

A Study on the Curing Characteristics, Tensile, Fatigue, and Morphological Properties of Alkali-Treated Palm Kernel Shell-Filled Natural Rubber Composites

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Effects of alkali treatment of palm kernel shells (PKS) were investigated relative to curing characteristics, tensile properties, and fatigue of PKS-filled natural rubber (NR) composites. The PKS powder was subjected to alkali treatment using 5% sodium hydroxide. The treated PKS was incorporated into the NR composites during compounding, with the concentrations of the composites ranging from 5 to 20 phr. The properties of treated PKS-filled NR composites were compared with those of untreated PKS-filled NR composites. The cure times, scorch times, and maximum torque values were all lower for alkali-treated PKS/NR composites compared with those of untreated PKS/NR composites. Tensile strength and elongation at break were higher for treated PKS composites, while the moduli (M100 and M300) were lower than those of untreated PKS/NR composites. The fatigue tests for treated PKS/NR composites also showed higher fatigue values than the untreated PKS/NR composites. Scanning electron microscopy revealed that the higher tensile strength, elongation at break, and fatigue values of treated PKS/NR composites were due to the removal of hemicellulose and lignin in PKS fillers. This removal increased in the surface roughness of the filler and led to improved rubber-filler adhesion.

Keywords: Palm kernel shell; Alkali treatment; Tensile strength; Cure time; Fatigue; FTIR

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INTRODUCTION

The demand for bio-based products is growing as people seek environmentally safe alternatives to traditional approaches that use carcinogenic chemicals and non-biodegradable polymers. Ecological concerns have resulted in various studies seeking the best substitutes for hazardous commercial chemicals and non-degradable polymers. For example, there has been much research on lignocellulosic fillers from agricultural waste, such as wheat straw fiber (Le Digabel *et al.* 2004), rice husk ash (Sae-Oui *et al.* 2002), oil palm ash (Ismail *et al.* 2015), palm kernel husk (Egwaikhide *et al.* 2007), sugarcane bagasse (Bras *et al.* 2010), cocoa pod powder (Imanah and Okieimen 2003), and coconut shell (Onukak *et al.* 2013).

The use of natural renewable resources is the best solution to curb this environmental problem. One method uses lignocellulosic fibers as fillers in polymer composites. They have distinct physical and mechanical properties, including, problematically, that they are highly hydrophilic in nature. This feature is the disadvantage of using lignocellulosic fillers, as they are incompatible with hydrophobic matrices. The difference in the polarities between the filler and the matrix leads to reduced mechanical and dynamic properties in the composites. There are many methods of natural fiber/filler

surface treatment, such as alkali and silane treatment, acetylation, grafting methods, and chemical agents (Yusriah *et al.* 2014). These treatments partially remove impurities and extracellular materials to improve the interfacial adhesion to, and the compatibility with, polymer matrices by reducing the hydrophilicity of the fiber/filler (De Rosa *et al.* 2011). Alkali treatment, the most commonly used fiber surface treatment method, is also the most economical treatment.

Mercerization is an efficient chemical modification method whereby lignin and hemicellulose are removed, reducing particle agglomeration to produce a rough surface strongly anchored to the matrix. This process results in strong interfacial adhesion between the filler and the matrix. Natural fibers experience weight loss and an increase in the cellulose content following mercerization. Natural fibers have been successfully used as fillers in automotive parts, packaging, domestic applications, *etc.*

Cellulose consists of glucose monomers having three hydroxyl groups linked by β -1,4 glycosidic bonds, which contribute to the load-carrying mechanism in the tensile tests of natural fiber-filled polymer composites. The tensile strength is proportional to the cellulose content incorporated into the composites. Cellulose is not greatly affected by alkalization and oxidizing agents (Bismarck *et al.* 2005). Rather, the amorphous regions and the crystallinity regions greatly determine the properties of the filler. Increasing the crystalline content of the filler results in higher strength, whereas a larger amorphous region results in greater elongation and more sites available for chemical reaction (Sain and Panthapulakkal 2004). Accordingly, cellulose is highly hydrophilic in nature.

Hemicellulose consists of a highly branched polysaccharide connected to a cellulose molecule. The highly branched structure of hemicellulose makes it amorphous with a low degree of polymerization. Unlike cellulose, hemicellulose is soluble in alkali. In this research, palm kernel shell (PKS) was used as filler in NR composites. Palm kernel shell (PKS) is predominantly amorphous, due to a high lignin content, and its crystalline content is only 15% (Okoroigwe *et al.* 2014). Lignin is a complex aromatic biopolymer that functions as coupling agent binding woody plant cells together and providing support to the entire plant structure. Lignin, together with hemicellulose, gives toughness and stiffness to the fiber. Lignin has an amorphous structure and is highly hydrophobic. It is also soluble in alkali solutions and is affected by alkali treatment. The presence of a high lignin content can lower the composite elongation at break and speed up degradation upon exposure to thermal energy and sunlight (Reddy *et al.* 2007). The reaction of NaOH with PKS is described in Eq. 1.



Alkali surface treatment of PKS, as shown in Eq. 1, is an exothermic process by which a hydroxyl ion (OH^-) produced by a perhydroxyl ion (HO_2^-) undergoes hydrolysis to release more perhydroxyl ions (Modibbo *et al.* 2009). The PKS surface becomes rough because of the modification of the lignocellulosic filler, by reducing the amount of lignin and hemicellulose in the PKS filler under alkali conditions. This change results in an increased proportion of cellulose in the PKS filler, which increases the number of active reaction sites (Jayabal *et al.* 2012). The increase in the number of active sites can promote better interfacial adhesion between the PKS filler and the matrix.

