INVESTIGATION ON THERMAL BEHAVIOR OF ALKALI AND BENZOYL TREATED HEMP FIBER REINFORCED CELLULOSE FILLED EPOXY HYBRID GREEN COMPOSITES

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Natural fibers have recently become an affordable alternative to glass fiber reinforced thermoplastics used for reinforcement in the automotive industry. This research is focused on developing and evaluating the thermal behaviors of eco-friendly cellulose filled epoxy hybrid composites reinforced with treated hemp fibers for automotive applications. The thermal behavior of cellulose filled epoxy hybrid composites reinforced with hemp fibers was studied by means of thermogravimetric analysis, linear coefficient of thermal expansion, thermal conductivity and heat deflection temperature. The thermal stability of the composites was found to be higher than that of other natural fiber reinforced composites. The effects of fiber loading, fiber length, fiber orientation and fiber modification on the thermal properties of the composites were evaluated. Fiber modifications were achieved by benzoylation and alkalization to improve the fiber -matrix adhesion. The addition of cellulose powder considerably increased the thermal stability. The treated-fiber composites showed better properties than those of untreated-fiber composites.

Keywords: hybrid green composites, thermal properties, thermogravimetric analysis, heat deflection temperature, surface treatments of fibers

INTRODUCTION

Environmental awareness throughout the world has impacted materials engineering and design. Renewed attention in the application of natural materials has been spurred by ecological issues, such as recyclability and environmental safety. Currently, artificial fibres, such as glass, carbon and aramid, are widely used in polymerbased composite, owing to their high stiffness and strength properties. 1,2 However, carbon/glass fibres have serious drawbacks in terms of their biodegradability, initial processing levies, recyclability, energy consumption, machine abrasion, health hazards, etc.3 Most significantly, their adverse environmental impacts shift the concentration from artificial fibres natural/renewable fibers. The introduction of natural fibers from annually renewable resources is now popularly used as reinforcement in polymer matrices. They impart benefits to the

environment with respect to the degradability and utilization of natural materials.² The successful use of natural fibers is dependent on their well-defined structural and mechanical properties. The mechanical properties are influenced by the growth site, climate conditions, age of the plants and the extraction methods that are used.^{3–5}

Natural fibers, such as flax, hemp, jute and sisal, have been well recognized as good potential reinforcements for engineering fiber composites. The advantageous features of these fibers are their lightweight, high specific modulus, non-toxicity, easiness of processing and absorption of CO₂ during plant growth. These benchmarking properties open the opportunity of using natural fibers in the composite sector and challenge the replacement of artificial fibers. However, natural fibers are not a problem-free alterative as they have certain shortfalls in properties. Their

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structural composition (cellulose, hemicelluloses, lignin, pectin and waxy substances) allows moisture absorption from the environment, which leads to poor bonding with the matrix materials.⁶ Additionally, the chemical structures of the fibers and matrix are different and couplings between these two phases are challenging. This causes ineffective stress transfer throughout the interface of the composites. Therefore, certain chemical treatments on the surface of natural fibres are definitely needed. These treatments are usually based on the use of reagent functional groups that are capable of reacting with the fiber structures and changing their composition. As a result, the tendency of moisture absorption of the fibers is reduced and this facilitates greater compatibility with the polymer matrix.⁴ For the fabrication of fiber composites. various arrangements, such as short randomly oriented, long unidirectional and woven fabrics, are used. Natural fiber reinforced composites have been investigated by several researchers with respect to their mechanical and thermal properties. Many academic and industrial research activities are ongoing to develop better interfacial bonding properties of the composites. Experimental parameters were tested by using different chemical treatments to achieve stronger fibre surface adhesion to the surrounding matrix.

Fiber reinforced polymer composites have prevalent applications as structural materials on account of their ease of fabrication, relatively low cost and exemplary thermal properties compared to polymer resins. These composites are considered as alternatives for metal materials, the concurrence of metallic fiber with a polymeric matrix being attractive for electronic packaging applications. The combination of reinforcement with high thermal conductivity embedded in a resin matrix with low thermal conductivity is desirable to dissipate the heat flux for electronic packaging components. Studies on the thermal properties of short fiber reinforced polymer composites have proved that both fiber length distribution and fiber orientation distribution play major roles in determining the thermal properties. 7-11 A number of experimental models have been proposed to predict the thermal conductivity of short fiber composites. 12-15 Thermal conductivity is a bulk property analogous to mechanical modulus. Also, it is well accepted that a mathematical similarity exists between thermal conduction and the elasticity of fiber composites. It is observed that the thermal

conductivity of the composite increases with mean fibre length, but decreases with mean fiber orientation angle with respect to the measured direction.¹⁶

Composites having two or more fillers in the same matrix are called hybrid composites. ^{17,18} The reinforcement with glass fibre of a polyester matrix produces composites with impact strength comparable to that of reinforced thermoplastics. ¹⁹ Recently, there has been a growing interest in hybridizing different natural fibres in order to produce high performance composite materials. ²⁰⁻

A synergistic strengthening of fibers was observed in the case of filler filled hybrid fiber reinforced composites, where thermal properties showed a positive hybrid effect. ²²⁻²⁴ In this paper, the thermo-physical properties of cellulose filled hemp fiber reinforced epoxy composites were studied as a function of fiber volume fraction and fiber surface modification. The results will be useful for improving the process and utilizing natural fiber composite materials.

