EFFECTS OF PARTIAL REPLACEMENT OF RATTAN POWDER BY COMMERCIAL FILLERS ON THE PROPERTIES OF NATURAL RUBBER COMPOSITES

Komethi Muniandy, Hanafi Ismail,*and Nadras Othman

The effects of partial replacement of rattan powder (RP) by carbon black (CB), mica, and calcium carbonate ($CaCO_3$) on the curing characteristics, tensile properties, rubber-filler interaction, and morphological studies of natural rubber (NR) composites were investigated. Rattan powder with an average particle size of less than 180 µm was used in this study. NR/RP/CB, NR/RP/mica, and NR/RP/$CaCO_3$ composites with five different RP/commercial fillers loadings (*i.e.* 30/0, 20/10, 15/15, 10/20, 0/30 phr) were prepared using a laboratory size two-roll mill. Results showed that the maximum torque (M_H) of the NR/RP/CB, NR/RP/mica, and NR/RP/$CaCO_3$ composites increased with increasing the commercial filler-loading ratio. The scorch time (t_{s2}) and cure time (t_{90}) of NR/RP/CB composites decreased as the ratio of CB loading was increased, whereas, t_{s2} and t_{90} of NR/RP/mica and NR/RP/$CaCO_3$ composites increased as mica and $CaCO_3$ loading ratio were raised, respectively. The tensile strength, elongation at break (E_b), stress at 100% elongation (M100), and stress at 300% elongation (M300) of all the composites increased as the commercial filler-loading ratio increased. This is due to the presence of the commercial filler, which brought a better rubber-filler interaction, as confirmed by the rubber-filler interaction and scanning electron microscopy (SEM) studies.

Keywords: Natural rubber; Rattan powder; Commercial fillers; Tensile properties; SEM

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INTRODUCTION

Fillers are incorporated in rubber composites to improve certain properties and reduce the materials cost. Fillers are one of the most important components and are added at the second highest portion in the manufacturing of rubber products. Basically, fillers are grouped into two types, namely reinforcing and non-reinforcing fillers. Reinforcing fillers improve the modulus and strength of the rubber products, whereas, non-reinforcing fillers have little or no effect on the rubber properties (Osabohien and Egboh 2007). There are varieties of fillers available and used commercially in the rubber industry.

However, research on developing a new type of filler for rubber composites has shifted its attention toward natural resources, particularly renewable resources such as natural fibres. The availability of these inexpensive natural fibres in every part of the world could allow countries to use their own natural resources in their composite processing industries. In Malaysia, rattan is abundantly available and is considered the most important non-wood forest product, which has been extensively used in the furniture industry (Ali and Khoo 1995). The large amount of rattan canes waste from the furniture industry has spurred interest in its possible use as a filler in NR composites.

The cure characteristics, tensile properties, rubber-filler interaction, and morphological studies of rattan powder-filled natural rubber (NR/RP) composites were studied and reported previously (Ismail *et al.* 2012). The results indicated that the incorporation of rattan powder in natural rubber tended to reduce tensile properties due to the weaker rubber-filler interaction. Generally, natural fibres have problems in adhesion and compatibility with the polymer matrix. This is due to the inherent polar and hydrophilic characteristics of natural fibres that make them incompatible with non-polar polymer matrix materials. As a consequence, poor dispersion of fibres within the matrix and poor interfacial adhesion between the fibres and the matrix can result, creating poorer composite properties (John and Anandjiwala 2008).

Therefore, different approaches have been applied to improve the properties of natural fibre-reinforced polymer composites. In line with that, hybrid composites are becoming more common, as these composites are designed to benefit from the different properties of the fillers employed to give synergistic improvements in the properties of a composite (Matthews and Rawlings 1999). For example, a mixture of natural fibre and carbon black in a rubber composite gives relatively inexpensive composites, owing to the low cost of the natural fibre, but with the mechanical properties enhanced by the excellent stiffness of carbon black. Basically, these types of natural fiber/commercial filler hybrid composites can be used for applications requiring moderate performance products such as hoses, belts, soft inner tubes for application of metal braids and also for other industrial articles (Joseph *et al.* 2005).