EXPERIMENTAL

Formulations for PKS-Filled NR Composites

The formulations used in this research are shown in Table 1. Natural rubber (SMR L) was obtained from the Rubber Research Institute of Malaysia (RRIM) (Sungai Buloh, Malaysia), and the PKS was obtained from the United Oil Palm Industries Ltd. (Nibong Tebal, Penang, Malaysia). Other chemicals used, such as sulphur, zinc oxide, stearic acid, n-cyclohexylbenthiazolyl sulphonamide (CBS), tetra-methyl thiuram disulphide (TMTD), and 2,2 methylene-bis-(4-methyl-6-tert-butylphenol) (BKF) were all purchased from Bayer (M) Ltd. (Kelana Jaya, Malaysia). Sodium hydroxide (NaOH) for the pre-treatment of the PKS was obtained from Sigma-Aldrich (Kuala Lumpur, Malaysia). The PKS were collected, ground, and sieved until they reached the average size of 90 μm . The chemical composition of the PKS harvested from *Elaeis guineensis* oil palm trees is shown in Table 2 (Edmund *et al.* 2014).

Table 1. Formulations

Compound	Composition (phr)*								
	1	2	3	4	5	6	7	8	9
SMR L	100	100	100	100	100	100	100	100	100
Zinc Oxide	5	5	5	5	5	5	5	5	5
Stearic Acid	3	3	3	3	3	3	3	3	3
CBS	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
TMTD	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
BKF	1	1	1	1	1	1	1	1	1
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Untreated PKS	0	5	10	15	20	-	-	-	-
Treated PKS	-	-	-	-	-	5	10	15	20

phr: part per hundred rubber

Table 2. Composition of Palm Kernel Shell

	Component	Approximate Value (%)
carbohydrate polymers	Hemicellulose	26.16
	Cellulose	6.92
aromatic polymer	Lignin	53.85

The Treatment of PKS

Treated PKS was prepared from raw palm kernel shell powder by soaking it in 10% aqueous alkali (NaOH) for 72 h. The PKS filler was then heated in aqueous alkali media to 100 °C and continuously stirred for 1 h. The purpose of heating the PKS was to break down its lignocellulosic complex structure and reduce its lignin content in order to improve the adhesion between the filler and the matrix. After 1 h, the PKS was rinsed with distilled water several times, oven-dried for 24 h, and sieved.

Sample Preparation

Mixing was carried out in a laboratory, using a two roll mill (model XK-160, Shandong, China), in accordance with ASTM D3184 (1989). A silane coupling agent was incorporated into the second series, but not into the first. The cure characteristics of rubber compounds were studied using a Monsanto rheometer (model MDR 2000, Alpha

Technologies, Akron, OH, USA) at 150 °C. Cure times (t_{90}), scorch times (t_{s2}), and maximum torque values (M_H) were obtained from the rheographs. The rubber compounds were moulded into sheets at 1500 °C using a hot press machine (Kao Tieh Go Tech Compression Machine, Shandong City, Taiwan). The process continued for the duration of their respective cure times.

Measurement of Tensile Properties

Dumbbell-shaped test pieces were cut for the tensile properties test, in accordance with ASTM D412-2006a (2013), using an Instron Universal testing machine (model 3366, Canton, MA, USA) at the test temperature of 23 °C and the crosshead rate of 500 mm/min. Five samples were tested, and their tensile properties including tensile strength, tensile modulus, and elongation at break were measured.

Scanning Electron Microscopy (SEM)

The examination of the tensile fracture surface was carried out using a Zeiss Supra scanning electron microscope (model 35vp, Oberkochen, Germany). The fracture parts of tensile specimens were used. The fracture surfaces were sputter coated (Bio-Rad SEM Coating System, Hercules, CA, USA) with gold to avoid electrostatic charging and poor image resolution. The images of rubber and filler dispersion were evaluated from the micrograph.

Fourier Transform Infrared (FTIR) Spectroscopy

The spectrum was obtained using Perkin-Elmer Spectrum One Series equipment (Selangor, Malaysia), and the attenuated total reflection (ATR) technique was adopted. The selected spectrum resolution and the scanning range were 4 cm⁻¹ and 550 to 4000 cm⁻¹, respectively.

RESULTS AND DISCUSSION

Curing Characteristics

The Δ torque values, $M_H - M_L$, of treated PKS-filled NR composites decreased with increasing PKS loading (Fig. 1) compared to untreated PKS-filled NR composites. Torque differences determine the shearing modulus of the composites (Ismail and Poh 2000). As for untreated PKS-filled NR composites, the increased in torque indicated that the composites became hardened with the addition of PKS filler. Unlike untreated PKS-filled NR composites, the torque of treated PKS-filled NR composites decreased with increasing PKS loading.

Alkalization resulted in weight loss in lignin and hemicellulose, which both acted as cementing materials in palm kernel shells. The presence of treated PKS reduced the viscosity that was responsible for the stiffness of the composites. Increasing the loading of treated PKS did not restrict the mobility of macromolecular rubber chains, and thus promoted higher flexibility in the composites. The lower Δ torque of treated PKS-filled NR composites as increased in filler loading indicated the lower extent of crosslink density and modulus of the composites.

