

# Performance of Pineapple Leaf Fiber–Natural Rubber Composites: The Effect of Fiber Surface Treatments

Natinee Lopattananon,<sup>1</sup> Kuljane Panawarangkul,<sup>1</sup> Kannika Sahakaro,<sup>1</sup> Bryan Ellis<sup>2</sup>

<sup>1</sup>Department of Rubber Technology and Polymer Science, Faculty of Science and Technology, Prince of Songkla University, Pattani 94000, Thailand

<sup>2</sup>Department of Engineering Materials, Faculty of Engineering, University of Sheffield, Sheffield S1 3JD, United Kingdom

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**ABSTRACT:** Composites of natural rubber (NR) and short pineapple leaf fiber (PALF) were prepared on a laboratory two-roll mill. The influences of untreated fiber content and orientation on the processing and mechanical properties of the composites were investigated. The dependence of extent of orientation on fiber concentration was also established. Sodium hydroxide (NaOH) solutions (1, 3, 5, and 7% w/v) and benzoyl peroxide (BPO) (1, 3, and 5 wt % of fiber) were used to treat the surfaces of PALFs. FTIR and scanning electron microscope (SEM) observations were made of the treatments in terms of chemical composition and surface structure. The tensile strength and elongation at break of the composites were later studied. The fiber–matrix adhesion

was also investigated using SEM technique. It was found that all surface modifications enhanced adhesion and tensile properties. The treatments with 5% NaOH and 1% BPO provided the best improvement of composite strength (28 and 57% respectively) when compared with that of untreated fiber. The PALF–NR composites also exhibited better resistance to aging than its gum vulcanizate, especially when combined with the treated fibers. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1974–1984, 2006

**Key words:** rubber; biofibers; composites; mechanical properties; morphology

## INTRODUCTION

Short fiber reinforced elastomers are a class of composite materials. It has been recognized that they have great potential to serve a wide range of applications in domestic end uses, especially in the V-belt, hose, seal, and tire industries. It is well known that the incorporation of rigid fiber into a soft rubbery matrix provides a synergistic combination to the constituent phases. That is, their mechanical properties, such as modulus and strength, can be enhanced while the flexibility of the rubbery matrix is retained. Moreover, short fiber reinforcement in rubber composites gives an improvement in green strength, creep resistance, aging resistance, and dimensional stability during fabrication and in real-life service. Extensive work has been carried out to investigate the influence of different short fibers such as cellulose, rayon, nylon, polyester, glass, and carbon fibers on the mechanical properties of natural and synthetic rubbers.<sup>1–4</sup> According to these

findings, the properties of short fiber–rubber composites depend upon fiber type, fiber content, fiber aspect ratio, fiber orientation, fiber dispersion, and fiber–matrix adhesion.

Recently, the development of short fiber reinforced rubber composites has focused on using renewable plant-based natural fibers such as jute, silk, pineapple leaf, coir, sisal, oil palm, and bamboo as reinforcing materials.<sup>5–13</sup> Two of the main reasons for the use of natural fiber in rubber composites are economic and processing advantages. Besides its low cost and density, natural fiber is nonabrasive and non-hazardous when compared with synthetic fibers. It is also abundantly available, particularly in the tropical country such as Thailand. Since it also has flexibility when bending, there is less fiber breakage during rubber fabrication than usually occurs when using more brittle synthetic fibers. This results in better stress transfer capability or reinforcement. The general components of natural fibers are cellulose, hemicellulose, lignin, pectin, waxes, and water-soluble substances, with cellulose, hemicellulose, and lignin as the basic components.<sup>14</sup>

Pineapple leaf fiber (PALF) is an important natural fiber that exhibits high specific strength and stiffness.<sup>15</sup> This is attributable to the high cellulose content (70–80%) and relatively low microfibrillar angle. Because of its excellent mechanical properties, the PALF

Correspondence to: N. Lopattananon (lnatinee@bunga.pn.psu.ac.th).

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has been found to have a high reinforcing efficiency for application in polyester composites,<sup>16–18</sup> low density polyethylene (LDPE) composites,<sup>19,20</sup> and biodegradable plastic composites.<sup>21,22</sup> It is reported by these authors that the viscoelastic behavior, processing, tensile strength, flexural, and impact properties of the composites depend on many factors including fiber length, fiber loading, and fiber orientation. On the other hand, it has been highlighted that the full exploitation of pineapple fiber in these composite materials encounters some limitations because of an inadequate bonding between PALF and the hydrophobic matrix.<sup>17,18,23</sup> In addition, PALF has high susceptibility to water absorption,<sup>24,25</sup> particularly at elevated temperatures. These major problems are associated with the hydrophilic character of the cellulose structure of PALF. Consequently, this certainly affects the mechanical performance of the rubber composites, especially under long exposure to environmental conditions of elevated temperatures and atmospheric humidity. To overcome these problems, it is necessary to modify the fiber surface through the employment of physical and chemical methods to reduce the hydrophilic nature of the natural fiber and, hence, improve the fiber–matrix bonding. In general, the surface modification of practical interest is readily achieved by using suitable chemical treatments of the fiber. A significant increase in the strength of composites is reported after treatment of the PALFs.<sup>17</sup> Mishra et al.<sup>18</sup> have shown that the interface quality for PALF-polyester composites could be enhanced through different surface modifications, such as dewaxing, alkali treatment, cyanoethylation, and grafting of acrylonitrile monomer onto dewaxed PALF. Samal and Ray<sup>26</sup> have demonstrated that the treatment of pineapple fibers with alkali, for example, sodium hydroxide (NaOH), 2,4-dinitrochlorobenzene, benzoyl peroxide (BPO), BPO/acetylation, significantly increased the resistance to water uptake and the mechanical strength of the fibers. A decrease in moisture content of chemically modified PALF-reinforced LDPE composites was reported by George et al.<sup>24</sup> Bonding agents based on three components, that is resorcinol (reso), hexamethylene tetramine (Hexa), and silica, were found to be essential for PALF-natural rubber (NR) adhesion.<sup>7</sup>

Although the use of chemical methods has proved successful as a tool for promoting the fiber–matrix adhesion for many polymer materials, but there seems to be no previous attempt to use chemically modified pineapple fiber to improve the adhesion of NR. In the present work, we first analyzed the influence of short pineapple fiber content on curing, mechanical properties, and extent of fiber orientation of PALF-natural rubber composites. The alkalization and benzoylation were then applied to pineapple fibers and their influence on the chemical composition and surface structure of the fibers as well as fiber–matrix adhesion,

mechanical properties, and aging of the short PALF-reinforced natural rubber were assessed.

