Effects of Palm Ash Loading and Maleated Natural Rubber as a Coupling Agent on the Properties of Palm–Ash–Filled Natural Rubber Composites

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ABSTRACT: Natural rubber composites were prepared by the incorporation of palm ash at different loadings into a natural rubber matrix with a laboratory-size two-roll mill (160×320 mm^2) maintained at 70 ± 5°C in accordance with the method described by ASTM D 3184–89. A coupling agent, maleated natural rubber (MANR), was used to improve the mechanical properties of the natural rubber composites. The results indicated that the scorch time and cure time decreased with increasing filler loading, whereas the maximum torque exhibited an increasing trend. Increasing the palm ash loading increased the tensile modulus, but the tensile strength, fatigue life, and elongation at break decreased. The rubber–filler interactions of the composites decreased with increasing filler loading. Scanning electron microscopy of the tensile fracture surfaces of the composites and rubber–filler interaction studies showed that the presence of MANR enhanced the interfacial interaction of the palm ash filler and natural rubber matrix. The presence of MANR also enhanced the tensile properties and fatigue life of palm-ash-filled natural rubber composites. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 2867–2876, 2008

Key words: composites; mechanical properties; rubber

INTRODUCTION

The addition of filler materials to improve various properties of polymers while reducing their cost has become a popular field of research.[1] The reinforcement of rubber by a filler is associated with chemical and physical interactions between the rubber and filler.[2]

The most generally used fillers in rubber industries are carbon black, silica, calcium carbonate, zinc oxide, magnesium oxide, talc, and mica.[3–8]

Malaysia is one of the largest palm oil exporters in the world, and solid waste from the palm oil industry is very abundant. This solid waste poses a menace and hence needs to be used to solve the environmental problem. This waste is usually used as a fuel in palm oil factories. Then, after the combustion of oil-palm fibers and shells, which are normally used as boiler fuel for the generation of steam in palm oil mills, ash is produced. Every year, Malaysia generates huge loads of ash. Therefore, the objective of this work was to study the potential of palm ash as a new filler in natural rubber composites.

The main problem in the preparation of polymer composites is the compatibility of a hydrophilic filler and a hydrophobic polymer matrix, which yield composites of poor properties.[9] One method that can be generally used to improve compatibility between a filler and a polymer matrix is the use of coupling agents such as organofunctional silane and organotitanates.[10]

In this study, maleated natural rubber (MANR) was selected as a coupling agent for palm-ash-filled natural rubber composites, and its effects on the cure characteristics, tensile properties, fatigue life, morphology, and rubber–filler interaction of palm-ash-filled natural rubber composites were investigated.

EXPERIMENTAL

Materials, formulation, and mixing procedure

Standard Malaysian Rubber Grade L natural rubber was purchased from the Rubber Research Institute of Malaysia. Palm ash was obtained from the United Oil Palm Mill (Penang, Malaysia). Palm ash was dried in a vacuum oven at 80°C for 24 h to expel moisture and then ground with a ball mill to a powder form. An Endicott sieve was used to obtain an average filler size of 75 μm. Other compounding ingredients such as zinc oxide, stearic acid, sulfur, *N*-cyclohexyl-2-benzothiazole sulfonamide (CBS), and *N*′-phenyl-*p*-phenylene diamine (IPPD) were all purchased from Bayer (M), Ltd. Maleic anhydride was supplied by Fluka Chemica (Switzerland).

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TABLE I
Formulation of Natural Rubber Composites with Different Palm Ash Loadings

Material	Compound (phr)
SMR L	100
Sulfur	1.6
Zinc oxide	1.5
Stearic acid	1.5
CBS	1,9
IPPD	2.0
Palm ash	0, 10, 20, 30, 40

MANR was prepared before compounding through the grafting of maleic anhydride onto natural rubber chains with a Haake Rheomix Polydrive R600/610 at 135°C and 60 rpm according to a procedure reported by Nakason et al.[11] To prepare the graft copolymer in this work, 6 phr maleic anhydride was used. The formulations used in this study are shown in Tables I and II, respectively. Table III shows the results of a semiquantitative analysis of the palm ash in this study. Compounding was carried out on a laboratory-sized (160 × 320 mm) two-roll mill (model XK-160). The compounds were compression-molded at 150°C with a force of 10 MPa and a cure time determined with a Monsanto MDR 2000 moving die rheometer.

Measurements of the curing characteristics and dynamic properties

The cure characteristics of the rubber compounds were studied with an MDR 2000 according to ISO 3417 at 150°C. Vulcanizates were conditioned for 24 h in a closed container before testing. In addition to curing characteristics, the MDR 2000 provided digital output of dynamic properties such as the elastic torque, viscous torque, and tan delta.

Measurement of the tensile properties

Dumbbell-shaped samples were cut from the molded sheets, and tensile tests were performed at a crosshead speed at 500 mm/min with a Monsanto M500 tensometer according to ISO 37.

TABLE II
Formulation of Natural Rubber Composites with Different MANR Loadings

Material	Compound (phr)
SMR L/MANR	100/0 (control), 95/5, 90/10, 85/15, 80/20
Sulfur	1.6
Zinc oxide	1.5
Stearic acid	1.5
CBS	1.9
IPPD	2.0
Palm ash	30

TABLE III
Semiquantitative Analysis of Palm Ash with a Rigaku RIX 3000 X-Ray Fluorescence Spectrometer

Component	Weight (%)
Na_2O	0.13
MgO	3.0
Al_2O_3	0.84
SiO_2	10.0
P_2O_5	2.4
SO_3	1.8
Cl	4.1
K_2O	27.0
CaO	3.4
TiO_2	0.032
MnO	0.046
Fe_2O_3	0.29
CuO	0.012
ZnO	0.025
Br	0.011
Rb_2O	0.076
SrO	0.012
ZrO_2	Trace
C	46.0

Determination of the fatigue life

The vulcanized rubbers were cut into individual dumbbell-shaped samples with a BS type E dumbbell cutter. Fatigue tests of the vulcanizates were then carried out on a Monsanto fatigue-to-failure tester. Six specimens were used for each test. The samples were subjected to repeated cyclic strain at 100 rpm, and the extension ratio was 1.6. The number of cycles was recorded automatically. The fatigue life was calculated on the basis of the Japanese Industrial Standard (JIS) average, which was determined from the four highest values as follows:

$$\text{JIS average} = 0.5A + 0.3B + 0.1(C + D) \quad (1)$$

where A is the highest value followed by B, C, and D.

