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Research Article

Viscoelastic properties of alkaline treated walnut shell/rice straw fiber/epoxy biocomposite

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Abstract

The increasing demand for an eco-friendly environment has led to the recent development of polymer matrix/green plant fiber composites. In this present study, the viscoelastic performance of walnut/rice straw fiber/epoxy biocomposites was examined using a dynamic mechanical analysis (DMA) in three-point bending mode at a constant frequency (1 Hz) and temperature (25 °C to 240 °C). The surface morphology of the developed composites was analyzed using field emission scanning electron microscopy (SEM). The epoxy resin was incorporated with walnut/rice straw fiber in five proportions (2-10 wt%) using the hand lay-up technique. The hybrids of rice straw fiber/walnut shell ash particulates were added in equal ratios. The DMA results showed that epoxy/6wt% walnut/rice straw fiber biocomposite recorded the maximum storage modulus (> 8×10^3 MPa) with low loss modulus and damping factor. This indicates excellent stiffness and high energy storage capacity resulting from excellent interfacial bonding of molecules of epoxy, walnut shell particulates, and rice straw fiber. The epoxy/rice straw fiber biocomposite showed a high rate of molecular mobility, leading to high heat dissipation and damping capacity. The glass transition temperature (Tg) of the developed composites ranges from 70 °C to 130 °C, indicating the working temperature of the materials to be below 70 °C. The tan-δ curves indicate that walnut/rice straw fiber/epoxy biocomposites are heterogeneous materials with separate viscoelastic phases and glass transition temperatures, resulting from the addition of walnut shell particulates and rice straw fiber. These reinforcers are finally noted as critical factors affecting the extent of macromolecular mobility within walnut/rice straw fiber/epoxy biocomposites.

Introduction

In recent years, more structural failures have led engineers to focus on designing better fracture-resistant structures [1,2]. For instance, aircraft and automobile designers have had to rethink their methods for designing and manufacturing damage-tolerant products. As part of this evolutionary process, new products will inevitably require fracture resistance capabilities incorporated into lighter-weight materials to support greater fuel efficiency for vehicular technology [1,3]. Given these requirements, long fiber-reinforced polymer composites provide a suitable solution owing to their high specific strength, high stiffness, corrosion resistance, and low density. Natural fibers have recently dominated glass and carbon fiber as predominant materials for reinforcing polymer matrices due to their non-toxicity and inherent excellent mechanical properties [4-10]. Several researchers have explored the impact of natural fibers on mechanical behavior, but limited works have been reported on the viscoelastic behavior of natural fibers incorporated in epoxy matrix composites, especially with regard to walnut shells and rice straw fiber. A study by Satapathy, et al. [11] revealed improvements in tensile strength, flexural strength, and hardness of high-density polyethylene by incorporating hybrids of maleic anhydride-treated banana fiber/fly ash cenospheres eco-friendly materials. The study also recorded an increase in stiffness and high-energy dissipation of the biocomposite. Chee, et al. [12] in their study of the viscoelastic performance of epoxy/kenaf,

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epoxy/bamboo, and epoxy/bamboo charcoal biocomposites recorded a transition temperature range of 60 °C to 90 °C, with epoxy/bamboo charcoal biocomposites recording the maximum thermal stability at 348 °C while epoxy/kenaf biocomposite showed better stiffness and high energy storage capacity. The reinforcing materials play a significant role in determining the overall performance of the composites. Different approaches adopted to improve the performance of particulate-reinforced epoxy matrix include finding alternative and cheaper reinforcements for it. Industrial wastes and agro-waste derivatives are some of the alternative reinforcing materials that have been investigated. Plant fibers, because of their low density, their specific properties (property-to-density ratio), strength, and stiffness are comparable to the values of glass fibers. They are light compared to glass or carbon fibers. On the other hand, the biodegradability of plant fibers can contribute to a healthy ecosystem while their low cost and high performance fulfill the economic interest of the industry.

