

Research Article

Hybrid Composite Laminates from ESOA-BisGMA Blend and 2-Hydroxyethyl Acrylate (HEA) Treated Jute Fiber

A. Praharaj^{1*}, D. Behera¹, T.K. Bastia¹ and A.K. Rout²

¹School of Applied Sciences (Chemistry), KIIT University, Bhubaneswar, Odisha, India

²School of Mechanical Engineering, KIIT University, Bhubaneswar, Odisha, India

Abstract

The development of an inter-cross-linked polymer network of thermoset-thermoset blends have been extensively studied due to their enhanced mechanical properties. Among various polymer blends, modifications of vinyl ester resin (VER) i.e. styrene cross-linkable Bisphenol-A glycidyl dimethacrylate (BisGMA) with epoxidized soybean oil acrylate (ESOA) combinations are an attractive route to promote the performance of the thermoset matrix and to overcome the inferior properties of both the components. The primary goal of this research is to develop hybrid composite laminates from ESOA-BisGMA blend (50:50 wt%) using both untreated and 2-hydroxyethyl acrylate (HEA) treated jute fiber as reinforcement and then to characterize thereof. The mechanical properties like tensile strength, bending strength & bending E modulus, dynamic mechanical analysis, corrosion and ageing studies have been investigated. The results suggested improved properties of the hybrid systems with the incorporation of ESOA-BisGMA blend as the composite matrix. Moreover, HEA treatment of jute fiber enhanced the composite properties further, which interestingly, outperformed the parent ESOA-BisGMA blend and untreated jute-ESOA/BisGMA blend based composite. In this investigation 5 ply of jute fabric has been reinforced into ESOA-BisGMA blend matrix, so that at a low cost thin sheets can be produced. This may be used as an alternate material to wood, which has not been carried out elsewhere.

Keywords: ESOA-BisGMA blend; HEA, Jute fiber; Mechanical properties; Dynamic mechanical analysis; Corrosion and ageing studies

Academic Editor: Taihong Shi, PhD, PhD, Sun Yat-sen University, China

Received: December 16, 2014; **Accepted:** January 22, 2015; **Published:** January 29, 2015

Competing Interests: The authors have declared that no competing interests exist.

Copyright: 2015 A. Praharaj. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

***Correspondence to:** A. Praharaj, School of Applied Sciences (Chemistry), KIIT University, Bhubaneswar, Odisha, India

Email: ankita.praharaj017@gmail.com

1. Introduction

The synthesis of polymers from renewable resources has become a much preferred research topic nowadays. This is due to the increasing demand for eco-friendly sustainable materials and to diminish global warming by replacing petroleum-based resins with bio-based ones. However, it is difficult to fully replace petroleum based polymeric materials by those from renewable resources mainly due to their inferior mechanical and thermo-physical properties in comparison with conventional petroleum-based polymers that are intended to be replaced. Moreover, functionalized plant oils, when cured alone or even with styrene as reactive comonomer, yield rubberlike materials [1-4]. Thus, they need to be combined with such petroleum-based resins which show high stiffness, strength and T_g owing to their chemical build-up and tightly crosslinked structure. In this context, plant oils, such as soybean oil are being widely used for the “greening” of thermosets such as vinyl esters (BisGMA) which is well suited as it contains stiff aromatic units. ESOA, synthesized from the reaction of acrylic acid with epoxidized soybean oil [5], is an attractive resin for blending with vinyl esters because it is inexpensive, has good properties and low toxicity, biodegradable [5,6] and can be “genetically engineered” for polymer-related applications.

It is worth noting that ESOA-vinyl ester blends have already been synthesized and their properties have been reported [7, 8]. But less attention has been paid to incorporate ESOA-BisGMA blends as composite matrix. Accordingly, our work aims to incorporate the above blend system for the fabrication of low cost hybrid composite laminates by using both untreated and HEA treated jute fiber as reinforcement and then to investigate their properties so that they could be used for high strength structural purposes in various fields. Among all the natural fibers, jute appears to be the most useful inexpensive and commercially available fiber in India. Several work has been carried out using this fiber as reinforcement [9-15]. Despite of this attractiveness of jute fiber reinforcement, several disadvantages of jute such as poor wettability, poor fiber -matrix adhesion property, and low moisture resistance make them insufficient for proper reinforcement [16]. To overcome this kind of bottlenecks we have used HEA treated jute fibers in our hybrid composites.