Scanning electron microscopy (SEM) micrographs of the tensile fracture surfaces

The fracture surfaces of the palm-ash-filled natural rubber compounds were investigated with a Leica Cambridge S-360 scanning electron microscope. The fracture ends of specimens were mounted on aluminum stubs and sputter-coated with a thin layer of gold to avoid electrostatic charging during examination.

Measurement of the rubber–filler interaction

Cured samples (30 mm × 5 mm × 2 mm) were swollen in toluene in a dark environment until equilibrium was achieved; this normally took 48 h at 25°C. The samples were dried in an oven at 60°C until a constant weight was obtained. The Lorenz

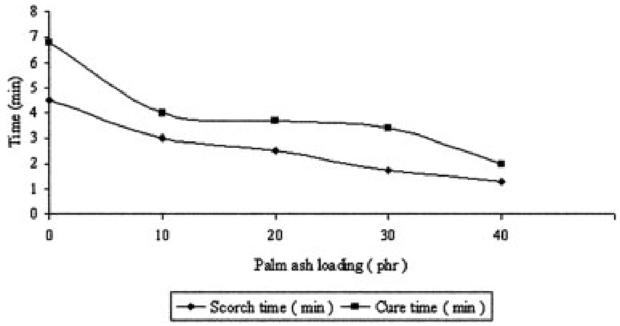

Figure 1 Effect of the filler loading on the scorch time and cure time of palm-ash-filled natural rubber composites.

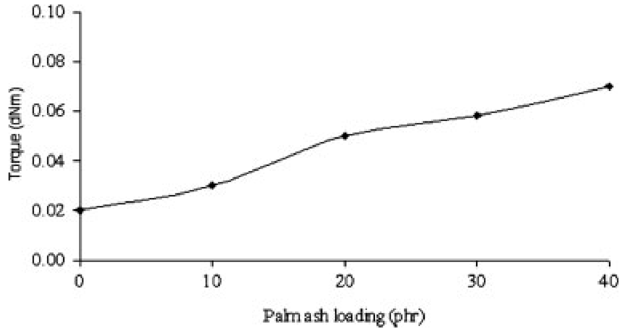

Figure 3 Effect of the filler loading on the minimum torque of palm-ash-filled natural rubber composites.

and Park equation[12] was applied to study the rubber–filler interaction:

$$Q_f/Q_g = ae^{-z} + b \quad (2)$$

where subscripts f and g refer to filled and gum vulcanizates, respectively; z is the ratio by weight of the filler to the rubber hydrocarbon in the vulcanizates; and a and b are constants. The higher the Q_f/Q_g values are, the lower the extent of interaction will be between the fiber and the matrix. In this study, we determined the weight of toluene uptake per gram of rubber hydrocarbon (Q) as follows:

$$Q = (W_s - W_d)/(W_i \times 100/\text{Formula weight}) \quad (3)$$

where W_s is the swollen weight, W_d is the dried weight, and W_i is the original weight.

RESULTS AND DISCUSSION

Effect of the palm ash loading on the natural rubber composite

Determination of the curing characteristics

Figure 1 shows the values of the scorch time and cure time of natural rubber composites with different palm ash loadings. The scorch time and cure time decrease with the palm ash loading increasing. The observed trend might be due to the longer time that the rubber remains on the mill during mixing. As the filler loading increases, the incorporation time of the filler into the rubber matrix also increases, and consequently, more heat is generated because of the additional friction. The other reason might be the presence of various metal oxides in the palm ash filler, which increase the curing rate. These metal oxides are aluminum oxide (Al_2O_3), ferrum oxide (Fe_2O_3), rubidium oxide (Rb_2O), and so forth. The presence of these metal oxides might enhance the curing rate of vulcanizates of rubber.[13] Table III shows the chemical composition of palm ash according to a Rigaku RIX 3000 X-ray fluorescence spectrometer.

Figures 2 and 3 show the maximum and minimum torques of the palm-ash-filled natural rubber composites, respectively. The figures show that the maximum and minimum torque values depend on the palm ash loading. The increase in the maximum and minimum torque values with an increase in the palm ash loading is due to an increase in the stiffness and hardness of the natural rubber composites and a reduction of the movement of the rubber macromolecule chains.[14] The higher the filler loading is, the more limited the movement of the

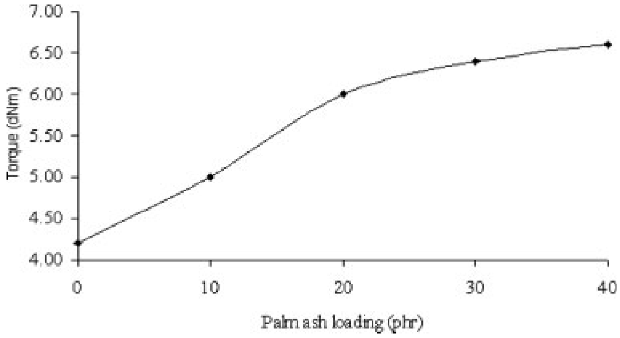

Figure 2 Effect of the filler loading on the maximum torque of palm-ash-filled natural rubber composites.