In light of recent global directives, such as 2009/33/EC and 2008/98/EC, Obande, et al. (2019), which require strict weight reduction targets in transport and a cross-sectoral reduction of landfill-bound waste streams, natural fibers-based reinforced composites offer a superior alternative to synthetics. Okafor, et al. (2022) suggest new ways of using natural fibers, which will prevent environmental concerns and create a second income for farmers. According to the literature, there is no research that relates the epoxy resin with the incorporation of walnut/rice straw fiber in five proportions (2-10 wt%) using the hand lay-up technique.

This study is aimed at investigating the viscoelastic behavior of epoxy matrix incorporated with hybrids of rice straw fiber/walnut shell particulate using dynamic mechanical analysis in three-point bending mode at a constant frequency (1 Hz) and operating temperature range 25 °C to 240 °C. This will help to explore the economic importance of eco-friendly green plant fibers and widens their applications in engineering.

Experimental procedure

Materials sourcing: Waterborne transparent epoxy resin (LY556), hardener (HY-951), and sodium hydroxide (NaOH) solution used in this study were procured from Herenba Instruments and Engineers (Chennai - 600053, Tamil Nadu, India). The reinforcing materials: rice straw fibers and walnut shells were sourced from Abakiliki, Ebonyi State, Nigeria, while the distilled water was sourced from the Department of Industrial Chemistry, Nnamdi Azikiwe University, Awka, Nigeria.

Materials preparation and chemical treatment: The sourced rice straw fibers (RSF) were washed with distilled water and allowed to dry at an elevated temperature of 30 °C for 24 h. The dried fibers were chemically treated with NaOH (alkalization) to enhance epoxy-fiber molecular interactions. The walnut shells were thoroughly washed with distilled water, sun-dried for 24 h, and carbonized in an enclosed alumina crucible at a temperature of 900°C for 5hrs using a muffle furnace. This was done to reduce the carbonaceous matter and increase the percentage of silica content.

Material fabrication: Before the molding process, a mold release agent (silicon spray) was applied on the mold surface to ensure easy removal of composite samples. For the epoxy/rice straw fiber composites, a mold with dimensions 400 × 400 × 4 mm^3 was stacked with rice straw fiber of an average length of 400 mm at total fiber loading of 2, 4, 6, 8, and 10 wt%. The waterborne transparent epoxy resin (LY556) and hardener (HY-951) were mixed properly in a ratio of 10:1 for 20 min and impregnated into the mold. Air bubbles were carefully removed with the aid of a roller. The mixture was consolidated using a hand lay-up technique and cured at constant temperature and pressure of 110 °C and 25×10^6 Pa respectively for 10 min. The consolidated samples were cooled slowly in a cold press at a constant pressure of 25×10^6 Pa for 5 min to avoid warpage. The epoxy/walnut/rice straw fiber hybrid biocomposites were fabricated using the same processes with the walnut/rice straw fiber (WSAp/RSF) added in the same proportions.

Dynamic Mechanical properties Analysis (DMA): The dynamic mechanical properties of the pure epoxy matrix, epoxy/rice straw fiber composites, and epoxy/walnut/rice straw fiber hybrid biocomposites were determined in accordance with ASTM D4065-01 standard using a dynamic mechanical analyzer Perkin Elmer (8000). The composite samples with dimensions 25 ×12 × 2 mm^3 were subjected to a three-point bending mode at an applied load of 10 N, constant frequency (1 Hz), temperature (25 °C to 240 °C), with a heating rate of 2°C/min, and 10 μm displacement amplitude. The fractured surfaces of the developed composites were analyzed using field emission scanning electron microscopy (SEM) (Carl Zeiss, Germany) to examine the fracture mechanism of the composite samples.