Extensive studies on the reinforcement effect of hybrid composites have been conducted by many researchers. The use bagasse fiber ash as a secondary filler in silica or carbon black filled natural rubber composites have been investigated by Kanking *et al.* (2012). AlMaadeed *et al*. (2012) also studied the mechanical and thermal properties of date palm wood flour/glass fibre reinforced hybrid composites of recycled polypropylene. Many interesting research works on partially replacing natural fibers such as palm ash (Ismail and Haw 2010), oil palm wood flour (Ismail and Khalil 2001), and wood sawdust (Saramolee and Bunloy 2009) with commercial fillers have been reported.

Thus, the current study focuses on the incorporation of commercial fillers such as carbon black (CB), mica, and calcium carbonate ($CaCO_3$) into rattan powder-filled natural rubber (NR/RP) composites. The curing characteristics, tensile properties, rubber-filler interaction, and morphological studies were investigated in the hybrid of commercial and RP filler in the NR composites.

EXPERIMENTAL

Materials and Formulation

Natural rubber (STR 5L) was purchased from Rubber Research Institute, Malaysia (RRIM). Waste rattan canes were collected from Seng Huat Shop, Penang, Malaysia. Then, waste rattans were cleaned, ground, and sieved into an average particle size of less than 180 µm. The particle size distribution was determined using a Sympatec Helos/BF Particle Size Analyzer (Muniandy *et al.* 2012). Zinc Oxide, stearic acid, sulphur, N-cyclohexyl-2-benzolthyazolsulfenamide (CBS), 2,2 methylene-bis-(4-methyl-6-tert-butylphenol) (BKF), carbon black (N330), mica, and calcium carbonate were obtained from Bayer (M) Ltd. The physical properties of rattan powder, carbon black, mica, and calcium carbonate are listed in Table 1. The formulations used to prepare the composites are tabulated in Table 2.

Table 1. Physical Properties of Rattan Powder, Carbon Black, Mica, and Calcium Carbonate

Filler	Average Particle Size (µm)	Surface Area (m^2/g)	Density (g/cm^3)
Rattan powder	24.84	0.68	1.60
Carbon Black (N330)	2.02	2.38	1.80
Mica	4.06	1.45	2.50
Calcium carbonate	5.93	0.81	2.70

Table 2. Formulation Used in the Preparation of NR/RP/CB, NR/RP/mica, and NR/RP/$CaCO_3$Composites

Ingredients	**Formulation (phr)**
Natural Rubber (STR 5L)	100
Zinc oxide	1.5
RP/CB, RP/mica, RP/$CaCO_3$	30/0, 20/10, 15/15, 10/20, 0/30
Stearic acid	1.5
CBS	1.9
BKF	2
Sulfur	1.6

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

Sample Preparation

Rattan powder was dried in an oven at 70°C for an hour to expel the moisture prior to the compounding process. Based on the formulation shown in Table 2, mixing of five different compositions of NR/RP/CB, NR/RP/mica, and NR/RP/$CaCO_3$ composites was carried out in a laboratory model two-roll mill (model XK-160) according to American Standard of Testing Material (ASTM) designation D 3184-80. The cure characteristics of rubber composites 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 composites were moulded into sheets with respective cure time, t_{90},at 150°C using a hot press machine.

Measurement of Tensile Properties

A tensile test was conducted on dumbbell shaped samples cut from vulcanized rubber sheets with a thickness of approximately 2 mm using a Wallace die cutter. The tensile test was carried out according to ASTM D 412 using an Instron Universal testing machine (model 3366) at test temperature of 23°C with a crosshead speed of 500 mm/min. Five samples were tested and the 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 (SEM)

Examination of the tensile fracture surfaces of NR/RP/CB, NR/RP/mica, and NR/RP/$CaCO_3$ composites was carried out using a scanning electron microscope (SEM), Zeiss Supra 35vp. The fracture surfaces were sputter-coated with gold to avoid electrostatic changing and poor image resolution. The fractured surface of the sample was placed on an aluminium mount with double-sided sticky tape and observed under the SEM. Only one sample was examined for each composite. The rubber-filler interactions and filler dispersion were evaluated from the micrograph.