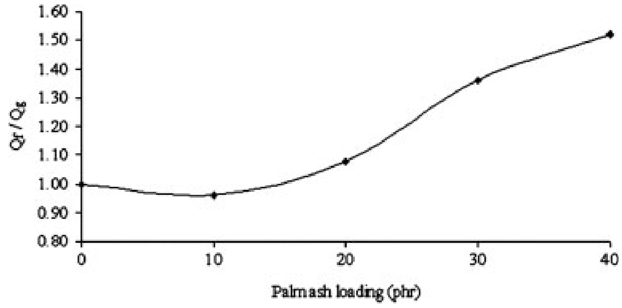

Figure 4 Effect of the filler loading on the rubber–filler interaction of palm-ash-filled natural rubber composites.

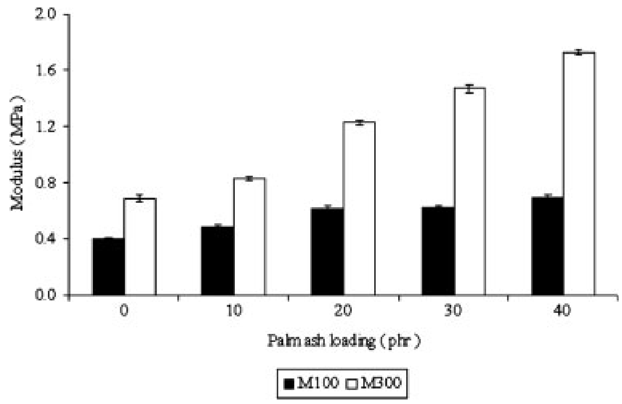

Figure 5 Effect of the filler loading on the stress at 100% elongation (M100) and stress at 300% elongation (M300) of palm-ash-filled natural rubber composites.

macromolecules will be, and then the maximum and minimum torques will be increased.

Rubber–filler interaction

The effect of the filler loading on the rubber–filler interaction (Q_f/Q_g) of the natural rubber composites is shown in Figure 4. The Q_f/Q_g values increase with increasing filler loading, and this indicates that the rubber–filler interaction weakens with an increase in the filler loading. This might be due to the hydrophilic nature of palm ash and the hydrophobic nature of the natural rubber matrix.[14]

Tensile properties

Figure 5 shows that the tensile modulus, stress at 100% elongation, and stress at 300% elongation increase with an increase in the filler loading. This observation indicates that the incorporation of palm ash into the rubber matrix improves the stiffness of the composites. The incorporation of palm ash filler into the rubber matrix reduces the elasticity of the rubber chain and consequently produces more rigid and tough natural rubber composites.

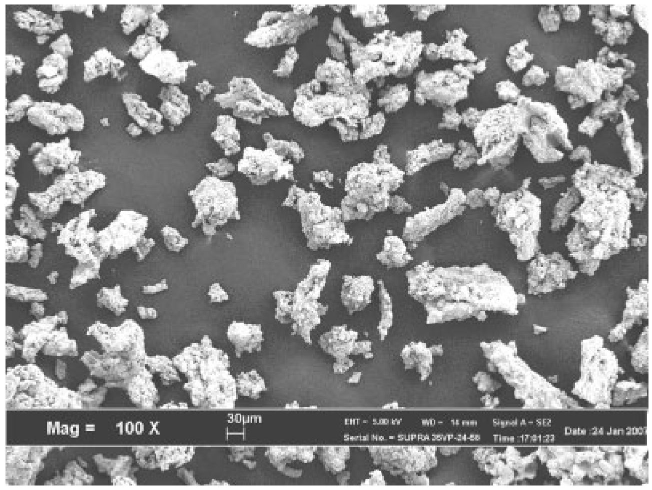

Figure 7 SEM micrograph of palm ash (magnification = 100×).

Figure 6 shows the effect of the filler loading on the tensile strength of palm-ash-filled natural rubber composites. The tensile strength of the composites decreases with the filler loading. The reduction of this property may be attributed to the geometry of the palm ash filler. For irregularly shaped fillers, the strength of the composites decreases because of the inability of the filler to support stress transferred from the polymer matrix. The presence of such filler is evident from the SEM study in Figure 7. This factor, together with the poor adhesion of the palm ash filler to the natural rubber matrix, is responsible for the reduction of the tensile strength with increasing filler loading.

The incorporation of palm ash into the natural rubber composites reduces the elongation at break, as shown in Figure 8. With increasing palm ash loading, the stiffness and brittleness of the composites increase gradually with an associated decrease in the elongation at break.[15] The application of a filler in a high quantity to a rubber matrix will tend to block the flow of the rubber chain, and

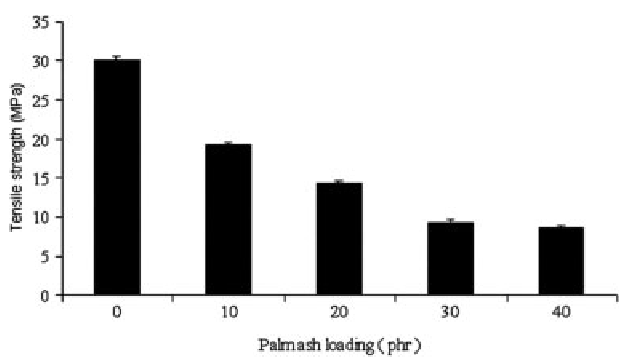

Figure 6 Effect of the filler loading on the tensile strength of palm-ash-filled natural rubber composites.

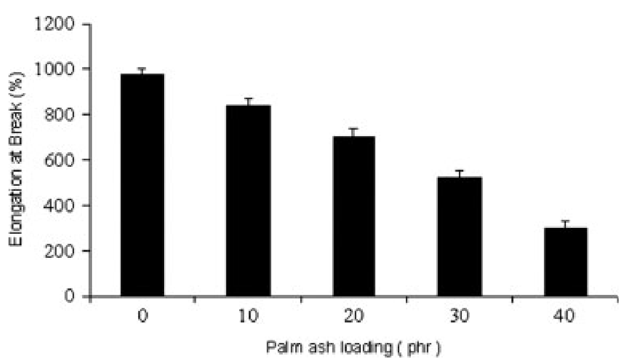

Figure 8 Effect of the filler loading on the elongation at break of palm-ash-filled natural rubber composites.