Previously, we had reported Hydroxyethyl Acrylate (HEA) Treated Jute-ESOA Composite Laminate: A New Development for Structural Materials [16]. Here, we aim to improve the properties of the above composite laminates by using the optimum composition of ESOA-BisGMA blend system (50:50 wt%) as composite matrix so as to incorporate the best properties of both the polymers into the hybrid laminates. The mechanical properties like tensile strength, bending strength & bending E.modulus, dynamic mechanical analysis, corrosion and ageing studies have been investigated. Moreover, comparative property studies are presented for HEA treated jute fiber/ESOA-BisGMA blend composites and untreated jute fiber/ESOA-BisGMA blend composites. This part of the research aims to develop high strength composite laminates which can specifically be used for low cost housing projects and members in marine application in saline environment.

2. Experimental

2.1. Materials

BisGMA prepolymer was synthesized from methacrylic acid and diglycidyl ether of bisphenol-A-type epoxy resin (DGEBA) by using a reported method in our laboratory [17]. It was styrene diluted (30 wt%) and had the following characteristics: Hydroxyl value ~158 mg (KOH)/g, acid value < 4 mg (KOH)/g, viscosity 94.25 mPa.s at 23 °C, and density 1.08 g/ml at 23 °C. The ESOA was purchased from Sigma Aldrich which had the following characteristics: Oxygen oxirane content-0.012, Iodine value- 8g/100 gm, Acid value-1.15 mg (KOH)/mg, Refractive index-1.4873 and viscosity- 25.336 mPa.s. Benzoyl peroxide (BPO with peroxide content-50 wt%) initiator, N,N-dimethyl aniline (DMA) accelerator, HEA, Dicumyl peroxide (DCP) were purchased from Sigma Aldrich. Jute fibers in the form of Hessian cloths were collected from Southern Jute Industries, India (207GSM). All chemicals and solvents were used without any modifications.

2.2. Methods

2.2.1. Surface treatment of jute fabric

The bleached jute (Hessian cloths) was cut into square sizes (18 cm × 10 cm) and temporarily fixed in a long square size plate (50 cm × 50 cm). Then the samples were subjected to soak a solution of 10% HEA and 1.2% DCP in methanol for 30 min. Finally they were dried at ambient temperature for 24 hours and then heated for 20 minute at 60⁰C.

2.2.2. Fabrication of ESOA-BisGMA blend and HEA treated Jute fiber based Hybrid Composite Laminates

The ESOA and BisGMA (50:50 wt%) were mixed together and stirred at 40⁰C for 30 minutes using a mechanical stirrer. Then a matrix formulation of 50:50 blend of ESOA-BisGMA, 2% BPO (w/w) and 0.5% DMA (w/w) on the bases of jute weight was prepared. Composites were fabricated using simple Hand-lay up for preparation of specimen. At the beginning of fabrication, gelcoat with uniformly brushed in to the finished side of male and female parts of the mould. Then each layer of fiber is pre-impregnated with matrix material and placed one over another as sandwich making system. Then the mould was subjected to hot-press (5 tons) with temperature of 110 °C for 2 hours and 160⁰C for 1 hour.

3. Characterization

3.1. Fourier transform infrared (FTIR) spectroscopy

FTIR spectra were collected using Thermo-Nicolate Model 400 instrument equipped with a controlled temperature cell (Model HT-32 heated demountable cell used with an Omega 9000-A temperature controller).

3.2. Scanning electron microscopy (SEM)

SEM was utilized to qualitatively examine the microstructure of unmodified and modified MWCNTs and the nanocomposites. The samples were gold coated and examined using a Philips 420T scanning transmission electron microscope with a secondary electron detector, operating at 15 KV in the SEM mode.

3.3. Mechanical testing

The tensile and bending properties of the composites were studied by universal testing machine (HOUNSFIELD; H10KS) in accordance with ASTM D-3039 and ASTM D-790. All the results were taken as an average of five samples.

3.4. Corrosion testing

For corrosion tests, five specimens ($12 \times 10 \times 3 \text{ mm}^3$ and exposed area of 372 mm^2) were tested according to ASTM B117 standard. The edges of the samples were sealed with BisGMA resin and their initial weights were taken in dry condition in an electronic balance of accuracy 0.00001 mg and model AY220. The test was then conducted by dipping the specimens in circulating salt water with 10 wt% NaCl concentration, pH value of 6.5 and at a temperature of $42 \text{ }^\circ\text{C}$. After a gap of 24, 48 and 72 hrs of testing, each time the specimens were rinsed, cleaned in deionized water, dried in an oven for 12 hrs and final weights were taken.