EXPERIMENTAL

Materials

Hemp fiber mats were purchased from "Sheeba Fibers and Handicrafts", Poovancode, Tamilnadu, India, and their properties are given in Table 1. The epoxy resin employed in the present study was LY556 and the hardener HY951 was purchased from the Modern Scientific Pvt Ltd, Chennai, Tamilnadu, India. LY556 resin is a bi-functional epoxy resin, i.e., diglycidyl ether of biphenyl-A (DGEBA), and HY951 is an aliphatic primary amine, viz., triethylene tetramine - TETA, with the mixing ratio of 10:1 w/w. Lyocell powder (1.7 decitex) of around 12 µm was supplied by Simtek Lab Agencies, Navi Mumbai, India. Chemicals used for the surface modification of fiber were commercial sodium hydroxide and benzoyl chloride, which were kindly supplied by Simtek Lab agencies, Navi Mumbai, India.

Treatment of fiber

First, the received hemp fibers were washed with distilled water to remove the surface dirt and then they were dried in an air circulating oven at a temperature of 100 °C until a fixed value of weight. The obtained fibers were named "raw hemp fibers".

Bleaching treatment

For this treatment, 25 g hemp fibers were added to a 2 L solution containing 320 mL (30% w/w) hydrogen peroxide and 1 g sodium hydroxide, and heated at 85 °C for 1 h.^{25,26} During this process, the fibers were cooked in the solution under gradual rise and fall of the temperature of the bath from 30 °C to 85 °C. This process of heating and cooling was done for a period

of 1 h. Finally, the cooked fibers were removed from the mixture at a temperature of 30 °C. In order to remove excess chemicals, the fibers were washed with distilled water. After washing, the fibers were again dried in an air circulating oven at a temperature of 100 °C until constant weight.²⁷ The obtained fibers were designated as "bleached hemp fibers".

Table 1
Properties of untreated hemp fibers used as reinforcement

| Density (g/cm ³) | 1.47 |
|------------------------------|------|
| Elongation (%) | 2-4 |
| Tensile strength | 690 |
| Elastic modulus | 70 |

Alkaline treatment

Alkaline treatment or mercerization is one of the most used chemical treatments of natural fibers when used to reinforce thermoplastics and thermosets. The important modification done by the alkaline treatment is the disruption of hydrogen bonding in the network structure, thereby increasing surface roughness. This treatment removes a certain amount of lignin, wax and oils covering the external surface of the fiber cell wall, depolymerises cellulose and exposes the short length crystallites.²⁸ The addition of aqueous sodium hydroxide (NaOH) to natural fiber promotes the ionization of the hydroxyl group to the alkoxide.²⁹ A water-ethanol solution (80:20) was prepared (6% NaOH) and stirred continuously for 1 hour. Later, fiber mats were immersed one by one in the solution. Finally, after immersing all the fiber mats, they were left undisturbed for nearly 3 hours. Then, the fiber mats were washed several times with distilled water followed by drying at 80 °C for 5 hours in a hot air oven. 30-33

Benzoylation

Benzoylation is an important transformation in organic synthesis.³⁴ Benzoyl chloride is most often used in fiber treatment. Benzoyl chloride includes benzoyl (C₆H₅C=O), which contributes to the decreased hydrophilic nature of the treated fiber and improved interaction with the hydrophobic polymer matrix.³⁴ The benzoylation of fiber improves fiber matrix adhesion, thereby considerably increasing the strength of the composite, decreasing its water absorption and improving its thermal stability. It was observed that the thermal stability of treated composites was higher than that of untreated fiber composites. The fiber was initially alkaline pretreated in order to activate the hydroxyl groups of the cellulose and lignin in the fiber; then the fiber was suspended in 10% NaOH and benzoyl chloride solution for 15 min. The isolated fibers were then soaked in ethanol for 1h to remove the benzoyl chloride and finally washed with water and dried in the oven at 80 °C for 24 h.