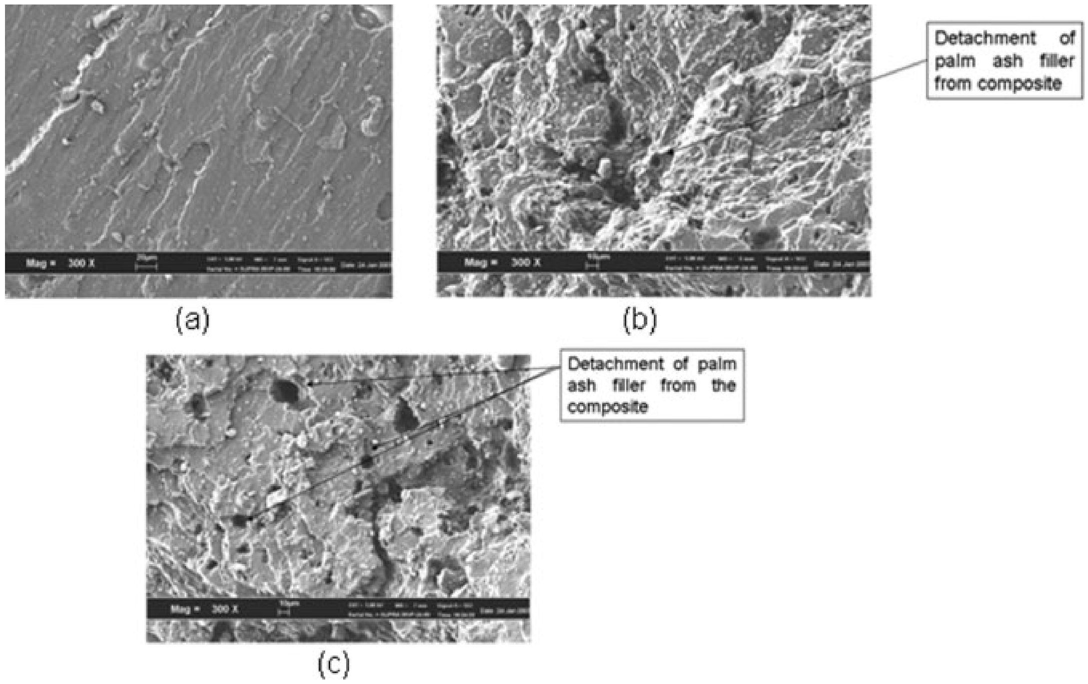

Figure 9 SEM micrographs of palm-ash-filled natural rubber composites after tensile fracture with (a) 0, (b) 10, and (c) 30 phr palm ash (magnification = 300×).

consequently, the rubber composites break at lower elongation.[16]

Morphology of the tensile fracture surface

Figure 9 shows SEM micrographs of palm-ash-filled natural rubber composites after tensile fracture with 0, 10, and 30 phr palm ash loadings. The SEM micrographs reveal that poor adhesion of palm ash (hydrophilic nature) to the natural rubber matrix (hydrophobic nature) is the main factor for the reduction of the tensile strength with an increasing filler loading in the palm-ash-filled natural rubber composites.

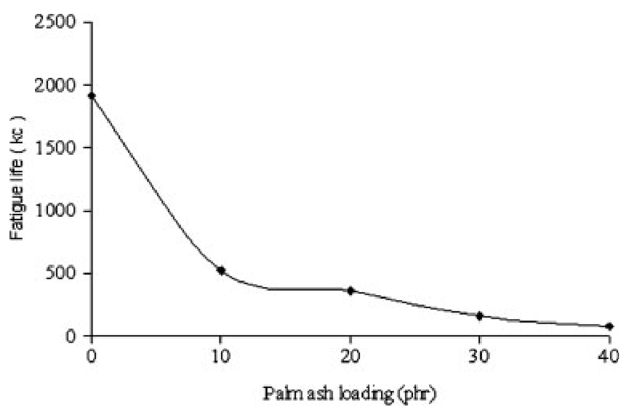

Figure 10 Effect of the filler loading on the fatigue life of palm-ash-filled natural rubber composites.

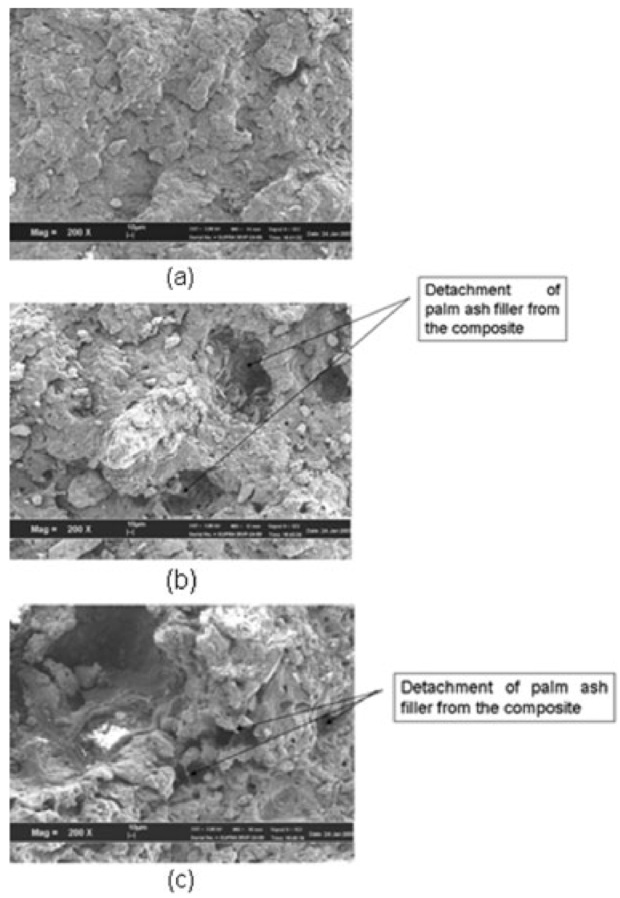

Figure 11 SEM micrographs of palm-ash-filled natural rubber composites after fatigue fracture with (a) 0, (b) 10, and (c) 30 phr palm ash (magnification = 200×).