3.5. Ageing studies

The ageing of composites on exposure to water was evaluated by keeping the samples immersed in water. Five specimens ($25 \text{ mm} \times 25 \text{ mm}$) of each sample were kept immersed in distilled water at $30 \text{ }^\circ\text{C}$ for 31 days. The samples were taken out, dried at room temperature and their weights were taken. Data reported is the calculated average value of the samples taken.

4. Results and Discussion

4.1. Preparation of ESOA-BisGMA blend

The present work mainly involves the synthesis of ESOA-BisGMA blend in its optimum composition i.e. 50:50 wt% and the incorporation of the above blend system as the matrix resin for the fabrication of hybrid composite laminates. Figure 1 depicts the FTIR spectrum of ESOA-BisGMA blend (50:50 wt%) with the characteristic peaks of both the blended polymers.

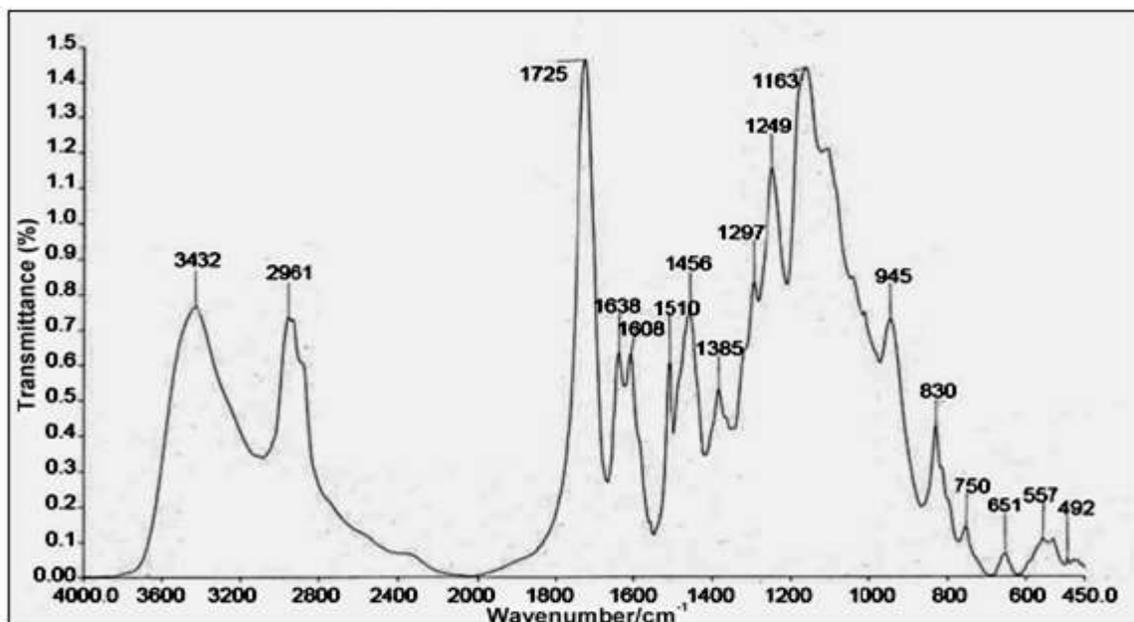


Figure 1 FTIR spectrum of ESOA-BisGMA blend (50:50 wt%)

The wide band at 3432 cm^{-1} , is due to the presence of hydroxyl group. The peak at 2961 cm^{-1} is due to the C–H stretching. The ester carbonyl stretching is observed at 1725 cm^{-1} where as the carbon carbon double bond (C=C) stretching is at 1638 cm^{-1} . The ring stretching vibrations of the aromatic nuclei are seen at 1608 and 1510 cm^{-1} respectively. The C–H scissoring band of ESOA is observed at 1456 cm^{-1} and the $\text{CH}_2=\text{CH}$ scissoring band for terminal alkene is observed at 1385 cm^{-1} . The peaks at 1297 and 1249 cm^{-1} are due to the C–O stretching. The C–C–O_{str} peak is observed at 1163 cm^{-1} . The C–H out of plane bending vibrations are observed at 945 , 830 and 557 cm^{-1} . All the peaks supported the formation of ESOA-BisGMA blend.