Rubber-Filler Interaction

The vulcanized sample (30 mm × 5 mm × 2mm) was accurately weighed, immersed in toluene, and allowed to swell in a closed bottle for 72 hours at room temperature (25^{o}C). The sample was removed and the surface of swollen sample was quickly wiped and weighed. The sample was dried in an oven at 70^{o}C for 15 minutes and weighed. *Q*, the weight of toluene uptake per gram of rubber hydrocarbon, was determined according to Equation 1.

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

The rubber-filler interaction was calculated using Lorenz and Park equation, as expressed by Equation 2 (Ismail *et al.* 2008):

$$\frac{Q_f}{Q_g} = a\mathrm{e}^{-\mathrm{z}} + b \qquad (2)$$

The subscripts *f* and *g* in Equation 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.

Fourier Transform Infrared Spectroscopy Analysis

The functional groups in rattan powder (RP) were detected using Fourier-transform infrared spectroscopy (FTIR; Perkin Elmer System 2000). RP was mixed with Potassium Bromide (KBr) using a mortar and pestle, and compressed into a thin pellet. The FTIR spectra were recorded in the range of 400 to 4000 cm^{-1} wave numbers.

RESULTS AND DISCUSSION

Fourier Transform Infrared Spectroscopy Analysis

The FTIR spectrum of rattan powder (RP) in the wavenumber range of 400 to 4000 cm^{-1} is displayed in Fig. 1. The major peaks are found in the region of 3399 cm^{-1}, 2929 cm^{-1}, 1737 cm^{-1}, 1611 cm^{-1}, 1242 cm^{-1}, and 1050 cm^{-1}. The strong and broad peak at 3399 cm^{-1} is attributed to the OH stretching from aliphatic (C-OH) and phenolic hydroxyl groups, with respect to the cellulose or hemicelluloses and lignin. The alkyl (C-H, CH_2, $C\text{-}CH_3$) groups that are found in the cellulose, hemicelluloses, and lignin were detected in the region of 2929 cm^{-1}. The frequency at 1737 cm^{-1} showed a weak intensity, which is principally attributed to the carbonyl group stretching from the hemicelluloses (Han and Jung 2008). The occurrence of a weak alkene C=C bond from lignin is found in the region of 1610 cm^{-1}. A complex lignin-carbohydrate structure was detected in the region of 1242 cm^{-1} with medium intensity. An absorbance at 1050 cm^{-1} is observed due to the presence of C-O-C bond; the intensity is sharp and strong (Dai and Fan 2011).

