INFLUENCE OF SURFACE MODIFICATION AND FIBER LOADING ON THE PROPERTIES OF RICE STRAW-REINFORCED EPOXY COMPOSITES

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Abstract

Fiber-reinforced composites have found extensive applications in construction, automotive, aerospace, and many fields. As a result of global sustainable development and environmental concern, however, natural fibers have become increasingly attractive over synthetic fibers due to their light weight, low cost, abundance, and biodegradability. This study has been carried out to evaluate the potential use of rice straw fiber as a reinforcement material for epoxy composite. Rice straw fibers were treated with NaOH aqueous solution and silane coupling agent, respectively, before they were applied into epoxy composites. The effect of surface modification and fiber contents on mechanical properties was investigated by flexural and impact tests. Compared with untreated rice straw fiber reinforced epoxy composite, fiber treated with 3% NaOH followed by 3% silane coupling agent showed the highest flexural strength and the maximum flexural strength was obtained at 15% fiber content. The untreated rice straw fiber reinforced epoxy composite, however, showed the highest impact strength as compared to all treated fibers and the maximum impact strength for untreated rice straw fiber filled epoxy composite was also obtained at 15% fiber content. The surface modified rice straw fiber composites exhibited lower water absorption values than those of untreated fiber-based composites.

Keywords: Fiber-reinforced composite, Rice straw fiber, Epoxy resin, Surface modification

Introduction

In the recent decades, the applications of natural fibers as reinforcement in polymer composites have drawn significant interest for scientists and researchers as an alternative to traditional materials as a result of environmental awareness (Maiti et al., 2022; Wambua et al., 2003). Natural fibers such as sisal, kenaf, bagasse, flax, hemp, and jute have been used as reinforcement in composite due to their low cost, low density, low weight, biodegradability, as well as good thermal and acoustic insulation properties (Goulart et al., 2011; Sanjay et al., 2019). Despite several advantages, natural fiber also poses few drawbacks such as poor wettability, high moisture absorption, and incompatibility with polymer matrices. The main concern in using natural fiber as reinforcement in polymer composite is insufficient adhesion between fiber and polymer matrix. The incompatibility between natural fiber and matrix arises from the hydrophilic characteristic of fiber and hydrophobic behavior of polymer matrix. Load transfer from matrix into fiber is not good due to low interaction between fiber and matrix, which lead to the undesirable properties of the composites (Ku et al., 2011). Many studies have been performed to improve the adhesion between fibers and matrix by modification of fiber and/or polymer matrix using physical and chemical techniques (Yousif et al., 2012; Mariatti et al., 2008). Chemical treatment is the most common technique used to improve the adhesion with a polymer matrix as studied by many researchers (Kabir et al., 2012; Sanjay et al., 2019). It has been found and reported that the interfacial bonding can be improved by the surface modification of the fiber through alkali treatment and chemical coupling method, which in turn will improve the overall performance of the composites (Suckley et al., 2017; Tingju et al., 2013; Uma et al., 2012).

This present work investigated the characteristic of rice straw fiber and rice straw-reinforced epoxy composite. The effect of sodium hydroxide and silane coupling agent treatment as well as fiber loading on the physical and mechanical properties of untreated and treated fiber reinforced epoxy composites were studied.

Materials and Methods

1. Materials

The raw rice straw fibers were obtained from the local farmer (Nakhonsawan Province, Thailand). The fibers were soaked in tab water for 3 h and then rinsed several times to remove any dirt. The fibers were then dried for 6 hrs in an oven at a temperature of 60°C. The clean rice straw fibers were crushed using a power blender into lengths of 2-3 mm and sieved through a 40-100 mesh sieve. Epoxy resin, obtained from Aditya Birla Chemicals (Thailand) Ltd, (Epoxy Division), was used as matrix and the curing agent used for the selected epoxy was an aliphatic amine for room temperature curing.

2. Fiber Treatment

For alkali treatment, the rice straw fibers were soaked in 3% NaOH (AR grade, KemAus) solution for 24 hrs. The alkali treated fibers were washed several times with water to remove any trace of NaOH from the fibers surface and dried in an oven at 60°C for 10 hrs. For silane treatment, pre-treated fibers with 3% NaOH were soaked in a solution of 1, 2, and 3% of 3-aminopropyltriethoxy silane (AR grade, Aldrich) in 80/20 ethanol: DI water mixture for 3 hrs. The pH of the solution was maintained between 3.50 to 4 using acetic acid (AR grade, RCI Labscan). The silane treated fibers were washed several times and dried in an oven at 60°C for 10 hrs.