4.2. HEA grafting of jute fabric

Grafting of jute fiber with HEA treatment results in the removal of lignin, hemicellulose and pith from the fiber to have better impregnation between fiber and matrix. It also increases fiber surface roughness (Figure 2(a) and 2(b)) to have a better interaction both with the matrix and filler. Such treated fibers are less dense and are capable to rearrange inter-fibril region when subjected to tensile deformation.

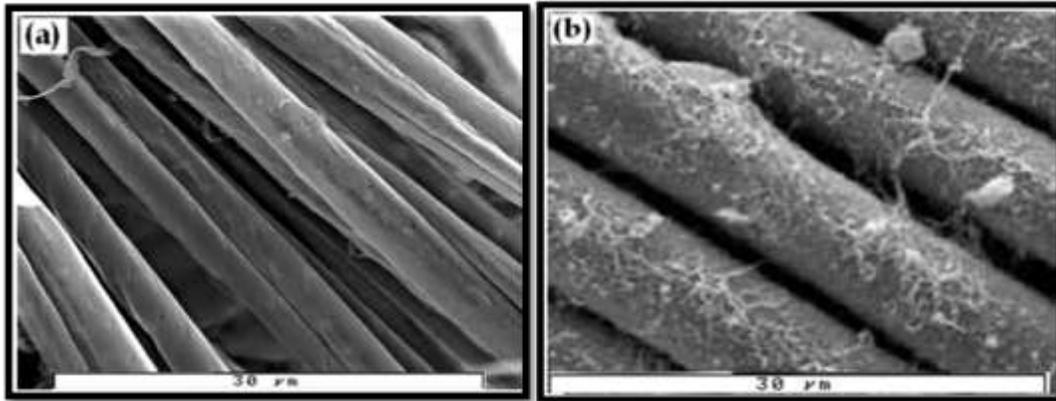


Figure 2 SEM of (a) Untreated jute fiber (b) HEA treated jute fiber

The effect of HEA treatment is also evident from FTIR spectra (Figure 3). HEA treatment results in the development of carbonyl groups which is evident from a peak at 1737 cm^{-1} and a C-O_{str} band is observed at 1371 cm^{-1} . The O-H band which should be observed above 3000 cm^{-1} is shifted to lower frequency side i.e. at 2926 cm^{-1} and 2852 cm^{-1} due to the presence of hydrogen bonding between cellulose and HEA.

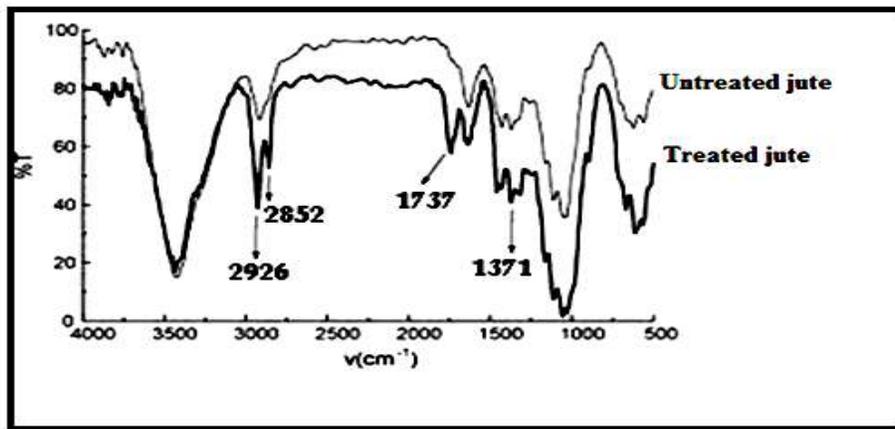


Figure 3 FTIR spectra of Untreated and HEA treated jute fiber

4.3. Mechanical properties of ESOA-BisGMA blend and HEA treated Jute fiber based Hybrid Composite Laminates

We have already reported the mechanical properties of ESOA, untreated jute-ESOA composite (UJEC) and HEA treated jute-ESOA composite (HJEC) in our previous work [16]. Here, we report the mechanical properties like tensile strength, bending strength and bending E-modulus of ESOA/BisGMA blend (EB₅₀),

untreated jute-ESOA/BisGMA blend composite (UJEBC) and HEA treated jute-ESOA/BisGMA blend composite (HJEBC) as presented in Table 1.

