Soil Burial Study of Palm Kernel Shell-Filled Natural Rubber Composites: The Effect of Filler Loading and Presence of Silane Coupling Agent

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Palm kernel shell (PKS) was incorporated into natural rubber composites at loadings ranging from 0 to 20 phr using a laboratory-size two-roll mill. A soil burial study of the PKS-filled NR composites as a function of filler loading and silane coupling agent incorporation was then conducted over a period of six months. The degraded composites were evaluated by means of tensile testing. To study the degradation of the composites after soil burial, their morphological properties were observed by scanning electron microscopy. Prior to the soil burial tests, as the PKS filler loading increased, the tensile strength and elongation at break of the composites both with and without the silane coupling agent decreased, while the tensile moduli (M100 and M300) increased. At identical filler loading values, the NR/PKS composites with the incorporated silane coupling agent exhibited better tensile properties than the NR/PKS composites without the silane. Following the soil burial tests, the tensile strength, elongation at break, and the tensile moduli (M100 and M300) all decreased because of microbial attacks on the composites. The addition of silane enhanced the retention of the tensile properties of the NR/PKS composites after soil burial because of the improved adhesion at the filler-rubber matrix interface.

Keywords: Palm kernel shell; Soil burial; Tensile strength; Silane coupling agent; FTIR; SEM

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INTRODUCTION

The degradation of a polymer is defined as the deterioration of polymer macromolecules resulting from bond cleavage in the backbone, chemical reactions in the side chains, and intermolecular crosslinking. Biodegradation is a chemical dissolution of materials by either living organisms, such as bacteria or fungi, or other biological processes, under certain conditions (Morelli 2008). Biodegradability, on the other hand, is the extent to which organic compounds can be broken down by living microorganisms (Ranalli and Zanardini 2009). Lately, biodegradable composites are becoming increasingly popular, given that biodegradable materials are an ideal solution to the environmental issues associated with polymer-based products. Many synthetic polymeric materials can withstand extreme temperatures and are durable. Nevertheless, most of them do not break down naturally. It is common knowledge that the increasing numbers of non-degradable polymer products have raised concerns globally. The decreasing available space for landfills and the global warming caused by increasing amounts of carbon dioxide in the atmosphere are very alarming issues (Stevenson and Stallwood 2008). Another concern is the issue of non-degradable solid waste, which also contributes to environmental pollution.

According to the Rubber Research Institute of Malaysia, the total global production of natural rubber in 2010 was around 10 million tons, increasing to more than 12.3 million tons in 2015 (LGM 2015). One of the most common natural rubber applications is in the tire industry. Tires, although made of rubber, are almost impossible to degrade because of their toughened structure, as well as the added fillers and stabilizers. Worn-out tires, as well as other used polymer products, are often discarded, causing pollution and inflicting other forms of damage on the environment.

The aerobic biodegradation of polymeric materials occurs in two stages, namely, depolymerization and mineralization. The preliminary stage of degradation of natural rubber in soil is caused by the attack of hydrogenase enzymes (involving oxygen), which split the long polymer molecules into shorter length and adhered themselves to rubber molecules. This causes the rubber molecules become hydrophilic, which provides suitable ambiance for microorganism attack. At this stage, hydrolysis, oxidation, and enzymatic microbial action can occur during the internal linkage cleavages of the polymer or during the sequential cleavage of the last monomer unit (Innocenti 2005). The final stage of biodegradation occurs when oligomeric segments are totally converted into biomass, minerals, and gases (Solaro 1996). Biodegradation is a time-consuming process. The degradation rate depends on the amount of additives present, as well as on the chemical and structural properties of the polymers. Regardless, biodegradable products at least help to reduce the effects of pollution caused by non-degradable products.

Aerobic biodegradation occurs as follows (Andrady 1994):

$$X_{\text{polymer}} + 0_2 \Rightarrow X_{\text{fragments}} \Rightarrow H_2O + CO_2 + X_{\text{biomass}} \tag{1}$$

The cis-1,4 polyisoprene elastomeric material, produced from rubber tree sap, makes up more than 90% of natural rubber (NR). It offers excellent flexibility and high gum strength. However, NR is highly prone to oxidation, ozonation, and high temperatures due to its unsaturated double bond (C=C), which has limited strength, as well as to the weak covalent bonds that make up its structure (Kothandaraman 2008). The degradation of NR causes chain scission, which can occur randomly, or at the ends of polymer chains. Natural fillers such as palm kernel shell, rattan, and kenaf, to name a few, have numerous advantages over commercial fillers, including low density, economy, biodegradability, easy availability, and customizability. Natural fillers are composed of several major constituents, namely cellulose, hemicellulose, and lignin (Bledzeki and Gassan 1999). The dominant component in most fiber fillers is cellulose (Bismarck *et al.* 2005). The main function of cellulose is to help the plant retain its strength and stiffness. Hemicellulose, on the other hand, is involved in moisture absorption, biodegradation, and the thermal degradation of the lignocellolusic filler (Thakur 2015). The major component of palm kernel shell is lignin, followed by hemi-cellulose and then cellulose. Lignin functions as a biochemical polymer that protects the cell wall from physical and chemical damage. It also fills the gaps between polysaccharide fibers and binds them together. Lignin contains high molecular-weight compounds that make it resistant to microbial attack. Lignin is notable for the presence of hydroxyl and methoxyl groups. High lignin content makes palm kernel shell resistant to biodegradation under normal environmental medium (Anike *et al.* 2016). Cellulose consists of linear chains of anhydroglucose, containing hydroxyl groups, which later bind to hydrogen and other cellulose macromolecules, making all natural fillers hydrophilic by nature (Bismarck *et al.* 2005).

