Curing Characteristics and Mechanical Properties of Rattan-Powder-Filled Natural Rubber Composites as a Function of Filler Loading and Silane Coupling Agent

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ABSTRACT: Curing characteristics, tensile properties, morphological studies of tensile fractured surfaces using scanning electron microscopy (SEM), and the extent of rubber filler interactions of rattan-powder-filled natural rubber (NR) composites were investigated as a function of filler loading and silane coupling agent (CA). NR composites were prepared by the incorporation of rattan powder at filler loading range of 0–30 phr into a NR matrix with a laboratory size two roll mill. The results indicate that in the presence of silane CA, scorch time (t_{s2}), and cure time (t_{90}) of rattan-powder-filled NR composites were shorten, while, maximum torque (M_H) increased compared with NR composites without silane CA. Tensile strength and tensile modulus of composites were enhanced whereas elongation at break reduced in the presence of silane CA mainly due to increase in rubber-filler interaction. It is proven by SEM studies that the bonding between the filler and rubber matrix has improved. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 2805–2811, 2012

Key words: natural rubber; rattan; silane coupling agent; cure characteristics; tensile properties; rubber-filler interaction; scanning electron microscopy

INTRODUCTION

Natural rubber (NR) has a very uniform microstructure that provides the material with unique and important characteristics, namely ability to crystallize upon stretching, a phenomenon known as "strain induced crystallization."[1] However, in most cases; fillers are added into NR to gain appropriate properties for specific applications. A wide variety of fillers are used in the rubber industry for various purposes, of which the most important are reinforcement, reduction in material costs, and improvements in processing.[2]

Recently the uses of natural fibers as replacement for man-made or commercial filler in fiber-reinforced composites have attracted the attention of scientists and technologists because of their advantages over commercial fillers. Natural fibers are environmentally friendly, fully biodegradable, readily and abundantly available, cheap and have low density. However, a notable drawback of natural fiber in composites is the polarity of natural fiber which results in poor compatibility with hydrophobic matrix.[3–5] Extensive works has been carried out to investigate the use of natural fibers such as bamboo, rice husk, and oil palm wood and fiber as filler in natural rubber composites. Results report that the downside of using these natural fibers is that it causes a drop in the mechanical properties of the composites and the effect is more drastic at higher filler loading compared with unfilled NR vulcanizates.[6–9]

This drawback can be remedied by few methods such as the use of coupling agents or compatiblizing agents and fiber surface treatments to improve the wettability of natural fiber by polymers and promote interfacial adhesion.[5,10,11] Silane coupling agent is recognized as one of an efficient coupling agent extensively used in polymer composites. Silane has bifunctional groups which can react with both natural fiber and polymer matrix and form a bridge between them. This brings to an enhancement in adhesion of natural fiber to polymer and forms a uniform composite structure.[11,12]

This paper highlights the use of rattan as new type filler and 3-aminopropyltrimethoxysilane (AMEO) as silane coupling agent in natural rubber composites. Rattans are abundant natural resource in Malaysia where it is used extensively in furniture industry. The furniture industries generates waste rattans every year, which is either land filled, burnt off or disposed. Moreover, rattan is lightweight, strong, and durable cane therefore spurred the interest to be use as rubber reinforcement.[13] Thus, for the

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TABLE I
Formulation of Rattan-Powder-Filled NR Composites

Ingredients	Formulation (phr)		Supplier
	Series 1	Series 2	
Natural rubber (STR 5L)	100	100	Rubber Research Institute 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-benzothiazolsulfenamide.
[b] BKF, 2,2 methylene-bis-(4-methyl-6-tert-butylphenol).
[c] AMEO, aminopropyltrimethoxysilane.

purpose of this research, waste rattan will be used. A successful use of rattan as filler will help ease the shortage of land besides creating a more environmentally friendly product. The effect of filler loading and silane coupling agent on curing characteristics, tensile properties, rubber-filler interaction, and tensile fracture surface study using scanning electron microscopy (SEM) of rattan-powder-filled natural rubber composites were investigated.