Composite fabrication

The composite material was fabricated by using the hand layup technique. Composite fabrication using double weave and non-woven hemp mats (150×150×1 mm³) was carried out in square moulds of the following volume 350x350x3, 350x350x6 and 350x350x10 mm³. Initially, the mould was polished and mould releasing agent was applied on its surface. Resin, hardener mixture and synthetic cellulose powder (10:1:4.3) were used for every layer. Figure 1 shows the treated hemp fiber mat used for the material preparation. Initially, the fibers were dried in sun light to remove the moisture. The mould surface was cleaned and releasing agent (wax) was applied. A thin layer of resin was also applied on the board. The woven roving NFRP was then completely filled with resin mixture, rolled to remove entrapped air and to uniformly spread the mixture. In this way, three layers of woven roving were placed one over the other to obtain top and bottom layers. A curing time of 24 h at room temperature was allowed for the structures to obtain good strength. Then, the required composite was obtained. By the same fabrication procedure, composites of different configurations by varying the ratio of cellulose powder and epoxy resin were fabricated. The same fabrication process was then carried out with chemically treated fibers. Thus, untreated and treated composites were prepared. Figure 2 shows the fabricated composite material.

Testing of composites

All the tests were carried out as per ASTM Standards at Central Institute of Plastics Engineering and Technology, Chennai, India, an ISO/IEC 17025:2005 – NABL Accredited Laboratory and ISO/IEC 17020 – NABCB Accredited Laboratory.

Thermogravimetric analysis (TGA)

The thermal decomposition of the neat polymer, fibers and composites were evaluated by thermogravimetric analysis (TGA) under ASTM Standard E 1131.

TGA measures changes in physical and chemical properties of materials as a function of increasing temperature (with constant heating rate). Using a Pyris 1 instrument from Perkin–Elmer, Italy, samples of ≤5



Figure 1: Treated hemp fiber mat

Heat deflection temperature/deflection temperature under load (DTUL or HDT)

Heat deflection temperature is defined as the temperature at which a standard test bar deflects a specified distance under a load. It is used to determine short-term heat resistance. It distinguishes between materials that are able to sustain light loads at high temperatures and those that lose rigidity over a narrow temperature range. Specimens of 127 mm×12.7 mm×3 mm size were placed under the deflection measuring device. A load of 1.80 MPa was placed on each specimen. The specimens were then lowered into a silicone oil bath where the temperature was raised at 2 °C per minute until they deflected 0.25 mm according to ASTM D 648.

Thermal conductivity

A material's thermal conductivity describes its ability to conduct and dissipate heat. This property influences the temperature distribution and the cooling behavior of the polymer melt. Thermal conductivity data are vital for high-end process simulation of extrusion and injection molding, as polymer thermal properties affect the process design, optimization, and the quality of finished parts. Testing was performed using a guarded-hot-plate apparatus. Two identical samples of 50 mm diameter and 10 mm thickness were placed on opposite sides of the main heater. The main heater and guard heaters were kept at the same temperature of 55 °C. Both auxiliary heaters were maintained at lower temperature. The guard heaters minimize the amount of lateral heat transfer from the main heater. Temperatures were monitored at each surface by thermocouples. The heat transferred through the specimens was equal to the power supplied to the main heater. Thermal equilibrium was established when temperature and voltage readings were steady. ASTM standard E 1530 has been followed for the above test.

Coefficient of linear thermal expansion

Linear thermal expansion is used to determine the rate at which a material expands as a function of mg weight were scanned from 40 to 900 °C at a heating rate of 50 °C per minute in nitrogen atmosphere, and the corresponding weight loss was recorded.



Figure 2: Fabricated HFRP specimen

temperature. This test can be used for design purposes and to determine if failure by thermal stress may occur. Understanding the relative expansion/contraction characteristics of two materials in contact can be important for successful application. The ASTM Standard D 696 has been followed. A dilatometer was used for this analysis. A specimen of 127 mm×12.7 mm×3 mm size was placed in the dilatometer at room temperature, and the height gauge was positioned and zeroed. The apparatus was placed in a temperature bath and the sample was measured from 30 °C to 70 °C.

Morphological study (FESEM)

Illustrating the effect of surface treatments of the fibre, the failure surfaces of the specimens subjected to the test were analyzed using a JEOL Quanta FEG field emission scanning electron microscope (FESEM). In FESEM, electrons are liberated from a field emission source and accelerated in a high electrical field gradient. Within the high vacuum column, these socalled primary electrons are focused and deflected by electronic lenses to produce a narrow scan beam that bombards the object. As a result, secondary electrons are emitted from the etch spot on the object. The angle and velocity of these secondary electrons relates to the surface structure of the object. Secondary electrons are detected or caught and an electronic signal is produced. This signal is amplified and transformed to a video scan-image or to a digital image. All specimens were sputtered with a 10 nm layer of gold prior to FESEM observations. Each specimen was mounted on the aluminum holder of the microscope using double sided adhesive electrical conduction carbon Accelerating voltage of 5-30 kV was employed. The FESEM analyses of both untreated and treated fiber composites were compared.