Results and discussion

The viscoelastic properties of pure epoxy, epoxy/rice straw fiber composites, and epoxy/walnut/rice straw fiber hybrid biocomposites are presented in Figure 1. These properties were examined using a three-point mode at a constant frequency (1 Hz), temperature range of 25 °C - 240 °C with a heating rate of 5 °C/min, and 10 μm displacement amplitude. The DMA curves were represented by storage modulus, loss modulus, and loss or damping factor (tan δ) as shown in Figure 1a,b and 1c respectively. The stiffness of the fabricated materials is described in terms of storage modulus. Material with maximum storage modulus has a better stiffness. The DMA curve showed that the incorporation of rice straw fiber into the pure epoxy significantly increased the storage modulus (stiffness) of the material. The increase in storage modulus became more significant with the addition of 4 wt% rice straw fiber. Analysis of Figure 1a shows that the storage modulus decreased after incorporating rice straw fiber into the epoxy in excess of 8 wt%. The epoxy/walnut/rice straw fiber hybrid biocomposites showed similar dynamic mechanical behavior. Comparatively, epoxy/walnut/rice straw fiber hybrid biocomposites demonstrated better dynamic mechanical behavior than pure epoxy and epoxy/rice straw fiber composites. This improvement can be attributed to excellent interfacial bonding between epoxy matrix, walnut shell ash, and rice straw fiber molecules as evidenced in the SEM images (Figure 2a,2b and 2c). The storage modulus of all

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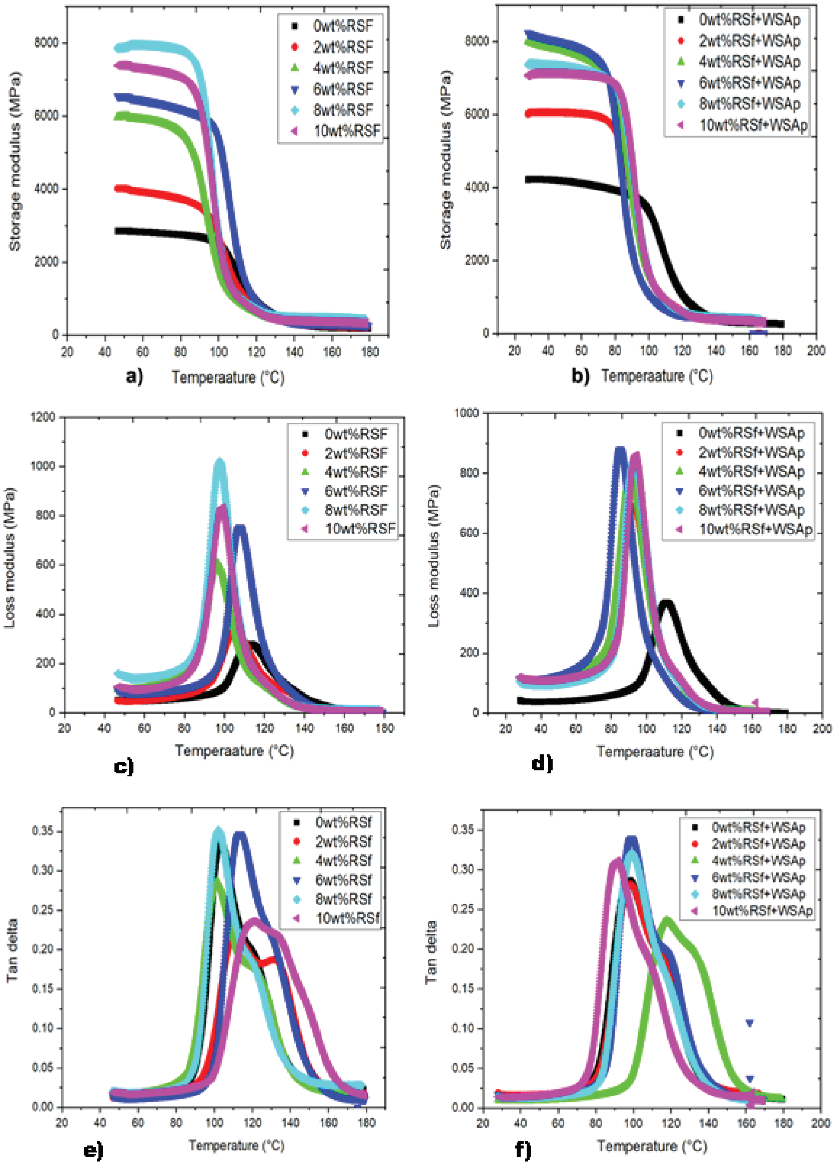

Figure 1: Dynamic mechanical behavior of the fabricated composites at different temperatures (a) storage modulus, (b) loss modulus and (c) damping factor (tan-δ).

the composites remained constant at the glassy region, but decreased progressively at increasing temperature across the glass transition and rubbery regions as described in [6,13,14].