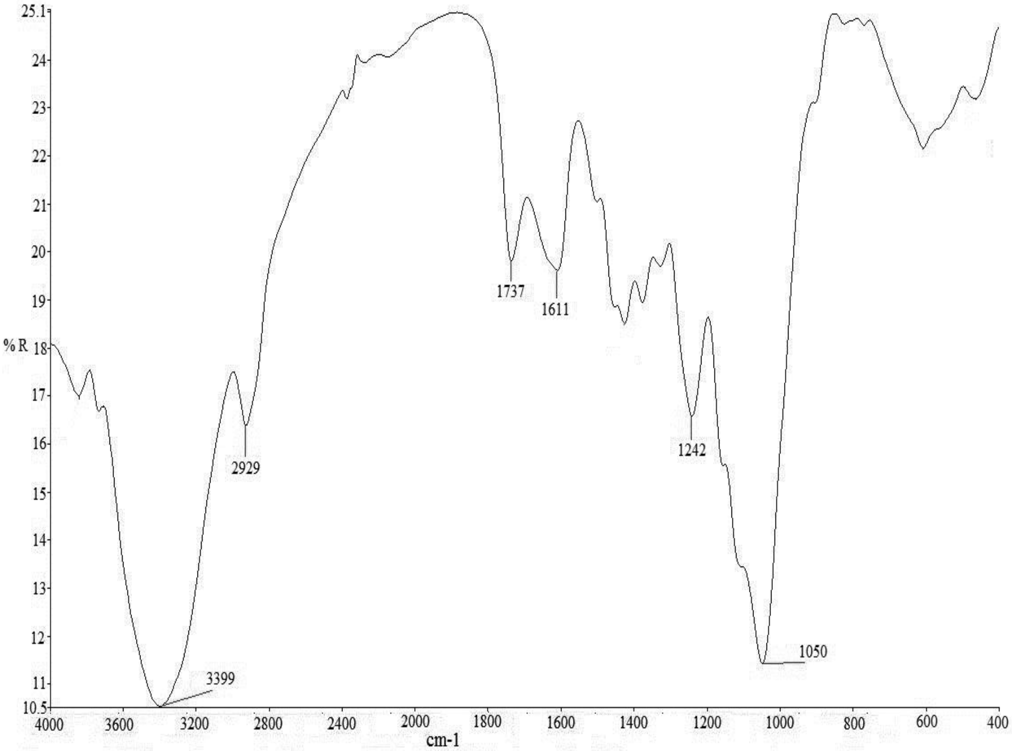

Fig. 1. Fourier transform infrared spectrum of rattan powder

Curing Characteristics

The curing characteristics of natural rubber (NR)/rattan powder (RP)/carbon black (CB), NR/RP/mica, and NR/RP/calcium carbonate ($CaCO_3$) composites are summarized in Figs. 2 through 4. Figure 2 depicts the maximum torque (M_H) of the partially filled natural rubber composites: NR/RP/CB, NR/RP/mica, and NR/RP/$CaCO_3$ composites. The three composites exhibited similar trends in M_H when the commercial fillers replace the RP. The composites experienced a reduction in M_H at 20/10 filler-loading ratio and then increased as the loading of commercial filler ratio is increased. Generally, the variation in torque depends on the nature and concentration of filler, its shape, size, and the interaction of the filler with the matrix (Wypych 2010).

The increase in M_H from 20/10 filler-loading ratio resulted from the good reinforcement or better interactions between the rubber matrix and the commercial fillers compared to the interaction between the rubber and the RP filler. The rubber-filler interaction will impose higher restriction in the mobility of the rubber's macromolecular chains, consequently increasing the value of M_H (Arayapranee and Rempel 2008). Even though the commercial fillers have the tendency to reinforce the composites compared to RP, the partial replacement of 10 phr rattan powder with commercial filler reduced M_H. This can be attributed to the dilution effect imparted by soft natured commercial filler compared to rattan powder, which is very stiff and coarse (Wypych 2010).

From Fig. 2 it can be concluded that the increment in M_H is more pronounced in NR/RP/CB composites, followed by NR/RP/mica and NR/RP/$CaCO_3$ composites. This observation is associated with the difference in the extent of reinforcement imparted by the three different types of fillers, which vary in particle size. CB has, on average, a smaller particle size that is 2.02 µm, followed by mica (4.06 µm) and $CaCO_3$ (5.93µm). Smaller particle sized fillers tend to form stronger rubber-filler interactions in the composites due to their high surface area per unit mass (Ismail and Shaari 2010; Wypych 2000). Thus, the addition of CB caused an extreme increase in M_H with increasing ratio of CB loading, while $CaCO_3$ created a relatively small increase in M_H as load of $CaCO_3$ ratio increased.

