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Original Article

Adhesion of pineapple-leaf fiber to epoxy matrix: The role of surface treatments

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Abstract

Natural fibers are considered to have potential use as reinforcing agents in polymer composite materials because of their principle benefits: moderate strength and stiffness, low cost, and be an environmental friendly, degradable, and renewable material. Due to their inherently hydrophilic nature, they are prone to absorb moisture, which can plasticise or weaken the adhesion of fibers to the surrounding matrix and by this affect the performance of composites used in atmospheric humidity, particularly at elevated temperatures. The surface treatments are often applied to the fiber to improve the bond strength between the fibers and matrix. This work discussed the effect of sodium hydroxide (NaOH) treatment and epoxy resin as a compatibilizing agent on interface properties of pineapple leaf fiber (PALF)-epoxy composites. A single-fiber fragmentation test coupled with data reduction technique was employed to assess interface quality in terms of apparent interfacial shear strength (IFSS or τ_a) of untreated, NaOH, and epoxy resin treated PALFs-epoxy composites. Tensile properties of untreated and treated PALFs were also examined. It was found that both treatments substantially increase τ_a, corresponding to an improved level of adhesion. The improvement in the level of adhesion for the alkali and epoxy treated fiber composites was due to an increase in the physical bonding between the alkali treated fibers and the matrix, and due to a promoted compatibility between the epoxy treated fibers and matrix, respectively.

Keywords: pineapple fiber (PALF), epoxy resin, single-fibre fragmentation test, fibre-matrix interfacial adhesion, surface treatments

1. Introduction

The use of natural fiber for reinforcing polymer composites has been increasingly found in wide range of applications, which is mainly because of their cost and ecological benefits. Besides, natural fibers also have some other advantages over traditional reinforcing fibers such as glass and carbon fibers: biodegradability, renewability, abundant availability, low density, relative non-abrasiveness, and ease of surface modification (Bledzki and Gassan, 1999). Among natural fibers, pineapple-leaf fiber (PALF) is one of the most important plant based fibers for composite materials due to its moderate specific strength and stiffness. This make them competitive to glass fibers as a reinforcing agent in composite applications (Van de Weyenberg *et al.*, 2006). In the past few years, several studies have reported the potential use of PALFs as reinforcing materials in wide range of polymers such as polyester (Uma Devi *et al.*, 1997; Mishra *et al.*, 2001), poly(hydroxybutyrate-co-valerate) (Luo and Netravali, 1999), polypropylene (Arib *et al.*, 2006), polyethylene (George *et al.*, 1995), and natural rubber (Lopattananon *et al.*, 2006). In PALF reinforced polymers, it has been well documented that the overall properties of composite materials are largely governed by adhesion between the PALFs and the matrix, which is a composite material with weak interfaces that have relatively low strength and stiffness. In addition, PALFs are reported to have high susceptibility to

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moisture absorption due to the inherent polar nature of the cellulose of the fibers (George *et al*., 1998; Uma devi *et al*., 2004). This results in weakening fiber-matrix adhesion and thus, adversely affecting the performance of natural fiber composites when using them at high humidity and elevated temperature. Thus, the surface treatment of fiber is always carried out to control the fiber-matrix adhesion to assure a good performance of the composites. An improved interface quality of composites is commonly achieved by treating surfaces of the fibers with suitable methods such as chemical modification and coupling or compatibility agents, which are reacted or deposited onto the fiber. Mishra *et al.* (2001) have shown that the interface quality of PALFs-polyester composites could be promoted through suitable surface modifications such as dewaxing, alkali treatment, cyanoethylation, and coating of acrylonitrile monomer onto dewaxed PALF. Recently, Lopattananon *et al.* (2006) have demonstrated that alkali treatment and benzoylation of PALFs resulted in better interfacial adhesion between PALFs and natural rubber matrix.