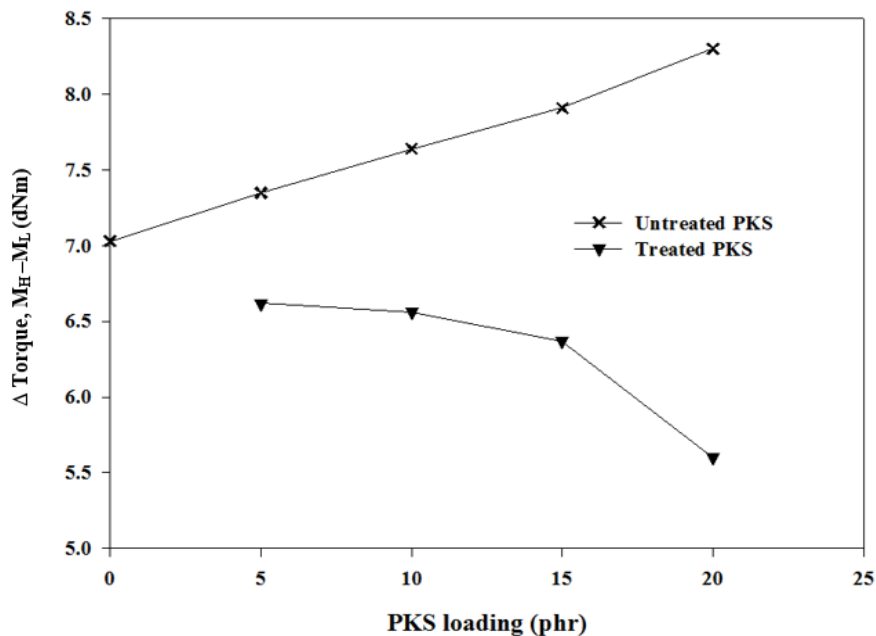


Fig. 1. The differences in torque (Δ Torque) of untreated and treated PKS-filled NR composites

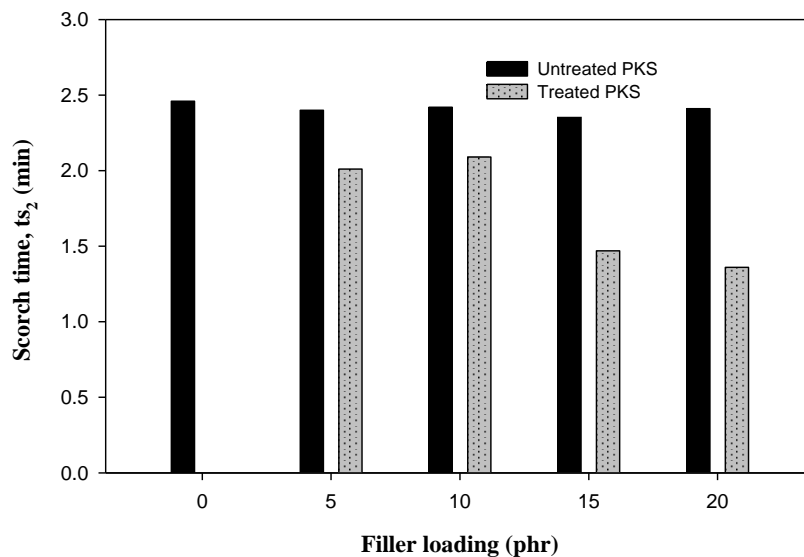


Fig. 2. The scorch time (t_{s2}) of the untreated and treated PKS-filled NR composites

The scorch time indicated the initial time for the composites to form cross links, and the cure time indicated the time required to fully vulcanize the composites. The scorch times (t_{s2}) and cure times (t_{90}) of treated and untreated PKS-filled NR composites are plotted in Figs. 2 and 3, respectively. Both untreated and treated PKS-filled composites showed a decreasing trend with increases in PKS loading. As more PKS was added to the rubber compounds, the rubber portion became less and the time to form crosslinks also decreased. The scorch enhancement of the composites also was related to the larger particle size of the filler and lower surface area that hinder the formation of more sulphur crosslinks during vulcanization. A similar result has been found using rattan powder into rubber matrix (Ismail *et al* 2012). As PKS loading was increased, the time for compounding on

two rolls mill also was longer. As a result, there was a reduction in scorch time (t_{s2}) and cure time (t_{90}) due to premature crosslinking. The t_{s2} and the t_{90} of the treated PKS-filled NR composites were shorter than those of the untreated PKS-filled NR composites. The shorter scorch times for the treated PKS-filled NR composites, compared with the untreated PKS-filled NR composites, could have resulted because of the absence of mostly stiff and hard components of the PKS (lignin and cellulose) eased compounding and larger surface area of the treated PKS increased chances for sulphur to form crosslinks during vulcanization. The cure times (t_{90}) of the treated PKS-filled NR composites were also lower than those of the untreated PKS-filled NR composites. The modified PKS had increased alkalinity, which encourages vulcanization and accelerates the curing of composites.