The loss modulus of the developed pure epoxy and composites represents the viscous behavior of the consolidated materials and the degree of energy dissipation in the system during the deformation process. The maximum peak of loss modulus indicates the transition (Tg) temperature of the materials. All the materials behaved alike at increasing temperatures. The loss modulus of both pure epoxy and composites increased correspondingly with the rise in temperature until the glass transition (Tg) temperature where the maximum peak is attained. Beyond the glass transition (Tg) temperature of the consolidated materials, the loss modulus decreased drastically along the rubbery region of the material. The glass transition (Tg) region of the composites fell between 70 °C to 140 °C. Figure 1 showed that pure epoxy resin recorded the lowest storage modulus and loss modulus, indicating poor stiffness and a low degree of heat dissipation compared with the composites. In comparison, epoxy/rice straw fiber composites recorded the highest loss modulus. This can be attributed to high molecular mobility, leading to increased heat dissipation. This behavior is expected and correlated with the reports of previous studies [13,15,16].

The loss or damping factor (tan δ) of the developed pure epoxy and composites indicates the non-elastic deformation behavior of the materials and the rate of energy dissipation in the system. The higher the damping factor, the higher the degree of energy dissipation in the system and the non-elastic properties. The damping factor increased correspondingly with the rise in temperature, reaching maximum peaks in the transition region before decreasing progressively in the rubbery region. Table 1 depicts the glass transition temperature peak, width, and area under the damping factor (tan δ) curve

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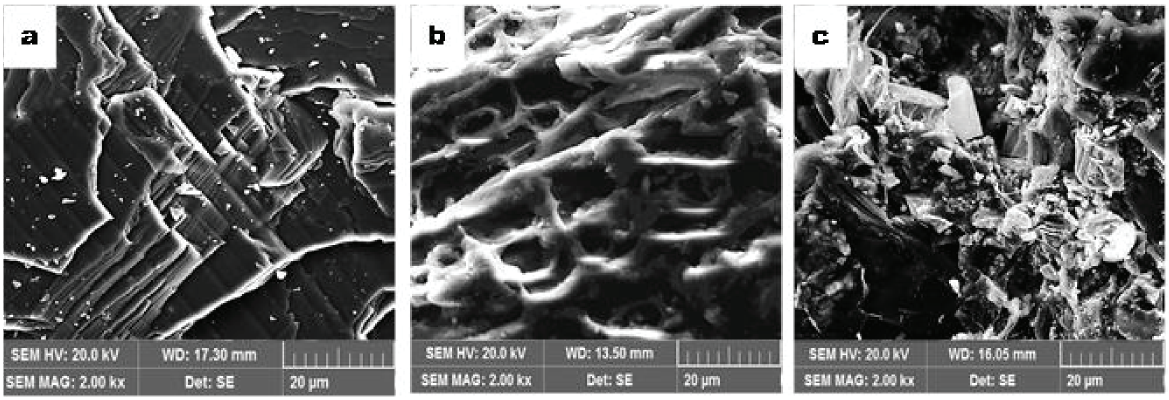

Figure 2: SEM images of fractured surfaces of (a) pure epoxy, (b) epoxy/8 wt% RSF and (c) epoxy/6 wt% (WASp+RSF).

of reinforced composite samples. It is noted from Table 1 that the composites have dual glass transition temperatures (Tg), especially the reinforced samples with significant margins, indicating differences in the deformation mechanisms of composites. The dual tan-δ peaks were indicative of two distinct viscoelastic phases with different glass transition temperatures. The areas under the tan-δ curve are the determinants of the molecular mobility of the composite and the rate of energy absorption and dispersion as described in [14,16]. Additionally, the width of the tan-δ peak at half height represents the heterogeneity of the material. The highest level of damping occurred at 6wt% walnut shell ash+ rice straw fiber [17,18].