Single-fiber fragmentation test is one of the most popular methods, which has been widely used to assess the effect of surface treatments on the composite properties in circular and rigid carbon fibers and glass fibers-epoxy resin composites (Cheng *et al*., 1994; Berg and Jones, 1998; Lopattananon *et al.,* 1999). Recently, the single-fiber fragmentation test has been successfully employed to evaluate the interfacial properties in various natural fibers reinforced with thermoplastic materials (Valadez-Gonzalez *et al.,* 1999; Zafeiropoulos *et al.,* 2002). In the test, a single fiber is embedded in a thin resin test piece. The tensile stress is transferred from the surrounding matrix to the embedded fiber by means of interfacial shear stress. As the applied strain increases until it is high enough to cause fracture, the fiber breaks repeatedly at points where its strength is exceeded. Continued application of load results in further fragmentation, until the length of the remaining fragment is not longer sufficient for further fractures to occur. This situation is defined as the saturation in the fiber-fragmentation process. The final fragment lengths in a transparent matrix composite can be measured using optical microscope. The analysis of the fragmentation test data for the determination of interface quality described by the constant shear lag model of Kelly-Tyson (Kelly and Tyson, 1965) is given as following,

$$\tau_a = \frac{r_f \sigma_{fu}}{l_c} \quad (1)$$

where τ_a is the apparent interfacial shear strength (IFSS), r_f is the fiber radius, and σ_{fu} is the fiber tensile strength at a length equal to l_c, the critical fiber length.

The application of Equation (1) requires the calculation of the critical fiber length, l_c, from the average fiber fragment length, $\bar{l}$, using Ohsawa's relationship (Ohsawa *et al.,* 1978) :

$$l_c = \frac{4}{3}\bar{l} \quad (2)$$

In this study, the characterization of the interface properties of PALF reinforced epoxy resin was investigated. The PALFs were treated with two reagents, i.e. NaOH and epoxy resin. The mechanical properties of untreated and the two different treated PALFs were examined. Single-fiber fragmentation test was used to evaluate the influence of surface treatments on interfacial shear strength of PALFs of epoxy resin composites. The fragmentation test data were analyzed by a conventional data reduction technique. A scanning electron microscope (SEM) was used to characterize the surfaces of both untreated and treated PALFs.

2. Experimental

2.1 Materials

PALF was extracted from parts of the pineapple leaf by scraping them, cleaned and dried in an oven at 70°C for 24 hrs. Due to the variability of the fiber diameter, the fibers having a diameter of 30 to 50 μm along the fiber length were carefully selected under a microscope. The epoxy resin used was a diglycidyl ether of Bisphenol A typed epoxy, Epikote 828 (Hexion Specialty Chemicals, USA). Tetraethylenetriamine (TETA) supplied by Yuka-Shell company was used as a hardener. Sodium hydroxide (NaOH), toluene, and acetone were AR-grade and used as received.

2.1.1 Fiber and surface treatments

Alkaline (NaOH) treatment

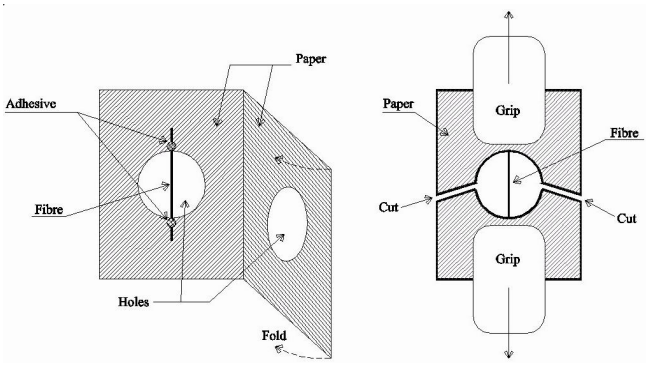
Untreated pineapple fibers were immersed in 5% NaOH solution for 1 hr and washed several times with acetone and distilled water to eliminate absorbed NaOH. The NaOH treated fibers were dried in a hot-air oven at 70°C for 24 hrs.

Epoxy resin coating

Epikote 828 in toluene (1 wt%) was prepared and added with untreated PALFs. The mixture was heated at 119°C for 1 hr. The fibers were removed from the epoxy solution, washed with toluene and dried at 70°C for 24 hrs.

2.1.2 Resin matrix

The Epikote 828 was mixed with TETA in the ratio of 100 to 11 parts. The matrix system was thermally processed at 80°C for 80 mins, followed by post-cured at 100°C for 60 mins.