3. Composites preparation

The rice straw-epoxy composites were prepared by casting technique. Epoxy/hardener (10:6 w/w) mixture was stirred and the fibers were added. After the matrix and fibers were thoroughly mixed, they were poured into a PTFE mould with dimensions 100 mm length x 30 mm width x 5 mm height. The mixtures were allowed to cure at room temperature for 24 hrs. Composites with amounts of rice straw fibers, ranging from 5, 10, 15 and 20 wt.% of treated and untreated fibers were prepared. For the neat epoxy resin, the material was fabricated in the same procedure to the composites procedure without adding the fibers.

4. Moisture content

The moisture content of untreated and treated rice straw fiber was determined. The initial weight of fiber was measured, then the fiber was heated in an oven at 105°C for 24 hrs, and weighed again. The moisture content was calculated as the measured weight loss after storage at 105°C divided by the weight before storage and multiply by 100.

5. Thermogravimetric analysis

Thermogravimetric analysis of untreated and treated rice straw fibers, neat epoxy resin and untreated and treated rice straw fibers-epoxy composites was carried out using Mettler Toledo Thermogravimetric Analyzer TGA/DSC1. The scanned temperature range was from 40 to 600°C with a heating rate of 10°C/min. The weight of the sample was maintained at approximately 10 mg. The analysis was conducted under the nitrogen atmosphere.

6. Mechanical Testing

Flexural tests were performed according to ASTM D 5943-56 using the three-point bending mode on a Universal Testing Machine (INSTRON 3369). The crosshead speed was at 2 mm/min and a support span length was set at 48 mm. Five specimens were used for each test and average values were recorded.

7. Scanning Electron Microscopy (SEM) analysis

The morphology of the fractured samples was examined using JEOL JSM 820 scanning electron microscope operating with secondary electron imaging at 5 kV. The fractured surfaces were sputter coated with gold to avoid charging before recording the micrographs.

8. Water absorption analysis

The specimens with the dimension of 30 mm x 50 mm x 5 mm were used for water absorption test. Specimens were oven dried at 60°C for 24 h to a constant weight *(M_0)*. The specimens were then immersed in the water tank and periodically taken out from tank, surface dried with absorbent paper and weighed using a digital balance (M_i). The percentage weight gain at any time (percent water absorption, M_t), as a result of water absorption was determined by using equation (1), where M_0 is the dry initial weight, M_i is the weight after immersion in water.

$$M_t\,(\%) = \frac{M_i - M_0}{M_0} x\ 100 \qquad (1)$$

Results

1. Characterization of untreated and treated rice straw fiber

1.1 Moisture content

Moisture content in fiber used for reinforced composite can affect mechanical properties of the composite materials, therefore, it should be investigated for both untreated and treated rice straw fibers. Untreated fibers had moisture content at 0.043%. Treated rice straw fibers had lower moisture content as compared to untreated fiber as shown in Figure 1. Moisture content of treated rice straw fiber slightly decreased with increasing the concentration of silane solution. The lowest moisture content was obtained at 0.036% for fiber treated with NaOH and followed by 3% silane coupling agent.

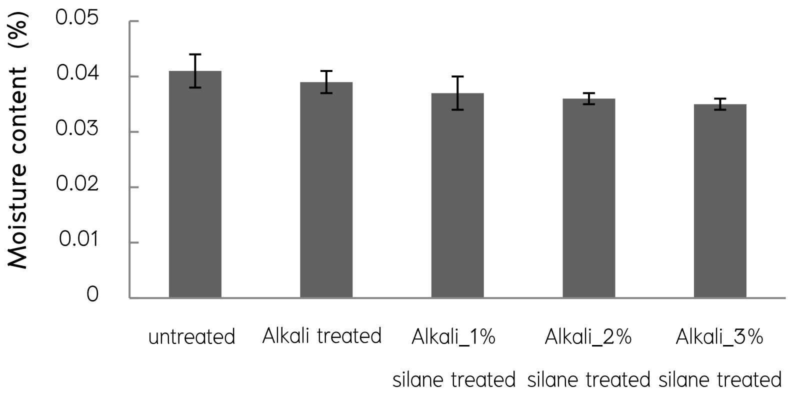


Figure 1 Moisture content of untreated, alkali-treated, and alkali-silane treated rice straw fiber.