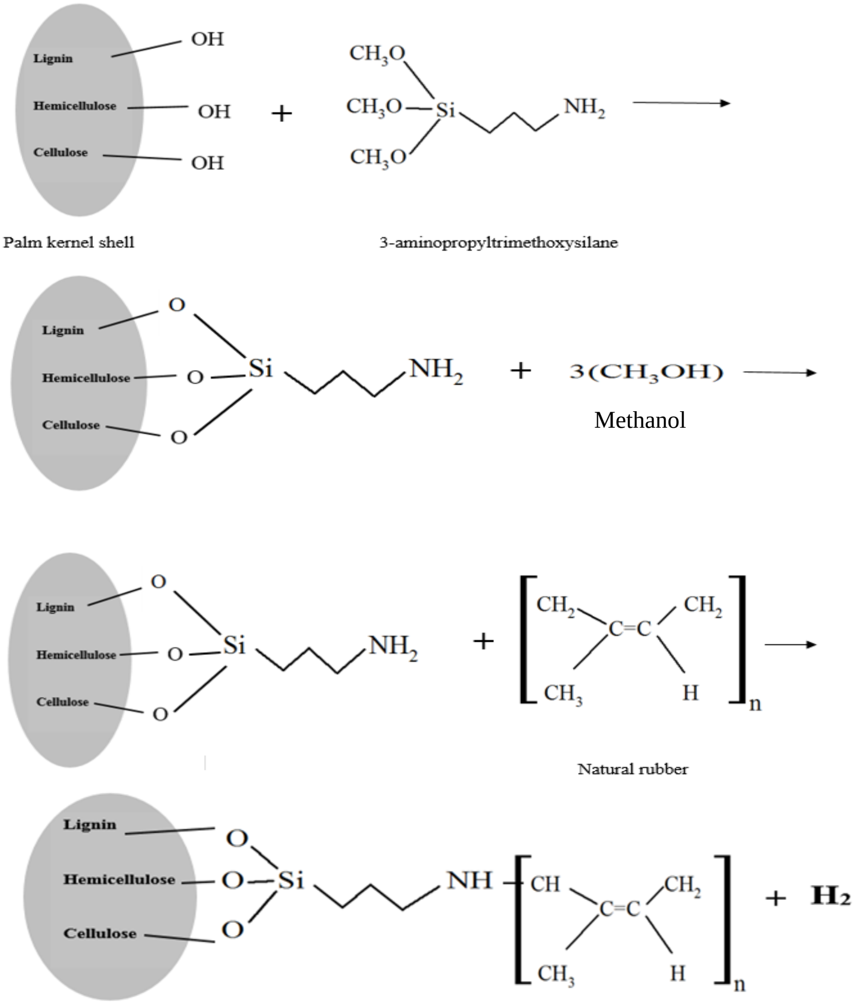

Fig. 1. The possible interaction of silane coupling agent (3-aminopropyltrimethoxysilane) with palm kernel shell and natural rubber

Natural rubber and palm kernel shell are totally incompatible because of their different polarities. Palm kernel shell is compatible with other natural fibers, which are hydrophilic, while natural rubber is hydrophobic (Ali Shah *et al*. 2013). Thus, to improve the interfacial adhesion and the compatibility between palm kernel shell and natural rubber, a silane coupling agent has been introduced into the system. The purpose of the present research is to study the extent of biodegradability of PKS-filled natural rubber composites, and the effect of a silane coupling agent on the NR composites following soil burial tests.

EXPERIMENTAL

Materials and Formulation

Natural rubber (SMR L) was obtained from the Rubber Research Institute of Malaysia (RRIM), and the palm kernel shells (PKS) were taken from United Palm Industries, Ltd, Penang, Malaysia. The palm kernel shells (PKS) were cleaned, dried, and ground, then sieved to an average particle size of 5.6 µm. The chemicals used, namely sulphur, zinc oxide, stearic acid, n-cyclohexyl-2-benzothiazol sulfenamide (CBS), 2-2 methylene-bis-(4-methyl-6-tert-butylphenol) (BKF), tetra-methylthiuram disulphide (TMTD), and AMEO (3-aminopropyltrimethoxysilane), were all from Bayer (M), Ltd. The formulations of the NR/PKS composites are illustrated in Table 1, and the composition of the palm kernel shell (PKS) is shown in Table 2.

Table 1. Formulations for Palm Kernel Shell Powder Filled-NR Composites

Ingredients	Formulation (phr)	
	Series 1	Series 2
Natural rubber	100	100
Palm kernel shell	0,5,10,15,20	5,10,15,20
Zinc oxide	5	5
Stearic acid	3	3
CBS	0.5	0.5
TMTD	0.1	0.1
BKF	1	1
Sulphur	2.5	2.5
Silane coupling agent (AMEO)	-	1

Table 2. Composition of Palm Kernel Shells (PKS) (Abdullah *et al.* 2010)

Fiber analysis:	By weight (%):
Cellulose	20.80
Hemicellulose	22.70
Lignin	50.50
Volatiles	4.80
Ash	1.00

Sample Preparation

Palm kernel shell powder was dried in an oven at 70 ^{o}C overnight to expel moisture prior to the compounding process. The mixing procedures for the two series of natural rubber composites were carried out in a laboratory two-roll mill (model XK-160) in accordance with the standard of the American Society for Testing and Materials (ASTM), designated D3184 (1994). The first series was mixed without the addition of a silane coupling agent, while the second series was prepared with the silane coupling agent incorporated. After the compounding process, the rubber compounds were kept in a freezer for 24 h prior to the curing assessment and the vulcanization. The curing characteristics of the rubber compounds were studied using a Monsanto Rheometer (model MDR 2000, Alpha Technologies, Ohio, USA), operated at 150 °C. The rubber compounds were molded into sheets for the duration of their respective cure times (t_{90}), at 150 °C using a hot press machine.

Soil Burial

The soil burial test was performed at the School of Materials and Minerals Resources Engineering, Universiti Sains Malaysia, over a period of six months. Dumbell-shaped samples were cut out of vulcanized rubber sheets, and the specimens were buried underground. After six months, the samples were withdrawn, washed with distilled water, and dried at room temperature. The degradation was assessed and evaluated by examining the tensile properties before and after soil burial.

Tensile Testing

Tensile testing was carried out according to ASTM D412-6a (2013) at a constant rate of 500 mm/min, using an Instron Universal Testing Machine (model 3366, Canton, Mass, USA). Five samples were tested, and average results were reported.

