Influence of Fiber Modification on Interfacial Adhesion and Mechanical Properties of Pineapple Leaf Fiber-Epoxy Composites

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ABSTRACT: Three kinds of surface treatment, that is, the alkalization (5% w/v NaOH aqueous solution), the deposition of diglycidyl ether of bisphenol A (DGEBA) from toluene solution (1% w/v DGEBA), and the alkalization combined with the deposition of DGEBA (5% w/v NaOH/1% w/v DGEBA) were applied to modify interfacial bonding and to enhance mechanical properties of pineapple leaf fiber (PALF) reinforced epoxy composites. The fiber strength and strain were measured by single fiber test and the fiber strength variation was assessed using Weibull modulus. Furthermore, a fragmentation test was used to quantify the interfacial adhesion of PALF-epoxy composite. It was verified that the interfacial shear strength of modified PALFs was substantially higher than that of untreated PALF by almost 2–2.7 times because of the greater interaction between the PALFs and epoxy resin matrix. The strongest interfacial adhesion was obtained from the fibers that had been received the alkalization combined with DGEBA deposition. Moreover, the flexural and impact properties of unidirectional PALF-epoxy composites were greatly enhanced when reinforced with the modified PALFs due to an improvement in interfacial adhesion, particularly in the synergetic use of 5% NaOH and 5% NaOH/1% DGEBA. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 433–443, 2008

Key words: adhesion; biofibers; composites; mechanical properties; morphology

INTRODUCTION

There has been a rapid growth in the use of natural fibers in polymer composite applications in the last two decades and there are enough indications for this trend to continue in coming years. Although natural fibers do not have clear advantages over other conventional glass fibers in terms of strength and stiffness, but their advantages appear when they are considered on the basis of strength per unit weight (specific strength) or modulus per unit weight (specific modulus). For many reasons, natural fibers have received considerable attention among researchers and composite related industry as alternative to glass fibers for reinforcement of plastics because of low price, weight reduction, and their sustainability as natural resources.

In recent years, pineapple leaf fibers (PALF) have successfully been used as effective and eco-friendly reinforcing agents for a polymer matrix to develop useful composites with good mechanical strength. This is because of their excellent mechanical properties. A number of research studies have been focused on reinforcing effect of PALF containing thermoset,[1–3] thermoplastic,[4] biodegradable plastics,[5,6] and natural rubber.[7,8] Uma Devi et al.[2] studied the potential of natural fiber-based polymer composites using PALF as reinforcing fibers in polyester. They showed that the PALF-based polymer composites possess superior stiffness and strength compared to other industrially used cellulose-based natural fiber composites. Mishra et al.[3] reported the significant improvement in tensile, flexural, and impact properties of polyester when reinforced with nonwoven PALF mat. Similar observation was presented by George et al.[4] where short PALFs were added into polyethylene to increase tensile and flexural properties of polyethylene composites. Luo and Netravali[5] used PALFs to strengthen biodegradable plastics (Biopol®).

Epoxy is the most common matrix for a variety of demanding applications, because of the excellent adhesion, strength, low shrinkage, corrosion protection, and many other properties.[9] In general, epoxy resin is rather expensive resin but their overall properties are excellent. Epoxy reinforced with natural fiber like jute, flax, sisal, and bamboo fibers have been

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studied by many researchers.[10–14] However, in the case of PALFs, there is no work has been made on the use of PALF for reinforcement of epoxy-based composites.

The most serious problem to be solved is that the adhesion of PALFs with many polymer matrices is usually very poor. PALFs have hydrophilic nature, which lowers their compatibility with hydrophobic polymer. In addition, the presence of natural waxy substances on their external surfaces contributes to low surface tension. Thus, these surfaces are not suitable for creating a strong bond with a polymer matrix. Theoretically, suitable surface treatment of fiber can improve bond strength by increasing the surface roughness and surface tension of fiber. One or more of the fiber surface treatments, i.e., cleaning the surface by dissolving the fatty substances and the layer of cuticle, reacting the fiber with reagents that would make it hydrophobic and grafting the fiber surface with some polymers compatible with the resin matrix, can be applied to fiber for improving bond strength.[15] Therefore, a numbers of research were carried out on the treatment of the fiber surface for the enhancement of interfacial interaction between PALFs and the surrounding matrix. For example, the chemical modification of PALFs, such as dewaxing, alkalization, cyanoethylation, and grafting of acrylonitrile monomer onto dewaxed PALF, was effective to promote the quality of PALFs and the adhesion with polymer matrix.[3] Alkali treated and benzoylated PALFs were used in composites to improve fiber–matrix adhesion and tensile properties.[8]

The purpose of this study is to assess the role of surface treatment on the interfacial shear strength and mechanical performance of unidirectional PALF-epoxy composites. Two reagents i.e., sodium hydroxide (NaOH) and diglycidyl ether of bisphenol A (DGEBA) and the combination were employed to treat the fibers. The DGEBA was used for the affinity increase because it is a main component of the epoxy matrix. In this study, the degree of fiber–matrix adhesion was evaluated by a single-fiber fragmentation test (SFFT). The tensile properties and the surface topography of untreated and treated PALFs were examined by single fiber strength test and SEM, respectively. The mechanical properties of unidirectional PALF reinforced epoxy composites were measured by flexural and impact tests. The fiber–matrix adhesion of PALF-epoxy composites was assessed by SEM.

EXPERIMENTAL

Materials

Chemicals

PALFs were extracted from part of pineapple leaf by scraping, cleaned, and dried in hot-air oven at 70°C for 24 h. The fiber diameters measured by an optical microscope are between 20 and 80 μm. The fibers were stored in dessicator at room temperature prior to the subsequent fiber surface treatment. Diglycidyl ether of Bisphenol A, DGEBA (Epikote 828, Hexion Specialty Chemicals, USA) was used for the study. Tetraethylenetriamine (TETA) was supplied by Fluka chemika (Switzerland). Releasing agent was obtained from Acmos Chemie GmbH (Germany). Sodium hydroxide (NaOH) (AR-grade, BDH Laboratory, England) and toluene (AR-grade, Lab Scan Asia, Thailand) were used as received.