Tab 1 Mechanical properties of different network systems

Network systems	Density (gm/cm ³)	Tensile strength (MPa)	Bending Strength (MPa)	Bending modulus (GPa)
EB ₅₀	1.065	87.05	95.23	4.1
UJEBC	0.92	98.11	140.11	7.3
HJEBC	0.89	120.23	198.50	10.5

From the recorded values it is concluded that tensile strength, bending strength and bending E-modulus of HJEBC system was increased significantly as compared to EB₅₀ and UJEBC system. Bending strength and bending E-modulus were increased by 41.7% and 45% compared to the UJEBC composite, respectively. Figure 4 depicts the graphical representation of the mechanical properties of the network systems.

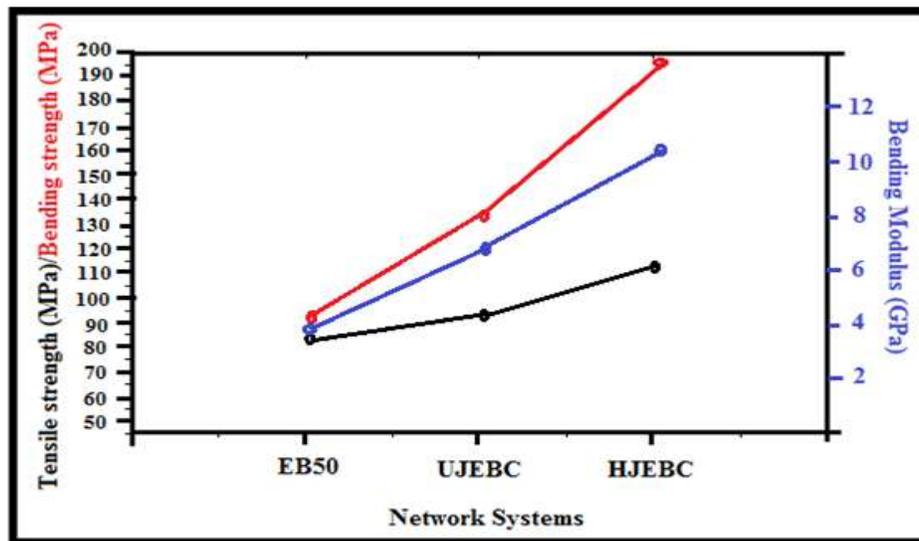


Figure 4 Graphical representation of Mechanical properties

Figure 5 represents the SEM micrographs of EB₅₀, UJEBC and HJEBC. The SEM of UJEBC shows ineffective fiber-matrix adhesion due to the untreated jute fiber used, thereby exposing the fiber surface. HEA treatment results in the development of rough fiber surface and increased fiber aspect ratio which offers a better fiber-matrix adhesion (Figure 5(c)) and higher mechanical properties. The reaction of HEA with the matrix and jute contribute to the increased mechanical properties and enhanced interfacial adhesion.