1.2 Thermogravimetric analysis

TGA curves of the untreated and treated rice straw fibers are shown in Figure 2. It can be seen that the thermal decomposition of untreated rice straw fiber occurred earlier than the other samples. The treated fibers exhibited an improvement in their thermal stability as compared to untreated fiber. The decomposition of NaOH treated fiber and alkali-silane treated fibers were initiated at 40°C and 44°C, respectively, higher than untreated rice straw fiber. The decomposition temperature of NaOH treated fiber, however, was slightly lower than that of alkali-silane treated fibers.

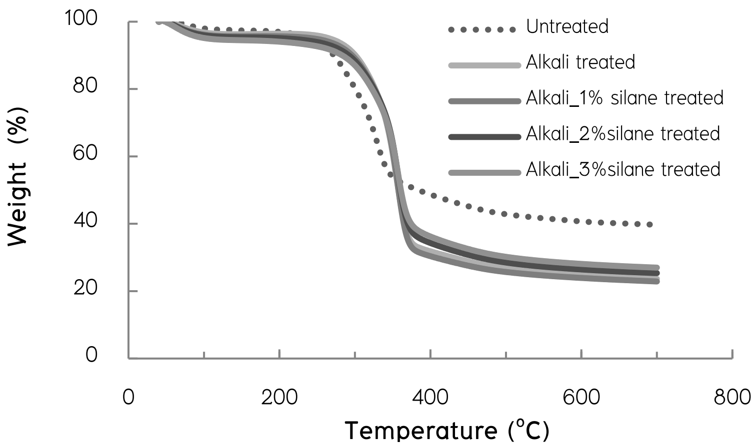


Figure 2 TGA curves of untreated, alkali-treated, and alkali-silane treated rice straw fiber.

The addition TGA study has been conducted to investigate the effect of silane treatment itself on neat fiber. The result is shown in Figure 3. It was observed that the decomposition temperature of silane-treated rice straw fiber was approximately 14°C higher than untreated fiber. The enhanced thermal stability of alkali-silane treated fibers could be attributed mainly to the effect of alkali treatment to the rice straw before the fiber was subjected to silane treatment. It is noted that the concentration of silane solution had no significant effect on thermal resistance of rice straw fiber. The percentage of weight reduction at 700°C reveals the amounts of residues left after the fibers were decomposed. Treated rice straw fibers had lower residue than untreated fibers. It can be seen that the alkalization process yield fiber with lower residual weight as compared to fiber treated with silane. TGA analysis indicates that the chemically modified rice straw fibers thermally stable below 330°C, therefore the fibers could be used effectively as reinforcement when the processing temperature was set under this temperature. The TGA data from the curves in Figure 2 and 3 are presented in Table 1.

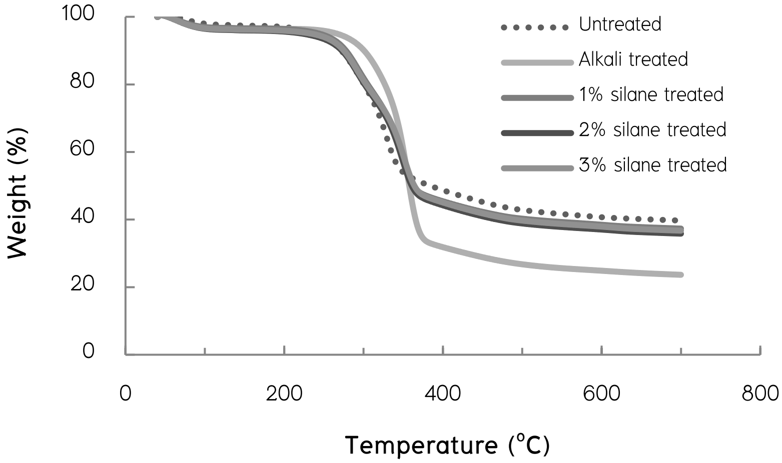


Figure 3 TGA curves of untreated, alkali-treated, and silane treated rice straw fiber.

Table 1 Decomposition temperature and charring of rice straw fibers.