## EXPERIMENTAL

### Chemicals

Pineapple leaf fiber (PALF) was washed with water, dried at 70°C in a hot-air oven for several days until the fiber weight remained unchanged, then combed, and cut into lengths of 6 mm. Thirty samples of fibers were subjected to diameter measurement using a scanning electron microscope (SEM). The measured values were averaged and found to be  $75 \pm 20 \mu\text{m}$ . Natural rubber (STR 5L) was obtained from Thavorn Industry Co. (Songkhla, Thailand). All the rubber additives were of commercial grade. Sodium hydroxide (NaOH), benzoyl peroxide (BPO), toluene, and acetone were AR-grade and used as received.

### Fiber treatments

#### Alkali treatment

The chopped PALFs were placed in a glass vessel containing NaOH solution of various concentrations (1, 3, 5, and 7% w/v). The fibers were soaked in NaOH solution at 28°C with continuous stirring for 18 h. The fiber was then washed several times with acetone and distilled water to eliminate the adsorbed alkali. The alkali-treated PALFs were later dried in a hot-air oven at 70°C and kept in a desiccator for subsequent analysis and fabrication.

#### Benzoylation

The untreated pineapple fibers (46 g) were mixed with 1 wt % of fiber BPO (0.46 g) dissolved in toluene (2 L) in a round-bottom glass vessel. The amounts of BPO used varied from 1, 3, and 5 wt % of fiber. The reaction was carried out at 80°C with stirring for 1 h under N<sub>2</sub> atmosphere. The fibers were removed from the reactor and washed thoroughly with toluene and dried at 70°C.

TABLE I  
Formulation of the Fiber-NR Composites

Ingredient	Parts by weight
Natural rubber (STR 5L)	100
Stearic acid	1
Zinc oxide	5
TMQ <sup>a</sup>	1
TBBS <sup>b</sup>	0.7
Sulfur	2.5
Untreated pineapple fiber	0, 10, 20, 30, and 40

<sup>a</sup> Polymerized 2,2–4-trimethyl-1,2-dihydroquinoline.

<sup>b</sup> *N-tert*-Butyl-2-benzothiazyl sulphenamide.

**TABLE II**  
**Mixing Schedule**

Mixing step	Mixing time (min)
Rubber mastication	2
Add stearic acid	1
Add zinc oxide, TMQ, and TBBS	3
Add PALF	5
Add sulfur	2
Sheet out (7 times)	5

### Fabrication of composites

The formulations of the fiber-NR composites using various types of vulcanizing chemicals are given in Table I. The composite materials were prepared on a two-roll mill (150 × 300 mm) at room temperature. Other ingredients were then mixed according to the time schedule given in Table II. The required amount of fiber was added into the rubber compounds at a mill opening of 1.5 mm. This value was chosen for maximizing fiber orientation in the mill direction. Finally, the fiber-NR composites were passed through the mill for seven times keeping the direction for each pass constant to ensure the alignment and uniform dispersion of fibers. Other mixing parameters such as temperature and mill/roll speed ratio were the same for all sets of experiments. The composites were then vulcanized at 150°C in a mold with hydraulic pressure for their respective optimal cure times obtained by using ODR test.

### Characterizations

#### FTIR spectroscopy

The chemical components of untreated and treated PALF were studied by using FTIR Spectrophotometer Nicolet 560 for ranges of wavenumbers 4000–400  $\text{cm}^{-1}$ . The FTIR spectra were recorded by using KBr pellet technique. The fibers (1.15 mg) were crushed into fine particles and mixed with KBr powder (3.45 mg). The mixtures (0.77 mg) were then pressed into thin discs.

#### Measurement of vulcanizate properties

Curing properties were measured on an Oscillating disc rheometer model ODR 100S at a vulcanization temperature of 150°C. The tensile properties were determined according to ASTM D 368–96 on the Hounsfield Tensometer model H10KS at the extension rate of  $500 \pm 50$  mm/min at room temperature.

#### Scanning electron microscopy

SEM model LEO145 VP was used to examine both the surface topography of untreated and treated PALF and fracture surfaces of PALF-natural rubber composites. For the analysis of fracture surfaces, the composite samples were immersed in liquid  $\text{N}_2$  for 15 min and then fractured. Prior to SEM investigation, the samples were gold-coated for 1 min by using gold coating sputter.

#### Anisotropic swelling measurement

The anisotropic swelling test was carried out on rectangular specimens (2.5 × 1.0 × 0.3 cm) in toluene at room temperature. After an immersion period of 48 h, the samples were taken out of the toluene and drained. The length and width were measured before and after immersion in toluene to determine the swelling ratio.

#### Thermal aging

Dumbbell test-pieces were heated at 100°C in a hot-air oven for 24 h, according to ASTM D 573–81. These samples were then conditioned at room temperature for 16 h prior to mechanical testing at room temperature.

## RESULTS AND DISCUSSIONS

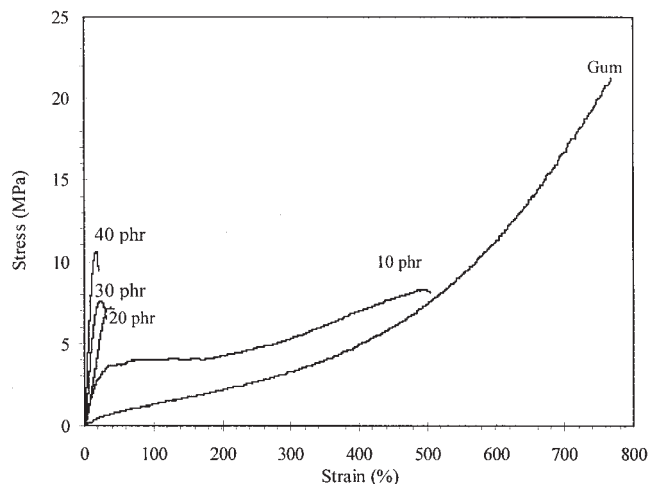
### Properties of untreated PALF-natural rubber composite

#### Effect of PALF concentration on the curing properties

Table III shows the effects of pineapple fiber loading on scorch time ( $t_{s1}$ ) and cure time ( $t_{90}$ ) obtained from

**TABLE III**  
**Vulcanization Characteristics of NR Composites with Different Concentrations of PALF**

Concentration of untreated PALF (phr)	Properties				
	Scorch time ( $t_{s1}$ , min)	Cure time ( $t_{90}$ , min)	Minimum torque ( $M_H$ , dN-m)	Maximum torque ( $M_L$ , dN-m)	$M_H - M_L$
0	7.21	13.48	2.5	20.70	18.20
10	4.46	11.53	2.1	23.80	21.70
20	4.32	11.24	1.1	21.63	20.53
30	4.06	9.06	1.1	24.30	23.20
40	3.48	11.02	2.3	32.90	30.64

