BIODEGRADATION, MORPHOLGICAL, AND FTIR STUDY OF RATTAN POWDER-FILLED NATURAL RUBBER COMPOSITES AS A FUNCTION OF FILLER LOADING AND A SILANE COUPLING AGENT

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Natural rubber (NR) composites were prepared by the incorporation of rattan *(Calamus Manan)* powder at filler loadings in the range of 0 to 30 phr into a natural rubber matrix with a laboratory size two roll mill. The particle size of rattan powder was less than 180 µm. The biodegradation of the rattan powder-filled natural rubber (NR) composites were investigated as a function of filler loading and a silane coupling agent. A soil burial test was carried out for six months, and the degradation of the NR compound and the NR composites was evaluated through tensile testing. Morphological properties were determined using scanning electron microscopy (SEM) to evaluate the degradation of the samples after six months of soil exposure. The results indicate that the tensile strength, elongation at break, and stress at 100% elongation (M 100) all decreased after soil burial testing due to the biological attack by microbes onto the sample. Improvement in tensile properties was seen with the addition of the silane coupling agent due to better adhesion between the rattan filler and the rubber matrix. The deterioration in tensile properties due to the biodegradation process was confirmed by SEM and FTIR studies.

Keywords: Biodegradation; Morphological Studies; FTIR; Natural Rubber; Rattan Filler; Silane Coupling Agent

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INTRODUCTION

Ecological concerns have renewed interest in compostable materials and materials made from natural, replenishable resources. Unlike commercial fillers, natural fibers, which are biodegradable and environmentally friendly, have become the centre of attraction in both the academic sector and the industry. Biological organisms recognize the carbohydrate polymers in the cell wall, thus degrading the natural fibers (Saheb and Jog 1999). In addition, natural fibers are cheaper, pose no health hazards, and provide a solution to environmental pollution by finding new uses for waste materials. Moreover, natural fibers, being available in many developing countries, would allow these countries the opportunity to use their own natural resources in their composite processing industries (Hassan et al. 2010; Joseph et al. 1999; Li et al. 2007).

In Malaysia, rattans are abundantly available and are considered the most important non-wood forest product. Rattans are spiny climbing plants belonging to the palm family (Ali and Khoo 1995). Rattan canes are extensively used in the furniture industry and account for a significant proportion of the export revenue for Malaysia. Early in the furniture manufacturing process, approximately 6 inches of each end of the rattan canes, known as rattan poles, must be cut off and thrown away. These rattan poles, which have contributed to waste even before the process begins, often become a burden to the environment through open burning and illegal dumping. At this stage, the waste could already be as high as 10 percent. Financially, 0.20 USD per pole is lost in the waste (Ariffin et al. 2001). Because the waste produced from rattan cane is lightweight, has high strength, and durable it has spurred the interest to be use as filler.

Natural rubber (NR) is a versatile raw material that has a very high structural regularity that provides the material with some unique and important characteristics, namely the ability to crystallize under strain, a phenomenon known as “strain induced crystallization”. The strain-induced crystallization gives NR its very high tensile strength (Chapman 2007; John et al. 2008). Natural rubber is biodegradable, but it is quiet resistant to biodegradation in comparison with other natural polymers as the actions of microorganisms are very low under normal ecological conditions (Rose and Steinbuchel 2005; Shubhra et al. 2010). Since both rattan filler and natural rubber are biodegradable, a composite made from these materials also be expected to be biodegradable.

Natural rubber and rattan filler are highly incompatible, resulting in poor interfacial bonding between the fillers and the matrix. This in turn leads to impaired mechanical properties of the composites (Saheb and Jog 1999). Thus, adequate adhesion across the interface is needed and can be achieved by better wetting and chemical bonding between the filler and the matrix. Generally, chemical coupling agents are used to improve the adhesion or interfacial bonding between the fillers and the matrix (Soykeabkaew et al. 2008). Many researchers have used a silane coupling agent in their research work, as it presents three main advantages: (i) they are commercially available at large scale, (ii) at one end, they bear alkoxysilane groups capable of reacting with OH-rich surfaces, and (iii) at the other end, they have a large number of functional groups that can be tailored as a function of the matrix to be used. The last feature ensures, at least, a good compatibility between the reinforcing element and the polymer matrix or even covalent bonds between them. Such modification was found to be effective in increasing the mechanical properties and durability of composites (Taj et al. 2007).

This paper highlights the use of waste rattan as new type of filler as well as 3-aminopropyltrimethoxysilane (AMEO) as a silane coupling agent in natural rubber composites. Successful use of waste rattan as filler will help create a more environmentally friendly product. The effects of filler loading and silane coupling agent on the biodegradation of rattan powder-filled natural rubber composites were investigated. The studies on curing characteristics, tensile properties, fracture surface morphology, and extent of rubber-filler interaction of rattan powder-filled natural rubber composites were reported in a previous paper (Ismail et al. 2011).

EXPERIMENTAL

Materials and Formulation

Table 1 shows the formulation, materials, and their manufacturer used in this research study (Ismail et al. 2011).