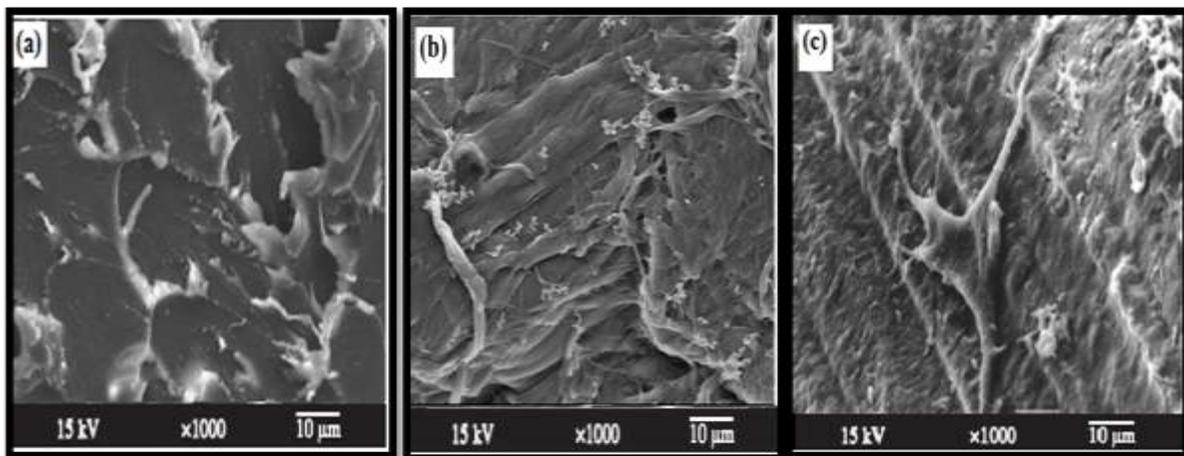


Figure 5 SEM micrographs of (a) EB₅₀ (b) UJIBC (c) HJIBC

4.4. Dynamic Mechanical Analysis

Dynamic mechanical properties like storage modulus (E') and $\tan \delta$ of ESOA, UJIBC and HJIBC were investigated as a function of temperature (Figure 6). It was found that storage modulus of HJIBC was significantly higher than that of UJIBC and EB₅₀. The value of storage modulus of HJIBC was found to be increased by 49% compared to the value of UJIBC. The presence of moisture in the UJIBC reduces the adhesion with ESOA-BisGMA blend matrix and promotes the formation of voids. This results in the untreated composite having lower stiffness and strength. The improved storage modulus of HJIBC was due to increased interfacial bond strength between the blended matrix and jute fiber. HEA treatment reduced moisture retention capacity of jute fiber and improved the compatibility with ESOA-BisGMA blend.

Figure 6(b) represents the $\tan \delta$ values with respect to temperature. $\tan \delta$ peak values of HJIBC shifted towards the lower temperature compared to both UJIBC and EB₅₀. So the glass transition temperature (T_g) of the HJIBC is lower than that of UJIBC and EB₅₀. In HJIBC, the strong interfacial fiber-matrix bonding results in lower glass transition temperature (T_g), higher modulus, higher tensile strength, and low fracture toughness than the bulk. The decrease of glass transition temperature indicates that coupling agent and other ingredients present in the composite reduces cross-linking density of mixture. Thus the composite of HEA treated jute fiber (HJIBC) is stiffer than both UJIBC and EB₅₀ because mobility of the molecular chain at the interface is reduced by strong interaction of fiber and matrix due to HEA treatment of fiber. Storage modulus indicates the interfacial bonding and thus the high values suggest enhanced interfacial and interlaminar shear strength in case of HJIBC.

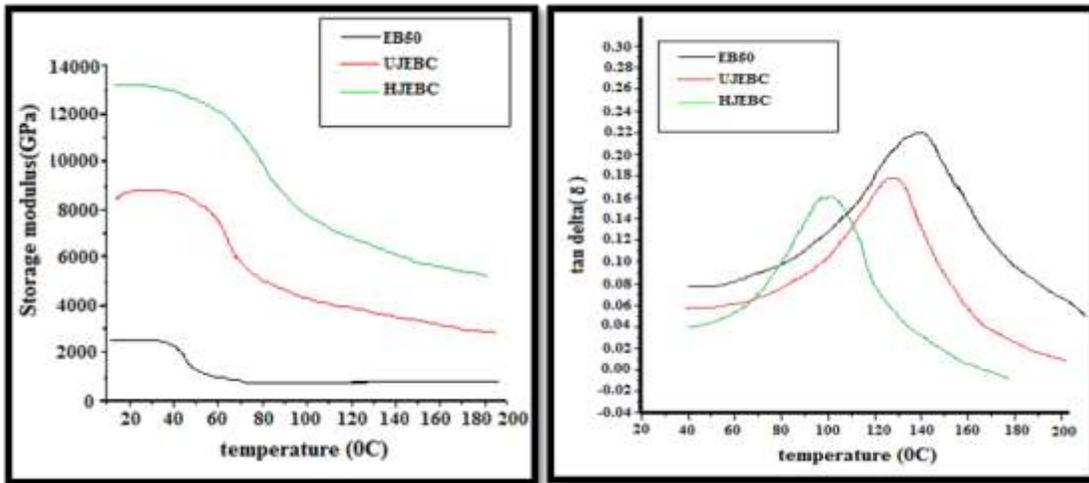


Figure 6 (a) Storage modulus (b) tan δ of EB₅₀, UJEBc and HJEBc

4.5. Corrosion test

The results of corrosion test reveal weight gain in all the specimens indicating oxidation. The graph showing the change in weight of hybrid composites has been plotted in Figure 7. There is a marked improvement in the absorption characteristics of the HEA treated hybrid composite laminates i.e. HJEBc compared to the untreated one i.e. UJEBc and EB₅₀. HJEBc shows less weight change compared to UJEBc due to its uniform surface characteristics confirmed from SEM images and the hybridization effect of grafted fiber. In UJEBc, the presence of voids result in easy passage of salt water into the matrix resulting in increased weight gain. However, the overall change in weight of the hybrid composite laminates is negligible even after increased hours of NaCl treatment.