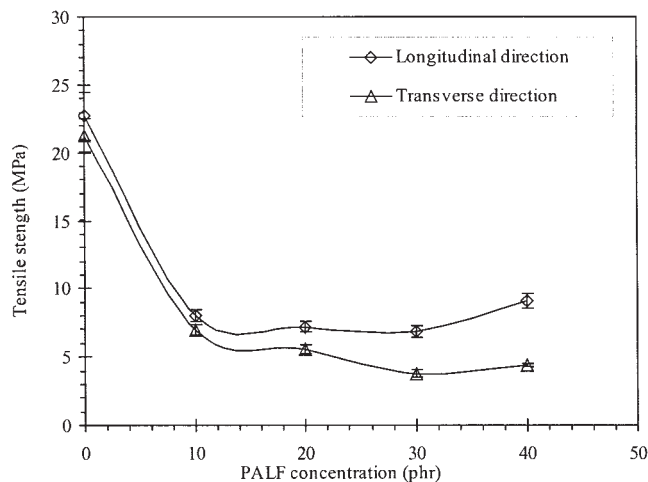


**Figure 1** Longitudinal forces–extension curve of PALF-natural rubber composites with various concentrations of pineapple fiber.

the ODR measurements. The  $t_{s1}$  and  $t_{90}$  are measures of the times at which vulcanization begins and when it reaches 90% of complete cure. It can be seen that all fiber-filled composites exhibit lower values of scorch and cure times than those of unfilled composites because the fiber introduced into NR composites causes an increase in mixing time.<sup>12,13</sup> However, it seems that both properties are not much affected by an increasing amount of fiber. Other researchers<sup>11,13</sup> also reported similar observations. The minimum torque ( $M_L$ ), a measure of initial viscosity of rubber compounds, is independent of fiber loading. But the maximum torque ( $M_H$ ) appears to increase as a function of fiber concentration, indicating a rise in stiffness of the vulcanizates. This was due to the restricted mobility of rubber molecules by the inclusion of fibers.<sup>10</sup> Moreover, the values of  $M_H - M_L$  of vulcanizates also increase with fiber loading, which implies a higher degree of fiber and NR matrix interaction.

#### Effect of PALF concentration on mechanical properties

The typical longitudinal stress–strain curves of PALF-natural rubber composites with various concentra-



**Figure 2** Tensile strength of PALF-natural rubber composite in longitudinal and transverse directions with various concentrations of pineapple fiber.

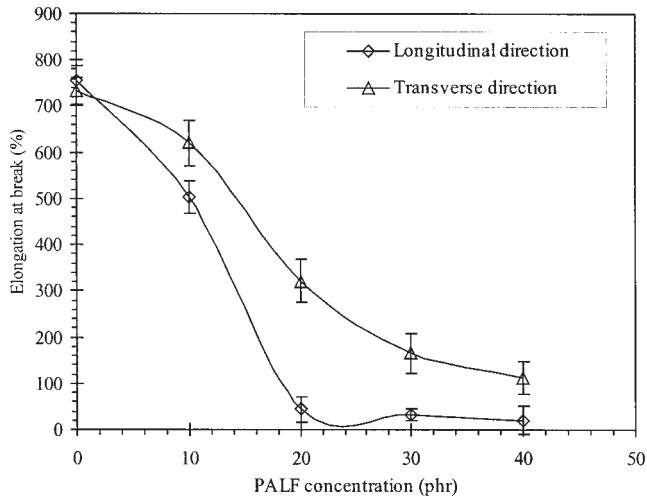
tions of pineapple fiber are illustrated in Figure 1. It is clearly seen that samples with an increasing fiber loading show higher stresses at a given level of strain, indicating that the rubber matrix becomes stiffer. The variation of tensile strength and elongation at break of PALF-natural rubber composites as a function of fiber load in longitudinal ( $L$ ) and transverse ( $T$ ) directions is tabulated in Table IV and graphically presented in Figures 2 and 3, respectively. From Table IV and Figure 2, it can be seen that the measurement of composite tensile strength in both directions gave similar trends, but the values of the composite strength in the longitudinal direction were greater than those tested in the transverse direction because the fibers mainly oriented in the direction of applied force. The presence of small amounts of fibers (10 phr) significantly reduced the tensile strength of composites below that of gum because the fibers acted as a rubber network defect. The drop in the tensile strength continued to occur until fiber content was greater than 30 phr. This could be attributed to the amount of fibers at that ratio was sufficient to carry the applied load. It has been previously noted that there appears to be a limiting amount of fiber that is required for reinforcement in

**TABLE IV**  
Tensile Strength and Elongation at Break of NR Composites with Different Concentrations of PALF

Concentration of fiber (phr)	Tensile strength (MPa) <sup>a</sup>		Elongation at break (%) <sup>a</sup>	
	$L$	$T$	$L$	$T$
0	22.71 ± 1.76	21.28 ± 1.20	755.00 ± 32.91	733.00 ± 28.87
10	8.00 ± 0.40	6.96 ± 0.39	503.57 ± 35.12	620.00 ± 50.23
20	7.20 ± 0.40	5.54 ± 0.35	43.75 ± 26.73	321.43 ± 45.70
30	6.80 ± 0.44	3.74 ± 0.27	32.14 ± 12.20	165.25 ± 43.22
40	9.06 ± 0.55	4.40 ± 0.13	20.71 ± 31.46	112.50 ± 35.60

<sup>a</sup>  $L$  denotes longitudinal and  $T$  denotes transverse orientation.





**Figure 3** Elongation at break of PALF-natural rubber composite in longitudinal and transverse directions with various concentrations of pineapple fiber.

natural rubber.<sup>4,9,27</sup> In this case, the minimum concentration of pineapple fiber for restraining the NR matrix was found to be 30 phr. The equivalent amount of fiber as found in the present work was also reported in the system of natural rubber containing coir fiber.<sup>9</sup> As the rubber matrix was stiffened by pineapple fiber, the longitudinal and transverse elongation at break decreased, as shown in Figure 3.