Swelling test

Swelling test (ASTM D471)(2013) was performed on a uniform circular cut from the compression-moulded rubber samples with 5 mm diameter and 2 mm thick. The samples were immersed in toluene at of room temperature for 48 hours to allow the swelling to reach equilibrium. Then, the test pieces were taken out and blotted using clean cloth. The swelling ratio was calculated following Eq. 1,

$$R = \frac{W_t - W_0}{W_0} \tag{1}$$

where W_0 and W_t are the weight of the test piece before swelling and after swelling, respectively. The swelling ratio is a direct measurement of degree of crosslinking.

Fourier Transform Infrared (FTIR)

Spectra were obtained using Perkin-Elmer System 2000 (Selangor, Malaysia), and the attenuated total reflection (ATR) technique was adopted. The spectrum resolution and the scanning range were 4 cm^{-1} and 550 to 4000 cm^{-1}, respectively.

Carbonyl Index

Carbonyl index (CI) is a parameter used to observe degree of degradation of NR/PKS composites. CI can be calculated following Eq. 2.

$$\text{Carbonyl Index} = \frac{A\ \text{carbonyl band}}{A\ \text{reference band}} \tag{2}$$

Scanning Electron Microscopy (SEM)

The examination of the surfaces of the samples was carried out using field emission scanning electron microscope (Zeiss Supra 35vp, Oberkochen, Germany). The fracture parts of the tensile specimens were used. The fracture surfaces were mounted on aluminum stubs and sputter-coated with thin layer of gold to avoid electrostatic charging and poor image resolution. The images of rubber and filler dispersion were evaluated from the micrographs.

Weight Loss

Each specimen was collected, cleaned and dried to a constant weight in a vacuum oven at 60°C. The biodegradation rate was estimated by measuring the weight of the specimens before and after testing. Using Equation (3), the percentage of weight loss was calculated as,

$$\text{Weight loss (\%)} = \frac{W_1 - W_0}{W_0} \tag{3}$$

where W_0 and W_1 are sample weights before and after the test respectively. Five measurements were taken for each compound.

RESULTS AND DISCUSSION

Fourier Transform Infrared Spectroscopy (FTIR)

Figures 2a(i) and b(i) show the FTIR spectra of palm kernel shell-filled natural rubber (NR) composites, with and without the silane coupling agent, before soil burial. Meanwhile, Figs. 2 a(ii) and b(ii) show the FTIR results for palm kernel shell-filled natural rubber (NR) composites with and without a silane coupling agent, respectively, after soil burial. The FTIR spectra show the formation and disappearance, presented in Figs. 2 a(ii) and b(ii), respectively, of new peaks following soil burial. Upon exposure to soil burial, various chemical reactions occurred in the composites, resulting in the changes observed in the FTIR spectrum. After the samples had been subjected to soil burial, an apparently broader peak of -OH at 3200 to 3700 cm^{-1} appeared. The presence of a carbonyl group (C=O), detected in the 1770 to 1710 cm^{-1} range, was attributed to changes in the chemical structure of the composites as a result of chain scission caused by oxidation (Stark and Matuana 2007). Additionally, a broad peak region that formed in the 1020 to 1300 cm^{-1} range following soil burial was attributed to the ether group (C-O-C). The intensity of the peak at 2917 cm^{-1}, which was attributed to $C\text{-}CH_3$, was slightly reduced following soil burial for composites with the silane coupling agent because the oxidation chain caused chain unzipping to occur on the side chains of the polymer (Yahya *et al*. 2014). In contrast, hardly any changes took place in the composites without the silane. Furthermore, it could be observed that the intensity of the peak at 830 cm^{-1}, attributed to the C=C bond of rubber, was reduced as a result of the deformation of the unsaturated double bonds. The changes in the peak at 1160 cm^{-1} indicated the formation of an aldehyde (Ali Shah *et al*. 2013).

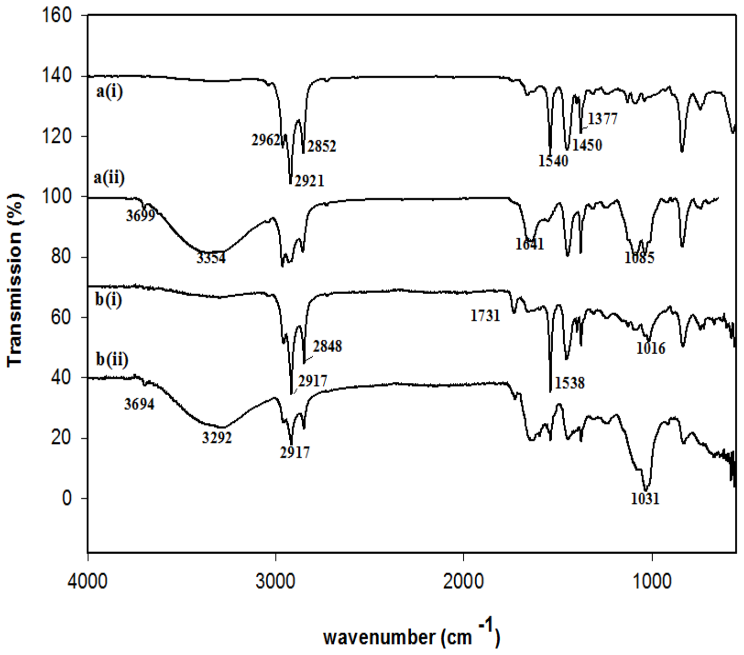

Fig. 2. FTIR spectra of 5-phr palm kernel shell-filled NR composites (a) without silane, (b) with silane, and (i) before and (ii) after soil burial

Soil burial causes the breakdown of important functional groups, such as carbonyl, methyl, and ether bonds. The hydroxyl peak was attenuated following soil burial. A peak corresponding to the cis-1,4 double bond at 835 cm^{-1} decreased in intensity after soil burial. The appearance new peak of carbonyl and ether groups was detected in FTIR spectrum. The formation of carbonyl after soil burial confirms that the degradation took place and the chemical structure of the polymers has been changed. The carbonyl index for NR/PKS composites with and without silane coupling agent are shown in Fig. 3. The composites with silane coupling agent has lower carbonyl index than composites without silane coupling agent. This is due to formation of strong rubber-filler interaction which was not susceptible to biodegradation. Overall, after the soil burial test, a reduction occurred in the number of 1,4-polyisoprene bonds, aldehyde, and ketone peaks that appeared. Hydroxyl, methoxyl, and carbonyl groups can also be found in lignin. Lignin is very hydrophobic, acts as a natural coupling agent, and increases the stiffness of cellulose in the filler (Taherzadeh and Karimi 2008).