RESULTS AND DISCUSSION

Seven specimens with different compositions, with three samples for each, were tested to find the thermal properties listed Table 2.

Thermal stability

The thermal stability of the treated and untreated hemp fiber reinforced cellulose filled epoxy matrix composites was studied by TGA under nitrogen in the range of 40-900 °C at a heating rate of 50 °C min. Similarly to some other fibers, the thermal degradation of hemp fibers was a two-stage process, the first associated to the degradation of hemicellulose in the temperature range of 230-360 °C and the second associated to lignin degradation in the range of 360-440 °C. 35,36 The degradation temperature of the neat epoxy was observed at 451 °C, and increased to 536 °C when treated fibers were incorporated into the cellulose filled polymer matrix at 25 wt% content (Table 3). The results of the thermogravimetric analyses for raw and polymer coated hemp fibers are shown in Figures 3 and 4.

The thermal analysis of the treated hemp fiber composite compared it to a binary system, comprising the thermal degradation of the neat epoxy and of the fibers. It was observed, after a series of tests, that there was a slight increase (15%) in the thermal degradation upon the addition of 25 wt% fibers to the neat epoxy. The observed increase in the thermal stability of both systems was due to the presence of fiber loading, which created a barrier to the polymer's exhausted gas formed during the thermal tests. Also, the formed ester bond in the ternary system leads to a good adhesion between the fibers and the polymeric matrix, which explains the thermal behavior of this system, compared to a binary one.

Table 2
Composition of different specimens (percentage of weight)

| No | Specimen | Hemp (%) | Cellulose powder (%) (1) | Epoxy resin (%) (2) | Hardener (%) (3) | Proportion 3:2:1 |
|----|---------------------|-------------|--------------------------|---------------------|------------------|------------------|
| 1 | U HFRP | 8 | 34.25 | 52.5 | 5.25 | 10:1:6.5 |
| 2 | V HFRP | 8 | 31.5 | 55 | 5.5 | 10:1:5.7 |
| 3 | W HFRP | 8 | 28.75 | 57.5 | 5.75 | 10:1:5 |
| 4 | X HFRP | 8 | 26 | 60 | 6 | 10:1:4.3 |
| 5 | Y HFRP | 8 | 23.25 | 62.5 | 6.25 | 10:1:3.7 |
| 6 | Z HFRP | 8 | 20.5 | 65 | 6.5 | 10:1:3.2 |
| 7 | UX (Untreated) HFRP | 8 | 26 | 60 | 6 | 10:1:4.3 |

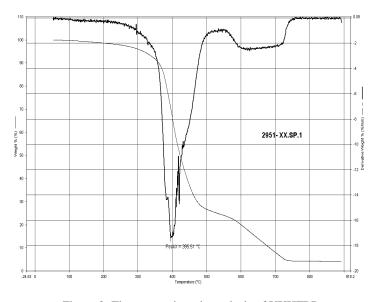


Figure 3: Thermogravimetric analysis of UXHFRP

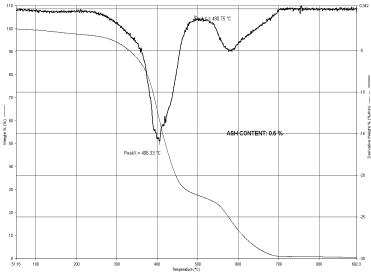


Figure 4: Thermogravimetric analysis of UXHFRP

Table 3
Real weight reduction percentage of treated and untreated HFRP composites at different temperatures