Structural analysis

Figure 2 shows the SEM analysis of the fractured surfaces of the investigated epoxy matrix and composites. The SEM image of pure epoxy reveals regions of matrix and cleavages, indicating a brittle failure mechanism at fracture. The micrograph of the epoxy/rice straw fiber composite reveals incomplete bonding of fiber with the epoxy matrix. De-bonding and porosity were also revealed in the SEM image. The micrograph of epoxy/walnut/rice straw fiber biocomposite demonstrated excellent interfacial bonding, leading to excellent dynamic mechanical properties.

It is obvious from the results of dynamic mechanical analysis of bio-composites reinforced with walnut/rice straw fiber that they are of extreme importance in many industries, including polymer and automobile. Therefore, it is an important composite for designing materials with high mechanical properties. Furthermore, the results provide remarkable insight into the different chemistries associated with the bio-composites reinforced with walnut/rice straw fiber. The importance of the dynamic storage modulus in many structural applications is well known. A clear understanding of the storage modulus–temperature curve obtained during a dynamic mechanical test provides valuable insight into the stiffness of a bio-composite reinforced with walnut/rice straw fiber as a function of temperature. The test curves are useful in assessing the molecular basis of the mechanical properties of bio-composite reinforced with walnut/rice straw fiber.

Table 1: Glass transition temperature peaks, width and area under the damping factor (tan-δ) curve of the developed bio-composites.

Composite formulation	Tg1 (°C)	Tg2 (°C)	Width of the tan-δ peak at the half-height (°C)	The area under the tan-δ curve (°C)
Pure epoxy	100	105	26.2	6.51
2 wt% RSF	115	135	29.6	6.93
4 wt% RSF	103	128	31.5	8.44
6 wt% RSF	115	130	32.1	8.46
8 wt% RSF	102	112	34.5	9.19
10 wt% RSF	120	136	34.2	8.66
2wt% RSF/WSAp	105	120	31.8	7.21
4 wt% RSF/WSAp	120	134	33.2	8.56
6 wt% RSF/WSAp	100	125	34.8	9.88
8 wt% RSF/WSAp	105	120	35.2	9.52
10 wt% RSF/WSAp	103	115	35.9	9.49

The curves are very sensitive to structural changes such as molecular weight, degree of cross-linking, and fiber–matrix interfacial bonding. It is noted that the storage modulus is linearly proportional to the loss modulus in terms of difference percentages under each reinforcing element. The behavior was predicted and corroborated by Onwumere, et al. [9] and Nwigbo, et al. [7] regarding predicted relationships between E′ and E″ in composites. The reinforced composites possess the same order of damping capabilities except for a few variations as a result of fillers content. The reason why reinforced composites possess low tan delta is because of the strong and rigid fiber/matrix interface due to improved adhesion, which reduces molecular mobility in the interfacial zone. Moreover, the presence of bonding agents results in a greater number of crosslinks being formed, and alkali treatment strengthens these crosslinks. Due to this, molecular motion is severely hindered within the rubber macromolecular chain, resulting in low damping characteristics. Jacob, et al. and Datta, et al. [19,20] have reported similar results.

Conclusion

The dynamic mechanical performances of the pure epoxy matrix, epoxy/rice straw fiber composite, and epoxy/walnut/rice straw fiber biocomposites have been investigated experimentally. Both composites demonstrated excellent

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dynamic mechanical properties better than the pure epoxy matrix. The hybrid's epoxy/walnut/rice straw fiber biocomposites recorded the maximum storage modulus with low loss modulus and damping factor, indicating excellent stiffness and high energy storage capacity. This excellent dynamic mechanical behavior was attributed to excellent interfacial bonding between the epoxy matrix, walnut shell ash particulates, and rice straw fiber. The glass transition temperature of the composites is in the range of 70 °C to 130 °C, above which they exist as soft and rubbery materials.

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