Rice straw fiber	Decomposition temperature, (°C)	Increment in thermal stability, (%)	Weight loss at 100°C, (%)	Residual weight at 700°C, (%
Untreated	284.9	-	2.01	39.70
Alkali treated	325.6	14.27	3.22	23.65
Alkali-1% silane treated	328.9	15.44	3.84	22.88
Alkali-2% silane treated	329.5	15.62	4.06	25.36
Alkali-3% silane treated	328.5	15.27	4.84	26.99
1% silane treated	298.6	4.79	3.43	35.59
2% silane treated	299.1	4.97	3.62	35.69
3% silane treated	300.8	5.56	3.92	37.34

2. Properties of rice straw fiber-epoxy composites

In order to study the effect of fiber loading on mechanical and physical properties of rice straw fiber composites, alkali-3% silane treated fiber was selected to use as reinforcement due to its high thermal stability and low moisture content.

2.1 Flexural Strength

Flexural strength of the untreated and treated rice straw fiber composites with varying fiber content is shown in Figure 4. The application of rice straw fiber as reinforcement in epoxy composite exhibited the improvement of flexural strength for both untreated and treated fibers. The use of chemical treated fiber, moreover, was found to enhance the flexural properties of epoxy composites more than the untreated one. The results also show that alkali-silane treated rice straw fiber composite had slightly higher flexural strength than alkali treated fiber composite for all fiber content. The maximum flexural strength was observed at 15% fiber content at 59 MPa and 54 MPa for alkali-3% silane treated and alkali treated rice straw fibers, respectively. The maximum flexural strength of chemical treated fibers composites were twice as much as compared to neat epoxy resin.

On the other hand, the flexural strength of untreated rice straw fiber composites decreased with increasing fiber content. This could be attributed to the bulky volume of the untreated rice straw fiber as compared to treated fiber.

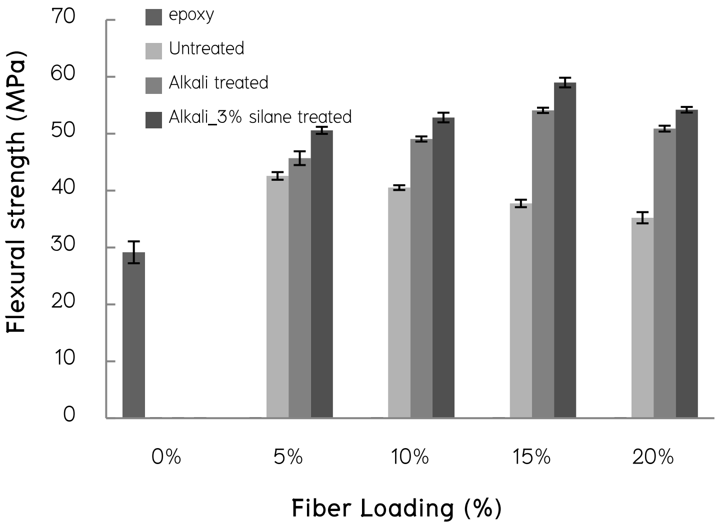


Figure 4 Flexural strength of untreated and alkali treated rice straw fiber epoxy composites at different fiber loading.

2.2 Impact Properties

Surface modification of rice straw fiber composites showed lower impact strength as compared to untreated fiber composites as seen in Figure 5. Alkali treated rice straw fiber composite had higher impact strength as compared to silane coupling agent treated fiber composites. The rice straw reinforced epoxy composites, however, had higher impact strength than those of neat epoxy resin. Increasing of fiber content showed no significant difference for impact strength up to 15% fiber loading. The reduction of impact strength was observed at 20% fiber loading for both untreated and treated rice straw fiber composites.