Fiber surface treatments

Alkaline (NaOH) treatment on PALF. PALFs were immersed in 5% (w/v) NaOH aqueous solution at 30°C for 1 h, and washed several times with distilled water to eliminate absorbed NaOH until pH of water was neutral. The NaOH treated fibers were then dried in hot-air oven at 70°C for 24 h.

DGEBA resin treatment. Two different PALFs, which are untreated and 5% NaOH treated fibers, were used for epoxy resin treatment. The treatment was carried out by refluxing the fibers with DGEBA in 1% (w/v) toluene solution at 119°C for 1 h, followed by drying in hot-air oven and in vacuum oven at 70°C for 24 h and at 50°C for 3 h, respectively.

Resin matrix

The resin matrix used in this study is a mixture of DGEBA and TETA curing agent. This was obtained by blending epoxy resin and TETA in the ratio of 100 to 11 parts. The matrix system was thermally cured at 80°C for 80 min, and postcured at 100°C for 60 min.

Single fiber test

The single fiber test was carried out using the method described by Tripathy et al.[16] The fibers having the diameter in the range of 30–50 μm were carefully selected under microscope to minimize the complexity of diameter irregularity in the test. Single fiber was selected at random from the untreated, 5%NaOH, 1%DGEBA, and 5%NaOH/1%DGEBA treated PALFs by hand and carefully mounted onto light, thin 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 gluing the opposite cards with adhesive. In this test, the samples with fiber misalignment at the center of the holes were discarded. The specimens were then pulled in uniaxial direction using a 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

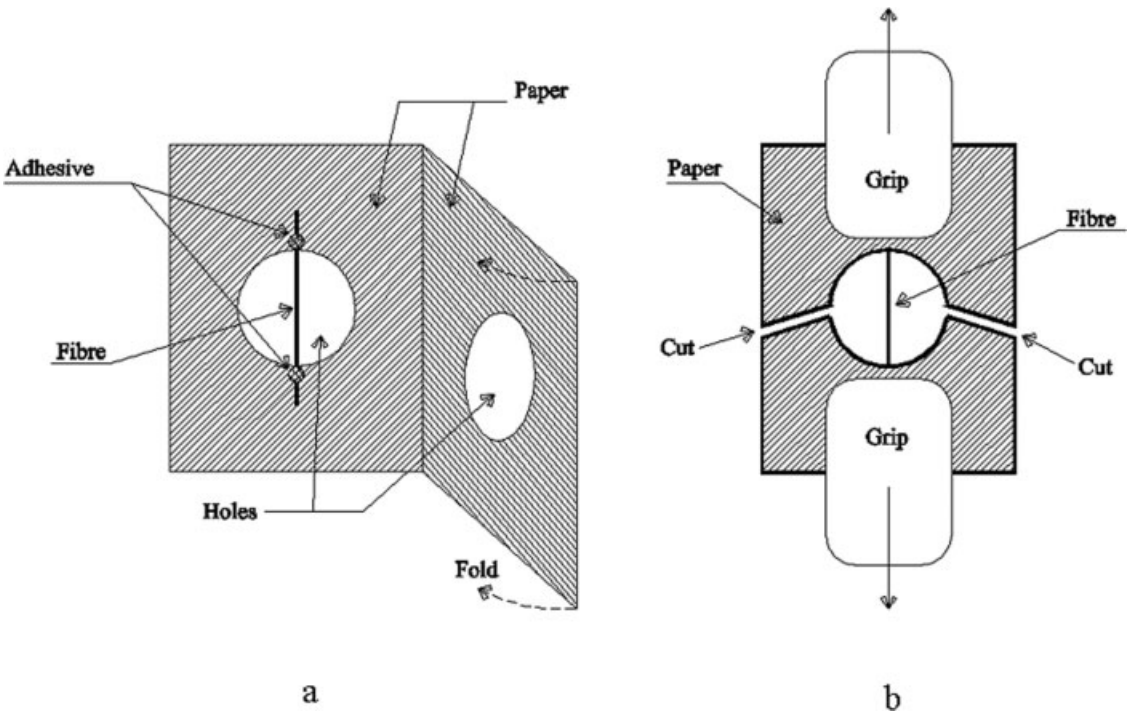


Figure 1 Schematic diagram for (a) preparation and (b) testing of single fiber strength test specimen.

cut prior to testing as illustrated in Figure 1(b). Although the specimens were tested, they were carefully monitored to ensure that only data were collected from the fibers that failed in tension. Tensile tests on each of sets of the single fiber were carried out with 30–40 samples. The estimation of the Weibull modulus (m) corresponding to statistical fluctuation of the fiber strength for a series of tensile strength tests was obtained using the method of maximum likelihood given in literature.[17] The statistics of fiber strength at gauge length (L) was analyzed using Weibull function given in eq. (1).[18]

$$P_f(\sigma) = 1 - \exp\left[-L\left(\frac{\sigma}{\sigma_0}\right)^m\right] \quad (1)$$

where $P_f(\sigma)$ is the cumulative probability of failure at stress (σ) for gauge length (L), σ_0 is a scale parameter or the upper limiting strength, m is shape parameter, usually referred to the Weibull modulus.

Single-fiber fragmentation test

Single-fiber fragmentation test (SFFT) specimens were prepared by the method outlined by Cheng et al.[17] SFFT uses a specimen that has a single fiber embedded longitudinally in a resin matrix. Single fiber was carefully aligned in the middle of silicone rubber mold cavity (12 mm × 80 mm × 1.6 mm) prior to casting the epoxy resin (Epikote 828 and TETA in the ratio of 100 parts resin to 11 parts curing agent). The samples were cured at 80°C for 80 min, and postcured at 100°C for 60 min before cooling down in the sealed oven over night to minimize thermal stress effects. Prior to testing, each specimen was investigated under optical microscope to verify defects such as fiber cracks, voids, and fiber deformation. The testing was performed using Instron universal testing machine at the cross-head speed 0.50 mm/min. The samples were stretched to 16% strain so that saturation in fiber fragmentation process was achieved. The fiber-fragment length and fiber diameter were measured under transmitted light using an Olympus light microscope fitted with a graduated eye-piece. The average fiber fragment length for each PALF was obtained using 10–15 specimens. For the measurement of fiber diameter, three reading were taken at different points of the fiber along the samples and the average values were reported. The interfacial failure mode at the locus of fiber fracture was examined using transmitted polarized light microscope Nikon model DN100 Digital Net Camera. The determination of interfacial shear strength (τ) was achieved using the Kelly-Tyson model[19] given in eq. (2);

$$\tau = \frac{\sigma_{fu} d}{2 l_c} \quad (2)$$

where τ is the interfacial shear strength (Ifss), d is the fiber diameter, l_c is the critical fiber length, σ_{fu} is average fiber strength at critical fiber length (l_c).