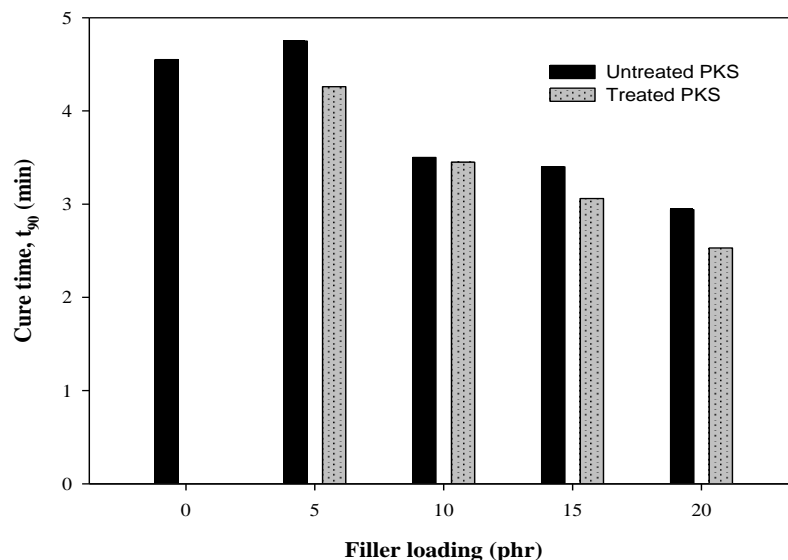


Fig. 3. The cure time (t_{90}) of the untreated and treated PKS-filled NR composites

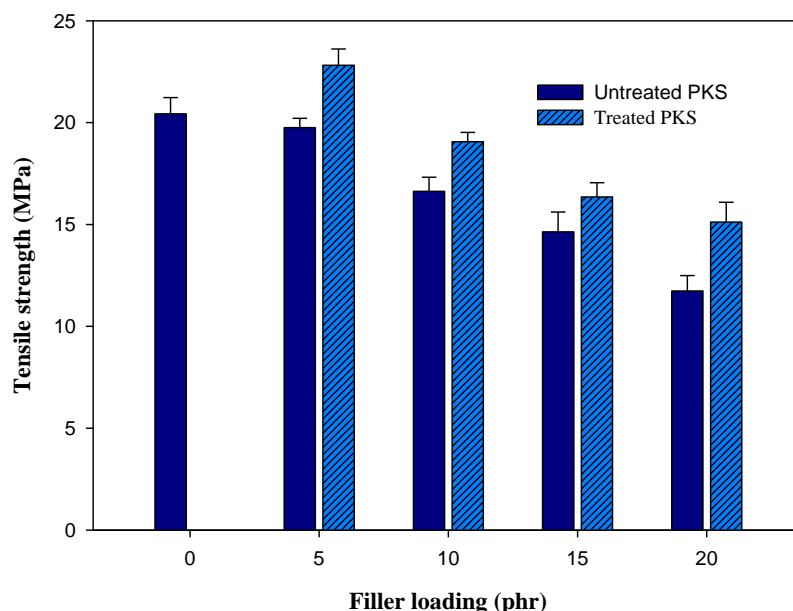


Fig. 4. The tensile strength of untreated and treated PKS-filled NR composites

Tensile Properties

As Fig. 4 demonstrates, the tensile strength of the NR composites with the NaOH-treated PKS were higher than those of the untreated PKS-filled NR composites. The higher tensile strengths for the NaOH-treated PKS-filled NR composites resulted from the removal of impurities, wax, adhesive pectin, and lignin from the filler. The removal of these constituents in the natural filler changed the physicochemical properties of cellulose (Mwaikambo and Ansell 2001). Palm kernel shell underwent alkaline treatment, and the lignin, waxes, and fats were dissolved, increasing the surface area contact. The increased surface area improved the chances of interlocking between the filler and the matrix by increasing surface roughness. The surface roughness, in turn, improved the rubber-filler adhesion, resulting in higher tensile strengths of the composites compared with those of the untreated PKS-filled NR composites. The most important alkali treatment modification to the PKS was the removal of hydrogen bonds in the PKS lignin structure. As the PKS filler loading increased, the probability of PKS agglomeration also increased, resulting in points of stress concentration that lowered the resistance to deformation during the tensile test. Both the untreated and the treated PKS-filled NR composites showed decreasing trends with increased PKS loading.

The elongation at break (EB) of both the untreated and the treated PKS-filled NR composites are shown in Fig. 5. The EB of the treated PKS-filled NR composites were higher than those of the untreated PKS-filled NR composites because of changes in the cellulose structure, as it was converted from cellulose I into cellulose II. This change was particularly evident at 15 and 20 phr as the result of the alkali treatment responsible for the low stiffness value of cellulose II, which enabled it to easily detach upon stretching (Gassan *et al.* 2000). Alkali treatment increased the moduli, as well as the tensile strengths, of the composites. The hydroxyl group present in the filler reacted with the sodium hydroxide during alkali treatment. The partial removal of lignin and hemi-cellulose of the natural filler embedded in the rubber matrix resulted in the low resistance to stretching during tensile deformation, improving the elongation at break of the composites (Dhanalakshmi *et al.* 2015).