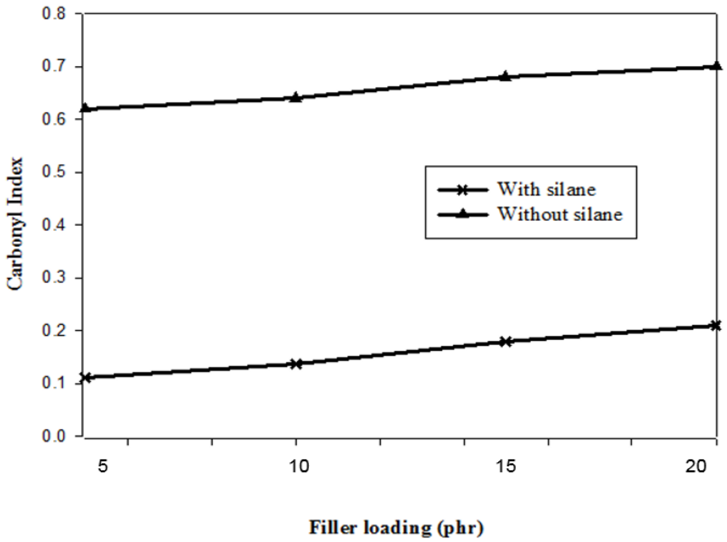

Fig. 3. Carbonyl index of NR/PKS composites with and without silane weathered for 6 months

Tensile Properties

The tensile properties of the unfilled NR and NR/PKS composites, such as tensile strength, elongation at break (E_b), tensile moduli at 100% elongation (M100) and at 300% elongation (M300), with and without the silane coupling agent prior to soil burial, are shown in Figs. 4, 5, 6, and 7. For samples both with and without the silane coupling agent, the tensile strength and the elongation at break (E_b) showed decreasing trends, whereas the tensile moduli showed increasing trends with increasing filler loadings. The results for the tensile strengths of all samples are shown in Fig. 4. The reduction in the tensile strength resulted from the poor rubber-filler interaction. This can be attributed to the strongly polarized nature of the lignocellulosic fillers, which are not particularly compatible with hydrophobic polymers, especially natural rubber. The addition of palm kernel shell into the NR compounds was expected to reduce the flexibility of the natural filler, as unfilled natural rubber possesses strain-induced crystallization properties that allow it to crystallize under stress (Ismail *et al.* 2010). Thus, increasing the natural filler loading should result in stiffer composites and lower the resistance of the composites to breakage. Accordingly, with increased filler loading, the elongation at break decreased, and the modulus increased, as presented in Figs. 5, 6, and 7. However, introducing a silane coupling agent can help to facilitate and maximize the interaction at the interface between the filler and the rubber matrix. The silane coupling agent can enhance the wettability of the filler on the rubber matrix. The silane coupling agent has bi-functional groups that at one end can react with the -OH groups in the cellulose while at the other end can react with the functional groups of the matrix by forming a bridge of chemical bonds between the filler and the matrix, which consequently creates interfacial adhesion (Ismail *et al*. 2001). As the interaction between the rubber and the filler increased, the ability of the composites to resist deformation also increased. As can be seen in Figs. 6 and 7, the tensile moduli at 100% elongation (M100) and at 300% elongation (M300) increased with the addition of the silane coupling agent, which was be attributed to the better adhesion between the filler and the rubber matrix, as has been demonstrated by the FTIR results.

After six months of soil burial, some deterioration in the tensile properties was observed for samples both with and without the silane coupling agent compared to samples before the soil burial test, as shown in Figs. 5 through 7. This was caused by the degradation of the natural rubber, as well as that of the natural filler incorporated into it. Vulcanized rubber degrades more slowly due to the interlinking of the poly(cis-1,4 polyisoprene) chains and the presence of additives (Ali Shah *et al.* 2013). Rubber biodegradation is a slow process; a process of consuming hydrocarbon as a source of carbon. The filled samples subjected to the soil burial test showed lower tensile strength compared with the unfilled NR compounds because of the lower resistance to microbial attack of the filled NR composites compared with the unfilled ones (Abraham *et al*. 2013).

The incorporation of a natural filler enhances the biodegradation of rubber composites underneath the soil, as cellulose degrades faster than natural rubber. The cellulose in natural fillers is consumed by bacteria and other microorganisms, resulting in porosity, the formation of voids, and the loss of the mechanical properties of the rubber matrix (Rose and Steinbuchel 2005). Studies have shown that the only strain of microorganisms that is able to decompose natural rubber and use rubber hydrocarbons as a source of carbon is the *Actinomycete* (Jendrossek *et al*. 1997; Steinbuchel 1998). Natural rubber and cellulose are two of the main sources of carbon for these microorganisms. Rubber degradation starts with the natural filler and later spreads to the rubber matrix. The destruction of the natural filler increases the number of active sites and increases the surface area, which accelerates the degradation of the rubber matrix. The filler particles of vulcanized rubber composites are connected to rubber chains by combinations of strong/weak and long/short linkages (Blanchard and Parkinson 1952). The reduction of the high molecular weight of rubber into shorter chains partially degrades the compound and, upon longer exposure, causes biodegradation (Jendrossek *et al.* 1997). Shorter chains reduce the frequency of rubber chain entanglements, resulting in lower resistance to breakage. Hence, the tensile strength was reduced after soil burial, as presented in Fig. 4. In addition, the presence of voids and shorter chains lowered the elongation at break of the NR/PKS composites. The increase in the tensile moduli with increased filler loading was attributed to the increase in the number of linkages between the fillers and the rubber chains, as shown in Figs. 6 and 7. The increase in the moduli was greater for the NR/PKS composites with the silane coupling agent incorporated. The incorporation of the silane coupling agent improved the adherence of the filler to the rubber matrix. This reinforcement was due to the load-sharing effect arising from the attachment of several molecules to one filler particle. When a highly stressed molecular chains breaks, the tension it carried is distributed equally among the other chains by the filler particles, instead of being imposed upon its immediate neighbours (Samsuri 2009). As the filler was able to distribute the load more and more effectively due to the improved rubber-filler interaction imparted by the silane coupling agent, the tensile strength of the NR/PKS composites incorporated with the silane coupling agent increased.