Table 1. Formulation of Rattan Powder Filled NR Composites

Ingredients	Formulation [phr]		Manufacturer
	1st Series	2nd Series	
Natural Rubber	100	100	Rubber Research Institute of Malaysia
Rattan	0, 5, 10, 15, 30	5, 10, 15, 30	Seng Huat Shop
Zinc Oxide	1.5	1.5	Bayer (M) Ltd
Stearic Acid	1.5	1.5	Bayer (M) Ltd
CBS[a]	1.9	1.9	Bayer (M) Ltd
BKF[b]	2.0	2.0	Bayer (M) Ltd
Sulphur	1.6	1.6	Bayer (M) Ltd
Silane coupling agent (AMEO)[c]	-	1.0	Bayer (M) Ltd

[a]CBS - N-cyclohexyl-2-benzolthyazolsulfenamide
[b]BKF - 2,2 methylene-bis-(4-methyl-6-tert-butylphenol)
[c]AMEO – 3- aminopropyltrimethoxysilane

Sample Preparation

Rattan (*Calamus Manan*) wastes were collected, cleaned, ground, and sieved for an average particle size of less than 180 µm. The chemical composition and physical and mechanical properties of rattan are shown in Table 2 (Ismail et al. 2011). Mixing for both series was carried out in a laboratory model two-roll mill according to American Standard of Testing Material (ASTM) designation D 3184-80. The first series did not include the addition of the silane coupling agent, while the second series involved the addition of silane coupling agent. The cure characteristics of rubber compounds were studied using a Monsanto Rheometer, model MDR 2000 at 150°C. Cure time (t_{90}), scorch time (t_{s2}), and maximum torque (M_H) were obtained from the rheographs. The rubber compounds were molded into sheets with the respective cure time, t_{90} at 150°C using a hot press machine.

Table 2. Chemical Composition, Physical and Mechanical Properties of Rattan, *Calamus Manan*

Properties		Approximate Value
Physical Properties	Specific gravity	0.55
	Density	0.54 g/cm^3
Mechanical Properties	Tensile strength	690 kg/cm^2
	Bending strength	636 kg/cm^2
	Compressive strength	216 kg/cm^2
	Modulus of elasticity	31302 kg/cm^2
Chemical Composition	Holocellulose	78.43 %
	Lignin	21.97 %
	Ash	1.37 %
	Hot water soluble	6.01 %
	Cold water soluble	3.63 %
	1% alkali soluble	22.47 %
	Alcohol-benzene soluble	2.9 %

Soil Burial Test

Dumbbell-shaped samples were cut from vulcanized rubber sheets, placed in a polybag containing decomposed soil, and buried in garden soil for six months. After six months, the samples were withdrawn, washed with distilled water, and dried at room temperature. The degradation was assessed and evaluated by measuring the tensile properties before and after soil burial. Tensile testing was carried out according to ASTM D 412 at a constant rate of 500 mm/min using an Instron Universal testing machine (Instron, model 3366, United States of America). Five samples were tested, and the average three results were reported.

Scanning Electron Microscopy (SEM)

Examination of the soil buried surfaces was carried out using scanning electron microscopy (Zeiss Supra 35vp, Germany). The fracture surfaces were sputter-coated with gold to avoid electrostatic changing and poor image resolution. The degradation of the samples was determined from the micrograph. Only one sample was examined for each condition.

Fourier Transform Infrared (FTIR)

The chemical changes in samples before and after soil burial were detected using Fourier-transform infrared spectroscopy (Perkin Elmer System 2000, United States of America). The FTIR spectra were recorded in the range of 550 to 4000 cm^{-1} wave numbers with an average of 24 scans. Only one samples tested for each composites.

RESULTS AND DISCUSSION

Tensile Properties

Figures 1, 2, and 3 display tensile properties such as tensile strength, elongation at break, and stress at 100% elongation (M 100) of the unfilled natural rubber compound and the rattan-powder filled NR composites with and without the silane coupling agent and before and after soil burial.

The tensile strength and elongation at break showed a decreasing trend, whereas, M100 showed an increasing trend with increasing filler loading for both samples with and without the silane coupling agent, before and after the soil burial test. The results of tensile strength of all of the samples are shown in Fig. 1. The reduction in tensile strength was due to poor adhesion between the rattan filler and the rubber matrix. As a result, the ability of matrix to transfer stress efficiently to the rattan filler was reduced. Therefore, the tensile strength decreased with increasing filler loading. The inclusion of unstrained rattan fillers into the rubber matrix reduced the flexibility of the composites, resulting in stiffer composites and leading to poorer resistance to break. Thus, the elongation at break decreased and the modulus increased with increasing filler loading, as presented in Figs. 2 and 3, respectively. Tensile strength was seen to improve with the addition of the silane coupling agent. For instance, at 5 phr rattan loading, the tensile strength was improved about 4 MPa and comparable to the unfilled NR compound. This showed that the silane coupling agent enhanced the wettability of the rattan filler by the rubber matrix and consequently promoted the interfacial adhesion. Rubber-rattan interaction increased, and the effectiveness of stress transferred from the matrix to the rattan also improved. Based on Figs. 2 and 3, the elongation at break further dropped, whilst, M 100 increased with the addition of the silane coupling agent. Again, this can be attributed to the better adhesion between the rubber matrix and the rattan fillers, which has been demonstrated by an FTIR study (Ismail et al. 2011). The FTIR result will be explained in detail under the FTIR subsection.