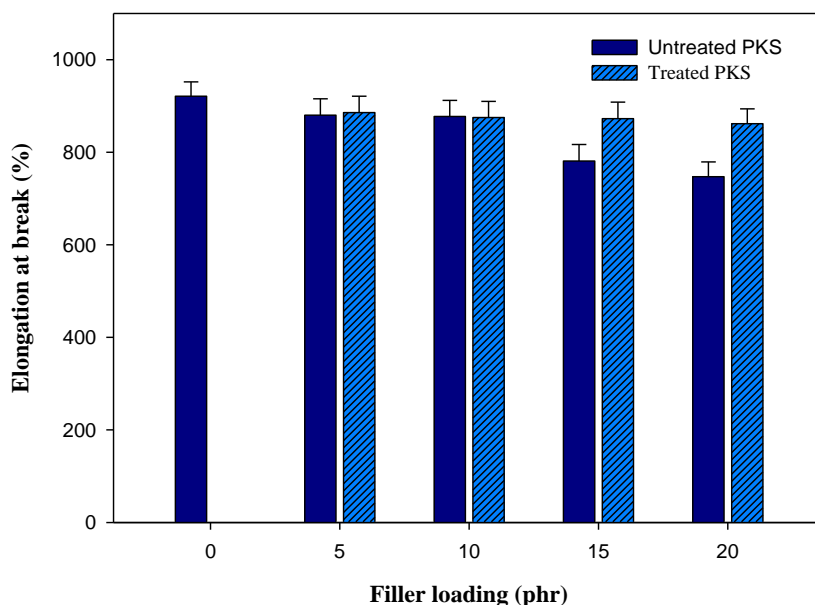


Fig. 5. The elongation at break of untreated and treated PKS-filled NR composites

Figures 6 and 7 show that moduli at 100% elongation (M100) and 300% elongation (M300) were lower for the NR composites with treated PKS than those of the untreated PKS/NR composites.

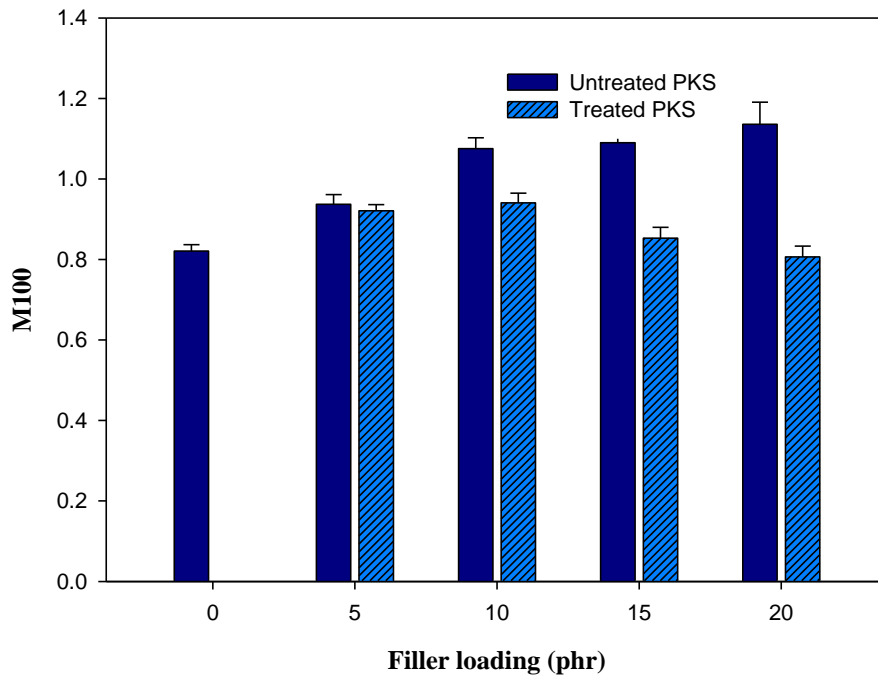


Fig. 6. The modulus at 100% elongation (M100) of untreated and treated PKS-filled NR composites

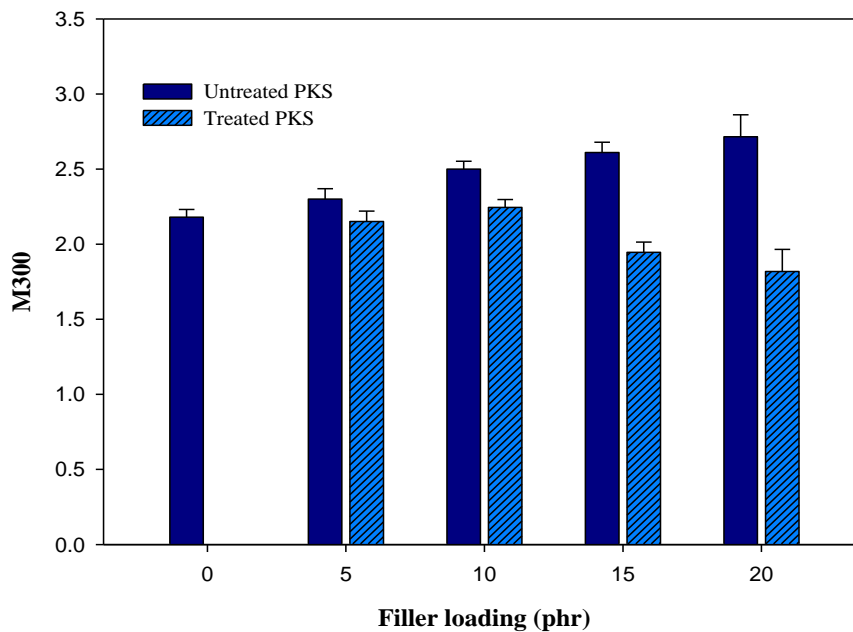


Fig. 7. The modulus at 300% elongation (M300) of untreated and treated PKS-filled NR composites

A previous study by Yusriah *et al.* (2014) that used alkali-treated betel nut waste showed that the tensile strength and moduli of the treated composites decreased as the betel

nut filler loading increased. Thus, the lower stiffness values of treated PKS-filled NR composites indicated a reduction in the stiffness of the composites because of the removal of lignin and hemi-cellulose from the filler. Lignin acted as a cementing medium that provided toughness to the natural filler. Thus, an increase in the delignification of filler NR composites overall reduced the moduli (M100 and M300) of the composites.