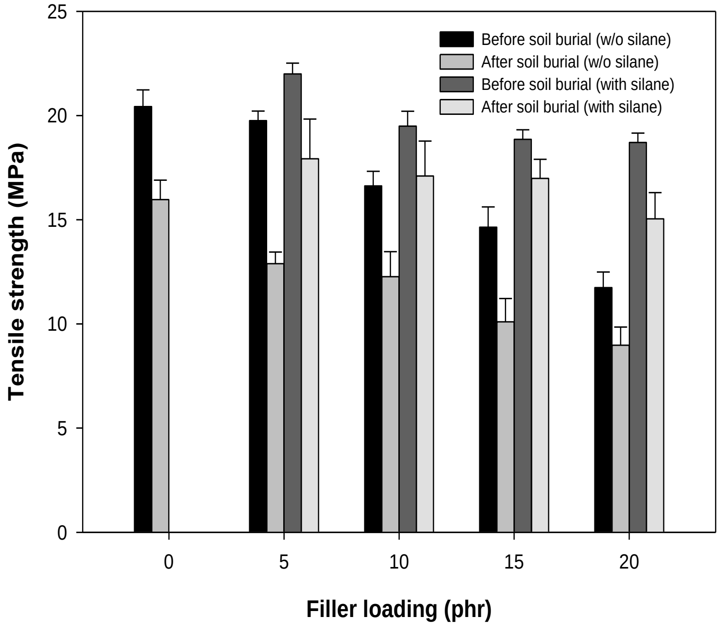

Fig. 4. The effects of filler loading and the incorporation of a silane coupling agent on the tensile strength of palm kernel shell-filled natural rubber composites before and after soil burial

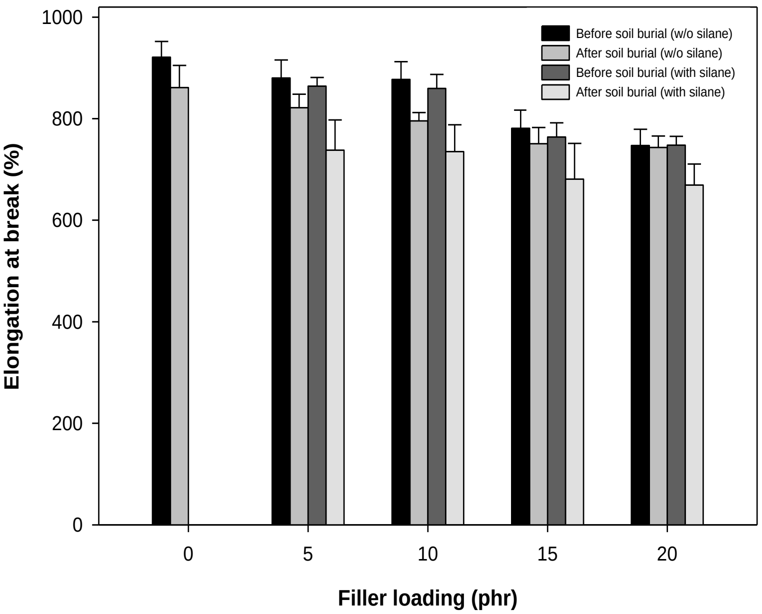

Fig. 5. The effect of filler loading and the incorporation of a silane coupling agent on the elongation at break of palm kernel shell-filled NR composites before and after soil burial

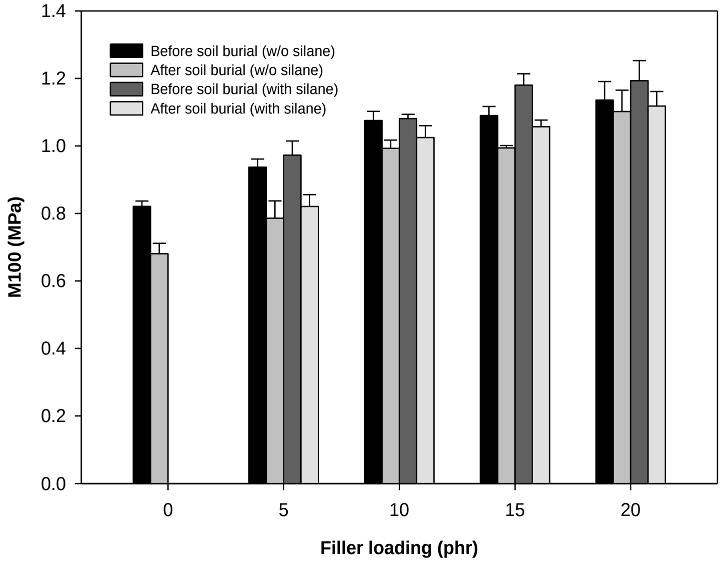

Fig. 6. The effect of filler loading and the incorporation of a silane coupling agent on modulus at 100% elongation (M100) of palm kernel shell-filled NR composites before and after soil burial

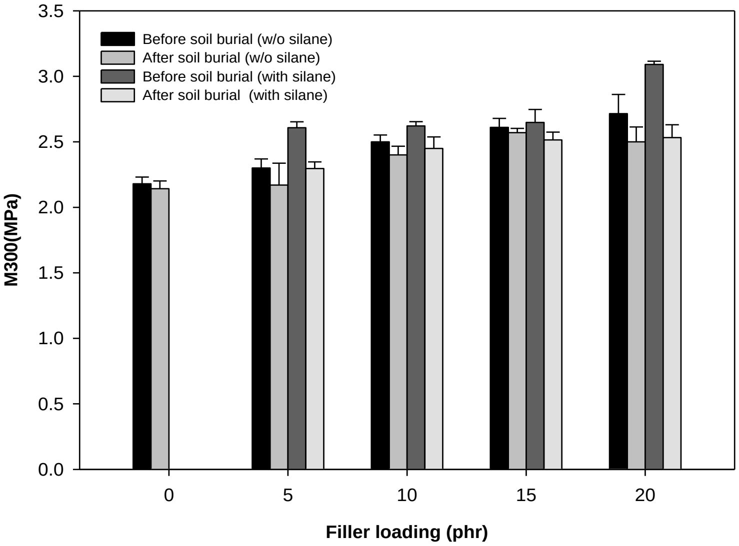

Fig. 7. The effects of filler loading and the incorporation of a silane coupling agent on the modulus at 300% elongation (M300) before and after soil burial