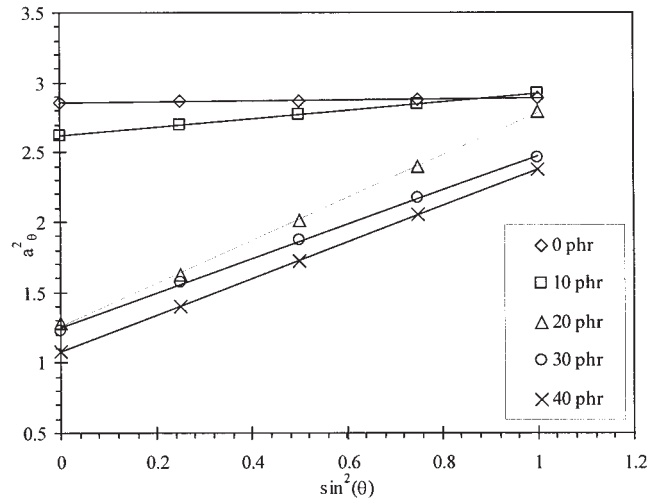
#### Effect of PALF concentration on fiber orientation

The solvent swelling of unidirection short fiber–rubber composite has been used to estimate the extent of fiber orientation and fiber–matrix adhesion in natural and synthetic rubber containing short coir fiber,<sup>8–9</sup> sisal/oil plam fibers,<sup>13</sup> and sisal fiber.<sup>27</sup> The analysis of data obtained from the equilibrium swelling test was first described by Coran et al.<sup>28</sup> In the test, the swelling of matrix containing preferred aligned fibers is anisotropic, leading to the progressive increase in swelling upon increasing angle ( $\theta$ ) relative to fiber orientation as can be expressed in eq. (1)

$$a_{\theta}^2 = (a_T^2 - a_L^2)\sin^2\theta + a_L^2 \quad (1)$$

where  $a_{\theta}$ ,  $a_L$ , and  $a_T$  are dimensional swelling ratios in the angle ( $\theta$ ), longitudinal, and transverse directions, respectively.

By assuming various values of  $\theta$ , the dimensional swelling of natural rubber containing 10, 20, 30, and 40 phr at any  $\theta$  were calculated by using eq. (1), and it is usual to present data in the form of Figure 4.<sup>8,9,13</sup> For all fiber-filled samples, the increase in value of  $\theta$  caused an increase in swelling, which obeys eq. (1), and the greatest extent of swelling was found at an angle of  $90^\circ$ . The swelling of NR matrix is isotropic in

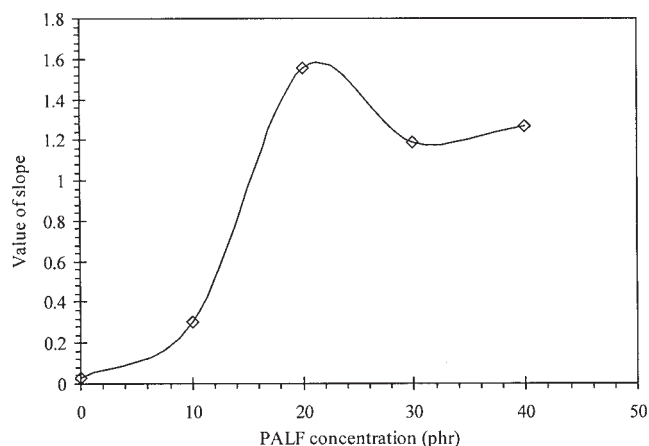


**Figure 4** Variation of dimensional swelling ratio ( $a_{\theta}^2$ ) with varying angle ( $\theta$ ) to the preferential orientation of fiber.

the absence of fibers. At any fixed angle, the swelling of natural rubber obviously became lesser as the fiber amounts were increased. This observation has demonstrated that the penetration of solvent into rubber composite is inhibited by the PALF. By using eq. (1) and measured values of  $a_L$  and  $a_T$  (Table V), the slope for each swelling curve has been evaluated to give the information of fiber orientation and plotted with fiber content as shown in Figure 5. With an increase of the slope, greater orientation is obtained.<sup>8,29</sup> The maximum preferred orientation was obtained in composites containing 20 phr pineapple fibers. At lower amounts of fiber, the movement of fibers in any direction in the mold could possibly be more because of the action of shear flow during compression molding and result in poor fiber alignment. For higher fiber loading (i.e., 30 and 40 phr), the agglomeration of fibers might occur, leading to a lower level of alignment than that of 20 phr fiber loading. Considering that the best fiber orientation along with acceptable processing results and moderate mechanical properties were observed in the mix reinforced with 20 phr fibers, this loading was chosen for subsequent study.

**TABLE V**  
Anisotropic Swelling Values of NR Composites with Different Concentrations of PALF

Concentration of fiber (phr)	$a_L$	$a_T$	Slope
0	1.69	1.70	0.03
10	1.62	1.71	0.29
20	1.11	1.67	1.51
30	1.13	1.57	1.18
40	1.04	1.54	1.29

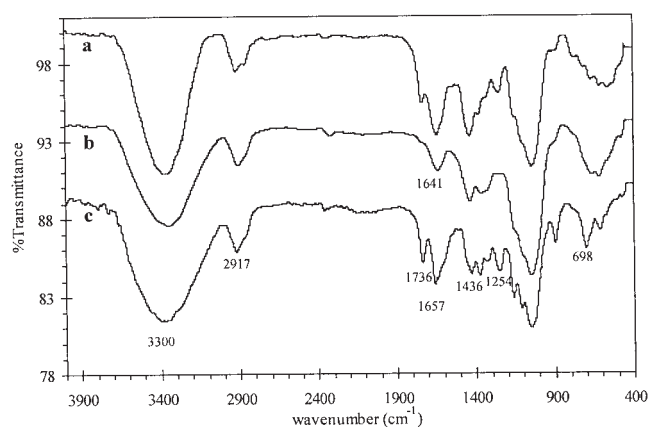


**Figure 5** Extent of fiber orientation in PALF-natural rubber composite with various concentrations of pineapple fiber.