The application of eq. (2) requires the calculation of the critical fiber length (l_c) and fiber strength at l_c (σ_{fu}). On the basis of Ohsawa relationship,[20] the critical fiber length can be obtained by the following equation:

$$l_c = \frac{4}{3}\bar{l} \tag{3}$$

where $\bar{l}$ is the average fiber fragment length.

The average tensile strength of fiber with the length of l_c (σ_{fu}) can be calculated by using eq. (4)[17]

$$\frac{\sigma_{fu}}{\sigma_1} = \left(\frac{l_1}{l_c}\right)^{1/m} \tag{4}$$

where σ_1 are the average tensile strength at the length l_1.

Preparation of unidirectional PALF-epoxy composites

Unidirectional composite sheets were prepared using a steel mold having dimension of 150 mm × 150 mm × 2 mm. First, the PALFs were separated into single filaments by gently combing, and unidirectional arranged by hand. The fibers were then placed in the mold coated with a mold-releasing agent, and poured over with degassed Epikote 828 resin containing TETA curing agent in the ratio of 100 parts to 11 parts. A roller was used to make the fiber wet to the resin. After the fiber was completely wet with the resin, the roller was again applied to remove the trapped air-bubbles. The composite samples were cured at 50°C for 80 min in the oven and postcure at 100°C for 60 min. The volume fraction of fiber in all the composite samples was kept constant at 15%.

Mechanical testing of unidirectional PALF-epoxy composites

Composite specimens were cut from the cured composite sheet to determine mechanical properties. The specimens of 120^{l} mm × 13^{w} mm × 2^{t} mm dimension with a span length of 95.5 mm were used for flexural testing. The flexural tests were performed using Instron Universal testing machine model 1121, in accordance with ASTM-D790, at a crosshead speed of 2.8 mm/min. The Izod impact test on unnotched specimens was determined using a pendulum impact testing machine, according to ASTM-D256. The specimens were 80^{l} mm × 13^{w} mm × 2^{t} mm in dimension. In this study, the reported data were the average values of six successful tests for each PALF composite.

Scanning electron microscopy

The changes in the fiber surface topography due to surface treatment and fracture surfaces of PALF-epoxy composites were characterized using a LEO145 VP SEM scanning electron microscope (SEM). Prior to SEM investigation, the samples were gold-coated for 1 min using a sputtering device. The SEM photomicrographs were taken at magnification of 100× and 300×.

RESULTS AND DISCUSSIONS

SEM characterization of PALFs

The effect of surface treatment on the fiber surface topography was studied using SEM. Figure 2 shows each surface of the untreated and treated fibers. The raw PALF [Fig. 2(a)] exhibits multifibrillar structure, in which the fibrils are bound together by chemical constituents i.e., hemicellulose and lignin.[21] It is well established that sodium hydroxide is the most commonly used chemical for bleaching and/or cleaning the surface of plant fibers.[22] After the fibers were treated by the 5%NaOH aqueous solution [Fig. 2(b)], the binding materials were partially removed and separated individual cellular element was revealed on the surface. It is also apparent that external surface of the PALF becomes cleaner because of dissolution of impurities such as waxy substances in the 5%NaOH solution. This made the fiber surface rough, and increased the interaction with the resin matrix. Figure 2(c,d) show the photomicrographs of 1%DGEBA treated fibers prepared from the virgin and 5%NaOH treated fibers, respectively. In both the figures, it can be noted that substantial amount of epoxy were deposited on the fiber surfaces, and filled the intercellular regions of each PALF. However, it is clearly observed that the binding materials between cells of the 1% DGEBA modified fiber [Fig. 2(c)] remain intact, as indicated by less separation of microfibrils when the 5% NaOH [Fig. 2(b)] and DGEBA modified 5% NaOH fibers [Fig. 2(d)] are compared.

Single fiber strength measurement

The average fiber fracture stress (σ_f) and failure strain obtained from each type of pineapple fibers are listed in Table I. The values of Weibull modulus (m) corresponding to statistical fiber strength distribution after various treatment of the virgin PALFs are also given. The untreated pineapple fibers generally show large scatter in tensile properties due to their inherent irregularity or defects. The average tensile strength and strain measured on the untreated fibers were 533 MPa and 4.83%, respectively. When the treated fibers are compared with the untreated fibers, there is a certain level of improvement in average tensile strength for the fibers due to the immersion in 5% NaOH solution,