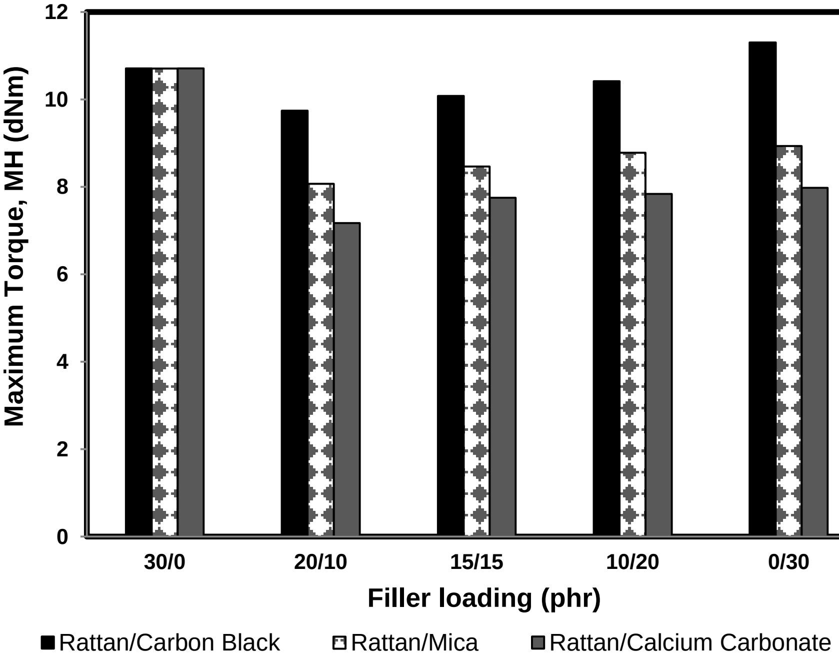

Fig. 2. Effect of partial replacement of rattan powder with commercial fillers on the maximum torque (M_H) of natural rubber composites

Figures 3 and 4 show the effects of partial replacement of RP with CB, mica, and $CaCO_3$ on scorch time (t_{s2}) and cure time (t_{90}) of natural rubber composites. It can be seen that the t_{s2} and t_{90} of NR/RP/CB composites decreased as the ratio of CB loading was increased, whereas, t_{s2} and $t_{90}$of NR/RP/mica and NR/RP/$CaCO_3$ composites increased as mica and $CaCO_3$ loading ratio were raised, respectively. The reduction of t_{s2} and t_{90} in NR/RP/CB composites suggest that the inclusion of CB accelerated the vulcanization process (Wampler *et al.* 2004). Sae-Oui *et al*. (2002) also reported similar findings in their research work. Carbon black is able to trigger the vulcanizing process by the formation of hydrogen sulphide and the rupture of S-N linkage when heated with sulphonamides (accelerator) in rubber, consequently speeding up the vulcanization process (Ismail *et al.* 2011). Thus, decrement in t_{s2} and t_{90} is achieved when rattan powder is partially or fully substituted by carbon black.

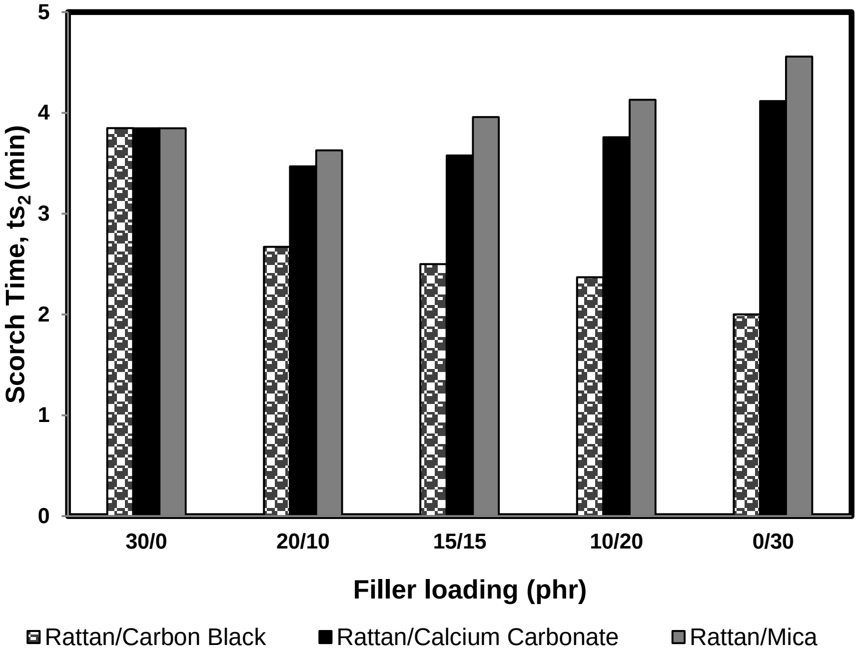

Fig. 3. Effect of partial replacement of rattan powder with commercial fillers on the scorch time (t_{s2}) of natural rubber composites