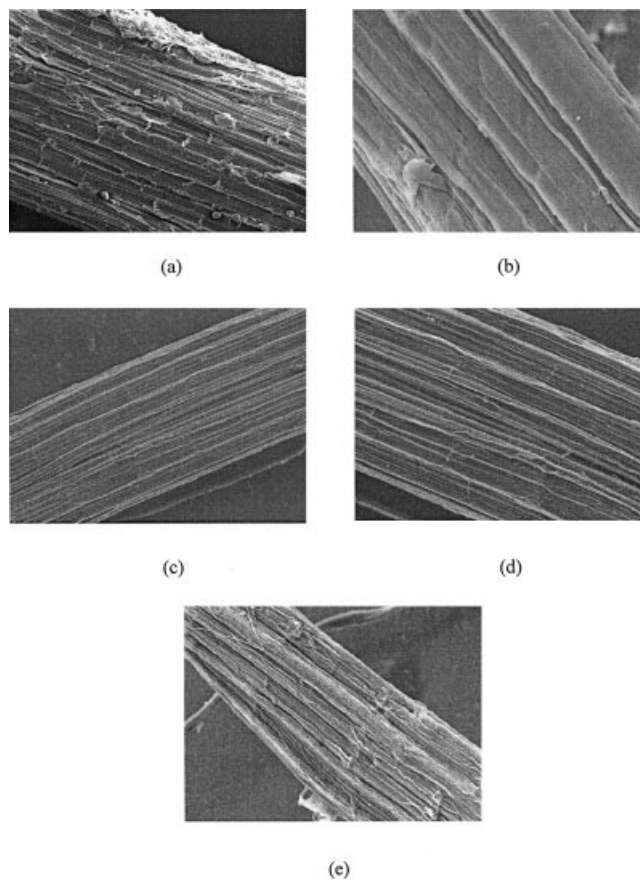
### Effect of chemical modifications

#### FTIR spectra

The effect of chemical modifications on the fiber surface was observed by using FTIR spectroscopy. The comparison of the representative FTIR spectra of untreated PALF before (a) and after NaOH (b) and BPO treatment (c) is shown in Figure 6. For untreated fiber, an intense and broad band ranging from 3100 to 3800  $\text{cm}^{-1}$  was due to hydrogen bonded  $\text{—OH}$  vibration of the cellulose structure of pineapple fiber. The peak at 2917  $\text{cm}^{-1}$  has been assigned to the  $\text{C—H}$  stretching vibration from  $\text{—CH}_2$  group of cellulose and hemicellulose. The characteristic peak at 1736  $\text{cm}^{-1}$  was attributed to  $\text{C=O}$  stretching of carbonyl groups ( $>\text{C=O}$ ) in hemicellulose. The peak at 1641  $\text{cm}^{-1}$  was due to absorbed water.<sup>26</sup> The peaks centered around 1436 and 1254  $\text{cm}^{-1}$  indicated the existence of lignin and

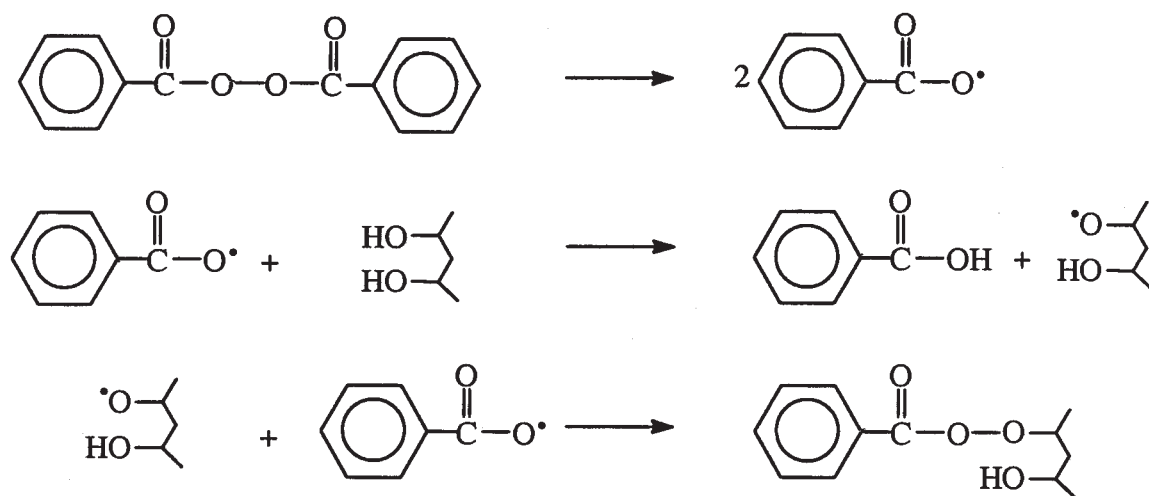


**Figure 6** FTIR spectra for (a) untreated, (b) NaOH-treated (at 5% w/v for 18 h), and (c) BPO-treated (at 1 wt % of fiber for 3 h) pineapple fibers.



**Figure 7** SEM photomicrographs of (a) untreated, (b) 1%, (c) 3%, (d) 5%, and (e) 7% (w/v) NaOH-treated pineapple fibers.

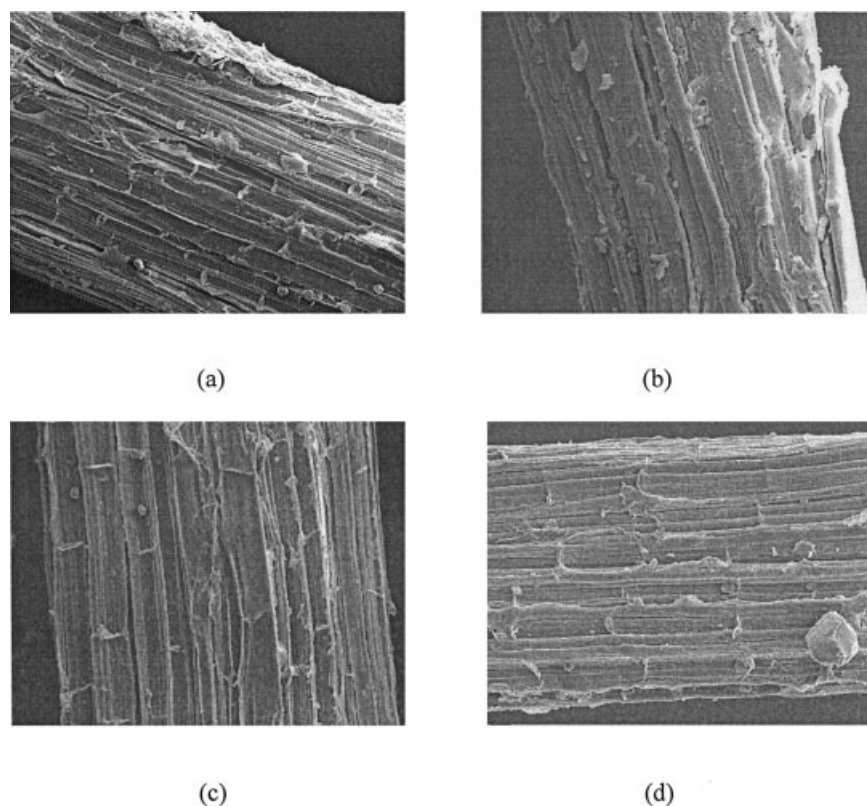
hemicellulose structure, respectively.<sup>30,31</sup> The most remarkable change in FTIR spectrum of NaOH-treated PALF [Fig. 6(b)] is noted to be the absence of characteristic peaks at 1736 and 1254  $\text{cm}^{-1}$ . This was accompanied by a reduction in peak intensity at 1436  $\text{cm}^{-1}$ . This is because of complete decomposition of hemicellulose and partial leaching out of lignin by the NaOH. These results indicate that the ester type in hemicellulose is more easily removed by an alkali solution. Mwaikambo and Ansell<sup>31</sup> have also reported that the alkali treatment is prone to attack the hemicellulose in sisal and jute rather than lignin. The benzylation of pineapple fiber introduces the new absorption peaks at about 1657 and 698  $\text{cm}^{-1}$  owing to the presence of phenyl nucleus in BPO.<sup>32</sup> It is apparent that the absorption at 3300  $\text{cm}^{-1}$  was broader than that of the untreated fiber, resulting from the participation of  $\text{—OH}$  group in the grafting reaction of BPO, while the peak intensity at 1735–1736  $\text{cm}^{-1}$  increased relative to that of untreated fiber. This observation is indicative of grafting of the benzoyl radical at OH sites of the cellulose, which may be represented by the following set of reactions:



### Surface topography

SEM micrographs for the untreated and treated PALF with various concentrations of NaOH and BPO are shown in Figures 7 and 8, respectively. It is well established that the cellulose chains of natural fiber are strongly bound by chemical constituents, lignin, and hemicellulose, resulting in the formation of multicellular fiber.<sup>33</sup> By comparing treated fibers with the untreated fibers [Fig. 7(a)], it can be seen that the

NaOH treatments [Figs. 7(b)–7(e)] resulted in separation of the microfibrillar structure of fiber because of the removal of cemented materials (i.e., lignin and hemicellulose).<sup>30,34</sup> The extraction of alkali-soluble materials observed from SEM analysis clearly corroborates the FTIR spectra of treated PALF. This phenomenon appeared to increase with higher concentrations of alkali solution. The other noticeable impurities have also been removed from the fiber surface. Conse-



**Figure 8** SEM photomicrographs of (a) untreated, (b) 1%, (c) 3%, and (d) 5% (by weight of fiber) BPO-treated pineapple fibers.

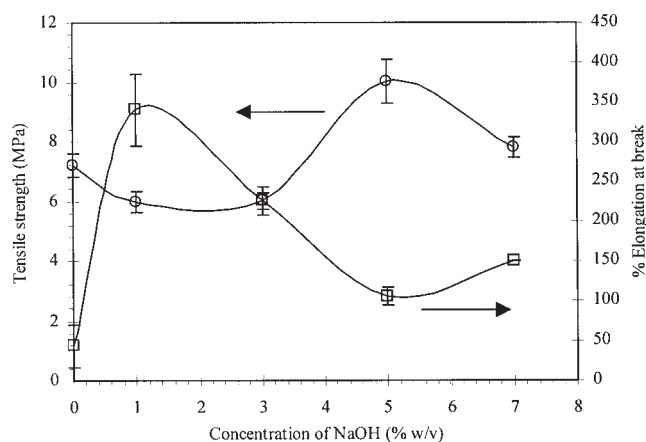
**TABLE VI**  
Longitudinal Tensile Strength and Elongation at Break of NR Composites Containing Different Percentage of NaOH-Treated PALF

Concentration of NaOH (% w/v)	Tensile strength (MPa)	Elongation at break (%)
0	7.20 ± 0.40	43.75 ± 26.73
1	5.98 ± 0.34	340.00 ± 45.41
3	6.01 ± 0.26	225.00 ± 17.68
5	10.02 ± 0.75	105.00 ± 11.18
7	7.79 ± 0.34	150.00 ± 0.00

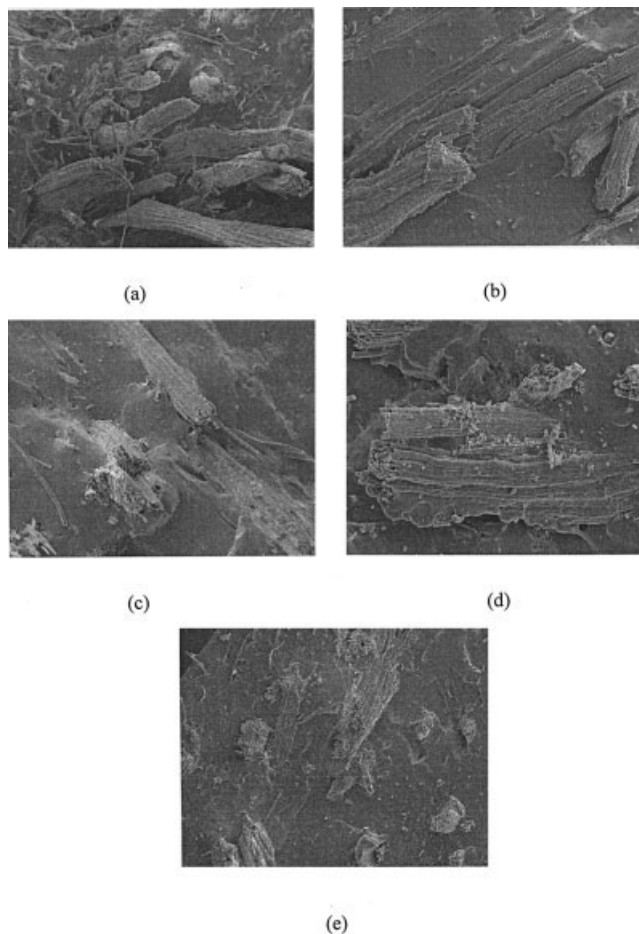
quently, the effective fiber surface area available for bonding with the matrix would be increased. The SEM photomicrographs of fiber surfaces treated with different percentage of BPO (weight of fiber) are shown in Figures 8(b)–8(d). They reveal that the bonding between multicellulosic fibers remains intact when compared with that of parent fiber and the grafted BPO on these fiber surfaces.

#### Mechanical properties

**Alkali treatment.** The variation of tensile properties of treated PALF-NR composites in longitudinal direction as a function of NaOH concentration (1, 3, 5, and 7%) for 18 h is shown in Table VI and Figure 9. It can be seen that all of the alkali-treated fiber composites exhibited higher elongation at break in comparison to unmodified fiber-reinforced composites. It has been previously addressed that when the hemicellulose are removed, the interfibrillar region is likely to be less dense and less rigid, and thereby makes the microfibrils to be more capable of rearranging themselves along the direction of tensile deformation.<sup>35</sup> Consequently, the increased elongation at break is perhaps



**Figure 9** Tensile strength and percentage of elongation at break of PALF-natural rubber composites containing fibers treated with different concentrations of NaOH solution.



