materials were removed to obtain a homogeneous mass and measured P^H was 7.0. The soil was poured into a plastic pot up to a thickness of about 3 cm. Five specimens from each category were dried in a vacuum oven at 60°C for 5 hours and weighted (W_i) using a precision balance having accuracy 0.0001gm. Then the specimens were buried in the pots to a depth of 1 cm. Water was sprayed once a day to sustain the moisture. The samples were taken out from the soil after 20, 30, 60 and 90 days and washed with distilled water. Then dried in a vacuum oven at 60°C for 5 hours and weighted (W_f). The weight loss was calculated using eq. (2).

$$\text{Weight loss } (\%) = [(W_i - W_f)/W_i] \times 100. \qquad (2)$$

Storage modulus (E′) of jute-biopol samples before and after degradation for 60 days were obtained from the DMA tests under three point bending mode at a heating rate of 5

°C/min from 30 to 120 °C with an oscillation frequency of 1 Hz and an amplitude of 15μm according to ASTM D4065-01 standard. Three samples from each category were tested.

3. RESULTS AND DISCUSSIONS

Surfaces of treated and untreated fibers investigated using SEM micrographs (Fig. 1) revealed relatively rougher surfaces in treated fibers compared to untreated fibers. Removal of surface impurities, non-cellulosic substances, inorganic materials, and waxes resulted in cleaner and rougher surfaces in finally treated fibers. Chemical treatments converted the mesh-like structure of fibers to clean and rough single fibers which provided higher

(a) Untreated jute fiber   (b) Detergent washed jute fiber

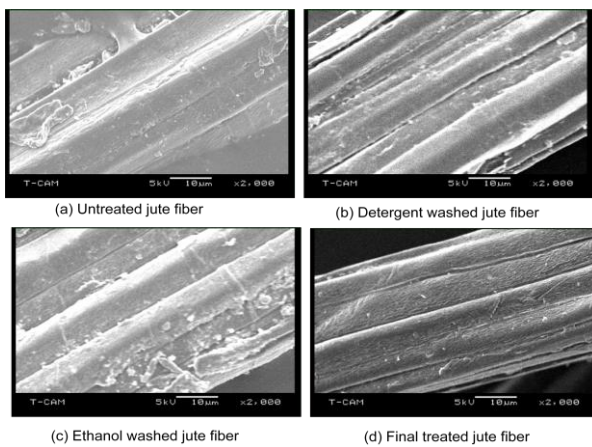(c) Ethanol washed jute fiber   (d) Final treated jute fiber

Figure1: SEM micrographs of jute fibers

strength to fibers. Rougher surface and defibrillation were also attributed to better interaction of fibers with matrix for larger surface area.

Figure 2 shows the percentage of moisture absorbed by the jute biopol composites at different time period. Most of the natural fibers have a tendency to absorb moisture when they are placed in a humid area which weakens the composites. The percentage moisture absorption for conventional and nanophased composites was almost same during initial 7-day conditioning period. As the conditioning time was increased, the amount of absorbed moisture was increased. After 20 days, it became almost saturated and there was no significant change in the moisture absorption data even after conditioning for 30 and 60 days. The amount of moisture absorbed by the UTJBC was higher compared to the TJBC and nanoclay infused TJBC, due to the presence of micro voids in the UTJBC for improper interaction between fiber and matrix. Nanoclay infused samples showed lower percentage of moisture absorption, because nanoparticles acted as a moisture barrier to the composites system.
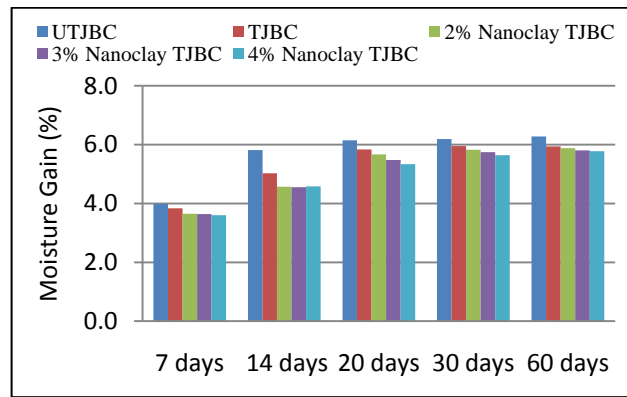

Figure2. Moisture absorption of jute biopol composites.