Fatigue

As shown in Fig. 8, the fatigue life values for the treated PKS-filled NR composites decreased with increased PKS filler loading. According to prior research, the composite with the highest filler loading has the lowest fatigue life, as the PKS filler does not deform during the straining of the composites. Therefore, the resulting strain of the rubber matrix is higher than the total strain in the composites (Payne *et al.* 1972). However, the fatigue life of the treated PKS-filled NR composites was slightly higher than in the untreated PKS-filled NR composites. Alkali treatment removed the unwanted waxy layer and the lignin. Thus, the treatment improved rubber-filler adhesion resulted because of the increase in surface roughness, which strengthened the adhesion between the filler and the rubber matrix after the alkali treatment. This observation agreed with the previous tensile strength results for untreated and treated PKS-filled NR composites in Fig. 4.

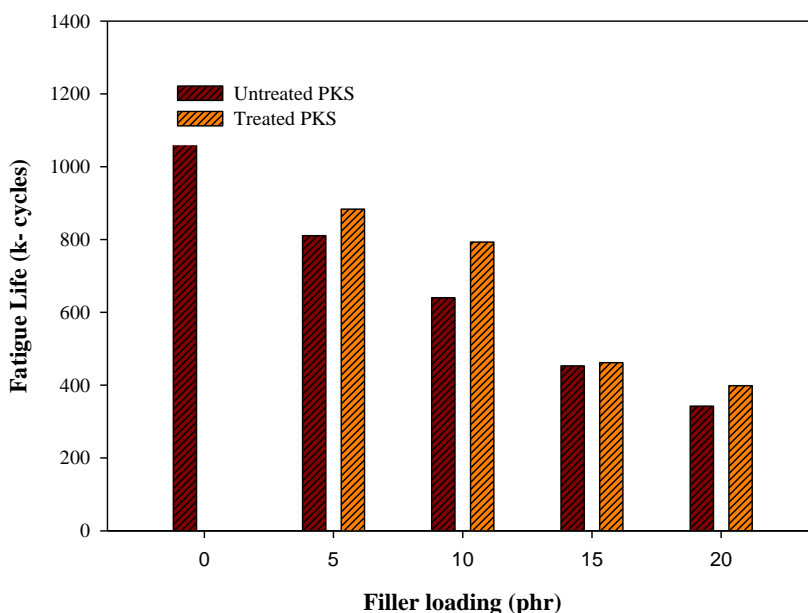


Fig. 8. Fatigue life of untreated and treated PKS-filled NR composites

FTIR Spectroscopy

Functional groups present in the untreated and the NaOH-treated PKS were confirmed using FTIR spectroscopy, with the scan range from 550 to 4000 cm^{-1} . The FTIR spectra of the PKS powders are displayed in Fig. 9. The treated PKS sample experienced a decrease in intensity at 3300 cm^{-1} , 2900 to 2800 cm^{-1} , 1700-1500 cm^{-1} , and 1034 cm^{-1} . The adsorption peaks present in both the untreated and the treated PKS were 3340 cm^{-1} , 1600 cm^{-1} , and 1035 cm^{-1} . The adsorption peak within the 3500 to 3200 cm^{-1} region was attributed to the -OH stretching of the alcohol or the phenol from the cellulose and the hemi-cellulose of the PKS (Dai and Fan 2011; Ismail *et al.* 2012). Moreover, the presence

of the alkyl group in the cellulose, hemicellulose, and lignin were detected within the range of 2922 to 2854 cm^{-1} . Figure 9 also shows that pectin and waxes in the PKS hemicellulose were no longer present. The adsorption peaks that disappeared after the treatment of the PKS occurred at 2854.06 cm^{-1} , 1725.64 cm^{-1} , 1242.46 cm^{-1} , and 770.98 cm^{-1} . Alkali treatment of PKS resulted in the partial removal of hemicellulose and lignin. Cellulose consists of glycosidic linkages, a hydroxyl group, and a carboxyl group (Bismarck *et al.* 2005). The cellulose was hardly affected by the alkali treatment, as indicated by the presence of corresponding lignin peaks in both untreated and treated PKS at 1160 cm^{-1} . Lignin is mainly comprised of ether bonds, while hemicellulose is distinguished by the presence of carboxyl groups (Taherzadeh and Karimi 2008). The disappearance of hemicellulose after the alkali treatment was seen in the 1730 cm^{-1} region, while the absence of the C–O stretching in lignin was seen at approximately 1263 cm^{-1} after the alkali treatment of PKS (Suryanto *et al.* 2014). The intensity of the ether (C–O–C) functional groups comprising the hemicellulose and the lignin complex at 1036 cm^{-1} also were diminished following the alkali treatment, demonstrating that delignification occurred after the silane treatment of PKS.