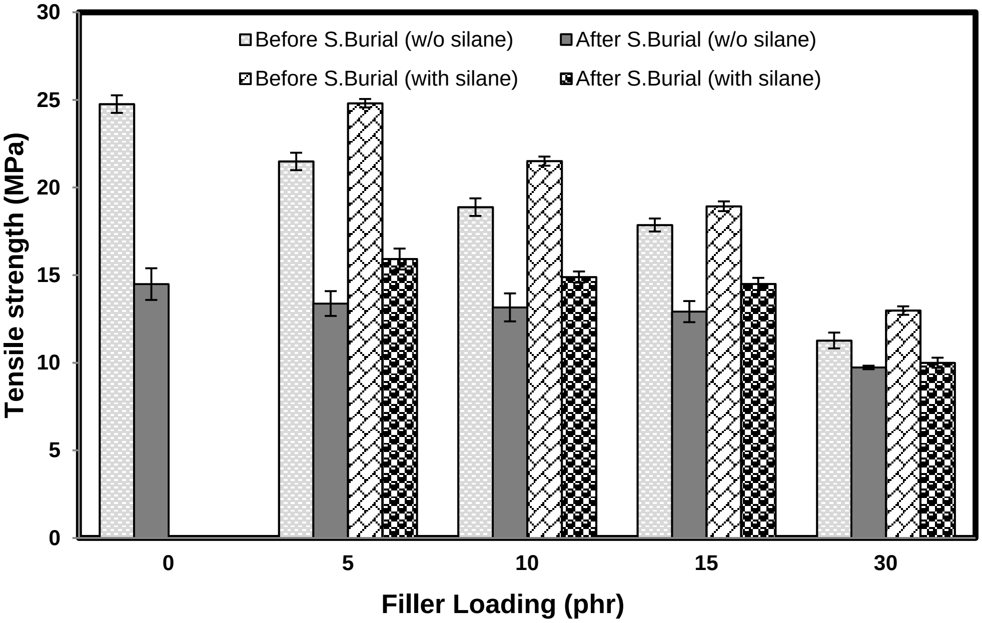


Fig. 1. The effect of filler loading and silane coupling agent on tensile strength of rattan powder-filled natural rubber composites before and after soil burial

After 6 months of soil exposure, the deterioration in tensile properties was observed for both samples with and without silane coupling agent as compared to the composites before soil burial test, as shown in Figs. 1 through 3. The deterioration in tensile properties was due to the degradation of the natural rubber and the rattan filler upon soil exposure. A reduction with an average of 30%, 25% and 8% was observed in tensile strength, elongation at break and M100 respectively for all samples. Biodegradation of vulcanized rubber is possible, although it is difficult due to the inter-linkages of the rubber chains. Natural rubber can be degraded by the action of specific microorganisms such as *Pseudomonas*. *Pseudomonas* is a commonly found gram-negative bacterium that has the capacity to utilize hydrocarbons (Jacob et al. 2007; Roy et al. 2006). Studies using various microorganisms indicate that during rubber biodegradation, as a first step, oxidative cleavage of the double bond in the rubber backbone should take place. This is because natural rubber is a high molecular mass compound and is too bulky to be effectively attacked by bacteria. Natural rubber, which is highly unsaturated and quite susceptible to oxidative degradation, produces short oligomers by the scission of longer polymeric chains of natural rubber (Rose and Steinbuchel 2005; Rifaat and Yosery 2004). Upon longer exposure, the short oligomers are metabolized by the microorganisms. Adding on, these shorter oligomers or chains also reduced the rubber chain entanglements. Consequently, the ability of the rubber matrix to transfer stress efficiently was also reduced. Hence, the tensile strength was reduced after soil exposure, as represented in Fig. 1. In addition, the reduction in rubber chain entanglements also tended to reduce the elongation at break and M100 of the samples. The elongation at break was reduced as the rubber chains were unable to entangle with each other and were not capable of stretching much, due to the shorter chains. Thus, the flexibility of the rubber chains was reduced and the elongation at break also decreased, as shown in Fig. 2. Meanwhile, the reduction of rubber chain entanglement with the loss of some shorter rubber chains during soil exposure made the rubber become soft and reduced in stiffness. Thus, M100 (Fig. 3) of all samples are noted to reduce after the soil exposure.

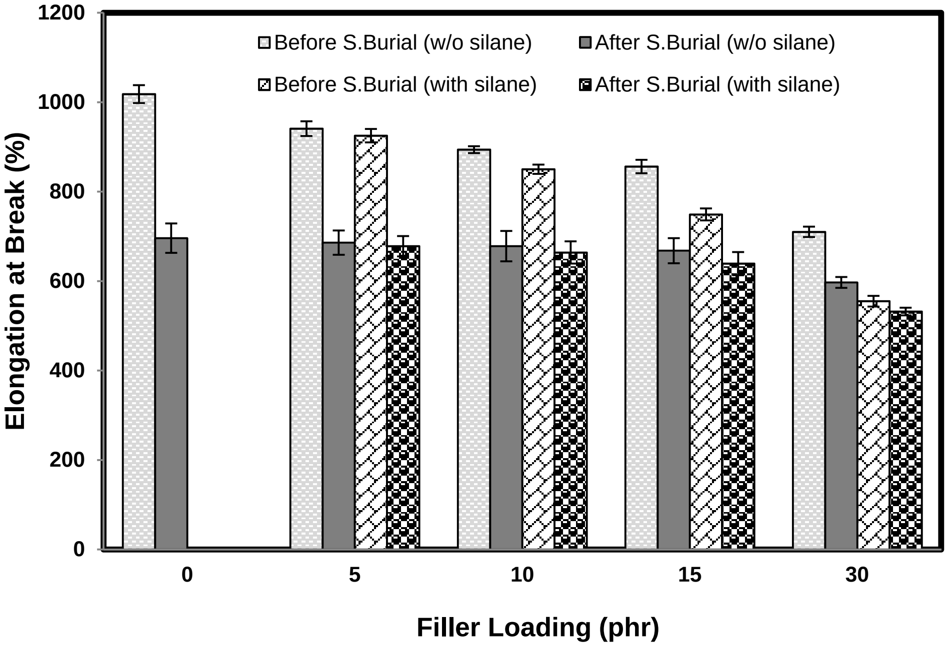


Fig. 2. The effect of filler loading and silane coupling agent on elongation at break of rattan powder-filled natural rubber composites before and after soil burial

During the soil exposure, the rattan fillers are also exposed to soil and degraded. Rattan is a type of natural fiber consisting of cellulose and lignin, which can degrade biologically, as they are more susceptible to decomposition by microorganisms (Huq et al. 2010). Microorganisms can recognize the carbohydrate polymers in the cell wall and have very specific enzyme systems capable of hydrolyzing these polymers into digestible units so that fiber structure is impaired and fiber strength decreased (Rowell 1995, Jacob et al. 2007). However, the extent of degradation of rattan filler is less, compared to the rubber matrix. This is because the biodegradation of natural rubber is a slow process, and the growth of bacteria utilizing rubber as a sole carbon source is also slow (Shubhra et al. 2010). The microbial attack will take place on the surface, leading to surface erosion. The rattan fillers are expected to degrade soon after the matrix degradation. Thus, not much rattan was observed to degrade, as illustrated in the SEM micrograph. The SEM results will be described in a later subsection. The major contribution of rattan fillers degradation towards the properties of samples are aesthetic effects such as surface checking and growth of hyphae, which can be clearly seen in SEM micrograph, Figure 7 (a).