| | | ***** | ***** | | | |
|-----------------|---------|--------|--------|--------|--------|--------|
| Temperature, °C | UX HFRP | X HRFP | Y HFRP | Z HFRP | V HFRP | W HFRP |
| 55 | 99.981 | 99.993 | 99.782 | 99.723 | 99.981 | 99.982 |
| 100 | 99.857 | 99.765 | 97.506 | 96.522 | 97.479 | 97.489 |
| 150 | 98.614 | 99.274 | 95.735 | 93.78 | 94.669 | 92.697 |
| 200 | 97.702 | 98.639 | 91.909 | 89.978 | 93.794 | 91.841 |
| 250 | 96.813 | 97.788 | 88.099 | 85.195 | 92.94 | 91.005 |
| 300 | 94.136 | 96.024 | 85.664 | 82.839 | 90.371 | 88.488 |
| 350 | 87.118 | 91.683 | 79.277 | 76.663 | 83.633 | 81.891 |
| 400 | 64.48 | 66.303 | 58.677 | 56.742 | 61.901 | 60.611 |
| 450 | 34.631 | 37.028 | 31.514 | 30.475 | 33.246 | 32.553 |
| 500 | 23.621 | 26.684 | 21.135 | 20.306 | 22.676 | 22.204 |
| 530 | 20.606 | 25.025 | 18.301 | 18.533 | 19.782 | 19.37 |
| 550 | 17.624 | 24.046 | 16.497 | 15.789 | 16.919 | 16.567 |
| 600 | 12.474 | 20.033 | 11.351 | 10.977 | 11.975 | 11.723 |
| 650 | 4.465 | 13.942 | 4.0631 | 3.929 | 4.286 | 4.212 |
| 700 | 1.005 | 8.025 | 0.915 | 0.884 | 0.965 | 0.945 |
| 750 | 0.865 | 4.342 | 0.787 | 0.761 | 0.83 | 0.813 |
| 800 | 0.769 | 4.253 | 0.6998 | 0.676 | 0.738 | 0.723 |
| 850 | 0.58 | 4.166 | 0.528 | 0.51 | 0.559 | 0.545 |
| 892 | 0.497 | 4.104 | 0.453 | 0.437 | 0.477 | 0.467 |

Heat deflection temperature

For further analysis of the dimensional stability, standardized heat deflection temperature (HDT) tests were performed. The standardized HDT analysis with a support distance of 100 mm only allows 0.25 mm deflection of the specimens, which puts up for much stricter requirements. ^{37,38} Heat deflection temperature (HDT) of untreated HFRP and treated HFRP composites was investigated using HDT analysis, and is depicted in Figure 5. The HDT values of HFRP are found to be lesser with the addition of 32 wt% of cellulose filler and untreated HFRP, whereas with

the incorporation of treated fiber in HFRP composites, a significant increase in thermal stability was observed from about 136 °C to 156 °C by using 43% volume of cellulose filled benzoyl treated hemp fibers. It revealed that the heat deflection temperature of the composite increases with the cellulose filler loading, as well as with fiber treatments. The heat deflection temperature of the composite increases from 136 °C to 156 °C (by 15%) with an increase in the filler-mass proportion. This improvement mainly stems from the increase in the modulus, as well as from the interaction between the filler in the

matrix and the fiber. The high heat resistance may also be due to the fact that the treated hemp fibers prevent deformation of the composite. The HDT value depends on the modulus and glass-transition temperature of a material. The modulus-temperature relationship plays a critical role in determining the HDT. Thus, the improvement in the HDT values for the HFRP composites is indicative of higher modulus values at elevated temperature. Figure 5 shows the dimensional stability of the HFRP composites, which was essential for automotive components. Figure 6 shows that HFRP exhibits better heat deflection temperature when compared with natural composites applied in the automobile industry.

Thermal conductivity

Thermal conductivity is the property describing a material's ability to transfer heat. It is well known that the thermal conductivity of a composite is dependent on such factors as polymer-filler interaction and characteristics, namely the type and shape of filler.³⁸ From the obtained results, it was observed that the composites filled with 43% vol. cellulose powder exhibited the least thermal conductivity. It may be due to the fact that while heating materials, a slow chemical reaction takes place in cellulose powder, releasing a small amount of water, and this released water resists the heat flow. Thus, it is possible that there is a fundamental difficulty in transferring the heat from the matrix to the fibers. Composites filled with 32% vol. cellulose powder exhibited higher thermal conductivity (0.22 W/mK).

The dependence of the overall conductivity on the particle diameter for spherical particles of equal size was investigated with several

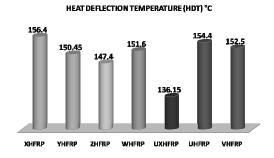


Figure 5: Heat deflection temperature of treated and untreated HFRP

predictions. 39-41 The reason for the decrease of the thermal conductivity values with decreasing grain size of filler can be attributed to the interfacial properties between the matrix and filler particles. It is obvious that decreasing the grain size results in a larger surface area between the matrix and filler particles. It is also possible that a greater number of interfacial reactions occur by increasing the interfacial surface area. It was stated⁴² that the interfacial reaction between filler particles and matrix can reduce the thermal conductivity of the composites. Although it was stated that⁴³ porosity can severely degrade the thermal and mechanical properties of the composites, the filler particles were distributed uniformly in the matrix, and no considerable amount of pores was observed in the present study when the amount of filler reached 43 wt%. Because of the lower thermal conductivity of cellulose itself (about 0.4 W/mK), compared with those of epoxy (0.8 W/mK) and hemp (0.48 W/mK), 42 the thermal conductivity of the epoxy matrix decreased with the increase of the cellulose content, so that the thermal conductivity of the composites exhibited a similar tendency of deviation. It can be concluded that the composites with 43 wt% cellulose content would exhibit low TC compared with those of the composites with 32 wt% to 37 wt% for a consistent level of porosity. From Figure 7, we can observe that, as cellulose powder has good thermal resistance, the increase in filler content results in good thermal resistance. Figure 8 reveals that XHFRP exhibits superior thermal conductivity to that of other natural composites used in automotive applications.