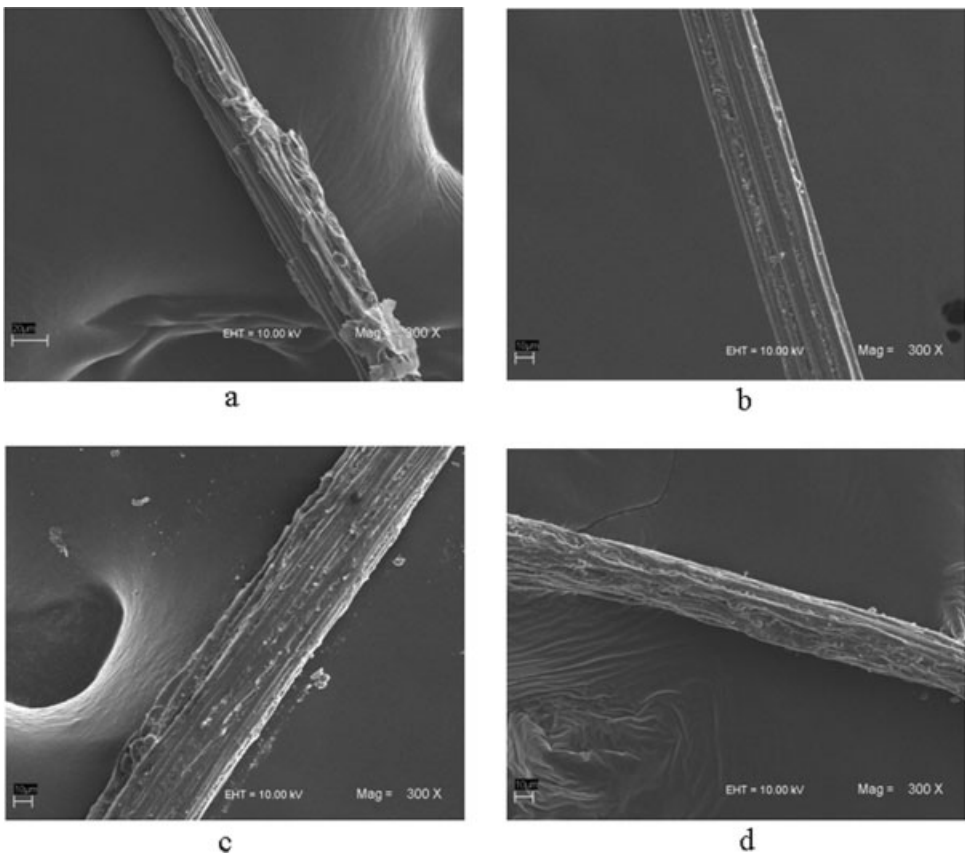


Figure 2 SEM photomicrographs of (a) untreated, (b) 5% NaOH, (c) 1% DGEBA, and (d) 5% NaOH/1% DGEBA treated PALFs.

although the improvement is not so clear. It has been well established that the removal of binding materials by alkali treatment accelerates the reorganization of fibrils along the direction of tensile force.[23] On the other hand, the tensile strain of each treated PALFs was comparable to that of the untreated fibers within the standard deviation. However, the Weibull modulus (m) of the treated PALFs clearly increased as compared to that of the untreated one (Table I). This indicates a reduced variability in strength of the untreated fiber after modification. It was found that the Weibull modulus of PALFs (m = 1.8–2.8) are in similar range as those reported for other natural fiber (m = 2.5–2.7).[24] It is also noteworthy that the strength of the treated PALFs substantially increased, especially in the range of lower strength as shown in Figure 3. In case of brittle synthetic fibers such as carbon and glass fibers, the

TABLE I
Tensile Properties and Corresponding Weibull Modulus (m) of Different Types of PALFs

Fiber types	Tensile strength (σ_f, MPa)	Strain (ε, %)	Weibull modulus (m)
Untreated fiber	533 ± 268	4.83 ± 0.84	1.80
5% NaOH treated fiber	635 ± 260	4.38 ± 0.64	2.50
1% DGEBA treated fiber	535 ± 240	3.86 ± 0.99	2.62
5% NaOH/1% DGEBA treated fiber	591 ± 190	4.51 ± 0.74	2.80

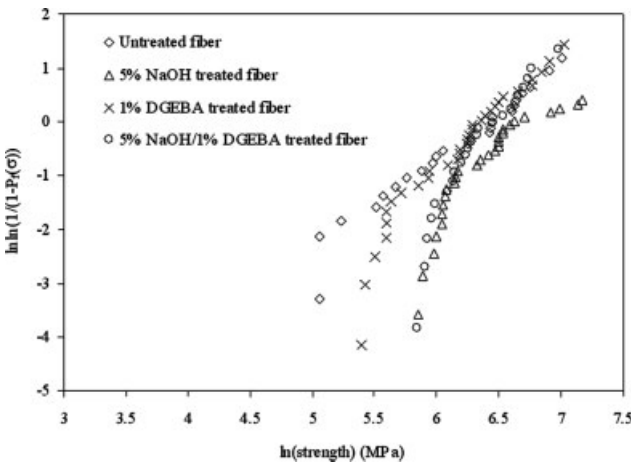


Figure 3 Weibull strength distribution for different types of PALFs.