EXPERIMENTAL

Materials and formulation

Table I shows the formulation, materials, and their suppliers used in this research study. Rattan wastes were collected, cleaned, grounded and sieved into average particle size less than 180 μm. The chemical composition, physical, and mechanical properties of rattan are shown in Table II. The rattan used in this study belongs to the species of *Calamus manan*.[14,15]

Sample preparation

Mixing for two series were carried out in a laboratory model two roll mill according to American Standard of Testing Material (ASTM) designation D 3184-80. The first series was without the addition of silane coupling agent while second series involve 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 respective cure time, t_{90} at 150°C using hot press machine.

Measurement of tensile properties

Dumbbell-shaped samples were cut from vulcanized rubber sheets using Wallace die cutter. Tensile test

was carried out according to ASTM D 412 using Instron Universal testing machine, model 3366 at test temperature of 23°C and at constant rate of 500 mm/min. Five samples were tested and average three results were reported. Tensile properties such as tensile strength, tensile modulus and elongation at break were obtained from tensile testing.

Scanning electron microscopy

Examination of the tensile fracture surfaces was carried out using a SEM, Zeiss Supra 35vp. The fracture surfaces were sputter coated with gold to avoid electrostatic changing and poor image resolution. The rubber-filler interactions and filler dispersion were evaluated from the micrograph.

Rubber-filler interaction

The vulcanized sample (30 mm × 5 mm × 2 mm) were accurately weighed and immersed in toluene and allowed to swell in closed bottle for 72 h at room temperature (25°C). The sample was removed

TABLE II
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 %
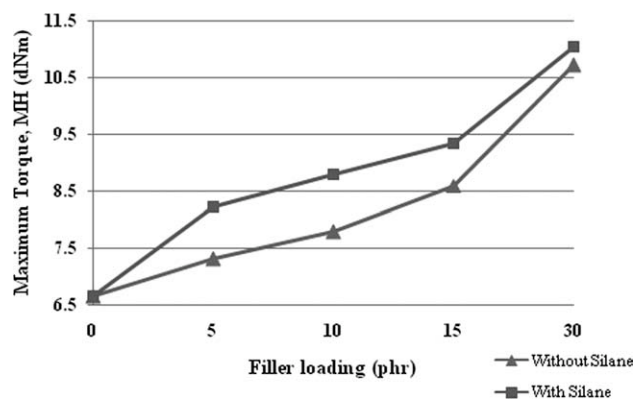
Figure 1 The effect of filler loading and silane coupling agent on maximum torque of rattan-powder-filled natural rubber composites.

and the surface of swollen sample was quickly wiped and weighed. The sample was dried in an oven at 70°C for 15 min and weighed. Q, the weight of toluene uptake per gram of rubber hydrocarbon was determined according to the eq. (1).

$$Q = \frac{\text{Swollen weight} - \text{Dried weight}}{\text{Original weight} \times 100/\text{Formula weight}} \quad (1)$$

The rubber-filler interaction was calculated using Lorenz and Park equation as eq. (2):

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

The subscripts f and g in eq. (2) refer to filled and gum vulcanizates, respectively. Z is the ratio by weight of filler to rubber hydrocarbon in the vulcanizate, while a and b are constants. The higher the Q_f/Q_g values, the lower will be the extent of interaction between filler and matrix.