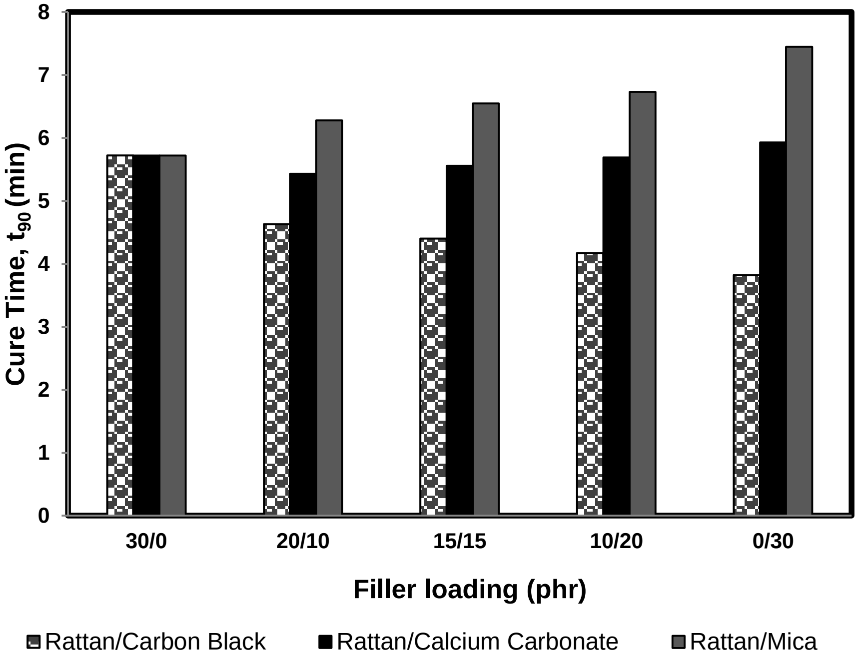

Fig. 4. Effect of partial replacement of rattan powder with commercial fillers on the cure time (t_{90}) of natural rubber composites

On the other hand, the addition of mica and $CaCO_3$ correspondingly to NR/RP/mica and NR/RP/$CaCO_3$ decelerated the vulcanization process and resulted in increased t_{s2} and t_{90} when the filler-loading ratio increased. Castro *et al*. (2004) obtained similar results in their study using mica and confirmed that mica has an ability to retard the vulcanization process. Moreover, the addition of $CaCO_3$ also results in cure retardation (Pasbakhsh *et al.* 2009). Both mica and $CaCO_3$ can interact with curatives such as activator and accelerator. Consequently, the amounts of active curatives necessary for sulphur vulcanization process are reduced and lead to cure retardation (Rattanasom and Prasertsri 2009).

Tensile Properties

The results of tensile properties of hybrid natural rubber (NR) composites are displayed in Figs. 5 to 8. The tensile properties of filled composites are generally governed by filler dispersion, particle size, or specific surface area of filler and rubber-filler interaction (Osman *et al.* 2010; Sae-Oui *et al.* 2002). The tensile strength of all the composites is increased with a higher loading of the commercial fillers, as shown in Fig. 5. The tensile strength of carbon black filled NR/RP/CB composites increased enormously with an escalation of CB filler ratio, whilst mica-filled NR/RP/mica composites exhibited a gradual increase with increasing mica loading ratio. The NR/RP/$CaCO_3$ composites showed little change in the tensile strength when the filler-loading ratio of $CaCO_3$ was increased.

From the results of tensile strength, it can be concluded that the inclusion of CB in NR composites showed a good reinforcement, followed by mica and $CaCO_3$. Fundamentally, finer or smaller filler particles pose high surface area that enables more wetting of the fillers by the rubber matrix, resulting in stronger rubber-filler interaction and good filler dispersion in the rubber matrix. Consequently, this could lead to a more efficient stress transfer from the matrix to the fillers under tensile loading, which is essential in achieving the highest possible tensile strength. Thus, the finer or smaller particle sized fillers can provide a higher degree of reinforcement than the coarse or bigger ones (Osman *et al.* 2010).