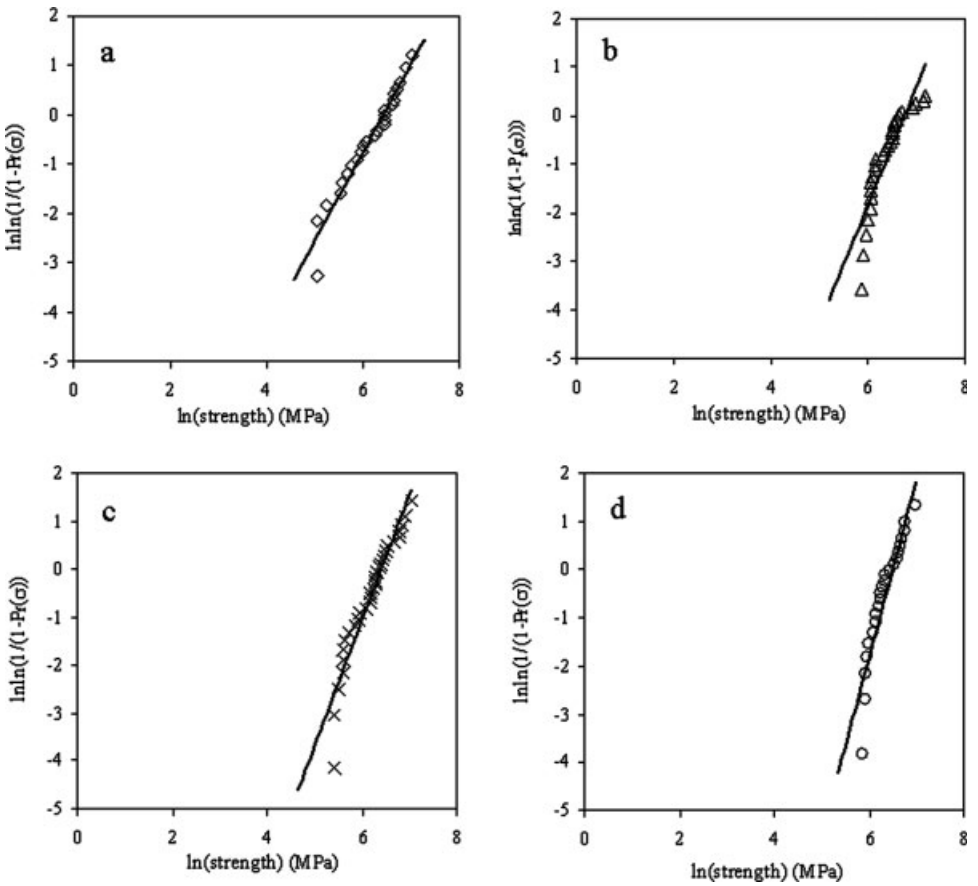


Figure 4 Comparison between Weibull strength distribution data and corresponding predictions from linear regression (solid line) for (a) untreated, (b) 5% NaOH, (c) 1% DGEBA, and (d) 5% NaOH/1% DGEBA treated PALFs.

strength distributions are closely associated to the degree of the imperfections such as voids, flaws, and cracks on the fiber surface.[25] However, the broad distribution of tensile strength of pineapple fibers obtained in this study would be attributed to the presence of considerable number of defects, mainly voids in the bonding material and weak links along the fiber length.[26] Owing to the alkalization on the fiber surface, the Weibull modulus improved mainly because of removing the weak bonding materials with defects. In case of fibers treated with 1%DGEBA and 5%NaOH/1%DGEBA, it is possible that the epoxy resin penetrated between the fibrils and filled to protect. The statistical strength distributions for the untreated and chemically modified PALFs were analyzed through the plot of ln(ln(1/(1 − $P_f(\sigma)$))) against ln(strength) where $P_f(\sigma)$ is experimental cumulative failure probability as shown in Figure 4. It is clearly seen that the trend obtained as the straight lines using linear regression showed good agreement with those of the experimental strength data for four different PALFs. This means that the validity of the fiber surface treatment can be evaluated by the Weibull statistical distribution.

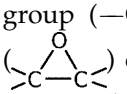
Single-fiber fragmentation test

The fragmentation test data of four kinds of fibers are given in Table II. The average fiber fragment length ($\bar{l}$) was measured from unloaded samples after removal of tension loading to 16% of applied strain. The critical fiber length (l_c) was simply obtained from eq. (3). The strength of each fiber at l_c (σ_{fu}) was then extrapolated from those measured at 4.5 mm according to the relationship given in eq. (4). The fiber diameter associated with the treated samples was found to be the same level of the untreated fibers. The interfacial shear strength (τ) was determined by Kelly-Tyson equation written in eq. (2). The τ values for different PALF-epoxy composites are listed in Table II and illustrated in Figure 5. SFFT data showed that shorter fiber fragment led to higher interfacial shear strength. Furthermore, from Table II, it is obvious that the average fiber fragment length and the critical fiber length of PALF-epoxy composites decrease according to the fiber surface modification used with 5% alkali aqueous solution as well as epoxy resin (1% DGEBA) in toluene solution, and in consequence, the τ values

TABLE II
Summary Results Obtained from Single-Fiber Fragmentation Test of Different Types of PALFs

Fiber types	d (μm)	$\bar{l}$ (mm)	l_c (mm)	σ_{fu} (GPa)	τ (MPa)
Untreated fiber	41.4 ± 3.2	0.73 ± 0.06	0.98 ± 0.08	1.25 ± 0.57	26.53 ± 2.50
5% NaOH treated fiber	40.0 ± 3.1	0.42 ± 0.02	0.55 ± 0.03	1.50 ± 0.29	52.98 ± 3.65
1% DGEBA treated fiber	42.4 ± 3.9	0.32 ± 0.04	0.42 ± 0.05	1.32 ± 0.69	66.69 ± 6.64
5% NaOH/1% DGEBA treated fiber	39.8 ± 3.3	0.29 ± 0.01	0.39 ± 0.01	1.42 ± 0.70	72.40 ± 7.72

d, $\bar{l}$, l_c, σ_{fu}, and τ are fiber diameter, average fiber fragment length, critical fiber length, fiber strength at critical fiber length, and interfacial shear strength.

significantly improved by 2 and 2.5 times, respectively. Good bonding between alkali treated fiber and epoxy matrix was brought by increased mechanical anchoring effects because the alkalization makes the fiber surface rough. Because it is well known that the epoxy resins can be reacted with a variety of functionalized compounds that contain hydroxyl, carboxyl, and amine groups,[27] Han and Drzal[28] studied the noncatalyzed reaction of glucose based resin with epoxy resin (DGEBA) by using FTIR and DSC. The reaction mechanism of hydroxyl group (—OH) in glucose resin and epoxide group () of epoxy resin was identified as etherification. In this study, it is proposed that the modification of fibers with epoxy solution resulted in grafting of the epoxy resin molecule at OH sites of the fiber as shown in Figure 6. Therefore, the high interfacial shear strength of epoxy treated composites may result from greater fiber surface affinity with the epoxy matrix. By applying alkali treatment in combination with refluxing in hot DGEBA solution (5% NaOH/1% DGEBA) to the fibers, the highest value of τ for the composites was obtained from this study. In this case, it is suggested that a number of grafting sites at —OH functional groups of the cellulose fibers were increased as a result of both treatments, leading to more reactivity of the fiber with the matrix. Regarding to the influence of the fiber–matrix adhesion,[29] it has been shown that transverse matrix cracks occur at high level of adhesion; interfacial crack growth at an intermediate level and frictional debonding at a low level, respectively. In Figure 7, the distinctive stress-birefringent patterns associated with fiber fractures were observed for the untreated and three differently treated PALFs. The transverse matrix cracking at the locus of fiber fragment is clearly seen in case of all treated PALFs [Fig. 7(b–d)], but not in case of the untreated fibers. In the case of the untreated fibers, only plastic deformation of the matrix around the fiber fracture was observed [Fig. 7(a)]. The presence of transverse matrix cracks indicates that stress concentration associated with energy release during fiber fracture causes the excessive stress in the matrix and hence the cracks propagate perpendicular to the fiber axis. These results verify that the composites with stronger interface were obtainable by the surface modifications of PALFs as shown in this study.