RESULTS AND DISCUSSION

Curing characteristics

The cure characteristics; maximum torque (M_H), cure time (t_{90}), and scorch time (t_{s2}) of unfilled NR vulcanizate and rattan-powder-filled natural rubber (NR) composites with and without silane coupling agent (CA) are presented in Figures 1–3 respectively. From Figure 1, it is clear that the maximum torque (M_H) for both cases increases with an increase in rattan loading. These probably due to the inclusion of rigid and hard rattan into soft rubber matrix which tends to immobilize the movement of macromolecular rubber chains. The more rattan is added, the more restriction in mobility is experienced by the rubber chains and as a result natural rubber composites become harder and stiffer.[16–20] Besides, Costa
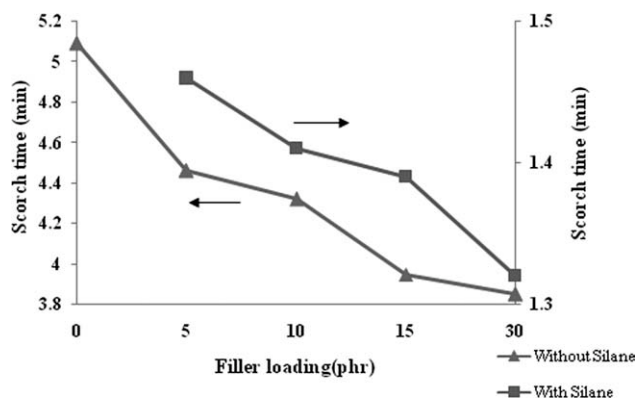
et al.[8] reported that this phenomenon leads to difficulties in mixing. Thus, M_H increases as rattan loading increases. On the other hand, at similar rattan loading, NR composites with the addition of silane CA show higher M_H value. This expected increase arises due to silane CA which promotes better rubber-rattan interactions leading to additional cross-links in the network structure.[21]

Figures 2 and 3 display the cure time (t_{90}) and scorch time (t_{s2}) of unfilled NR vulcanizate and natural rubber (NR)/ rattan powder composites. The t_{90} and t_{s2} of both NR composites with and without silane CA are shorter than of unfilled NR vulcanizates and slightly decreases as rattan loading increases. Several researchers[7,16,22] also reported similar results in their research work. Da Costa et al.[8] and Ismail et al.[23] explained that the cure enhancement usually can be related to filler associated parameters such as surface area and particle size. In this study, the probable reason for the decrease of t_{90} and t_{s2} as increasing rattan loading is the lower surface area of irregularly shaped rattan powders. The t_{90} and t_{s2} of NR composites in the presence of silane CA become
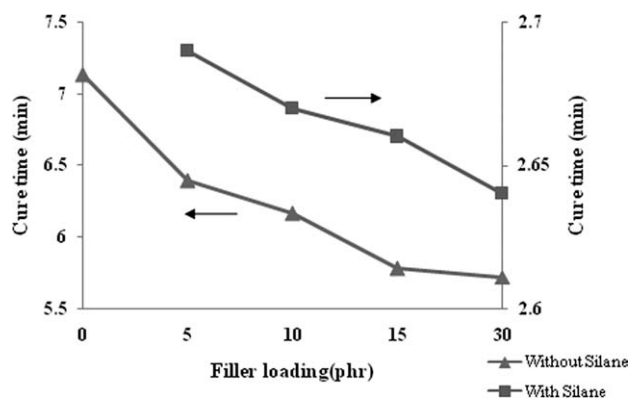

Figure 2 The effect of filler loading and silane coupling agent on scorch time of rattan-powder-filled natural rubber composites.

Figure 3 The effect of filler loading and silane coupling agent on cure time of rattan-powder-filled natural rubber composites.

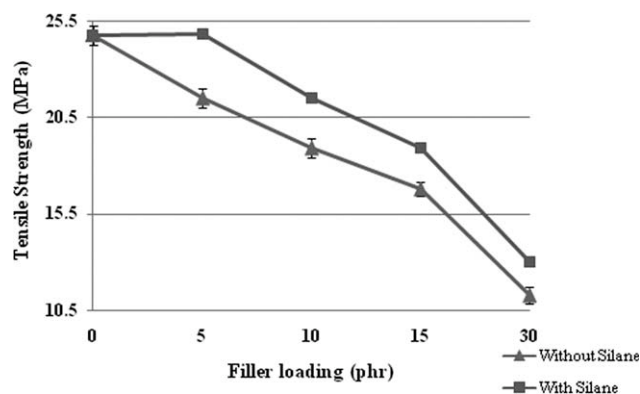**Figure 4** The effect of filler loading and silane coupling agent on tensile strength of rattan-powder-filled natural rubber composites.