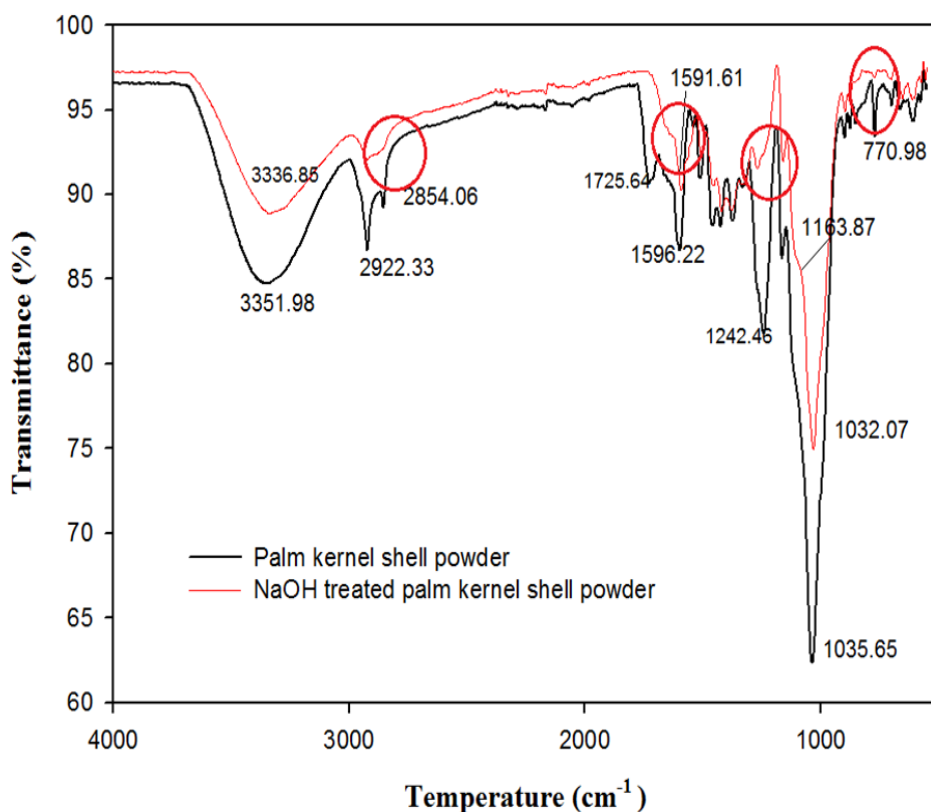


Fig. 9. FTIR spectra of untreated and treated palm kernel shell (PKS) powder

Morphological Properties

Figures 10a and 10b show SEM micrographs of the untreated and the treated PKS fillers, and Figs. 11a and 11b present the SEM micrographs of surface fractures of the untreated and the treated PKS-filled NR composites, respectively, at the loading of 5 phr. Figure 10a shows that the raw PKS particles had various smooth shapes, and dirt and impurities were present. The rough surfaces of the treated PKS particles (Fig. 10b) are apparent, with evidence of cementing material being removed after the alkali treatment

(Ray and Sarkar 2001). Pores can also be seen on the surfaces of the PKS particles, indicating exposed lumens as the result of the alkali treatment; lignin and hemicellulose, which provide a non-crystalline structure for the plant fiber, were removed. The fracture surfaces of the PKS-filled NR composites show that the PKS fillers that had not undergone alkali treatment showed extensive filler detachment and voids associated with poor rubber-filler adhesion. The micrographs also show poor interfacial adhesion in the composites, as the presence of crevices at the interface between the PKS filler and the matrix indicated. As for the treated PKS, the filler particles appear to be distributed evenly and cannot be seen clearly, as they are embedded in the rubber matrix as the result of better rubber-filler interaction. Less detachment and deeper fracture zones are seen, indicating high load-sharing upon rupture at the interface.