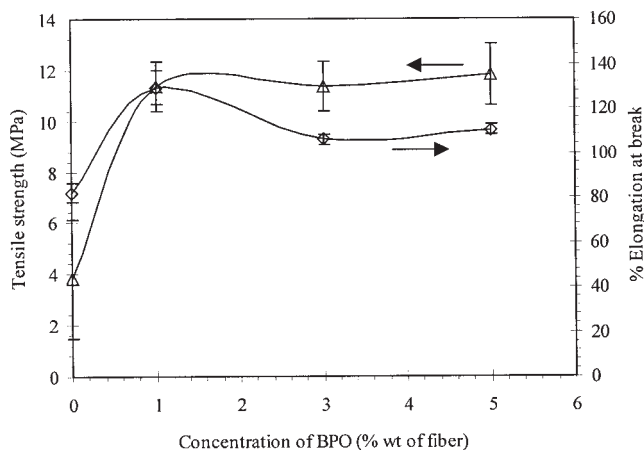
**Figure 10** SEM photomicrographs of fracture surfaces of PALF-natural rubber composites containing (a) untreated, (b) 1%, (c) 3%, (d) 5, and (e) 7% (w/v) NaOH-treated pine-apple fibers.

due to the improved degree of molecular orientation in the microfibrils. In addition, it is noted by Luo and Netravali<sup>21</sup> that the composites failed at the interface because of the weak interfacial bonding. The weak bonding is primarily determined by the void content present at the interface. In PALF-NR composites, the failure of the composite at interface would reduce because of the decrease in micro-void content upon surface treatment. Therefore, this indicates an en-

**TABLE VII**  
Longitudinal Tensile Strength and Elongation at Break of NR Composites Containing Different Percentage of BPO-Treated PALF

Amount of BPO (wt % of fiber)	Tensile strength (MPa)	Elongation at break (%)
0	7.20 ± 0.40	43.75 ± 26.73
1	11.32 ± 0.66	130.00 ± 11.18
3	9.28 ± 0.19	130.00 ± 11.18
5	9.65 ± 0.21	135.00 ± 13.69



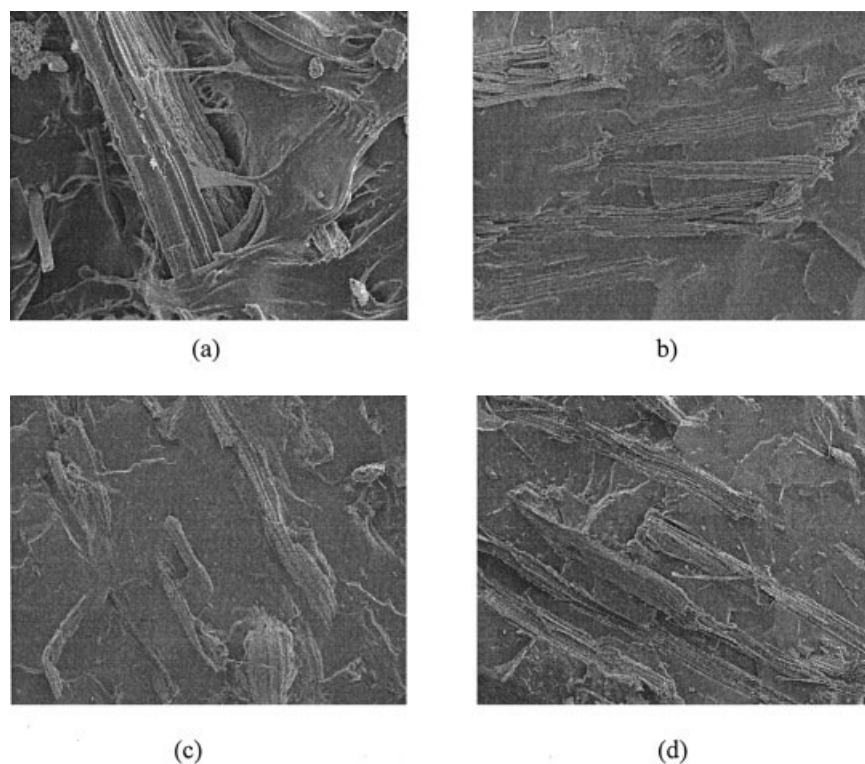


**Figure 11** Tensile strength and elongation at break of PALF-natural rubber composites containing fibers treated with different amounts of BPO.

hancement of fiber-natural rubber interfacial adhesion. Similar observation has been previously reported by Razera and Frollini.<sup>36</sup> However, the NaOH-treated composites do not show any improvement in tensile strength when using relatively lower concentrations, that is less than 5% (w/v). As the concentration of NaOH solution increased from 3 to 5% (w/v), the tensile strength of treated fiber composites increased by 28% over that of untreated fiber composites. The improvement in tensile properties was attributed to an

increase in effective surface area and roughness of the pineapple fibers, which increased the interfacial bond strength through mechanical interlocking between the fiber and natural rubber. Thus, this efficiently enhanced the stress transfer capability at fiber-matrix interface of the composites subjected to given tensile loading. This was verified by examining the SEM photomicrographs of fractured surfaces taken from the rubber specimens reinforced with different concentration of NaOH-treated fibers and comparing them with those containing untreated fibers. These SEM results are given in Figure 10. The fracture surface of untreated fiber composite shows clean long stems of fibers after pulling from the rubber matrix [Fig. 10(a)]. This is because of poor adhesion between the untreated fiber and the rubber. The fracture surfaces in the cases of rubber composites containing 1, 3, 5, and 7% NaOH-treated fibers show better adhesion between the fibers and rubber matrix [Figs. 10(b)–10(e)], as indicated by the presence of rubber phase adhering to the fibers. Comparing the results obtained for the different concentrations of NaOH solution, it was found that the 5% NaOH solution produced the best mechanical properties.

*Benzoylation.* The dependence of BPO concentration on tensile properties of benzoylated fiber composites is presented in Table VII and Figure 11. The composites reinforced with BPO-treated fibers (1, 3, and 5 wt



**Figure 12** SEM photomicrographs of fracture surfaces of PALF-natural rubber composites containing (a) untreated, (b) 1%, (c) 3%, and (d) 5% (by weight of fiber) BPO-treated pineapple fibers.