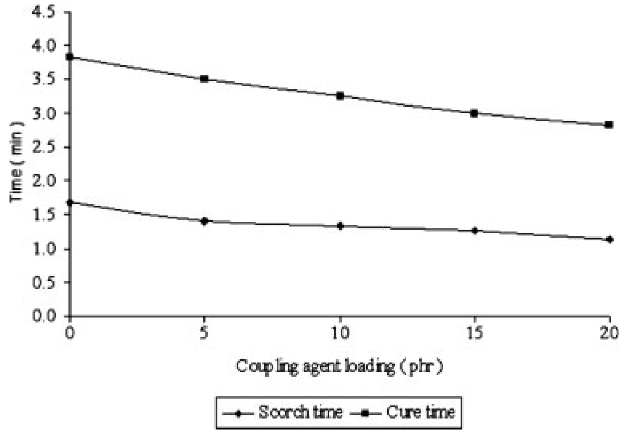

Figure 12 Effect of the coupling agent loading (MANR) on the scorch time and cure time of palm-ash-filled natural rubber composites.

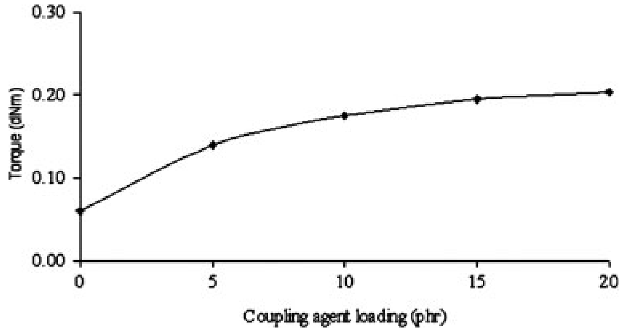

Figure 14 Effect of the coupling agent loading (MANR) on the minimum torque of palm-ash-filled natural rubber composites.

Figure 9(a) exhibits a smooth tensile-fractured surface as there was no filler. Figure 9(b,c) shows that the palm ash filler was pulled out from the natural rubber composites. The natural rubber composite in Figure 9(c), which had a greater palm ash loading, exhibited more detachment of palm ash from the natural rubber matrix. This might be due to the nonhomogeneous dispersion and poor wettability of the filler by natural rubber at the high palm ash loading in the rubber matrix. Also, the bigger sizes of the palm ash agglomerates contribute to the poor dispersion and wettability by the rubber matrix.

Fatigue life

Figure 10 shows the effect of the filler loading on the fatigue life of palm-ash-filled natural rubber composites. The fatigue life decreases as the filler loading increases, and this indicates the strong influence of a filler on the fatigue life of rubber composites. It is believed that the presence of a filler in a rubber matrix results in the friction of filler particles, which creates a crack in the rubber surface and consequently leads to catastrophic failure. As more and more filler is added to the rubber matrix, it can be anticipated that the filler particles and aggregates will not be dispersed and wetted efficiently by the rubber matrix. These inherent defects can act as stress concentration points and shorten the fatigue life of natural rubber composites. Similar observations have been reported by Ishak et al.[17] and Ismail et al.[18] for rubber composites filled with different types of natural fibers.

Figure 11(a–c) shows SEM micrographs of palm-ash-filled natural rubber composites after fatigue fracture with 0, 10, and 30 phr palm ash loadings. Figure 11(a) shows the surface of the fatigue-fractured surface of a rubber composite without the presence of palm ash. The composite exhibits a failure surface in which there is no pullout of the filler from the rubber composite.

However, there is detachment of the palm ash filler from the rubber composites in Figure 11(b,c). The increasing palm ash loading in the rubber composites increases the filler pulled out from the rubber matrix. Again, the reason might be the nonhomogeneous dispersion and poor wettability of the filler by the natural rubber at a high palm ash loading in the rubber matrix and consequently the decreased fatigue life of the rubber composites.

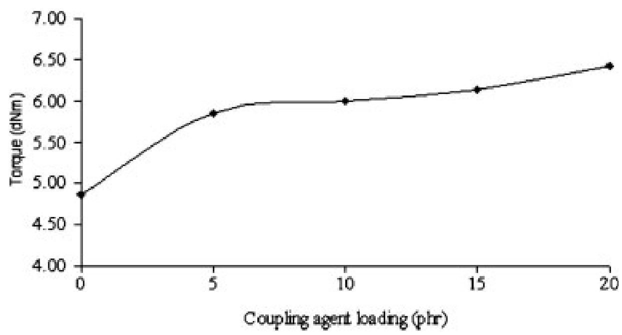

Figure 13 Effect of the coupling agent loading (MANR) on the maximum torque of palm-ash-filled natural rubber composites.

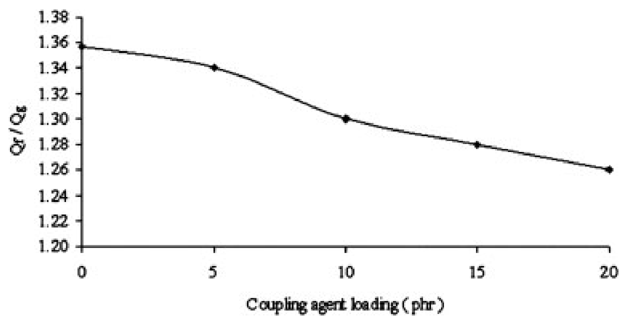

Figure 15 Effect of the coupling agent loading (MANR) on the rubber–filler interaction of palm-ash-filled natural rubber composites.