(a) (b)

Figure 1. Schematic diagram of the preparation of a single fiber-strength test specimen. (a) preparation, and (b) testing of single fiber strength test specimen.

2.2 Single fiber test

The single fiber test was carried out by the method outlined by Cheng *et al.* (1994). Single fibers were selected at random from the untreated, NaOH, and epoxy treated PALFs by hand and carefully mounted onto light, and thin window cards punched with a hole of 4.5 mm diameter as illustrated in Figure 1(a). The fiber was secured in place by folding and glueing the opposite cards with adhesive. In this test, the samples with fiber misalignment at the centre of the holes were discarded. The specimens were then pulled in uniaxial tension on the mini tester Lloyd LRX-Plus with 10 N load-cell at a displacement rate of 0.52 mm/min. The supporting paper for the fiber was cut before the test as illustrated in Figure 1(b). While the specimens were tested, they were carefully monitored to ensure that only data for the fibers that failed in tension were collected. In a typical test the load increases steadily to a maximum at which the fiber broke and the load instantaneously dropped to zero. In some cases, the fibers slipped within the windows because of improper adhesion, which allowed the fibers to pull out from the supports. In such cases, the load did not drop to zero instantaneously at fracture state so that these data were not included in the calculation of the fiber strength. 30 to 40 samples were measured. The tensile testing data were averaged and the values of weibull modulus (m) were calculated using the weibull statistical approach (Cheng *et al.*, 1994). The strength of untreated and treated PALFs at the critical length, l_c, was estimated using the following relationships (Cheng *et al.*, 1994):

$$\sigma_{fu} = \bar{\sigma}\left(\frac{l}{l_c}\right)^{\frac{1}{m}} \quad (3)$$

Where $\bar{\sigma}$ is the average tensile strength of the fibers, and l is the fiber length chosen for the strength measurements. For the untreated and treated PALFs, l = 4.5 mm.

2.3 Single-fiber fragmentation test

Single-fiber fragmentation test specimens were prepared by the method outlined by Cheng *et al.* (1994). The fragmentation test uses a specimen that has a single fiber embedded longitudinally in a resin matrix, having strain to failure two or three times greater than that of pineapple leaf fibers. The testing was performed on an Instron universal testing machine at a cross-head speed of 0.50 mm/min. The samples were stretched to 15% applied strain to achieve saturation to the fragmentation process. The fiber-fragment lengths were measured under transmitted light using an Olympus light microscope fitted with a graduated eye-piece. The interfacial failure modes that occurred at the locus of the fiber fractures were examined by using a transmitted polarized light microscope, Nikon, model DN100 Digital Net Camera. The determination of τ_a, was achieved by using the Kelly-Tyson model given in Equation (1).

2.4 Surface topography

The changes in fiber surface topography following surface treatments were characterized using a LEO145 VP SEM scanning electron microscope. Prior to SEM investigation, the samples were gold-coated for 1 min by using gold coating sputter.

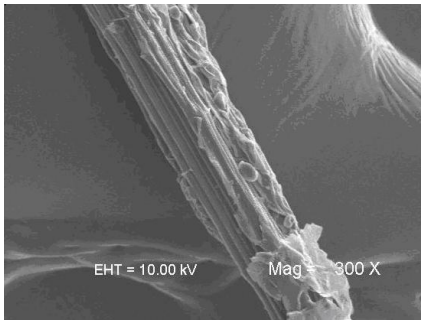
3. Results and Discussions

3.1 Surface treatments

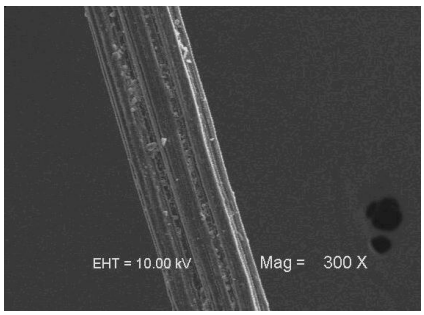
Changes in the surface topography of the fibers after treatments were studied by using a scanning electron microscopy. Figure 2 shows the surfaces of the untreated, alkali, and epoxy treated fibers. It is clear that the untreated PALFs exhibit a multifibrillar structure, where the fibrils are bound together by hemicellulose and lignin (Luo and Netravali, 1999). Upon alkali treatment of the PALFs, the hemicellulose and lignin were partially removed, resulting in surfaces with a higher degree of roughness and effective surface area (Figure 2(b)). However, in case of epoxy treated fibers (Figure 2(c)), the fibers kept their integrity with the epoxy resin coating onto the surfaces.