Nevertheless, the addition of the silane coupling agent improved the tensile strength and the durability of the composites. Based on Figs. 1 and 3, an improvement with an average of 10% was achieved for tensile strength and an average of 12% for M100 of samples with silane coupling agent as compared to without silane coupling agent after the soil exposure. Meanwhile, a reduction with an average of 5% was seen for elongation at break, shown in Fig. 2. As mentioned earlier, this improvement resulted from the proper wetting between the rubber matrix and the rattan filler by the silane coupling agent, leading to a better interfacial adhesion. The presence of silane coupling agent with the better adhesion between rubber matrix and rattan filler can act as a protective covering to the action of microorganism present in soil (Jacob et al. 2007).

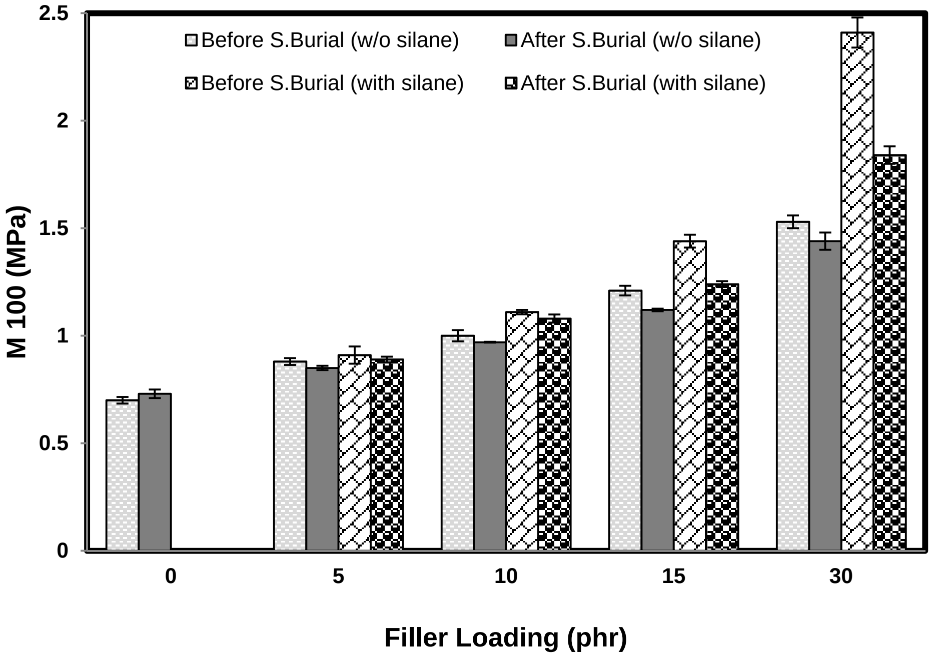


Fig. 3. The effect of filler loading and silane coupling agent on stress at 100% elongation (M100) of rattan-powder filled natural rubber composites before and after soil burial

Morphological Studies

Figure 4 shows SEM micrographs of soil buried surfaces of the unfilled natural rubber (NR) compound, while Figs. 5 (a) and 6 (a) represent SEM micrographs of soil buried surfaces of the rattan powder-filled NR composites at 5 and 30 phr rattan loading, respectively. SEM micrographs of composites with the addition of the silane coupling agent for both 5 and 30 phr loading are shown in Figs. 5 (b) and 6 (b). These SEM micrographs reflect the results obtained from tensile studies.