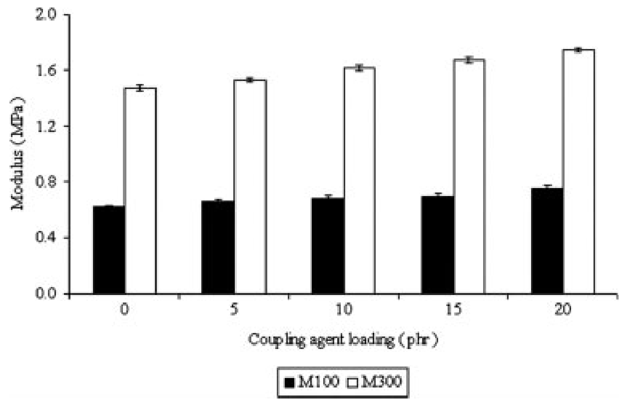

Figure 16 Effect of the coupling agent loading (MANR) on the stress at 100% elongation (M100) and stress at 300% elongation (M300) of palm-ash-filled natural rubber composites.

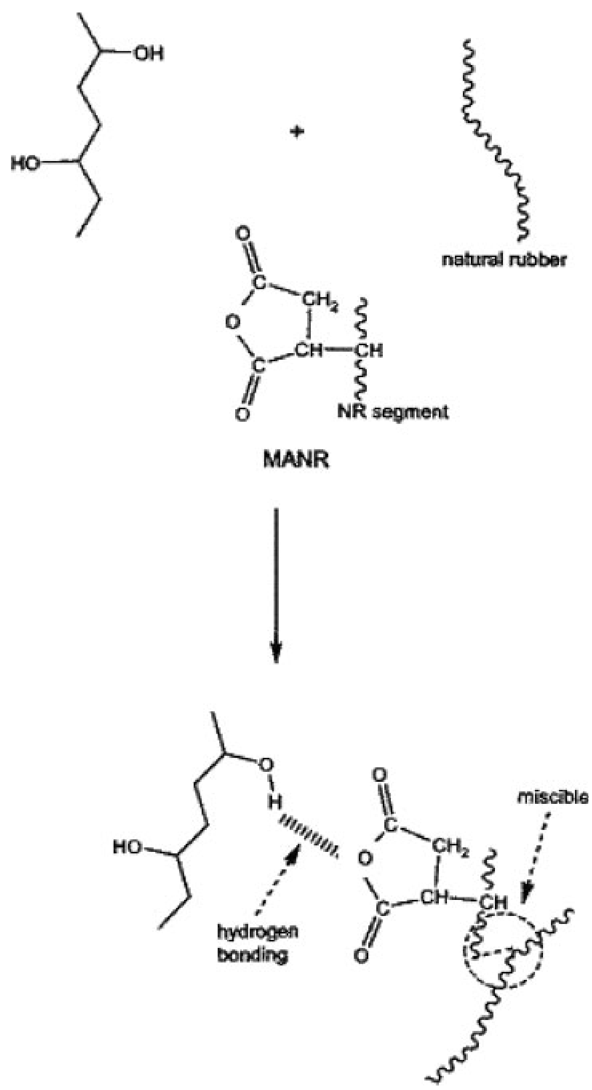

Figure 17 Possible interaction between MANR with fillers and a natural rubber matrix.

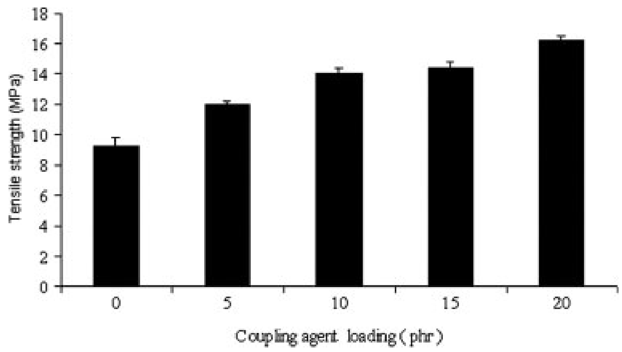

Figure 18 Effect of the coupling agent loading (MANR) on the tensile strength of palm-ash-filled natural rubber composites.

Effect of MANR as a coupling agent on the natural rubber composites

Determination of the curing characteristics

Figure 12 shows that the cure time and scorch time of palm-ash-filled natural rubber composites decrease with the addition of MANR as a coupling agent. This might be due to the formation of a good interaction between the palm ash and rubber matrix in the presence of MANR. According to Dannenberg,[19] the cure enhancement is due to an improvement of the filler dispersion in the rubber matrix by a coupling agent. Wagner[20] also reported that coupling agents generally reduce the cure and scorch times to a certain degree depending on the types of accelerator systems and elastomers.

Figures 13 and 14 indicate that the addition of a coupling agent increases the maximum and minimum torque values of palm-ash-filled natural rubber composites. The results show the advantage of using MANR to reduce the damping characteristics of the natural rubber composites.

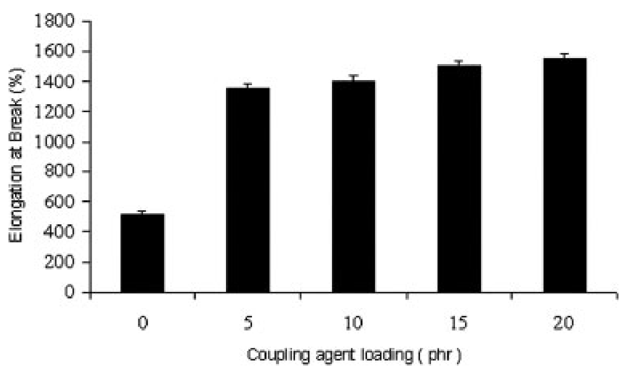

Figure 19 Effect of the coupling agent loading (MANR) on the elongation at break of palm-ash-filled natural rubber composites.