**TABLE VIII**  
**Tensile Strength and Percentage Retention in Tensile Strength of NR Vulcanizate and Composites Containing Untreated, 5% NaOH, and 1% BPO-Treated PALF before and after Thermal Aging at 100°C for 24 h**

Sample	Tensile strength (MPa)		Percentage retention in tensile strength
	Before	After	
Vulcanizate	22.71 ± 1.76	15.72 ± 1.81	69
Untreated fiber	7.20 ± 0.40	5.83 ± 0.46	81
5% (w/v) NaOH-treated fiber	10.02 ± 0.75	9.13 ± 0.72	91
1% (wt of fiber) BPO-treated fiber	11.32 ± 0.66	10.47 ± 0.59	92

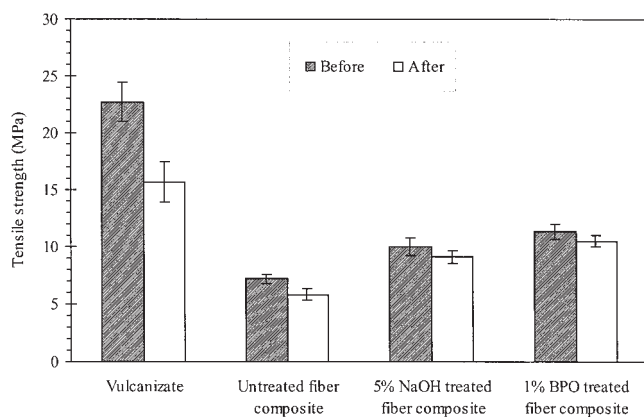
% of fiber) show increase in both tensile and elongation at break relative to untreated composites. This may be attributed to the increase in hydrophobic character on these fiber surfaces, therefore making the surfaces more compatible with natural rubber. From Figure 11, it is seen that the tensile strength and elongation at break of composites rapidly increase when using 1% BPO in the graft reaction. However, as the amount of BPO is further increased, the tensile strength started to fall off and became constant within experimental error. The 1% BPO-treated fiber composite improved in tensile strength and elongation at break by 57 and 197%, respectively, when compared with those of untreated fiber composites. The reason for the small reduction in tensile properties at concentrations of BPO greater than 1% warrants further study. For instance, the tensile properties of untreated and treated fibers should be measured to explain the mechanical behavior of BPO-treated fiber composites. But, it is clearly established that both tensile strength and elongation at break are increased by reinforcing natural rubber with BPO-treated PALF. The SEM micrographs illustrating the interface of the treated fiber composites are given in Figure 12. For all treated samples, the rubber matrices are more bonded with the fibers when compared with untreated fiber, suggesting

an enhanced adhesion over that of untreated fiber composites.

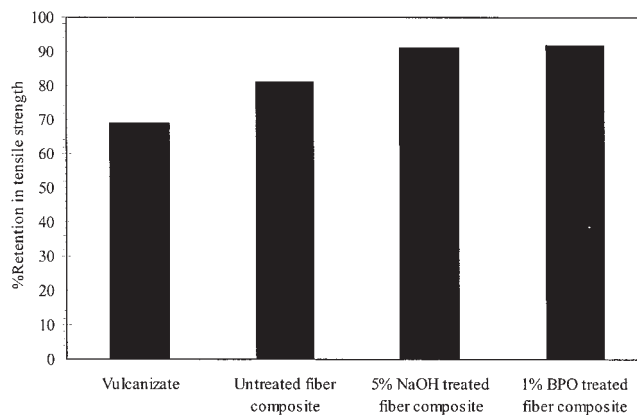
From these experimental results, the optimal concentrations for surface treatments of fibers by using alkali solution and BPO are 5% (w/v) and 1% BPO (by weight of fiber), respectively.

#### Thermal aging

The data obtained from tensile testing of the vulcanizates and composites reinforced with untreated, 5% (w/v) NaOH, and 1% (weight of fiber) BPO after thermal aging at 100°C for 24 h are shown in Table VIII and Figure 13. After thermal aging, tensile strength reduced in all cases. However, the incorporation of pineapple fibers in natural rubber resulted in an increased level of retention of tensile strength and is clearly seen in Figure 14. These results indicated that the rubber degradation was restricted to some extent by incorporated fibers. Furthermore, the increase in retention was greater in composites containing both 5% NaOH and 1% BPO-treated pineapple fibers. It has been stated that pineapple fibers might suffer because of decomposition of their volatile extratables present



**Figure 13** Comparison of tensile strength of natural rubber vulcanizate and PALF-natural rubber composites containing untreated, 5% NaOH-, and 1% BPO-treated pineapple fibers before and after thermal aging at 100°C for 24 h.



**Figure 14** Comparison of percentage of retention in tensile strength of natural rubber vulcanizate and PALF-natural rubber composites containing untreated, 5% NaOH-, and 1% BPO-treated pineapple fibers before and after thermal aging at 100°C for 24 h.

on the fiber surfaces upon heating at 100°C during aging, leading to formation of voids at fiber–matrix interface, and this would weaken fiber–matrix bond strength and therefore composite performance.<sup>25</sup> Thus, in the case of NaOH and BPO-treated fiber composites, the existence of good interfacial adhesion will provide the protection against void formation during aging, and an improvement of retention of tensile strength.

### CONCLUSIONS

The processing parameters of the short PALF-filled natural rubber compounds, such as scorch times, cure times, and minimum torques, are independent of fiber loading, but the maximum torques increase with increasing concentration of short pineapple fibers. The composite stiffness significantly increases while the tensile strength and elongation at break decrease with fiber content. In the case of tensile strength, there was an increase above 30 phr. The extent of fiber orientation measured by using anisotropic swelling test is highest at 20 phr of fibers, but this ratio does not provide the best mechanical properties. The alkali and BPO treatments were used to modify PALF, which generally exhibit poor adhesion with natural rubber. The FTIR and SEM results show increased surface area and roughness upon alkali treatment, leading to an enhanced fiber–natural rubber bonding through the mechanical interlocking mechanism. In the case of BPO treatment, the hydrophobic aspect of the fiber surface is increased, thus the fiber–matrix interaction and composite mechanical properties are improved. The 5% (w/v) NaOH solution and 1% BPO (weight of fiber) produce the greatest improvement in composite strength. The thermal aging properties of natural rubber were greatly improved by the presence of untreated fibers and can be further improved with treated fibers. The PALF-reinforced natural rubber offers several advantages such as improved tensile modulus, resistance to solvent swelling, and positive thermal aging properties. Thus, it could be a useful material for applications where such properties are required. However, novel surface treatment is worthwhile to explore for further improvement.

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