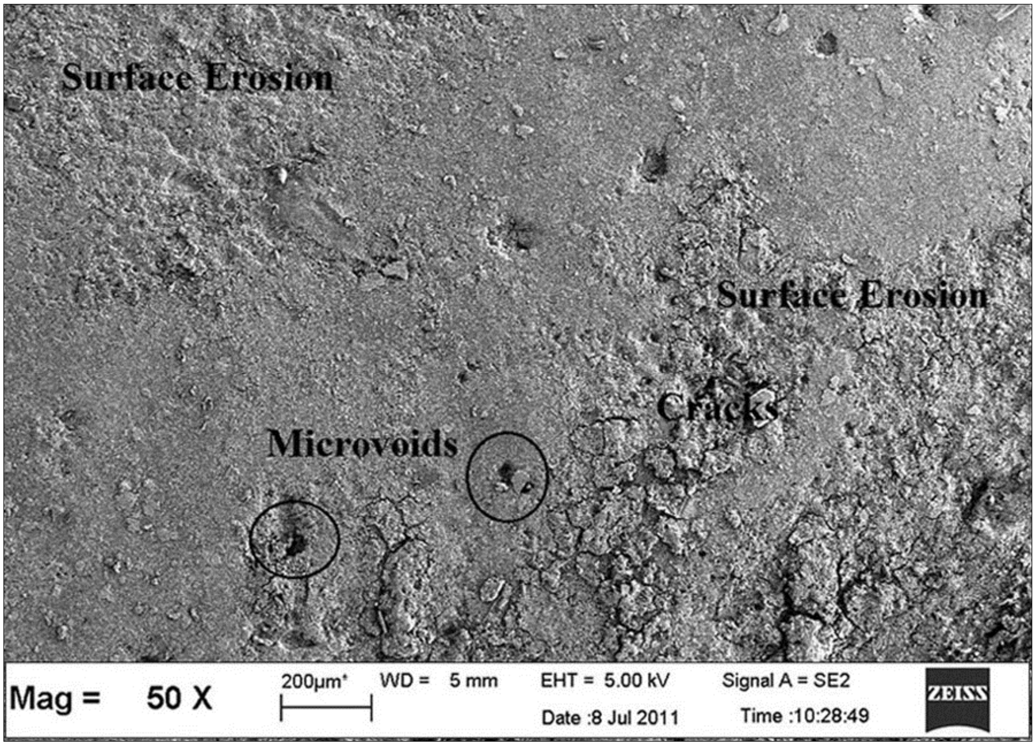


Fig. 4. SEM micrograph of soil buried surfaces of unfilled NR compound at magnification of 50×

The microbial attack took place on the sample surface, which was accompanied by massive loss of oligomers, leading to an eroded surface. This observation was evidenced through the increase in surface roughness and erosion, which was detectable in the rubber matrix as the filler loading increased. In addition, formations of cracks and micro voids were also found on the samples. As mentioned previously, short oligomers produced by oxidative degradation will be metabolized by the microorganisms leading to micro voids and an eroded surface. This occurrences was observed clearly in the SEM micrographs at a magnification of 50×, as seen in Figs. 4, 5 (a), 5 (b), 6 (a), and 6 (b). Manzur et al. (2004) reported similar observations in their study of biodegradation of polyethylene and suggested that the presence of cavities on the surface might be due to the absence of a uniform distribution of short branches in the polymer matrix.

A clearer picture of biodegradation of the composites is displayed in Figs. 7 (a) and 7 (b), at a magnification of 300×. The bacterial action on surface of filler and the degradation of the rattan filler in the composites are visible in Fig. 7 (a). Formation of hyphae in the sample surface along with surface checking such as formation of cavities on rattan surface and splitting of rattan filler are also found on the sample surface. This demonstrates that degradation of rattan has taken place. From Figs. 4 through 6, in all sample surfaces, the microorganism attacks are more on the rubber matrix compared to the rattan filler. This indicates that the extent of rattan degradation is less compared to the matrix degradation. Figures 5 (b), 6 (b), and 7 (b), illustrate that with the addition of the silane coupling agent, less degradation occurred than for the samples without the silane coupling agent. At 30 phr filler loading, samples without silane coupling agent showed higher degradation compared to samples with the silane coupling agent, as displayed in Figs. 7 (a) and (b).