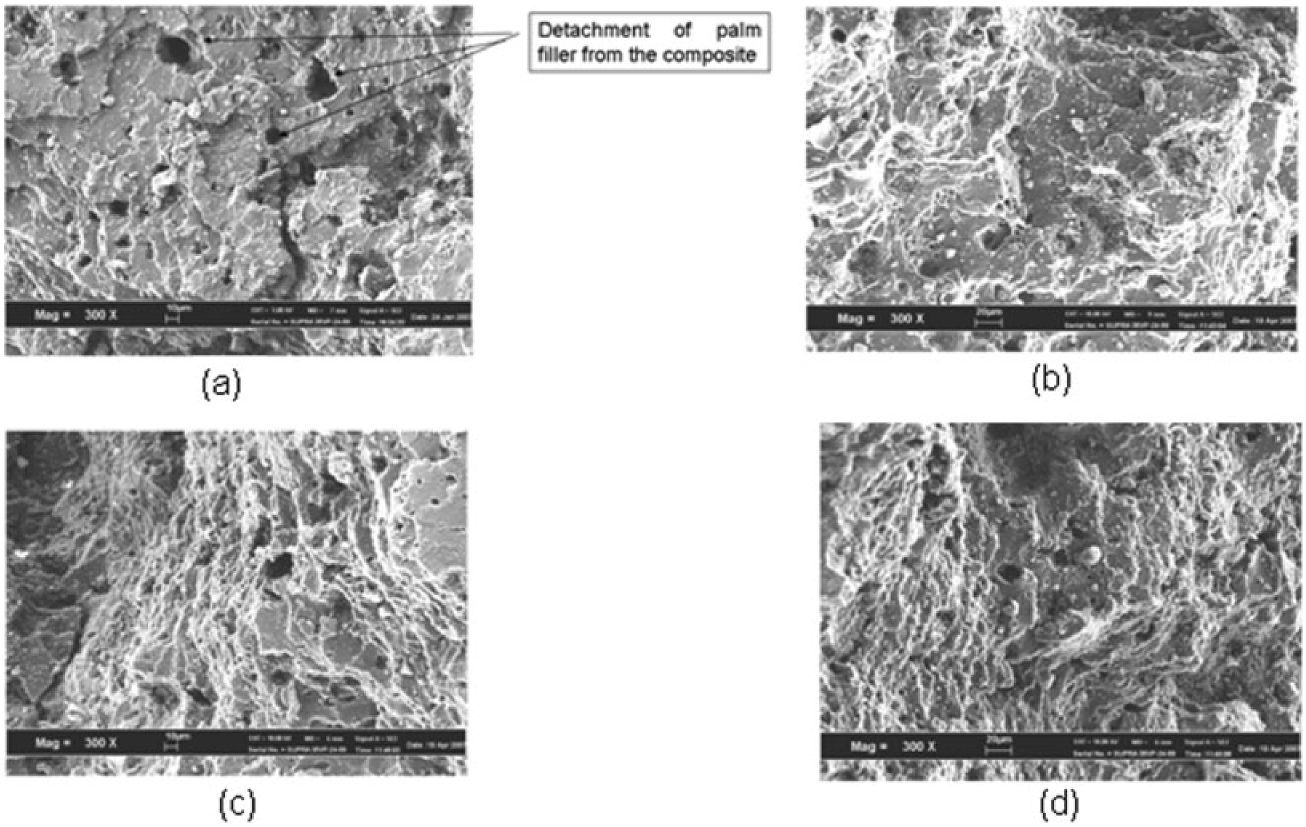

Figure 20 SEM micrographs of palm-ash-filled natural rubber composites after tensile fracture with (a) 0, (b) 5, (c) 10, and (d) 20 phr MANR (magnification = 300×).

Rubber–filler interaction

Figure 15 shows the effect of MANR on the rubber–filler interaction (Q_f/Q_g) of palm-ash-filled natural rubber composites. The Q_f/Q_g values of natural rubber decrease with the MANR loading increasing. In comparison with the control composite (without MANR), the incorporation of MANR produces lower values of Q_f/Q_g, and this confirms better interactions between the palm ash and rubber matrix. The higher the MANR loading is, the better the interaction is between the filler and rubber matrix.

Tensile properties

Figure 16 shows that the stress at 100% elongation and stress at 300% elongation increase with an increase in the MANR loading. This may be attributed to the improvement in the interfacial adhesion between the palm ash and natural rubber in the presence of MANR.

It is well known that a coupling agent works by interacting with both the filler and rubber matrix. In this work, it is believed that the natural rubber segments of MANR form miscible blends with the natural rubber, and the polar part of MANR (maleic anhydride) forms hydrogen bonds with the hydroxyl group of the filler at the interfacial region. Figure 17 shows the proposed interactions between MANR and both the palm ash and rubber matrix. Stronger adhesion at the filler–rubber matrix interface causes better stress transfer from the matrix to the filler, consequently leading to a higher tensile strength of the natural rubber composites (Fig. 18).

Figure 19 shows the effect of the MANR loading on the elongation at break of palm-ash-filled natural rubber composites. Because of the better interaction of the natural rubber matrix with the natural rubber segment of MANR, the increase in the coupling

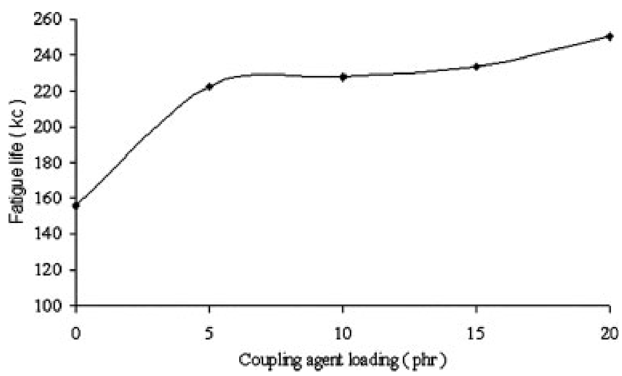

Figure 21 Effect of the coupling agent loading (MANR) on the fatigue life of palm-ash-filled natural rubber composites.