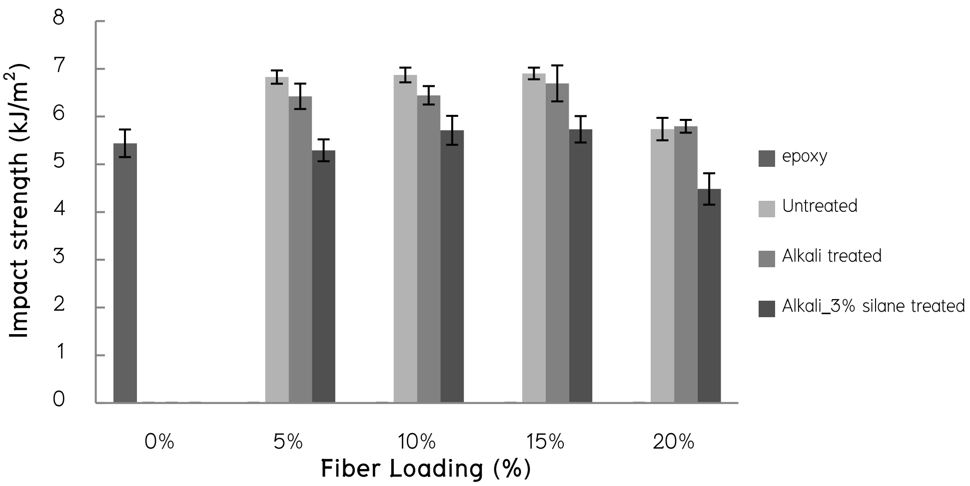
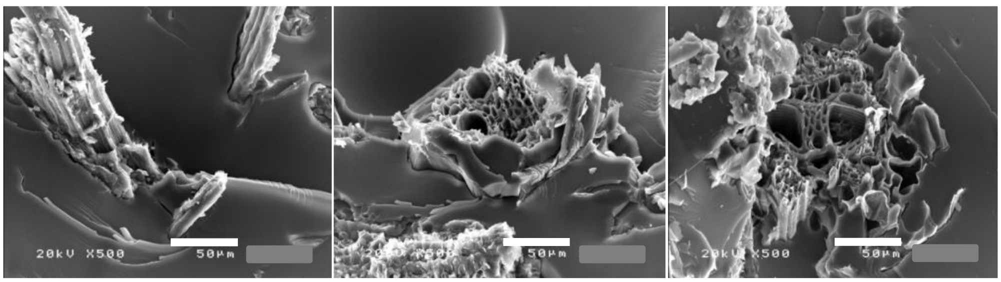


Figure 5 Impact strength of untreated and alkali treated rice straw fiber epoxy composites at different fiber loading.

2.3 Fracture surface

The fracture micrographs of the composites with 15% loading of rice straw fiber were observed by SEM. As seen in Figure 6(a) for untreated rice straw fiber epoxy composite, the phenomenon of pull-out fibers occurred more than those of treated rice straw fiber-based composite. It could be observed that alkali-silane treated rice straw fiber composite (Figure 6(c)) shows better interfacial adhesion between fiber and polymer matrix as compared to alkali treated fiber (Figure 6(b)) which leads to better flexural strength as mentioned above.



(a) (b) (c)

Figure 6 SEM micrograph of flexural fracture surface of; (a) untreated rice straw fiber epoxy composites; (b) alkali treated rice straw fiber epoxy composites; (c) alkali-silane treated rice straw fiber epoxy composites.

2.4 Water Absorption

The water absorption behavior of epoxy and rice straw fiber composites (15% fiber content) as a function of exposure time in water are shown in Figure 7. In all cases, the water absorption rate was high at the beginning of the process and leveled off for some period of time before it reached the equilibrium. The untreated rice straw fiber composite exhibited the highest absorption rate and weight gain. The alkali-silane surface treatment of rice straw fiber reduced more water uptake for the composite system as compared to alkali treated rice straw fiber.

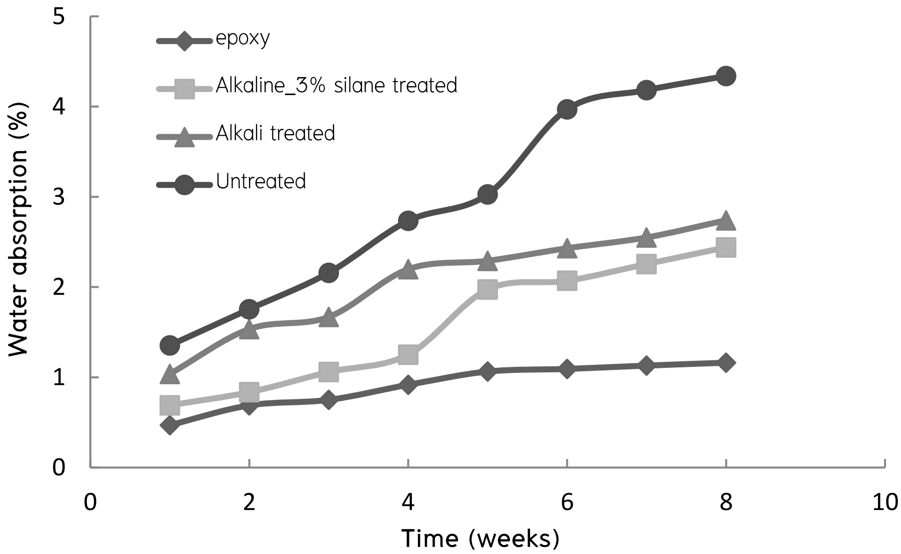


Figure 7 Water absorption behavior of epoxy and untreated and treated rice straw fiber composites.