Moisture absorption resulted in significant decrease in the flexural properties of the UTJBC and TJBC compared to the composites with nanoclay (Figures 3 & 4). Flexure tests showed 32% and 23% decrease in strength, and 21% and 21% decrease in modulus of the UTJBC and TJBC, respectively, for a conditioning period of 60 days. The respective values were 16% and 6% for 4% nanoclay infused TJBC.
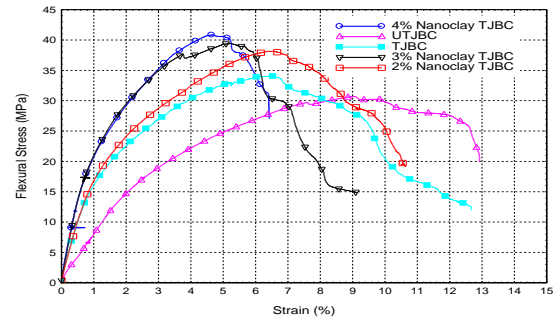

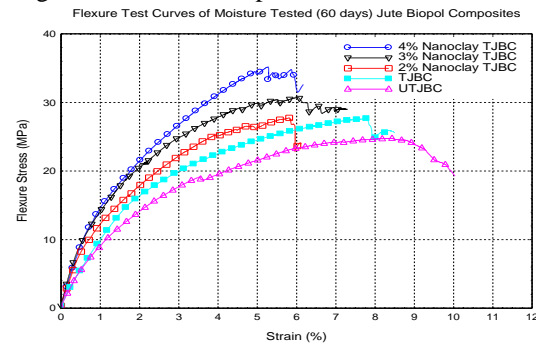Figure 3. Stress-strain plot of unconditioned JBC

Figure 4. Stress-strain plot of 60-days conditioned JBC.

Table 1 shows the biodegradation of jute biopol composites. After 20 days, about 1.7 and 1.8% weight loss was observed in UTJBC and TJBC, respectively. Whereas 1.6% weight loss were observed in nanoclay infused specimens. After 60 days, all the samples showed about 5 to 6 % weight loss. This loss was mainly due to the degradation of biopol. After 60 days, the degradation rate was higher and about 10% weight loss was observed after 90 days. Nanoclay showed no significant effect on the degradation of the biocomposites.

Table 1. Degradation of jute biopol composites.

	After 20 days	After 30 days	After 60 days	After 90 Days
UTJBC	1.74±0.31	2.06±0.44	6.17±0.89	10.65±0.93
TJBC	1.88±0.59	2.19±0.70	5.99±0.78	10.89±0.57
2% TJBC	1.60±0.11	2.05±0.45	5.60±0.76	10.59±0.97
3% TJBC	1.60±0.43	2.13±0.17	5.51±0.91	10.69±0.29
4% TJBC	1.60±0.01	2.09±0.30	5.56±0.79	10.92±0.13

UTJBC and TJBC had the storage modulus of 1467 and 1605 MPa before degradation and 587 and 677 MPa after degradation for 60 days (Fig. 5). Jute/biopol samples with 2, 3, and 4 wt.% nanoclay showed about 2550, 2900, and 3050 MPa storage modulus at 30 °C, respectively before degradation and the corresponding values were 891, 979 and 1088 MPa after degradation for 60 days.
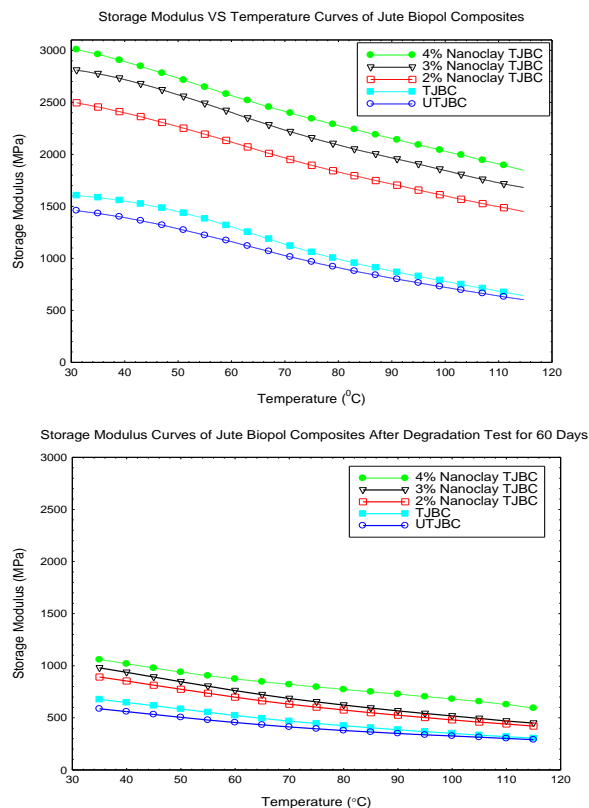

Figure 5. Storage modulus of JBC before and after degradation for 60 days.

3. CONCLUSIONS

Surface treatments resulted in the removal of pectin, hemicelluloses, and other non-cellulosic substances from the fibers and the higher percentage of celluloses in the final treated fibers. Rougher surface and increased effective surface area of the chemically treated fibers facilitated better interaction between the fiber and matrix. The 4% nanoclay infused composites showed lower moisture absorption, better flexural properties, and dynamic mechanical properties, compared to the 2%, 3% nanoclay infused composites as well as the conventional composites. The flexural properties decreased with the moisture absorption for all composites. Nanoclay infused specimens showed better properties. All categories of composites degraded about 10% after 90 days buried into soil. In case of degraded specimens, nanoclay infused samples showed better storage modulus as like before degradation.

Acknowledgement

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