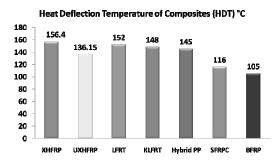


Figure 6: Heat deflection temperature comparison of FRP

Thermal Conductivity in W/mK 0.292 0.258 0.245 0.233 0.249 0.239 XHFRP YHFRP ZHFRP WHFRP UXHFRP UHFRP VHFRP

Figure 7: Thermal conductivity of treated and untreated HFRP

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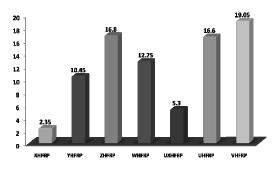


Figure 9: Coefficient of linear thermal expansion of treated and untreated HFRP

Thermal expansion coefficient

From the experimental results, it is observed that an increase in the addition of cellulose filler to HFRP composites reduces the thermal expansion coefficient. It has been noticed that the 43% vol. cellulose powder filled composite exhibited the least thermal expansion coefficient. This may be explained by the fact that adding more filler in a composite material provides good filler matrix interaction in the system, as the filler binds with the matrix and prevents it from expanding as much as it would on its own. Subsequently, this would affect the thermal expansion of the composite system. Many studies have shown that materials with higher filler content have a lower thermal expansion coefficient. The incorporation of cellulosic reinforcements polymeric in matrices composites generates residual stresses during cooling from the material processing temperature, due to the large difference between the coefficient of thermal expansion of the reinforcement and that of the matrix.⁴⁴ Residual stresses cause compressive stresses on the reinforcements and tensile stress on the matrix, and their magnitude varies with the characteristics of reinforcement

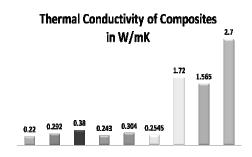


Figure 8: Thermal conductivity comparison of FRP

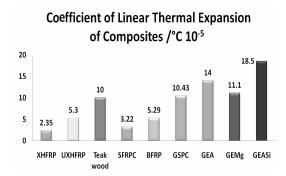


Figure 10: Coefficient of linear thermal expansion comparison of FRP

and matrix, as well as with the processing. 42,45-46 Ren et al. 42 stated that such a tensile stress is considered to be generated by a mismatch of the coefficient of thermal expansion between the matrix and the reinforcement, progressively diminishing and approaching zero during the heating stage. Therefore, the compressive stress in the matrix builds up with the temperature, since the expansion of the matrix is constrained by the vicinity of reinforcement particles. Accordingly, compressive stress begins to accumulate to such intensity until it surpasses the yield strength of the matrix, which lessens with temperature elevation, ensuing plastic relaxation. The tensile stress builds up throughout the reduction in temperature during the subsequent cooling period and new residual stresses will be generated. However, the matrix has deformed and hardened enough to result in less noticeable plastic relaxation of the matrix, arising from the new tensile stress, increasing with the reduction in temperature. 44,45,47

Introducing the third phase (cellulose) to the hemp reinforced epoxy composite induced residual strain in the epoxy matrix. Due to the thermal expansion mismatch between cellulose and the polymer phase, residual stresses are expected to be tensile in the polymer phase and compressive in the cellulose, and during heating, the residual stresses relaxed elastically or plastically. 48 This relaxation process was observed in this investigation with an increase in the cellulose content, resulting in an open hysteresis during the heating and cooling cycles. From Figure 9, it may be observed that the composites filled with 43% vol. cellulose filler exhibited low thermal expansion coefficient (2.35×10^{-5}) , when compared with other filled composites. This is due to the fact that cellulose particles have reduced thermal expansion and good dimensional stability. Thus, HFRP exhibits better coefficient of thermal expansion when compared with other natural composites used in automotive applications (Fig. 10).

Morphological analysis (FESEM)

Morphological analysis was done using field emission scanning electron microscopy. The interfacial adhesion between the matrix and the fiber is clearly seen from field emission scanning electron micrographs.