Figure 6 The effect of filler loading and silane coupling agent on stress at 100% elongation (M 100) of rattan-powder-filled natural rubber composites.

shorter compared to NR composites without silane. An average reduction of 55% is seen for cure time as well as reduction of 66% in scorch time. This is due to the ability of silane CA which helps to have better dispersion of rattan particles in rubber matrix apart from establishing molecular bridges at the interface between the NR matrix and rattan surface. Furthermore, the catalytic role of amine group in silane CA [3-aminopropyltrimethoxysilane (AMEO)] which is similar to commercial accelerator such as N-cyclohexyl-2-benzothiazolsulfenamide (CBS) has the ability to accelerate the vulcanization process causing reduction in t_{90} and t_{s2}.[6,8,11]

Tensile properties

Tensile properties such as tensile strength, elongation at break, and tensile modulus; stress at 100% elongation (M 100) and stress at 300% elongation (M 300) of unfilled NR vulcanizates and rattan-powder-filled NR composites are plotted as in Figures 4–7. According to Figure 4, tensile strength of rattan-powder-filled NR composites shows decreasing trend as increasing rattan loading as compared to
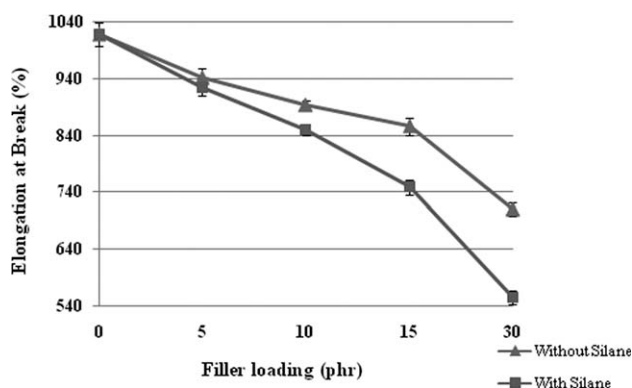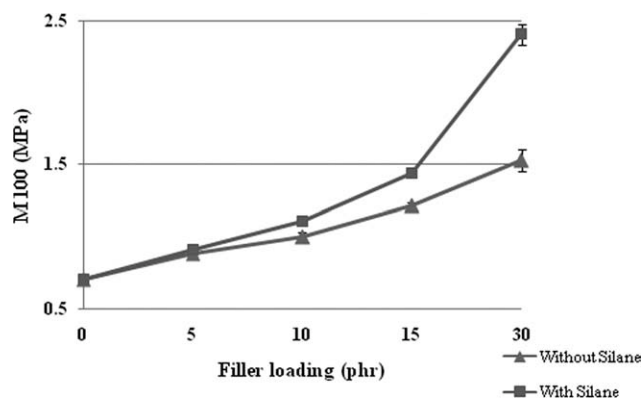
unfilled NR vulcanizate, however, improvement in strength is seen with the addition of silane CA. Suhaida et al.,[18] Nabil et al.,[24] and Ismail et al.[25] also have reported comparable view in their study. The reduction in tensile strength is owing to poor adhesion or incompatibility between rattan and rubber matrix. Referring to Yanjun et al.,[11] the hydrophilic nature of the filler tends to agglomerate into bundles and unevenly distribute throughout the nonpolar polymer matrix. In addition, there is also insufficient wetting of fillers by the nonpolar polymer matrices, resulting in weak interfacial adhesion. As a result, the stress transfer efficiency from the matrix to the fillers is reduced. Nonetheless, tensile strength of NR composites has improved about 15% for 5, 10, 15, and 30 phr rattans loading by silane coupling agent. For instance, at 5 phr rattan loading, the tensile strength is improved and slightly higher than the unfilled NR vulcanizates. Silane CA enhanced the wettability of rattan by rubber matrix and promoted interfacial adhesion. Rubber-rattan interaction increased and the effectiveness of stress transferred from matrix to rattan also improved.[20] Yet, tensile