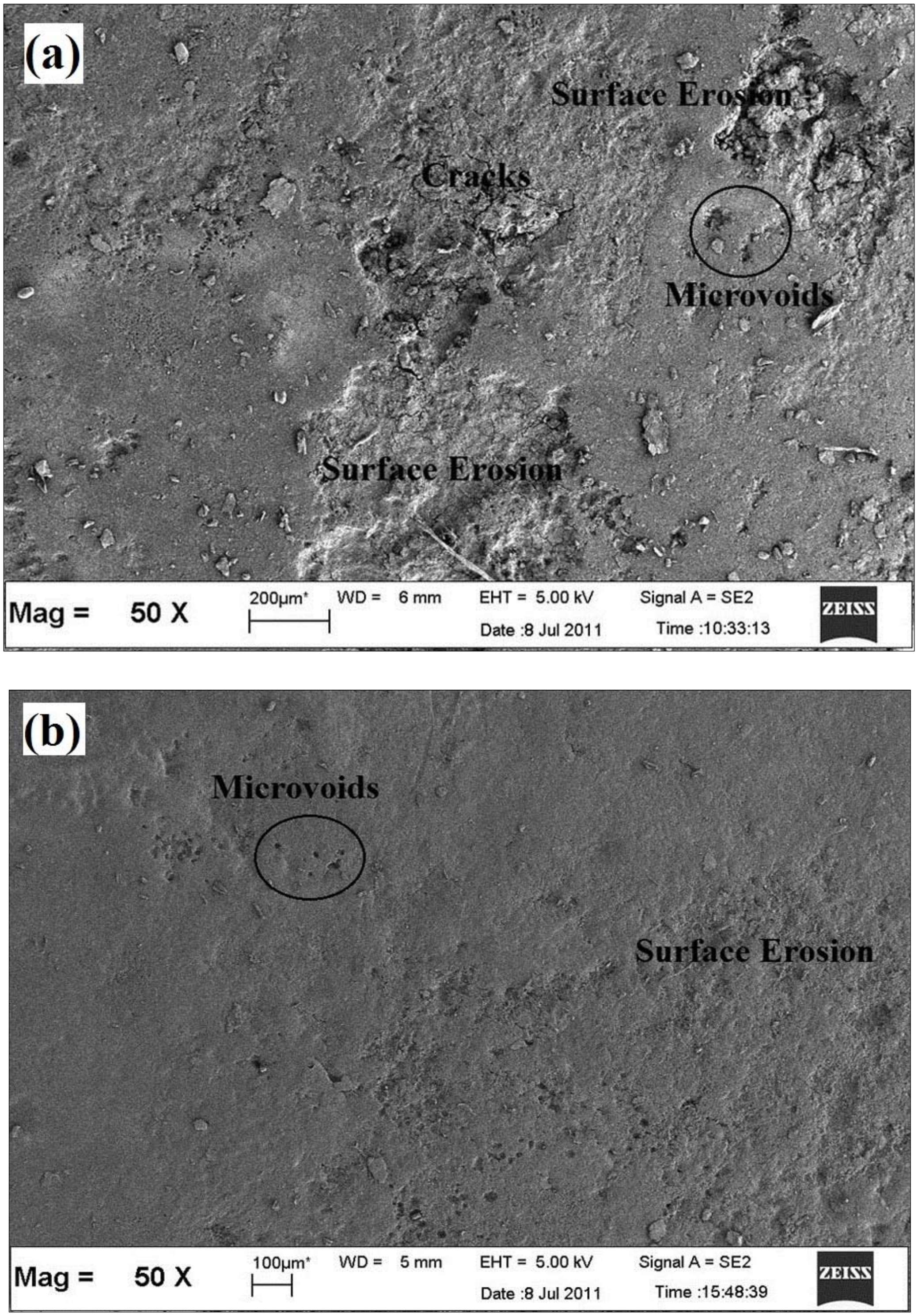


Fig. 5. SEM of soil buried surfaces of 5 phr rattan powder-filled natural rubber composites at magnification of 50× (a) without silane coupling agent (b) with silane coupling agent

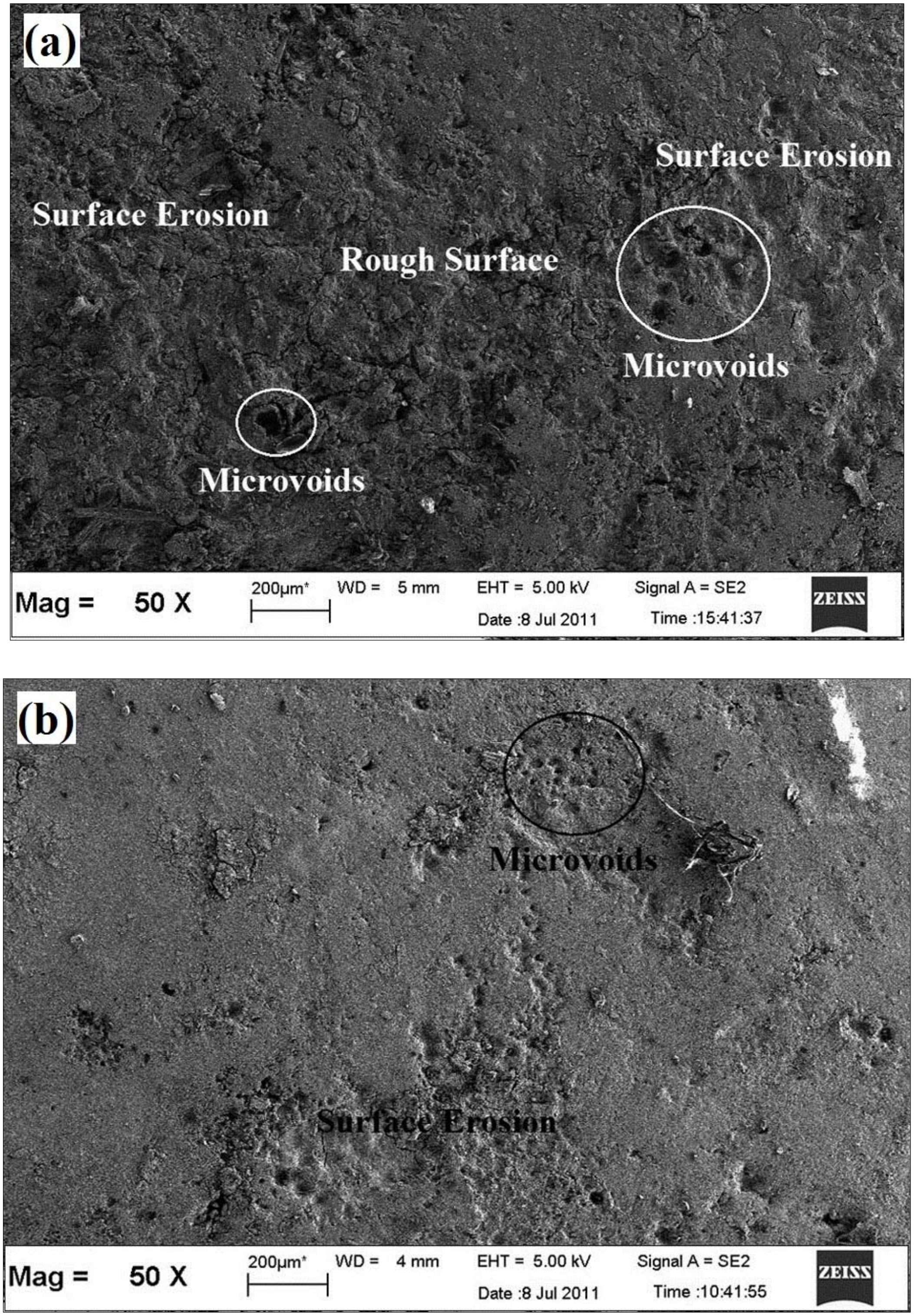
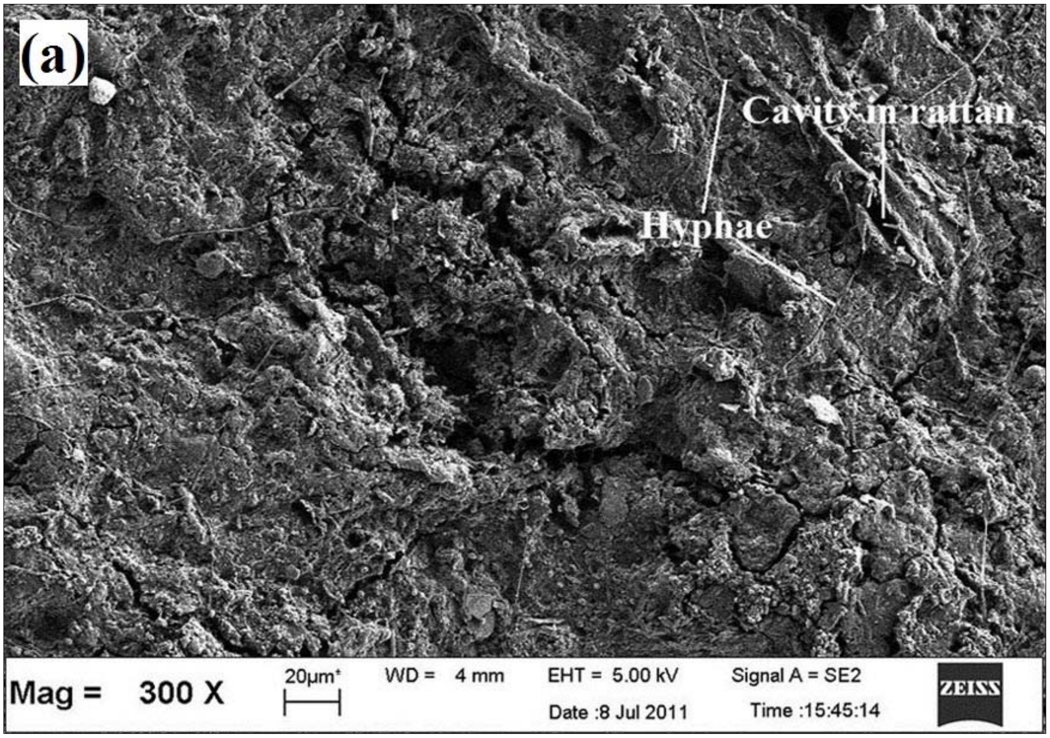
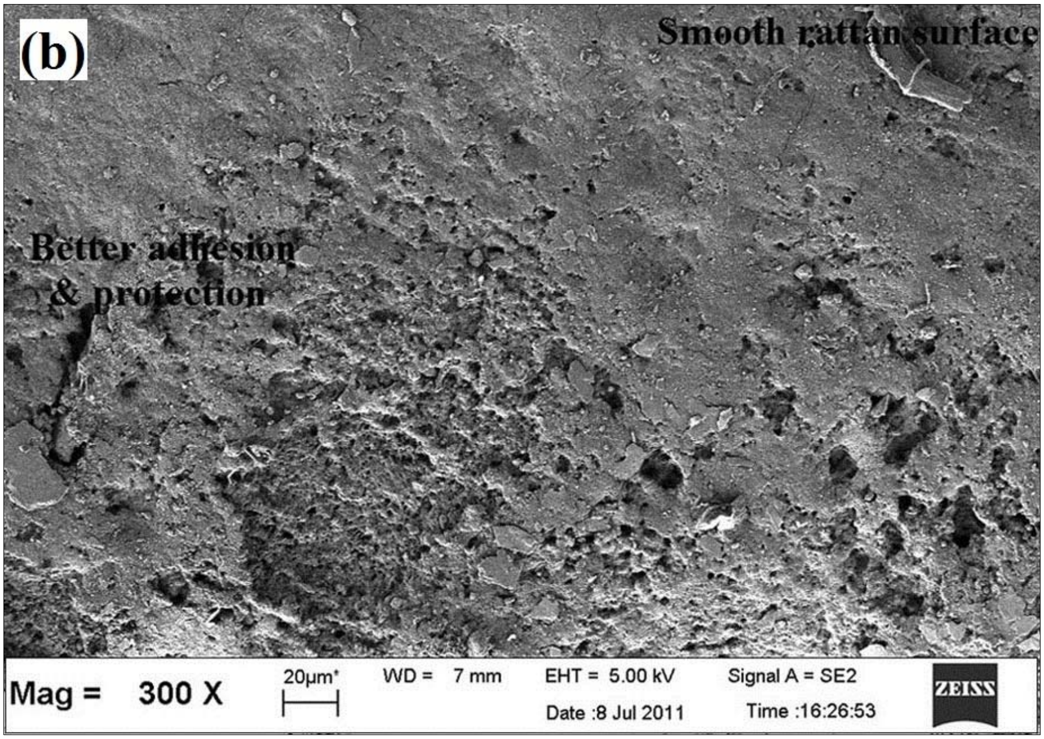