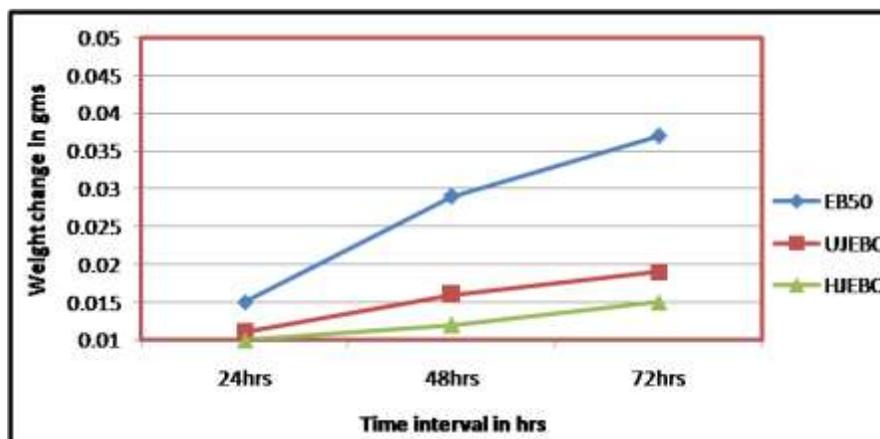


Figure 7 Corrosion test of EB₅₀, UJEBc and HJEBc

4.6. Ageing studies of Hybrid Composite Laminates in water

The major drawback in the use of natural fibers as reinforcement is that their sensitivity to water which increase the dimension of the composites and also reduce the mechanical properties [18]. Moisture absorption leads to swelling and degradation at fiber matrix interface which results in poor mechanical properties and dimensional instability [19]. Thus, the water ingress capacity of the composites was evaluated to find out whether they could be used in moist environment and the results are shown in Figure 8.

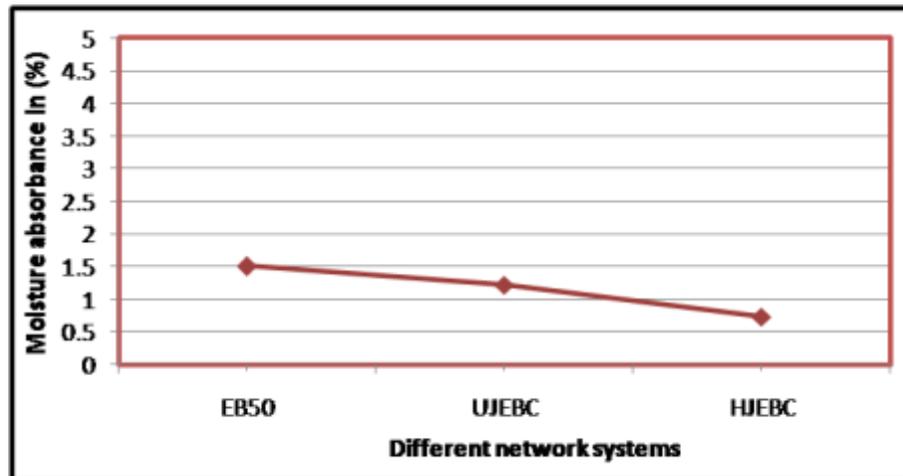


Figure 8 Ageing studies of EB₅₀, UJEBC and HJEBC in water

In UJEBC, untreated jute results in higher water uptake but after treatment with HEA (HJEBC), hydrophilic nature of jute fiber is reduced due to the removal of waxes, leading to better bonding between fiber and matrix. Improved adhesion reduces the rate of diffusion of water molecules. Thus, the HJEBC shows reduced water ingress into the system. But in UJEBC, the bad bonding between fiber/matrix causes cracks and micro-voids on the surface [20] leading to increased water leakage into the system.

5. Conclusion

In this work, we have blended both ESOA and Vinyl ester (BisGMA) in their optimum composition (50:50 wt%) and investigated the effect of both untreated and HEA treated jute fiber on the mechanical, corrosion and water ingress properties of the hybrid composite laminates. The blended system (EB₅₀) exhibited improved properties than ESOA and BisGMA which was further enhanced with the incorporation of jute fiber. However, HEA treatment of jute fiber led to improved mechanical properties of composite laminates including corrosion and water ingress properties compared to the ones with untreated jute fiber. Thus, the HJEBC laminates can be recommended for use in structural purposes specifically for low cost housing projects and members in marine application in saline environment.