As can be seen in Figs. 4, 6, and 7, for composites with the silane coupling agent, an improvement of 7% on average for tensile strength, of 6% for M100, and of 13% for M300 was achieved over those without the silane. Nevertheless, after soil burial, the elongation at break (E_b) in Fig. 5 had decreased by 8% more on average for the NR/PKS composites with the silane coupling agent in comparison to those without the silane. The addition of the silane coupling agent also provided a protective layer against microbial attack (Jacob *et al*. 2007). Swelling ratio of composites with silane coupling agent in Fig. 8 significantly reduced after swelling test indicates the presence of cross-links and improved rubber-filler interaction between filler and rubber matrix.

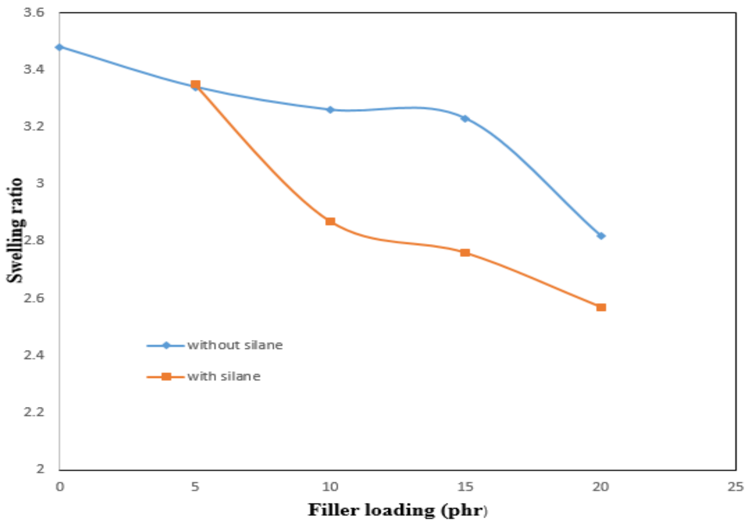

Fig. 8. The swelling ratio of NR/PKS with and without silane coupling agent

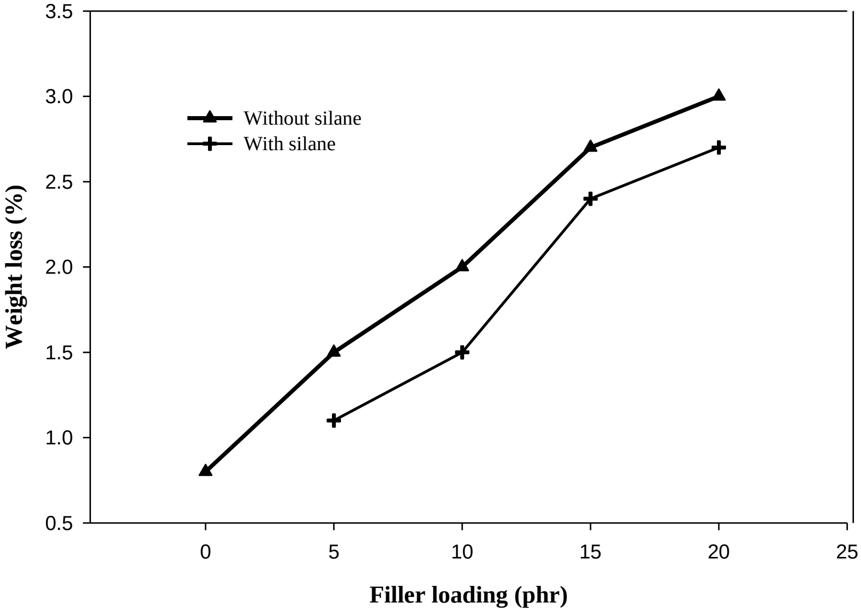

Fig. 9. The weight loss of NR/PKS composites with and without silane after soil burial

Morphological Studies

Figures 10 to 14 show the SEM micrographs of the soil-buried surfaces of the NR/PKS composites after soil burial. Figures 11b and 13b show the micrographs of soil-buried surfaces of NR/PKS composites without the silane coupling agent incorporated, while Figs. 12b and 14b represent the micrographs of soil-buried surfaces of palm kernel shell-filled natural rubber composites with the silane coupling agent added at 5 phr and 20 phr filler loadings, respectively. A study of the morphological properties of NR/PKS composites is beneficial in analyzing the degree of interaction between the filler and the matrix and the biodegradation levels of the composites. The samples were exposed to soil burial for 6 months. The microorganisms' attacks on the surface of the matrix led to surface roughness and the loss of the matrix and the filler (Sareena and Purushothaman 2014). The holes represent cavities in the composite structure that the filler formerly occupied. As the filler loading increased, the formation of voids, cracks, and cavities became more prominent. The effects of biodegradation consisted primarily of changes in the appearances of the NR/PKS composites, such as the spread of hyphae and surface erosion (Muniandy *et al*. 2012). It could be seen that at lower filler loadings, only micro-voids formed, and the surfaces of the samples were left porous. At higher consumption of the lingo-cellulosic components by microorganisms, the presence of surface erosion and hyphae were more pronounced (20 phr PKS). The improved interfacial adhesion of NR/PKS composites can be proved by the lower weight loss compared to composites without silane due to better resistance to the microorganisms and oxidation (Fig. 9).