Therefore, CB, which is the smallest compared to other fillers such as mica, $CaCO_3$, and RP, are able to provide the greatest reinforcement when substituted. Carbon blacks used in rubber industries are composed of fused primary aggregates, known as structured materials. Structure differs in degree of branching and the number of particles per aggregate. The higher the structure, the more carbon blacks that are wetted by the rubber matrix and a greater rubber-filler interaction is formed (Wampler *et al.* 2004). Moreover, CB is a non-polar filler and is more compatible with hydrocarbon rubber chains, therefore resulting in good contact to the rubber rather than the contact between filler and filler (Wypych 2000). Greater rubber-filler interaction is important to maximize the filler dispersion and provide reinforcement (Hassan *et al.* 2012). As a result, NR/RP/CB composite shows the highest tensile strength at 0/30 phr filler loading ratio, as well as an improvement in the tensile strength of rattan powder-filled NR composites are noted with increment in CB loading ratio.

On the other hand, calcium carbonate showed little reinforcement compared to RP due to its size, which is smaller than RP (24.84 µm). Thus, at 30 phr loading, NR/$CaCO_3$ composite exhibited higher tensile strength than NR/RP composite. However, NR/$CaCO_3$

composite did show lower tensile strength compared to CB and mica filled composites. This is because $CaCO_3$ has a larger particle size compared to CB and mica and the addition of $CaCO_3$ results in weaker rubber-$CaCO_3$ interaction. Thus, the weaker rubber-$CaCO_3$ interaction is unable to transfer more stress from the matrix to the filler upon tensile loading. Hence, $CaCO_3$ provides little reinforcement to the NR/RP/$CaCO_3$ composites.

The addition of mica in NR/RP/mica showed tensile strength in between NR/RP/CB and NR/RP/$CaCO_3$. Both $CaCO_3$ and mica are polar natured mineral fillers, but mica significantly enhanced the tensile strength by about 13 MPa compared to $CaCO_3$, which enhanced it by just 4 MPa. This is due to the flake- or plate-like mica filler with high aspect ratio as compared to $CaCO_3$, which is larger and round shaped. Thus, the mica filler with higher surface area increases the wettability by the matrix, thus creating fewer micro voids in rubber matrix compared to $CaCO_3$. Consequently, interaction with rubber and filler will increase and the filler will be able to bear the load transferred from the matrix.

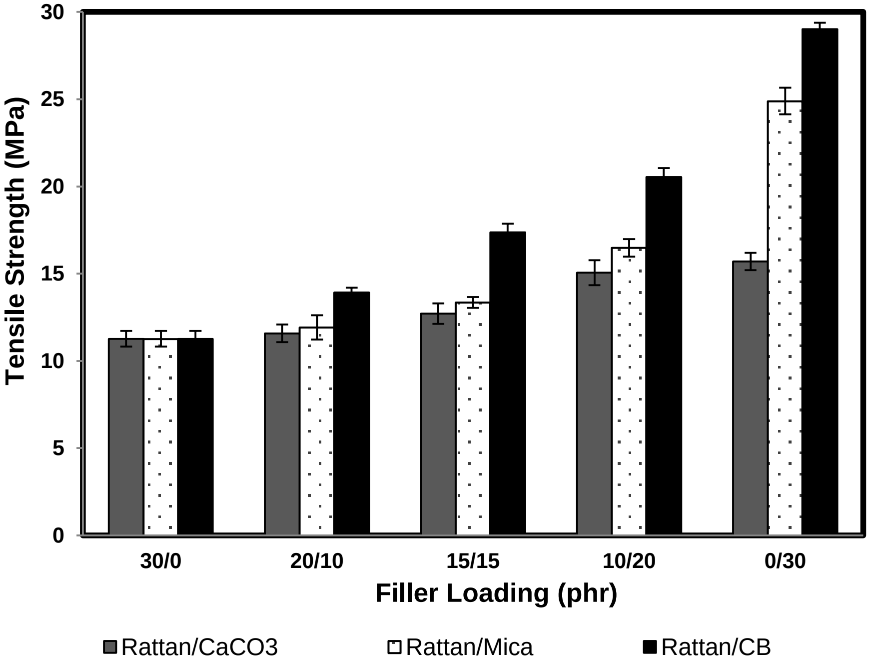

Fig. 5. Effect of partial replacement of rattan powder with commercial fillers on the tensile strength of natural rubber composites