6. Acknowledgement

The authors of this paper are thankful to KIIT University for their support and help. The assistance provided by IIT, Kharagpur during the characterization of some of the experimental work is greatly acknowledged.

7. References

1. Khot SN, Lascala JJ, Can E, Morye SS, Williams GI, Palmese GR, Kusefoglu SH, Wool RP. Development and application of triglyceride based polymers and composites. *Journal of Applied Polymer Science*. 2001, 82:703-723
2. Raquez JM, Deléglise M, Lacrampe MF, Krawczak P. Thermosetting (bio) materials derived from renewable resources: A critical review. *Progress in Polymer Science*. 2010, 35: 487-509
3. La Scala J, Wool RP. Property analysis of triglyceride- based thermosets. *Polymer*. 2005, 46: 61-69
4. Fu L, Yang L, Dai C, Zhao C, Ma L. Thermal and mechanical properties of acrylated epoxidized-soybean oil-based thermosets. *Journal of Applied Polymer Science*. 2010. 117: 2220-2225
5. Behera D, Banthia AK. Synthesis, characterization and kinetics study of thermal decomposition of epoxidised soybean oil acrylate (ESOA). *Journal of Applied Polymer Science*. 2008, 109:2583-2590
6. Lu J, Khot S, Wool RP. New sheet molding compound resins from soybean oil. Synthesis and characterization. *Polymer*. 2005, 46: 71-80
7. Grishchuk S, Karger K. Hybrid thermosets from vinyl ester resin and acrylated epoxidized soybean oil (AESO). *eXPRESS Polymer Letters*. 2011,1: 2-11
8. Alireza F, Abdul RR, Mat UW, Mustapha SNH, Tajulruddin WNW. Mechanical properties of hybrid thermosets from vinyl ester resin and acrylated epoxidized palm oil (AEPO). *Applied Mechanics and Materials*. 2015, 695: 73-76
9. Gassan J, Bledki AK. The Influence of Fiber Treatment on the Mechanical Properties of Jute-Polypropylene Composites. *Composites Part A*. 1997, 28:1001-1005
10. Sridhar MK, Basavarajjappa G, Kasturi S Sg, Balsubramanian N. Evaluation of jute as a reinforcement in composites. *Indian J Text Res*. 1982, 7:87-96
11. Roe PJ, Ansell MP. Jute reinforced polyester composite. *J. Mater. Sci*. 1985, 20:4015-4020
12. Mohanty AK, Khan MA, Hinrichsen G. Influence of Chemical Surface Modification on the Properties of Biodegradable Jute Fabrics–Polyester Amide Composites. *Composites Part A*. 2000, 31:143-150
13. Ray D, Sarkar BK, Basak RK, Rana AK. Study of the Thermal Behavior of Alkali-Treated Jute Fibers. *Journal of Applied Polymer Science*. 2002, 85:2594-2599
14. Tripathy SS, DI Landro L, Fontanelli D, Marchetti A, Levita G. Mechanical Properties of Jute Fibers and Interface Strength with an Epoxy Resin. *Journal of Applied Polymer Science*. 2000, 75:1585-1596
15. Winfield AG. **Proceedings of second symposium on new fibers and composites**, sponsored jointly by Dept. of Science and Technology, India, and UNIDO, January 10-11,1977
16. Behera D, Banthia AK, Bastia.TK. Hydroxyethyl Acrylate (HEA) Treated Jute–ESOA Composite Laminate: A New Development for Structural Materials. *International Journal of Plastics Technology*. 2011, 15: 86-92
17. Behera D, Satapathy H, Banthia AK. Synthesis, purification and curing studies of vinyl ester network. *Pigment and Resin Technology*. 2007, 32: 271-278

18. Dhakal HK, Zhang ZY, Richardson MOW. Effect of water absorption on the mechanical properties of hemp fiber reinforced unsaturated polyester composites. **Compos Sci. Technol.** 2007, 67: 1627-1639
19. Cheng S, Lau KT, Liu T et al. Mechanical and thermal properties of chicken feather fiber/PLA green composites. **Composites: Part B.** 2009, 40: 650-654
20. Abdul Khalil HPS, Jawaid M, Abu Bakar A. Woven hybrid composites: water absorption and thickness swelling behaviours. **Bioresources.** 2011, 6:1043-1052