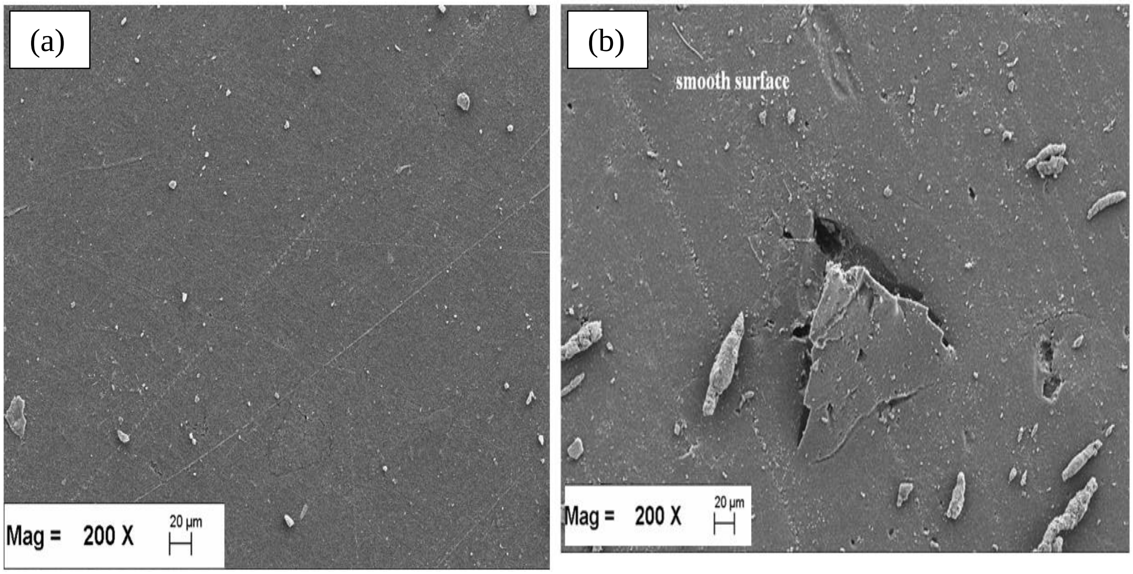

Fig. 10. SEM micrograph of unfilled NR compound (a) before and (b) after soil burial

The natural filler was more prone to bacterial attack than natural rubber, as natural rubber has a higher molecular weight, and it is more difficult to break down the polymer chains. The cellulose degrades first, leaving vacant space, which increases the surface area for the later biodegradation of the NR matrix. Through Figs. 10b, 11b, 12b, 13b, and 14b, the microbial action was more prominent on the filler than on the rubber matrix. This is indicated by the formation of voids and cavities, which were more concentrated in the location where the filler attaches to the rubber matrix.

The extent of filler degradation was also greater for the samples with higher filler loadings. Figures 12(b) and 14(b) illustrate that with the addition of a silane coupling agent, less degradation was observed than for samples without the silane coupling agent added. It can also be seen that the samples with the silane coupling agent had smoother surfaces, which indicated that there was no noticeable effect of bacterial action in these samples due to the strong rubber-filler interaction provided by the silane. The poor adhesion/interaction was indicated by the large amounts of filler extracted after the soil burial.

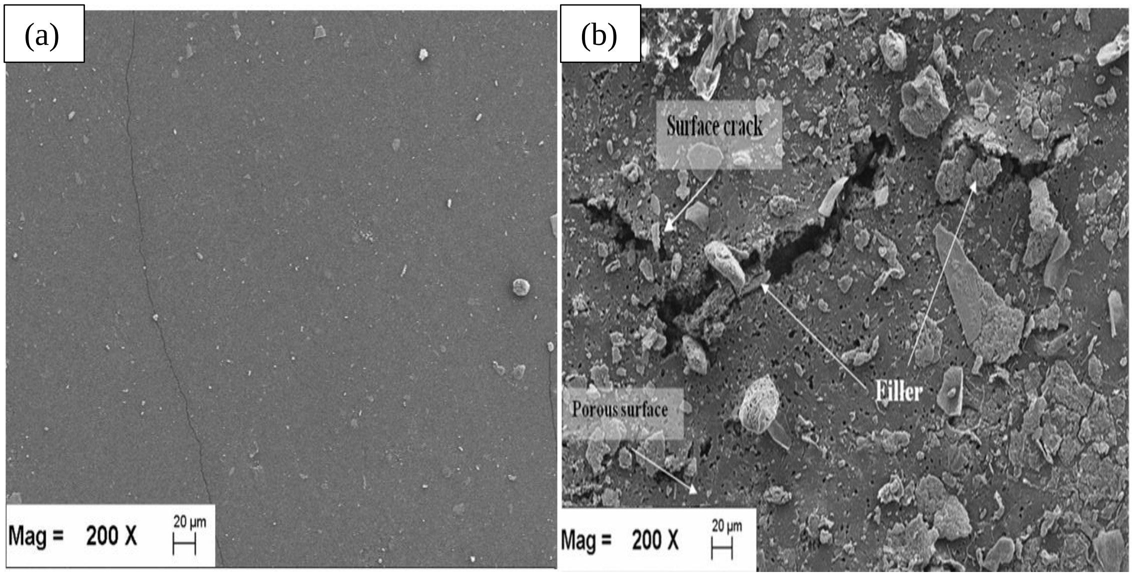

Fig. 11. SEM micrographs of soil-buried surfaces of 5-phr palm kernel shell-filled natural rubber composites without silane (a) before soil burial and (b) after soil burial