The morphology of the fractured surfaces of untreated (UXHFRP) and treated (YHFRP and ZHFRP) composites is illustrated in Figures 11, 12 and 13, respectively. From Figure 11, it may be seen that in the untreated composite there are a number of gaps between the fibers and the matrix, resulting from fiber pullouts. This indicates poor interfacial adhesion and inadequate wetting of the untreated fibers within the matrix, which is probably due to a difference in the surface energies between the fibers and the matrix. On the contrary, alkali and benzoyl treated composites manifested improved fiber matrix adhesion. As may be observed from Figures 12 and 13, the treated fibers are uniformly coated by layers of matrix material, which considerably reduces the gaps between them. It is also observed that the layers of matrix material were pulled out together with the fibers during fracture, which further substantiates cohesive coupling between the alkali and benzoyl treated fibers and matrix.

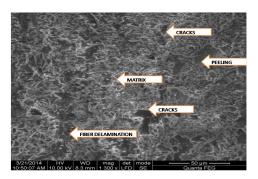


Figure 11: FESEM photographs of UX HFRP

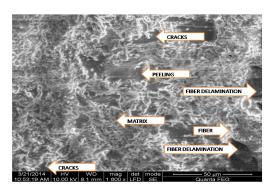


Figure 12: FESEM photographs of Y HFRP

CONCLUSION

This study is focused on the thermal properties of a hemp fiber reinforced composite to be

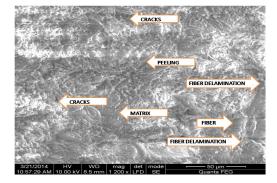


Figure 13: FESEM photographs of X HFRP

applied in automotive components. The influence of fiber treatments (*i.e.* washing, bleaching and chemical treatments) on the thermal properties of

hemp fiber composites was analyzed. All the treatments removed surface impurities from the fibers, producing modifications on the surface and improving the thermal stability of fiber-reinforced composites. The results were supported by FESEM analysis. The composites made with treated hemp fibers had better thermal behavior than those made with untreated fibers. Also, the considerable former showed improvement in thermal conductivity and a 15% improvement in heat deflection temperature, compared to the untreated composites. The thermal stability of untreated and treated hemp fiber reinforced cellulose filled epoxy hybrid composites has also been studied. The results showed that the degradation begins at a higher temperature of 400 °C and decomposition is almost complete at 700 °C. The thermal stability of the treated fiber composites was found to be higher than that of the untreated fiber composite and can be explained based on the better thermal stability of treated fibers and improved fibermatrix interactions in treated fiber composites. The XHFRP hybrid material, which presents superior thermal properties can be associated to the commercial LFRT material. The results obtained suggest that natural long fiber hemp reinforced composites can be utilized in automotive structural components, such as bumper beams, front end modules and in interior part of automobiles, and thus can undeniably replace the commercial LFRT applications.

ABBREVIATIONS:

NFRP – natural fiber reinforced polymers, XHFRP – treated hemp fiber reinforced synthetic cellulose filled epoxy composites, UXHFRP – untreated hemp fiber reinforced synthetic cellulose filled epoxy composites, LFRT – long fiber reinforced thermoplastics

REFERENCES

- ¹ M. M. Kabir, H. Wang, K. T. Lau and F. Cardona, *Composites: B*, **43**, 2883 (2012).
- ² J. Rout, M. Misra, S. Tripathy, S. K. Nayak and A. K. Mohanty, *Compos. Sci. Technol.*, **61**, 1303 (2001).
- ³ A. K. Bledzki and J. Gassan, *Progress Polym. Sci.*, **24**, 221 (1999).
- ⁴ M. Abdelmouleh, S. Boufis and M. N. Belgacem, *Compos. Sci. Technol.*, **67**, 1627 (2007).
- ⁵ V. Tserki, N. E. Zafeiropoulos, F. Simon and C. Panayiotou, *Composites: A*, **36**, 1110 (2005).
- ⁶ T. T. L. Doan, S. L. Gao and E. Mader, *Compos. Sci. Technol.*, **66**, 952 (2006).