Figure 5 The effect of filler loading and silane coupling agent on elongation at break of rattan-powder-filled natural rubber composites.
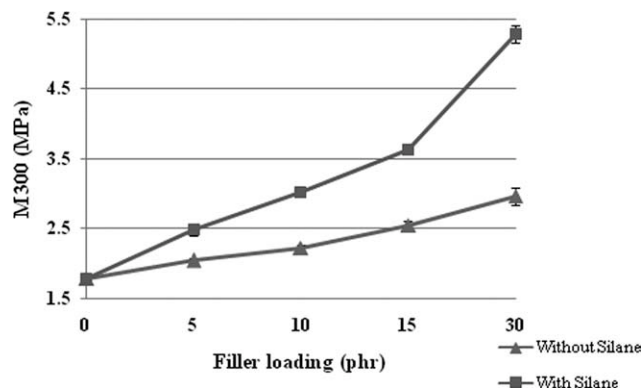

Figure 7 The effect of filler loading and silane coupling agent on stress at 300% elongation (M 300) of rattan-powder-filled natural rubber composites.
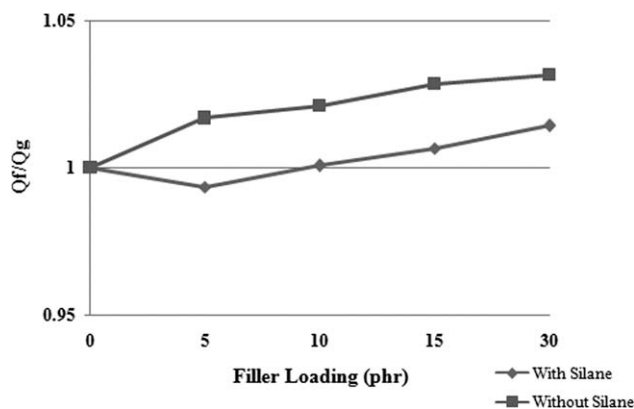
Figure 8 The effect of filler loading and silane coupling agent on rubber-rattan interaction of rattan-powder-filled natural rubber composites.

strength experiences reduction at high rattan loading. This attributed to the inadequacy of rubber matrix to hold the high volume rattan together, thus leads to poor tensile strength.[18,24]

Figures 5–7, respectively, exhibit the elongation at break (EB) and tensile modulus, stress at 100% elongation (M 100), and stress at 300% elongation (M 300) of unfilled NR vulcanizate and rattan-powder-filled NR composites for both with and without the silane coupling agent. Compared with unfilled NR vulcanizate, elongation at break decreases as increasing rattan loading, whereas, the opposite trend is observed for the tensile modulus of composites. As mentioned earlier, the incorporation of unstrained rattan particles into rubber matrix tends to form aggregates in between flexible rubber chains and restricts the mobility. The elasticity of composites is reduced resulting in more stiff and rigid composites. This leads to lower resistance to break.[6,8,17–18,20] M 100 and M 300 increased while elongation at break reduced further as silane CA added into the composites. This modulus enhancement accredited to the better bonding between rubber matrix and rattan apart from the existence of rattan particles. The reduction in elongation at break and increment in M100 and M 300 is more evident at 30 phr rattan loading, a drop of 28% for EB, rise of 36 and 44% is observed for M 100 and M 300, correspondingly. For 5, 10, and 15 phr rattan loading, EB dropped in the range of 2–14%, M 100, and M 300 increased in the range of 3–16% and 17–30%, respectively.

Rubber-filler interaction

The rubber-filler interactions, Q_f/Q_g of rattan-powder-filled NR composites for both series are illustrated as in Figure 8. The Q_f/Q_g for both series increases as increased rattan loading. It is known that, the lower the Q_f/Q_g value, the higher the extent of interaction between filler and matrix.[26] At similar

rattan loading, the Q_f/Q_g value of composites without silane is higher compared with composite with silane. It is clear that the different nature of rubber and rattan which is hydrophobic and hydrophilic respectively, results in lower extent of rubber-rattan interactions as rattan loading increased. The increase in toluene uptake can be taken as a sign of reduction in rubber-rattan interaction. This is because formation of fewer crosslink per rubber chain will increase the ability of rubber to swell in toluene.

On the other hand, addition of silane noticeably improves the extent of adhesion between rattan and rubber. This is basically due to the ability of silane coupling agent in reducing rattan–rattan interaction and promoting enhancement in rubber–rattan interaction. This increases the possibility of more crosslink to form in rubber chain. As a consequent, improvement in tensile properties of rattan-powder-filled NR composites is achieved.