3.2 Single fiber test

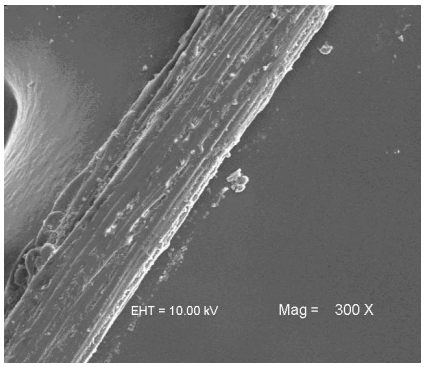
Table 1 shows the mechanical properties of the untreated, NaOH, and epoxy treated pineapple fibers. It is apparent that the modulus and tensile strength of alkali treated fibers are higher than those of untreated fibers, whereas the failure strain of the alkali treated fibers is not different from those of the untreated fibers. The epoxy treatment did not significantly change the mechanical properties of the fibers. For the alkali treatment, the improved modulus and tensile strength can be explained like following. When the binding



(a)



(b)



(c)

Figure 2. SEM photomicrographs of (a) untreated fiber, (b) alkali treated fiber, and (c) epoxy treated fiber.

materials are removed, the interfibrillar region is likely to be less dense and less rigid and thereby makes the fibrils more capable of rearranging themselves along the direction of the tensile deformation. Therefore, if the fiber was subjected to uniaxial stretch such rearrangements would result in better load sharing and hence higher stress development in the fibers (Gassan and Bledzki, 1999).

3.3 Mechanical properties of epoxy resin matrix

In the single-fiber fragmentation test, the failure strain of epoxy matrix must be three times greater than those of untreated and treated PALFs. This is to ensure that saturation is achieved. Therefore, the properties of cured resin were determined and given in Table 2. From Table 2 the Young's modulus, tensile strength, and failure strain of the matrix resin are 5.54±0.23 GPa, 75±5 MPa, and 18%, respectively. By comparing the value of failure strain of cured resin with those of different PALFs reported in Table 1, the matrix has sufficient failure strain to reach the saturation in the fiber fragmentation process.

3.4 Single - fiber fragmentation test

The interfacial shear strength, τ_a, of different fiber composites are compared in Figure 3. As expected, both alkali and epoxy treated fiber composites present much higher interfacial shear strength corresponding to the level of interfacial adhesion relative to that of the untreated fiber composites. The epoxy treatment gives the best improvement in level of adhesion. The improvement in level of adhesion for the NaOH treated fibers is attributed to increasing surface roughness and area, and thus promotes interaction between the fiber and epoxy through the mechanical interlocking. For the epoxy treated fiber composites, the relatively strong

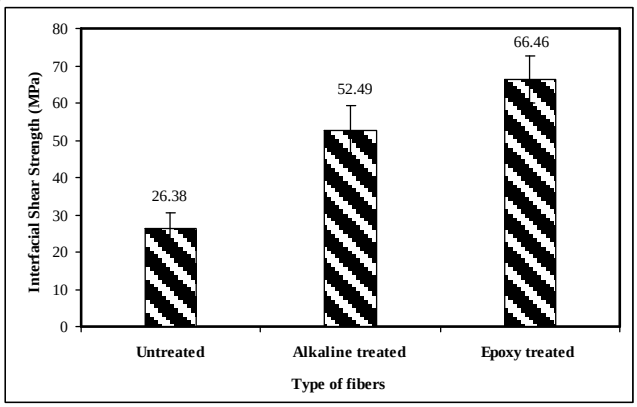


Figure 3. Comparison of interfacial shear strength for untreated and treated pineapple leaf fibers reinforced epoxy composites. (Figure is given with average value as well as standard deviation.)