- ⁷ M. Idicula, A. Boudenne, L. Umadevi, L. Ibos, Y. Candau *et al.*, *Compos. Sci. Technol.*, **66**, 2719 (2006).
- M. R. Piggott, J. Compos. Mater., 28, 588 (1994).
- ⁹ S. Y. Fu and B. Lauke, *J. Mater. Sci.*, **32**, 1985 (1997).
- B. Lauke and S. Y. Fu, Compos. Sci. Technol., 59, 699 (1999).
- ¹¹ F. U. Shao-Yun and B. Lauke, *Compos. Sci. Technol.*, **58**, 1961 (1998).
- ¹² J. R. Willis, J. Mech. Phys. Solids, **25**, 185 (1977).
- ¹³ S. Normura and T. W. Chou, *J. Compos. Mater.*, 14, 120 (1980).
- ¹⁴ H. Hatta and M. Taya, J. Appl. Phys., **58**, 2478 (1985).
- ¹⁵ C. H. Chen and Y. C. Wang, *Mechan. Mater.*, **23**, 217 (1996).
- ¹⁶ S. Y. Fu and Y. W. Mai, *J. Appl. Polym. Sci.*, **88**, 1497 (2003).
- ¹⁷ C. Pavithran, P. S. Muckerjee, M. Brahmakumar and A. Damodaran, *Mater. Sci. Lett.*, **6**, 882 (1987).
- ¹⁸ N. L. Hancox, "Fiber Composite Hybrid Materials", Macmillan Publishers, 1981.
- ¹⁹ J. R. Vinson and T. W. Chou, "Composite Materials and their Uses in Structures", Applied Science Publishers Ltd., London, 1975.
- ²⁰ C. Z. Paiva Jr, L. H. de Carvalho, V. M. Fonseca, S. N. Monteiro and J. R. M. Almeida, *Polym. Testing*, 23, 131 (2004).
- ²¹ M. Jacob, K. T. Varghese and S. Thomas, *J. Appl. Polym. Sci.*, **93**, 2305 (2004).
- ²² M. Idicula, N. R. Neelakantan and S. Thomas, in *Procs. USM JIRCAS Joint International Symposium*, 2001, p. 368.
- ²³ M. Idicula, S. K. Malhothra, K. Joseph and S. Thomas, *Compos. Sci. Technol.*, **65**, 1077 (2005).
- D. Nabi Saheb and J. P. Jog, *Adv. Polym. Technol.*,
 18, 351 (1999).
- ²⁵ M. A. Maleque, F. Y. Belal and S. M. Sapuan, *Arabian J. Sci. Eng.*, **32**, 359 (2007).
- ²⁶ P. Wambua, J. Ivens and I. Verpoest, *Compos. Sci. Technol.*, **63**, 1259 (2003).
- ²⁷ G. Karam, *J. Compos. Technol. Res.*, **16**, 154 (1994).
- ²⁸ A. K. Mohanty, M. Mishra and L. T. Zal, *Compos. Interfac.*,**8**, 313 (2001).
- ²⁹ R. Agarwal, N. S. Saxena, K. B. Sharma, S. Thomas and M. S. Sreekala, *Mater. Sci. Eng. A*, **277**, 77 (2000).
- ³⁰ J. Katz, US Patent number 4,060:386 (1977).
- ³¹ J. Rout, S. S. Tripathy, S. K. Nayak, M. Misra and A. K. Mohanty, *J. Appl. Polym. Sci.*, **79**, 1169 (2000).
- J. Rout, M. Misra, S. S. Tripathy, S. K. Nayak and A. K. Mohanty, *Compos. Sci. Technol.*, 61, 1303 (2001).
 S. P. Shukla and P. S. Pai *Biorescur Technol.* 96.
- ³³ S. R. Shukla and R. S. Pai, *Bioresour. Technol.*, **96**, 1430 (2005).
- ³⁴ K. C. Manikandan Nair, S. Thomas and G. Groeninck, *Compos. Sci. Technol.*, **61**, 2519 (2001).

- ³⁵ I. C. Finegan and R. F. Gibson, Compos. Struct., **44**, 89 (1999).
- ³⁶ R. F. Gibson, J. Mater. Eng. Perform., 1, 11
- (1992).

 37 S. Jeyanthi and J. Rani, *Int. J. Phys. Sci.*, **7**, 5765
- (2012).

 38 T. Tábi, P. Tamás and J. G. Kovács, *eXPRESS* Polym. Lett., 7, 107 (2013).
- ³⁹ H. J. Böhm and S. Nogales, *Compos. Sci. Technol.*,
- **68**, 1181 (2008).

 D. Hasselman and L. Johnson, *J. Compos. Mater.*, **21**, 508 (1987).

 Y. Benveniste, *J. Appl. Phys.*, **61**, 2840 (1987).
- 42 X. Ren, S. He, X. Qu, I. Humail and Y. Li,

- Compos. Sci. Technol., **67**, 2103 (2007).

 43 H. S. Lee and S. H. Hong, *Mater. Sci. Technol.*, **19**, 1057 (2003).
- 44 S. C. Tjong and K. F. Tam, *Mater. Chem. Phys.*, **97**, 91 (2006).
- ⁴⁵ S. Q. Wu, Z. S. Wei and S. C. Tjong, *Compos. Sci.* Technol., 60, 2873 (2000).
- ⁴⁶ B. G. Kim, S. L. Dong and S. D. Park, *Mater*. *Chem. Phys.*, **72**, 42 (2001).

 T. Huber, H. P. Degischer, G. Lefranc and T.
- Schmitt, Compos. Sci. Technol., 66, 2206 (2006).
- T. Etter, M. Papakyriacou, P. Schulz and P. J. Uggowitzer, Carbon, 41, 1017 (2003).