Scanning electron microscopy

SEM is a common method to analyze the level of matrix and filler adhesion. The SEM micrograph of rattan powders shown in Figure 9 proves that the rattan powders are in irregular shape, vary in size and length.

Figures 10 presents SEM micrographs of tensile fracture surfaces of rattan-powder-filled NR composites at 5, 10, and 30 phr rattan loading with and without silane coupling agent. SEM micrographs support our previous result of tensile properties; tensile strength, elongation at break, and tensile modulus. These micrographs reveal that as increasing filler loading, the fracture surfaces become rougher. At lower rattan loading, 5 phr, more matrix tearing is seen as compared to 10 phr and 30 phr rattan loading. Besides, the tensile fracture surfaces also exhibits evidence of filler agglomeration and uneven distribution
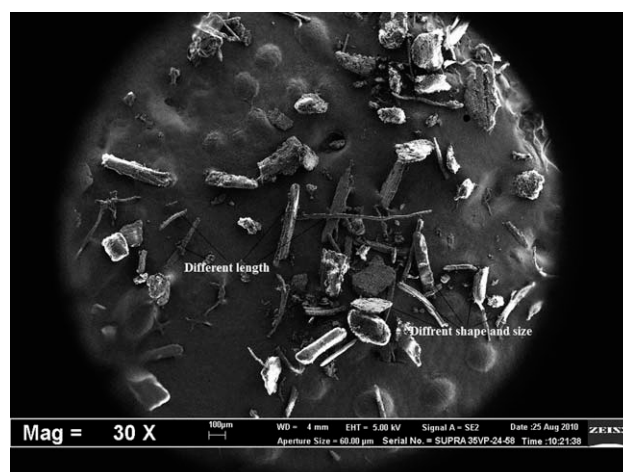

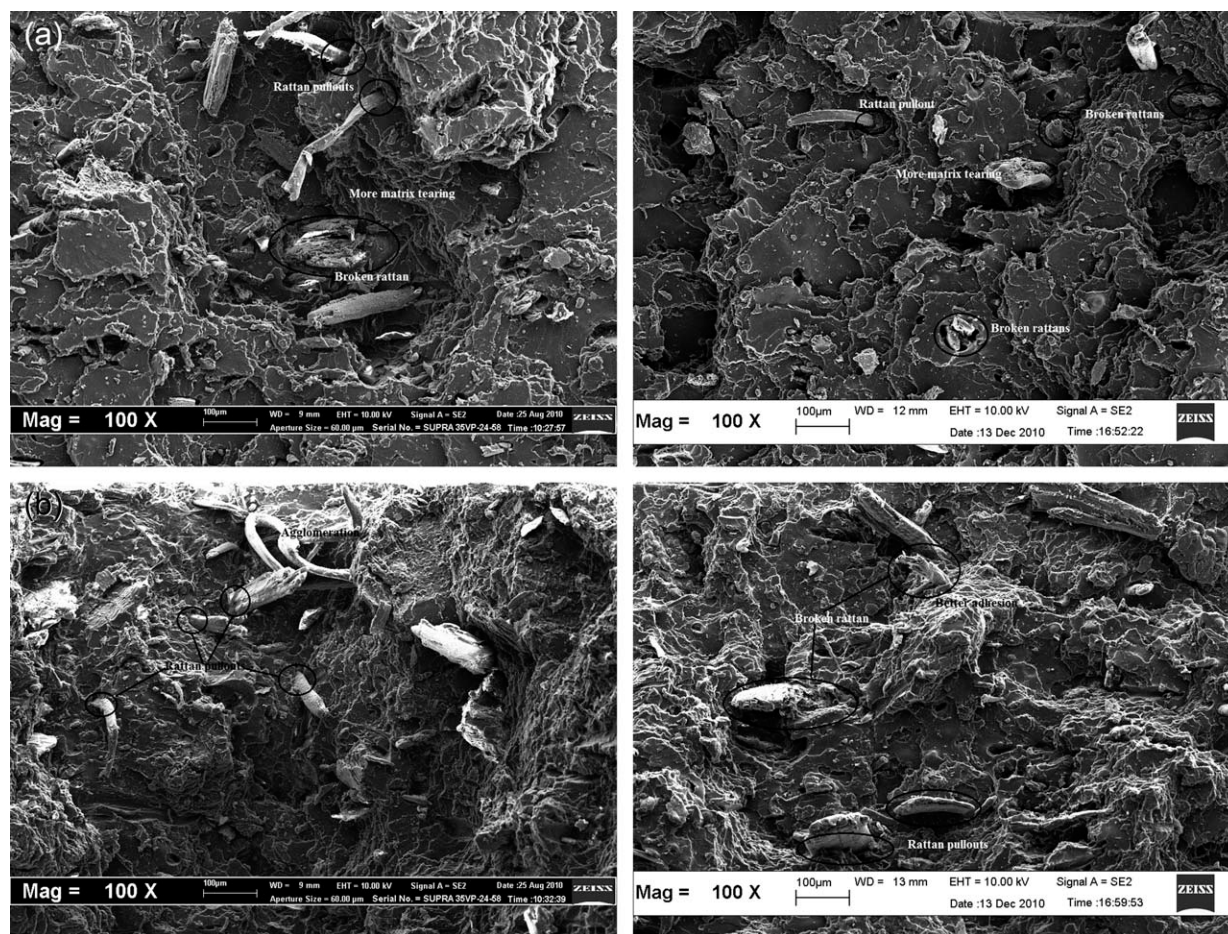**Figure 9** Scanning electron microscopy (SEM) micrograph of raw rattan powder at magnification of 30×.