Fig. 6. SEM micrograph of soil buried surfaces of 30 phr rattan powder-filled natural rubber composites at magnification of 50× (a) without silane coupling agent (b) with silane coupling agent



(a)



(b)

Fig. 7. SEM of soil buried surfaces of 30 phr rattan powder-filled natural rubber composites at magnification of 300× (a) without silane coupling agent (b) with silane coupling agent

Rattan filler was found to have a smoother appearance, revealing that it was less attacked by microorganisms. This is due to good interaction between the rattan and the matrix, resulting in the formation of a better interfacial adhesion. Apart from that, the silane coupling agent protects the rattan and prevents it from degradation.

Fourier Transform Infrared (FTIR)

Figures 8 a(i) and 8 a(ii) show the FTIR spectra of rattan powder filled natural rubber (NR) composites without and with silane coupling agent, respectively, before soil burial. The FTIR results of samples after the soil burial test are presented as in Figs. 8 b(i) and 8 b(ii), in accordance with samples without and with silane coupling agent. Based on Figs. 8 a(ii) and 8 b(ii), sample with the silane coupling agent before and after soil exposure showed two additional peaks in the FTIR spectrum as compared to samples without silane coupling agent (Figs. 8 a(i) and 8 b(i)). These peaks are found in the region of 1172 cm^{-1} and 1586 cm^{-1} which corresponds to C-N stretching and silanes (Si-O-C) respectively, as displayed in Fig. 8a(ii) and 8b(ii). The formation of these bonds shows that the silane coupling agent resulted in better interaction between the rattan filler and the rubber matrix.