Table 1. Mechanical properties of untreated, alkali, and epoxy treated pineapple leaf fibers (PALF).

PALF	Young's Modulus (GPa)	Tensile strength (MPa)	Strain to failure (%)
Untreated PALF	12.58±7.61	532.74±268.40	4.83±0.84
Alkali treated PALF	15.72±8.05	635.44±259.51	4.38±0.64
Epoxy coated PALF	14.33±6.37	534.88±239.91	3.86 ±0.99

Table 2. Mechanical properties of cured epoxy resin.

Epikote 828	Properties
Strain to failure (%)	18
Tensile strength (MPa)	75±5
Young's modulus (GPa)	5.54±0.23

adhesion between the fiber and epoxy may be caused by the promoted compatibility of the treated fiber and epoxy matrix.

Figure 4 shows the mode of failure occurred at the region of interface between the different fibers and epoxy matrix. It is evident that the untreated fiber composites show plastic deformation at the interface between the fiber and matrix, associated with fibre fractures, indicating relatively poor interfacial adhesion. In case of treated fibers, transverse matrix cracking occuring near the fiber fragment of the treated fibers is observed, which is an indication of relatively strong adhesion (Lopattananon *et al*., 1999). The change in mode of failure corresponding to a change in level of adhesion is in good agreement with the IFSS values of epoxy composite reinforced with untreated and treated PALFs determined in the previous section.

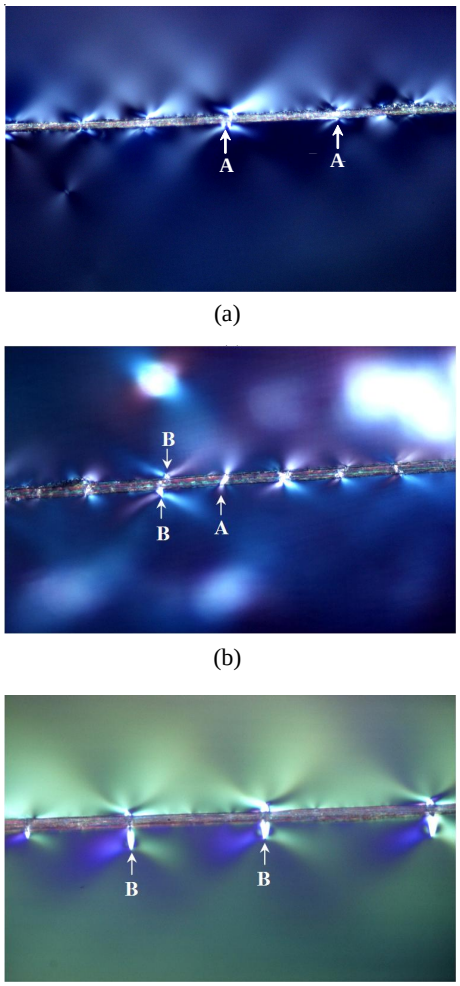


Figure 4. Polarized microphotographs presenting the fragmentation process of (a) untreated fiber, (b) alkali treated, and (c) epoxy treated fiber composites (A = fiber fractures, B = transverse matrix cracking).

4. Conclusions

Two chemical reagents, NaOH and a commercial epoxy resin were used for the modification of PALFs. Single-fiber fragmentation test was used to examine the interfacial shear strength corresponding to the level of interfacial adhesion between PALF and epoxy resin matrix. The NaOH treatment increased the tensile modulus and strength of the PALFs over those of the untreated fibers, whereas the coating of epoxy resin did not. The NaOH and epoxy resin treatments of the PALFs modified the stress transfer efficiency at the interface of composites and improved the IFSS of epoxy composites by 98.97% and 151.38%, respectively, when compared with the untreated fibers. These observations suggest that the surface treatments with NaOH and epoxy resin as a compatibilizing agent effectively promote interface quality, and would also increase the strength of PALFs-epoxy composites. Future work needs to be carried out to determine the effect of surface treated PALFs on the unidirectional PALFs-epoxy composites.

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