Discussion

Surface modification of rice straw fiber by alkali treatment and alkali-silane coupling agent treatment resulted in the decrease of moisture content. This can be attributed to the reduction of the hydroxyl group in the cell wall of the fiber molecule, thus decreasing the water content of the fiber (Mariatti et al., 2008; Xue, Lope & Satyanarayani 2007). The concentration of silane coupling agent solution slightly affected the moisture content of modified fiber. The treatment with silane coupling agent increases the hydrophobicity of the fiber by adding functional groups to their surface (Panaitescu et al., 2016), therefore increasing the concentration of silane solution lead to the reduction of moisture content. Chemical treatment can also improve thermal stability of treated fiber. From TGA analysis, it was found that the enhanced thermal stability could be largely affected by alkali treatment. According to Mariatti et al. (2008) the alkali treatment destroyed the cellular structure of the fiber resulted in a compressed structure which could act as thermal insulators. Many researchers have also reported improvement in decomposition temperature of natural fibers after alkalization (Azwa & Yousif, 2013) and silane treatment (Panaitescu et al., 2016; Xie et al., 2010) due to the removal of lignin, wax and oils from the surface of the fiber.

The superior flexural properties of chemically modified rice straw fiber composites as compared to untreated rice straw fiber composites are attributed to the improvement of fiber surface adhesives characteristic by fibrillation process. Cao, Shibata & Fukumoto (2006) reported that the alkali treatment decreased fiber diameter by the compression of cellular structure which could enhance the mechanical properties of the composite. The samples with fiber treated with alkali-silane coupling agent showed slightly better flexural strength than the sample with fiber treated only with alkali. This could be attributed to improved quality of the fiber/matrix interface from silane coupling agent. Silane coupling agent reacts with the hydroxy group on the surface of the fiber and it is compatible with the matrix, therefore contributing to good interfacial bonding and enhancement of the mechanical properties. The effectiveness of silane coupling agent in improving the adhesion between matrix and natural fiber has been reported in many works (Panaitescu et al., 2016, Pickering et ai., 2016). Impact strength of untreated rice straw fiber composites was higher than composites with treated fibers. This could be ascribed to the loose structure of untreated fiber that can absorb more impact energy (Tingju et al., 2013). More loading of fiber at 20% resulting in the reduction of impact strength due to poor dispersion of the fibers in the matrix (Tingju et al., 2013).

As mentioned previously, chemical treatment can reduce the hydroxyl group in the cell wall of the natural fiber molecule, thus decreasing the water absorption of the composites. The results are in accordance with works by Fraga et al. (2006); Mariatti et al. (2008).

Conclusions

Effects of surface modification and fiber loading on the properties of rice straw-reinforced epoxy composites were investigated. The alkalization followed by silane treatment increased thermal stability and reduced moisture content of rice straw fiber. The use of chemical treated fiber was found to improve the flexural properties of epoxy composites owing to better interfacial adhesion between fiber and polymer matrix. The maximum flexural strength was observed at 15% fiber content. Treated rice straw fiber composites, however, showed lower impact strength as compared to untreated fiber composites. It was also observed that the surface modified rice straw fiber composites had lower water absorption values than those of untreated fiber-based composites.

The over all results from this research work show that modified rice straw fiber using alkali-silane treatment has potential utilization as reinforcement for natural fiber composite because of its enhancement of thermal stability, better interaction between fiber and the matrix, improvement of flexural strength as well as reduction of moisture content. The replacement of synthetic fiber by natural fiber in polymer composite can make a better impact for the environment as it is biodegradable and also give value-added to the agricultural waste. Modified rice straw fiber reinforced epoxy composite can be applied as windmill or drone blades, construction materials, furniture, and automotive components.

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