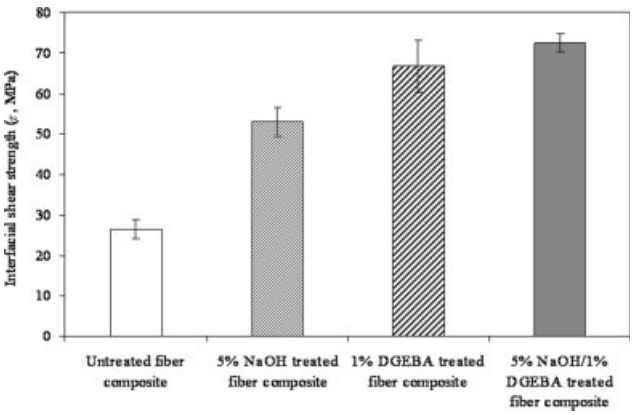


Figure 5 Comparison of interfacial shear strength (τ) of PALF-epoxy composites containing untreated, 5% NaOH, 1% DGEBA and 5% NaOH/1% DGEBA treated PALFs.

Mechanical properties of unidirectional PALF reinforced epoxy composites

Flexural strength

Table III and Figures 8 and 9 show the flexural properties of the epoxy composites reinforced with the untreated and differently treated PALFs. The incorporation of the untreated PALFs into the epoxy resin matrix at volume fraction of 0.15 produced the increase of flexural moduli by about 90% and strength by about 9% when those of the cured epoxy matrix were compared. The fiber surface treatment further increased the flexural modulus and strength of the epoxy composites by about 14–52 and 7–33%, respectively. The general improvement in flexural modulus of the treated fiber composites is attributed to the enhancement of fiber–matrix interaction and more effective transfer of stress. It is also noted that the trend in flexural modulus of the differently treated PALF composites was closely related to the trend in the interfacial bond strength (Fig. 5). For the

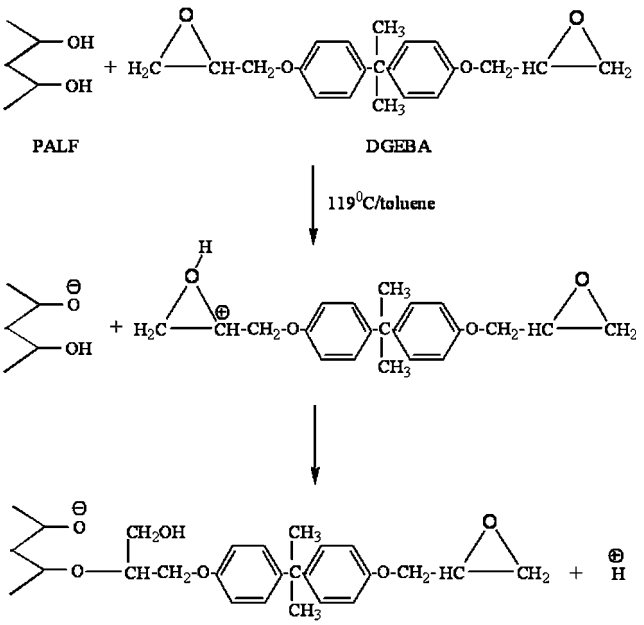


Figure 6 Proposed mechanism of reaction between hydroxyl group of pineapple fiber and DGEBA from toluene solution.

flexural strength, it can be seen from Figure 9 that the maximum improvement was achieved, when the composites were reinforced with the PALFs which were applied to alkalization and combination of alkalization and DGEBA deposition. However, both of the treatment gave the similar improvement level in strength (about 33% over the untreated PALF composite), although the fiber treatment using alkalization coupled with DGEBA allowed strongest adhesion at interface. This observation implies that the flexural strength improves because the alkalization increases the fiber strength by the enhancement of the orientation in the cellulose chain as discussed previously. Similar results were reported for natural fiber reinforced polyester composites.[30] The reason why there exists no significant improvement in flexural strength between the 1%DGEBA treated composites and the untreated fiber ones can be explained by the fact that the strength of PALF itself was not improved by the DGEBA treatment (Table I). In other words, the increase in flexural strength of alkali-modified composites is primarily due to the improvement in the strength of fibers by alkalization.

Impact strength

Table III and Figure 10 shows the impact strength obtained from the neat epoxy matrix, untreated and differently treated PALF-epoxy composites. From Table III and Figure 10, it is obviously seen that the addition of untreated PALF in the epoxy matrix