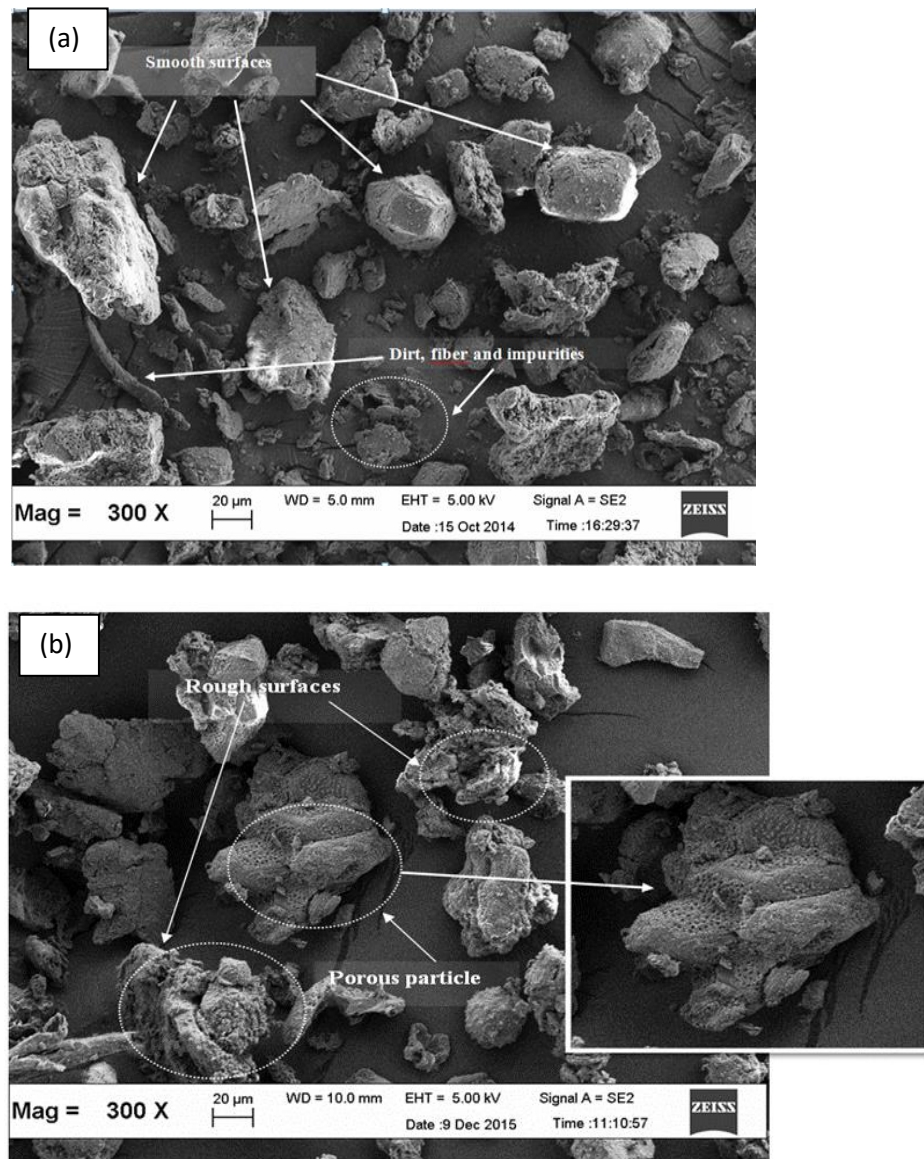


Fig. 10. SEM micrographs of (a) untreated and (b) alkali-treated PKS powder

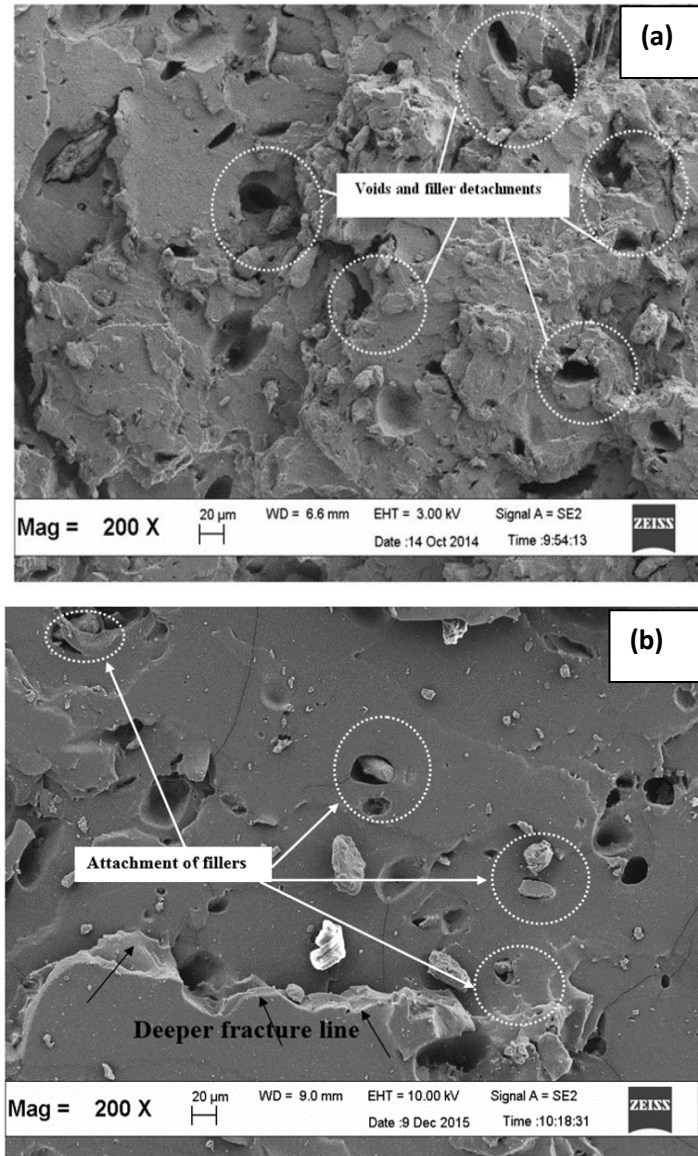


Fig. 11. SEM micrographs of (a) untreated and (b) treated PKS-filled NR composites at 5 phr filler loading

CONCLUSIONS

1. Enhanced tensile strength in treated palm kernel shell (PKS) – natural rubber (NR) composites was due to good interfacial adhesion between the rubber and the PKS filler. The alkalization of the PKS filler increased surface roughness, which facilitated attachment to the rubber matrix. The absence of hard and rigid components in the PKS also contributed to the increased flexibility of the composites upon straining; hence, the composites exhibited improved E_b . The moduli (M_{100} and M_{300}) of the alkali-treated PKS-filled NR composites were lower than those of untreated PKS-filled NR composites because lignin and hemicellulose, the dominant constituents of the PKS, were removed during alkali surface treatment. The presence of treated PKS in the NR composites did not provide stiffness to the composites.

2. The fatigue life of the treated PKS-filled NR composites was slightly higher than those of the untreated PKS-filled NR composites. The alkali treatment removed the unwanted waxy layer and the lignin. Thus, enhanced rubber-filler adhesion resulted.
3. The SEM results of treated PKS showed that the surface roughness increased, which increased the chances of adhesion between the filler and the rubber matrix after the alkali treatment.

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