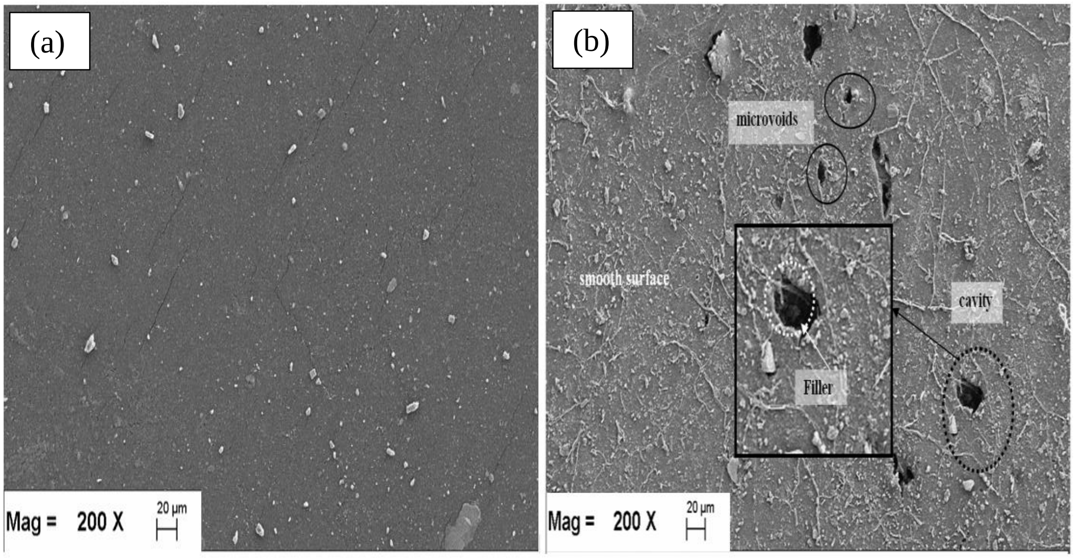

Fig. 12. SEM micrographs of soil-buried surfaces of 5-phr palm kernel shell-filled natural rubber composites with silane (a) before soil burial (b) after soil burial

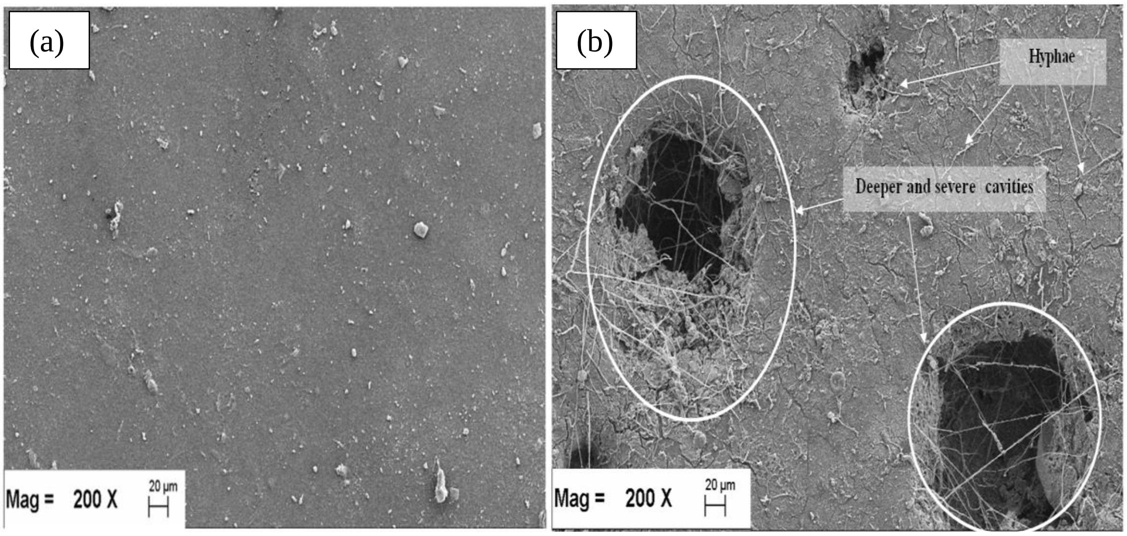

Fig. 13. SEM micrographs of soil buried surfaces of 20 phr palm kernel shell-filled natural rubber composites without silane (a) before and (b) after soil burial

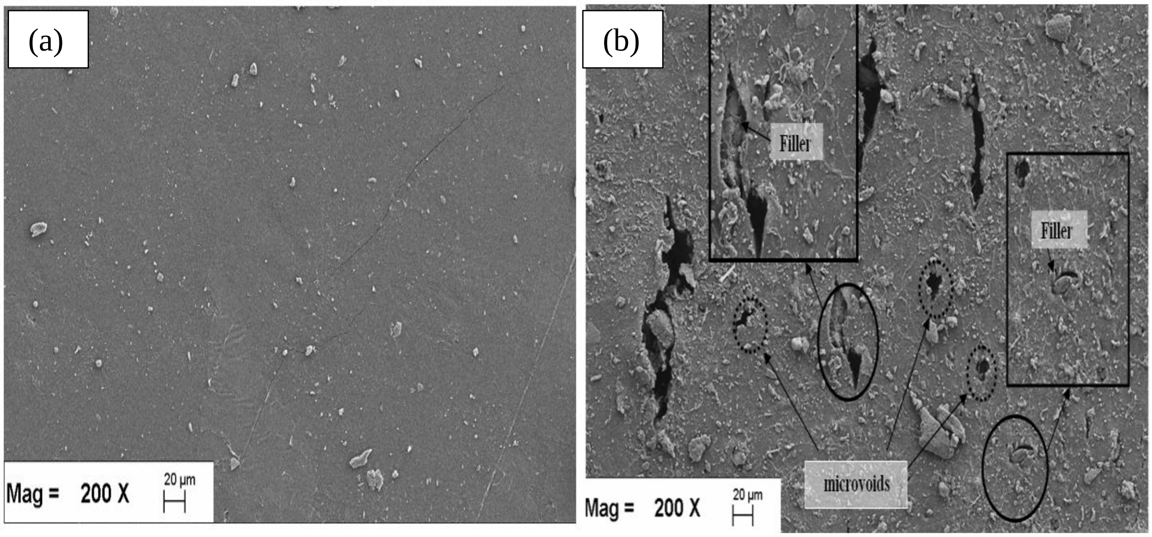

Fig. 14. SEM micrographs of soil buried surfaces of 20 phr palm kernel shell-filled natural rubber composites with silane (a) before (b) after soil burial

CONCLUSION

1. The tensile properties of the NR/PKS composites, namely tensile strength, elongation at break, and moduli M100 and M300, decreased following the soil burial test because of the microbial action on the rubber and the palm kernel shell filler.
2. As the incorporation of the silane coupling agent increased, the tensile properties of the NR/PKS composites, namely tensile strength, elongation at break, and tensile moduli (M100 and M300), improved relative to those without the silane coupling agent because of the better rubber-filler interaction imparted by the silane coupling agent.

3. The IR spectra and SEM showed that the palm kernel shell filler was more prone to microbial attacks than was the natural rubber matrix because of the highly decomposable polysaccharide content in the PKS.

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