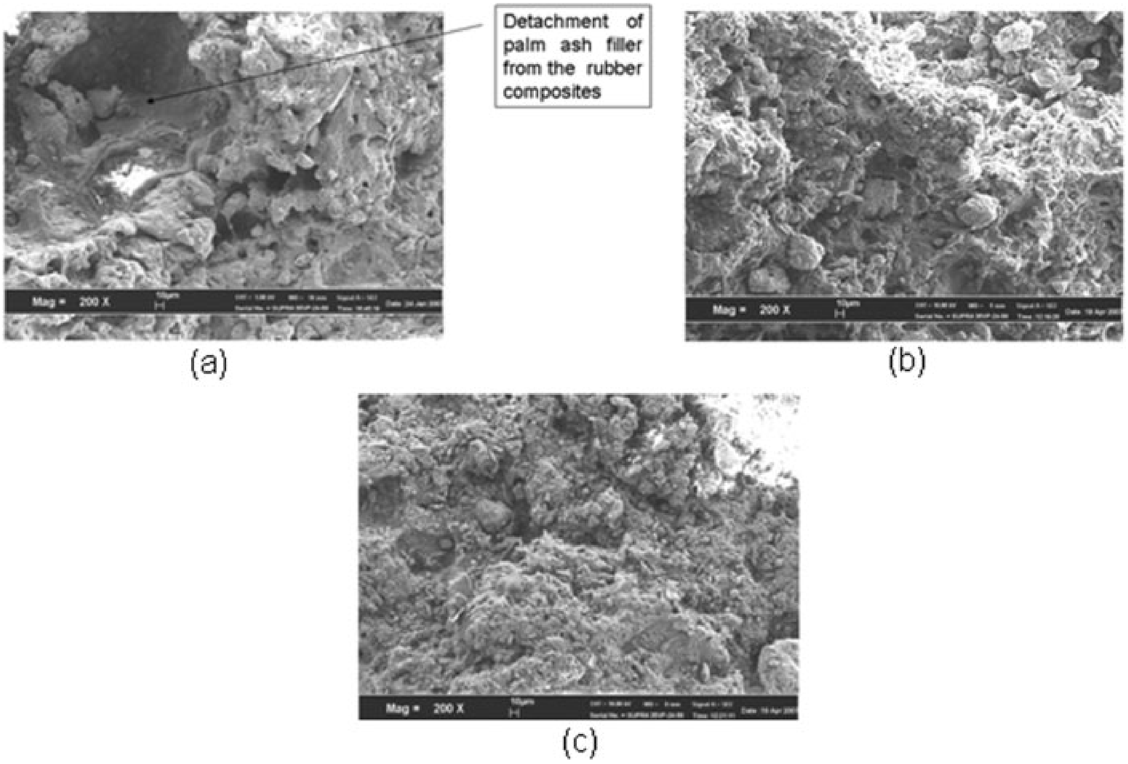

Figure 22 SEM micrographs of palm-ash-filled natural rubber composites after fatigue fracture with (a) 0, (b) 5, and (c) 10 phr MANR (magnification = 200×).

agent loading increases the elongation at break of natural rubber composites.

Morphology of the tensile-fractured surface

An SEM micrograph of the tensile failure surface of a palm-ash-filled natural rubber composite without MANR as a coupling agent is shown in Figure 20(a). The failure surface of the rubber composite exhibits weak interfacial adhesion between the palm ash and the rubber matrix. The failure surface shows that many holes were left after the palm ash was pulled out from the rubber matrix when stress was applied, and the failure occurred at the weak palm ash filler and rubber matrix interface. With the addition of MANR, there was less pullout of the palm ash from the natural rubber matrix because of the strong interaction between the filler and rubber matrix [Fig. 20(b)–(d)].

Fatigue properties

Figure 21 shows the effect of the MANR loading on the fatigue life of palm-ash-filled natural rubber composites. The fatigue life increases as the coupling agent increases, and this indicates the strong influence of MANR on the fatigue life of natural rubber composites. As discussed before, natural rubber segments of MANR form a miscible blend with the natural rubber, and the polar part of MANR (maleic anhydride) forms hydrogen bonds with hydroxyl groups of the filler at the interfacial region, as shown in Figure 17. These interactions cause an improvement in the fatigue life due to the increase in the effectiveness of the stress transferred from the rubber matrix to the filler, which reduces the progression of damage. In addition, the higher interfacial adhesion helps to reduce the amount of heat buildup during deformation, and this reduces the chain scission and consequently enhances the fatigue life. The better filler dispersion and wettability improvement of the filler by the matrix reduce the formation of stress concentration points and consequently increase the fatigue life of the composites.

Figure 22(a) shows that the dispersion of the filler and the wettability of the filler by the rubber matrix of the composites are poor without the presence of MANR (control composite). However, the presence of MANR causes a reduction in filler pullout, and less aggregate is formed [see Fig. 22(b,c)]. Figure 22(c) shows that the fillers are well wetted and do not detach from the rubber matrix. This might be due to the better interaction between the filler and matrix in the presence of MANR.

CONCLUSIONS

1. The incorporation of palm ash into a natural rubber matrix decreases the scorch time and cure time but increases the maximum torque and minimum torque.

2. The tensile modulus increases with increasing palm ash loading, but the tensile strength, fatigue life, and elongation at break exhibit the opposite trend. The reduction of these properties can be attributed to the poor filler–matrix interaction.
3. The presence of MANR enhances the tensile properties and fatigue life of palm-ash-filled natural rubber composites.
4. SEM micrographs of tensile-fractured surfaces of the composites show that the presence of MANR causes a reduction in filler detachment and better interfacial interaction between palm ash and natural rubber.

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