Figure 10 (a-i): SEM micrograph of tensile fracture surface of 5 phr rattan-powder-filled natural rubber composite without silane CA at magnification of 100×. (a-ii) SEM micrograph of tensile fracture surface of 5 phr rattan-powder-filled natural rubber composite with silane CA at magnification of 100×. (b-i) SEM micrograph of tensile fracture surface of 10 phr rattan-powder-filled natural rubber composite without silane CA at magnification of 100×. (b-ii) SEM micrograph of tensile fracture surface of 10 phr rattan-powder-filled natural rubber composite with silane CA at magnification of 100×. (c-i) SEM micrograph of tensile fracture surface of 30 phr rattan-powder-filled natural rubber composite without silane CA at magnification of 100×. (c-ii) SEM micrograph of tensile fracture surface of 30 phr rattan-powder-filled natural rubber composite with silane CA at magnification of 100×. (d) SEM micrograph shows better rattan-rubber interaction of rattan-powder-filled natural rubber composite with silane CA at magnification of 300×.

of rattan in rubber matrix as more filler are added. Ismail et al.[6] reported similar observation.

Figure 10(a-i, b-i, c-i) display the tensile fracture surfaces of rattan-powder-filled NR composites in the absence of silane CA. More rattan pullouts from rubber matrix and cavities are noticed as the rattan loading increases. This indicates that the level of adhesion between the irregular shaped rattan particles and NR matrix is poor and when stress is applied it causes the rattan to be pulled out from the rubber easily leaving gaping holes. The presence of cavities is clearly visible at 30 phr rattan loading as confirmed by Figure 10(c-i). However, short broken rattan is visible at 5 phr rattan loading [Fig. 10(a-i)], suggests that at lower filler loading, rattan is able to sustain a reasonable tensile properties. This is coupled with an improvement in tensile properties of NR composite with silane compared with unfilled NR vulcanizates.

At the same time, in the presence of silane, as increasing rattan loading, minimal rattan pullouts are present. Broken rattan projecting out of rubber matrix can be seen from the fracture surfaces. When stress is applied, rattan is likely to break due to strong adhesion between rattan and matrix. This proves that with the help of silane, the rattans are well wetted by the matrix phase and a great improvement in adhesion is achieved between two phases as demonstrated by Figure 10(d).