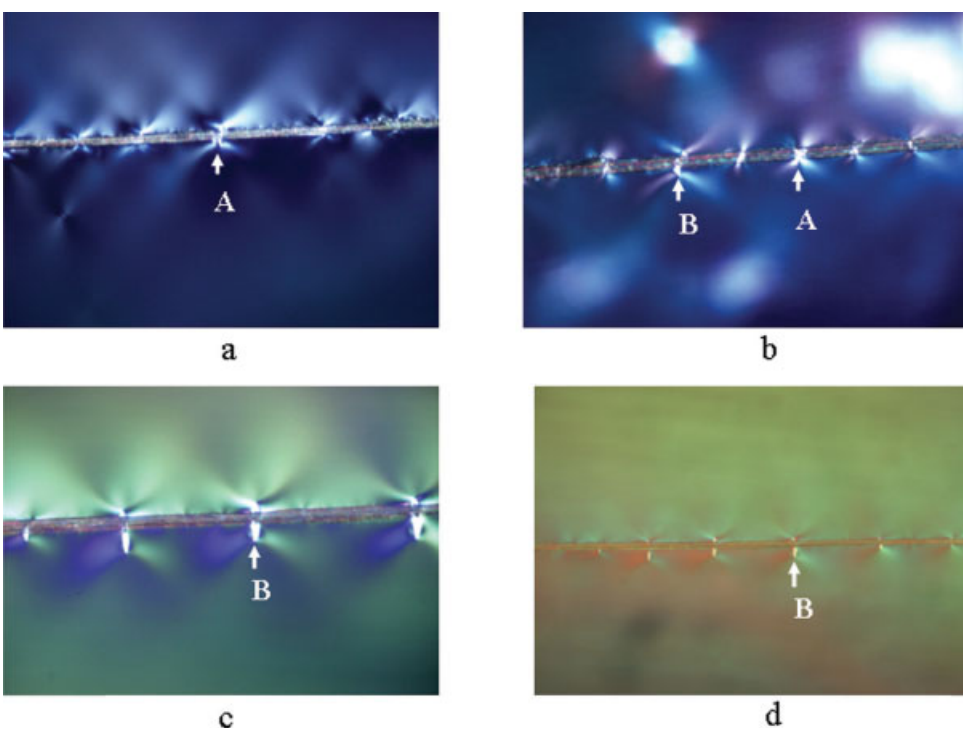


Figure 7 Typical interfacial failure modes of PALF - epoxy composites containing (a) untreated, (b) 5% NaOH, (c) 1% DGEBA, and (d) 5% NaOH/1% DGEBA treated PALFs observed from single-fiber fragmentation test. Fiber fracture and transverse matrix cracking are represented by A and B, respectively. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE III
Flexural and Impact Properties of Cured Epoxy Resin and Unidirectional PALF-Epoxy Composites Containing Different Types of PALFs

Samples	Modulus of elasticity (GPa)	Flexural strength (MPa)	Impact strength (KJ/m^2)
Epoxy matrix	2.37 ± 0.45	107 ± 8	11.00 ± 1.03
Untreated fiber composites	4.51 ± 0.74	117 ± 13	22.51 ± 4.25
5% NaOH treated fiber composites	5.15 ± 1.24	156 ± 15	39.35 ± 3.91
1% DGEBA treated fiber composites	6.26 ± 1.11	125 ± 10	31.96 ± 7.01
5% NaOH/1% DGEBA treated fiber composites	6.87 ± 0.88	155 ± 10	41.96 ± 8.52

made impact strength increased by 105%, which is same as PALF reinforced polyester composites.[2] Furthermore, all kinds of the fiber surface treatments resulted in the increase in impact strength of each composite. The impact strength of 5% NaOH, 1% DGEBA, and 5% NaOH/1% DGEBA treated fiber composites was 75, 42, and 86% higher than that of the untreated fiber composites, respectively. The maximum impact strength of composites was obtained from the combinatorial treatment with NaOH and DGEBA. Figure 11 shows SEM observation of each fractured surface by impact. From Figure 11, it is clear that the fibers with the clean surface were pulled out as shown in case of untreated PALF composites [Fig. 11(a)], which indicates poor interfacial bonding. On the other hand, in case of treated PALF composites [Fig. 11(b–d)], the fibers were pulled out connecting with the epoxy matrix, which means strong adhesion between the fibers and matrix. From these results, the increase in impact strength of treated PALF composites was attributed to the improved bonding between the fibers and the epoxy matrix. Moreover, it is generally accepted that the impact properties of various fiber reinforced composites are directly related to the fiber–matrix adhesion and fiber toughness, which can be evaluated by stress–strain curves of the fibers.[31] Figure 12 shows the typical stress–strain data of various fibers used in this study. NaOH and NaOH/DGEBA treatments brought about fiber toughness increase, just as stated previously (section flexural strength). In consequence, the great improvement in impact strength of NaOH/DGEBA treated PALF composites is due to synergistic effects combined with the adhesion and fiber toughness.

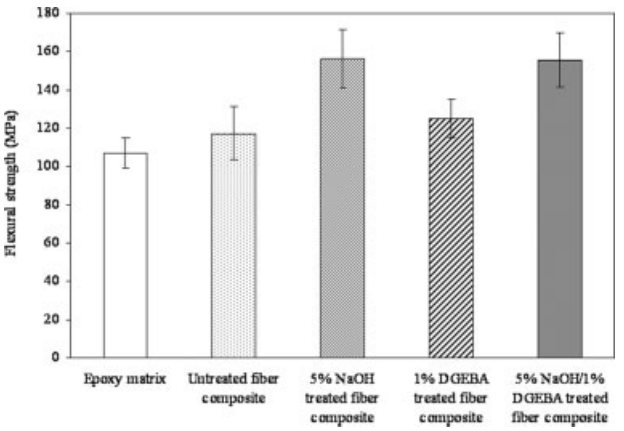


Figure 9 Comparison of flexural strength of cured epoxy matrix and PALF-epoxy composites containing untreated, 5% NaOH, 1% DGEBA, and 5% NaOH/1% DGEBA treated PALFs.

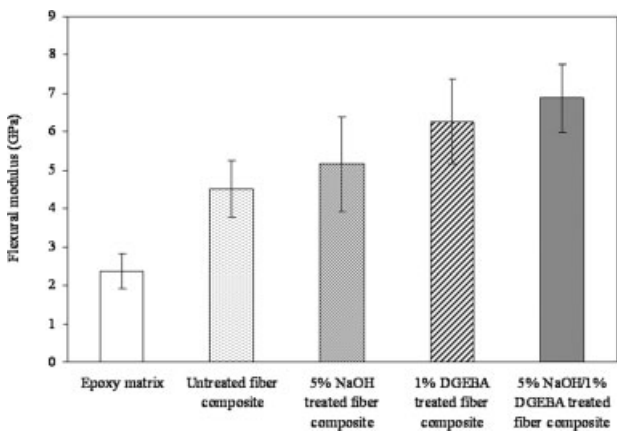


Figure 8 Comparison of flexural modulus of cured epoxy matrix and PALF-epoxy composites containing untreated, 5% NaOH, 1% DGEBA, and 5% NaOH/1% DGEBA treated PALFs.