Changes in the FTIR spectra are seen after the soil burial (Figs. 8 b(i) and 8 b(ii)) with formation and disappearance of some peaks. Carbonyl (C=O) and ether (C-O-C) groups are apparent in the region of 1717 cm^{-1} and 1020-1050 cm^{-1}, respectively, before and after soil burial. After soil exposure, the intensity of carbonyl and ether bonds was increased. New peaks were also spotted at 3200-3400 cm^{-1} and 1632 cm^{-1}, which were attributed to hydroxyl (OH) and carbonyl (C=O) groups, respectively. The intensity of peaks at 2916 cm^{-1}, 2845 cm^{-1}, and 1456 cm^{-1} was attenuated, while the intensity of peaks in the regions of 744 cm^{-1} and 723 cm^{-1} disappeared with soil exposure. These peaks are assigned to C-H bonds from alkyl groups. These changes confirm the degradation of sample.

CONCLUSIONS

1. Tensile properties such as tensile strength, elongation at break, and stress at 100% elongation (M 100) decrease after soil burial testing due to the biological attack or biodegradation process of the rubber matrix and the rattan filler.
2. The presence of a silane coupling agent improves the tensile properties of NR composites compared to composites without a silane coupling agent owing to the better rubber-rattan adhesion.
3. The deterioration and improvement of tensile properties was confirmed by analyzing the degradation on the surface of soil-buried samples by use of SEM studies.
4. The FTIR results showed evidence of the degradation process.

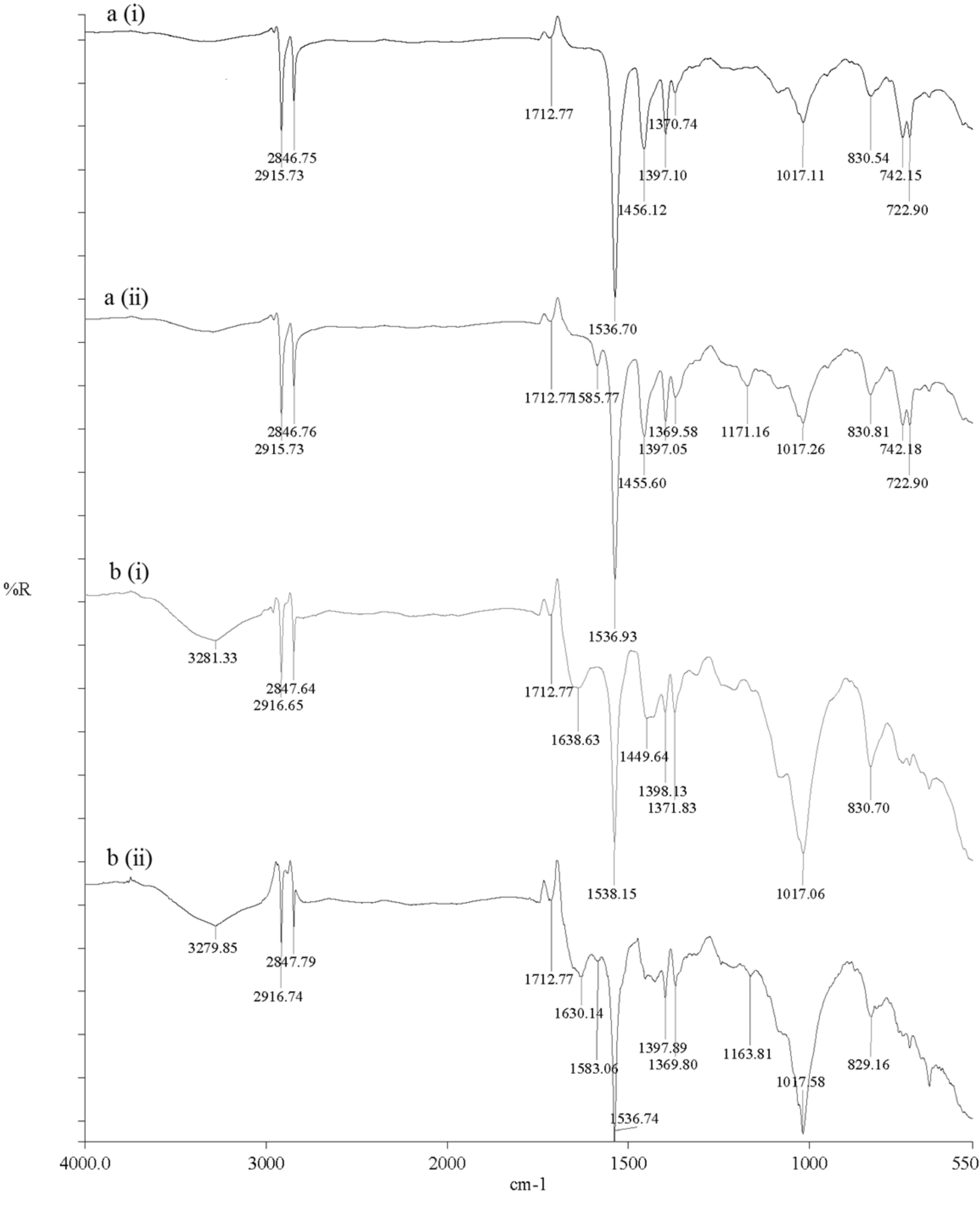


Fig. 8. FTIR spectrum of 30 phr rattan powder-filled natural rubber composites (a) before (b) after soil burial test; (i) without silane coupling agent (ii) with silane coupling agent

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