CONCLUSIONS

As filler loading increases, a drop in tensile strength and elongation at break is noted due to poor rubber rattan adhesion. However, the presence of silane coupling agent (CA) decreases the scorch time and cure time but increases the maximum torque of rattan-filled
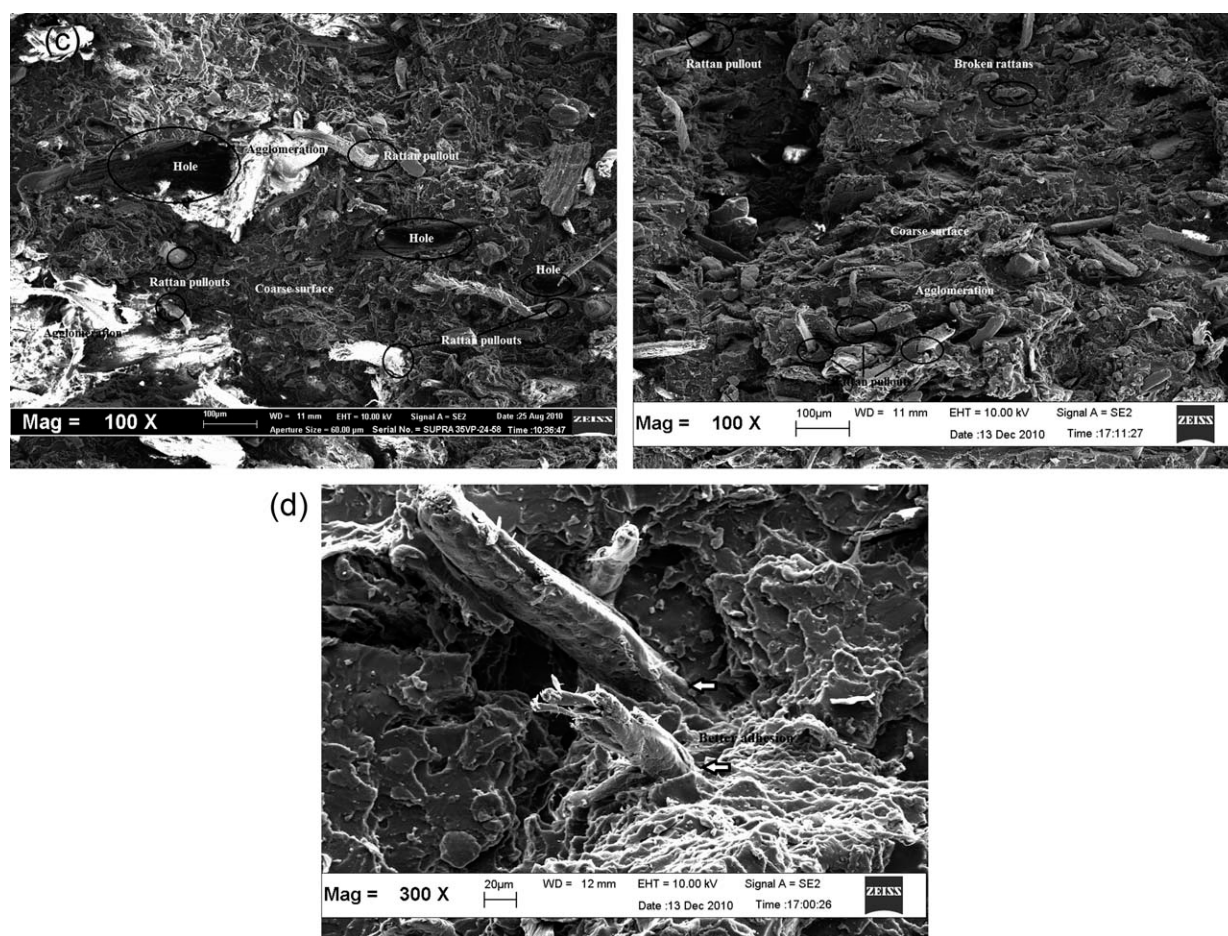
Figure 10 Continued

NR composites as rattan loading is increased. The presence of silane coupling agent also has improved the tensile properties of NR composites compared to composites without silane CA owing to the better wetting and dispersion imparted by silane CA. Improvement in the rubber–rattan interaction leads to minimal rattan pullouts and fewer holes in fracture surface of rubber matrix as shown by SEM micrographs.

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