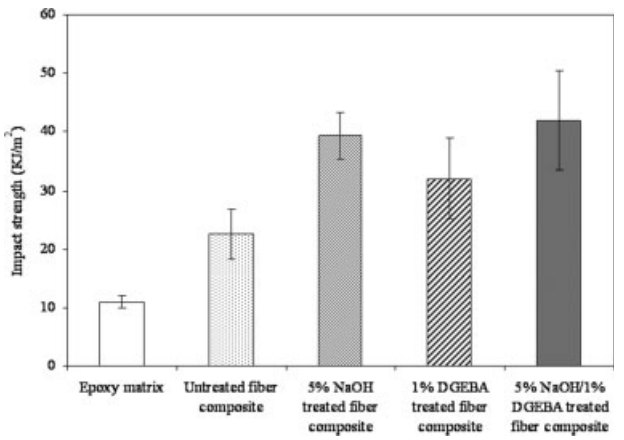


Figure 10 Comparison of impact strength of cured epoxy matrix and PALF-epoxy composites containing untreated, 5% NaOH, 1% DGEBA, and 5% NaOH/1%DGEBA treated PALFs.

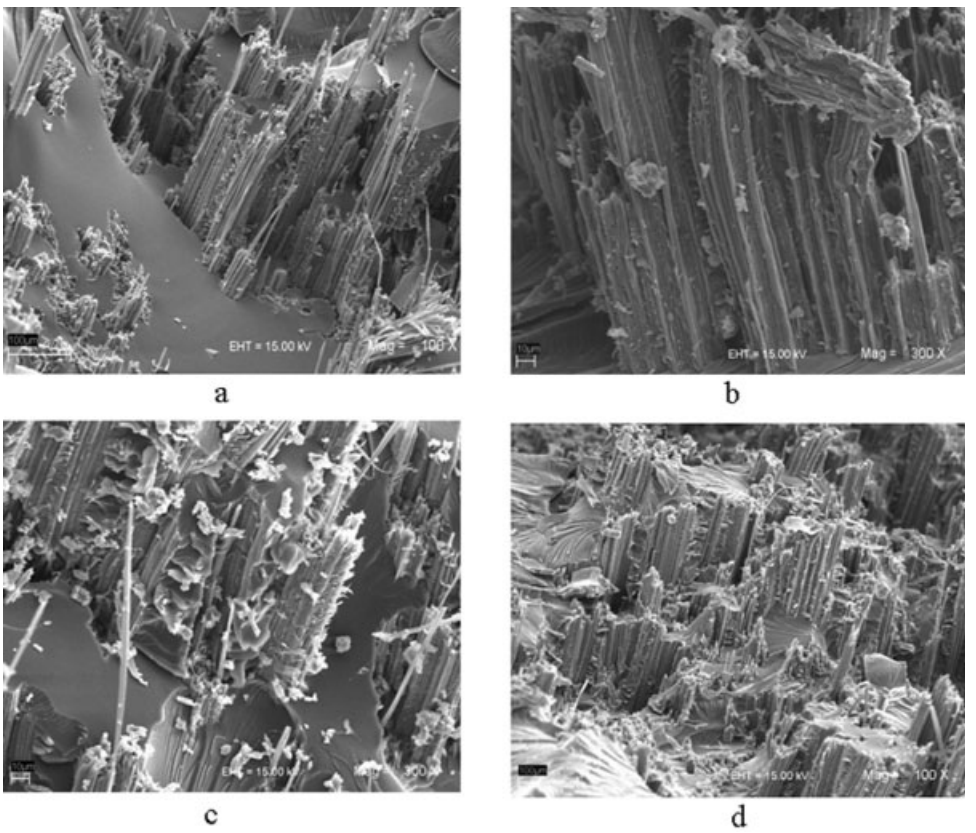


Figure 11 SEM photomicrographs of fracture surfaces for (a) untreated, (b) 5% NaOH, (c) 1% DGEBA, and (d) 5% NaOH/1% DGEBA treated composites.

CONCLUSIONS

About 5% aqueous solution of NaOH, 1% toluene solution of diglycidyl ether of bisphenol A (DGEBA), and 5% NaOH solution together with 1% DGEBA in toluene were applied to modify the surface of PALFs and adhesion of PALFs to epoxy matrix. As a result, the fluctuation of fiber strength of the PALFs has been clearly reduced, and the interfacial adhesion between PALFs and epoxy matrix was improved after each treatment. The alkalization strengthened the level of fiber–matrix adhesion by increasing surface roughness and better mechanical anchoring. The deposition of DGEBA resin on fiber surface has greatly increased the affinity with the epoxy matrix, resulting in the strong interfacial adhesion. Furthermore, the combination of alkalization and DGEBA solution resulted in the highest degree of the interfacial adhesion of PALF-epoxy composites. The flexural and impact properties of epoxy composites were greatly increased by three kinds of surface treatment proposed in this study. This study will provide valuable contributions to the development of high-value-added fiber reinforced composites based on natural PALFs as one of sustainable resources and epoxy resin.

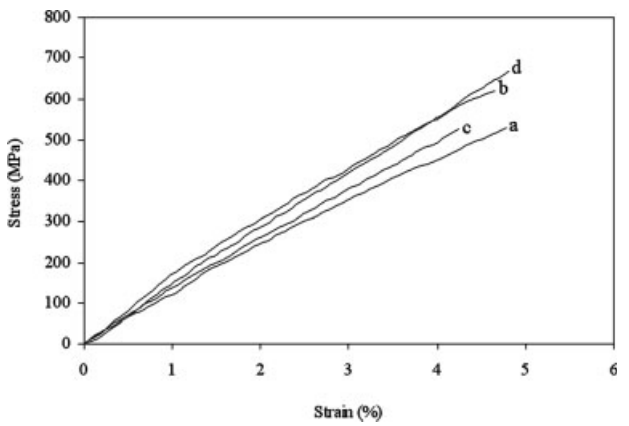


Figure 12 Typical stress–strain curves for (a) untreated, (b) 5% NaOH treated, (c) 1% DGEBA treated, and (d) 5% NaOH/1% DGEBA treated PALFs.

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