Figure 6 illustrates the effect of partial replacement of RP with commercial fillers on the elongation at break (E_b) of NR composites. At first, all the composites (NR/RP/CB, NR/RP/mica, and NR/RP/$CaCO_3$) experienced a reduction in E_b at 20/10 (RP/commercial filler) hybrid filler-loading ratio, and then, the E_b increased as the load of commercial filler was enlarged while the rattan powder loading decreased. The reduction in E_b might be due to the dominant effect of rattan filler agglomeration, which also reduced the interaction between the commercial fillers and rubber matrix. At a filler-loading ratio of 15/15 onwards, the E_b was dominated by the effect of commercial fillers. As discussed previously, higher loading of CB, mica, and $CaCO_3$ increased the interfacial interaction between the rubber matrix and the fillers along with enhanced filler dispersion. Hence, the ability to resist the fracture accumulates, leading to an increase in the E_b.

At similar filler loading, it is observed that NR/RP/CB composites showed the lowest E_b due to the greater adhesion between CB and matrix leading to a stiffer composite, whilst the NR/RP/mica composites showed the highest E_b. This is because, unlike CB, the inclusion of mica did not make the composite rigid. Under the tensile force, platy mica fillers can slide past each other, resulting in a higher percentage of E_b (Wang *et al.* 2010). Meanwhile, the E_b of NR/RP/$CaCO_3$ obtained is lower than NR/RP/mica. This might be due to the lower rubber-filler interaction that leads to filler agglomerations and lowered the E_b.

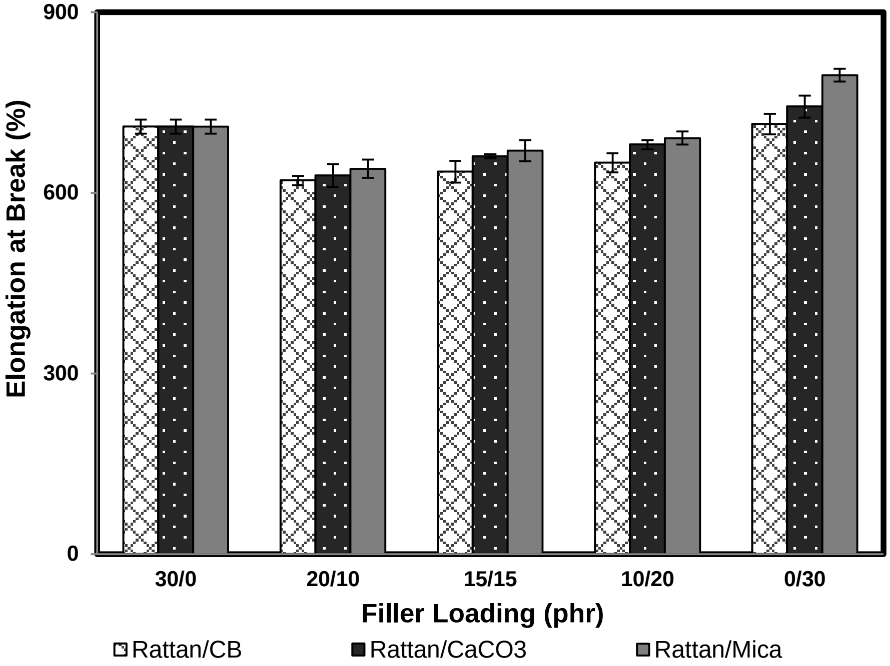

Fig. 6. Effect of partial replacement of rattan powder with commercial fillers on the elongation at break of natural rubber composites

The tensile modulus, stress at 100% elongation (M100), and stress at 300% elongation (M300) of NR/RP/CB, NR/RP/mica, and NR/RP/$CaCO_3$, are presented in Figs. 7 and 8, respectively. The result of tensile modulus is similar to that of elongation at break except for a 20/10 filler-loading ratio, where the M300 of the NR/RP/CB is higher than the NR/RP composite. Again, the rubber-filler interaction plays an important role in the increment of M100 and M300 of the composites. The tensile modulus of composites increases as the rubber-filler interaction is increased. Apart from that, the incorporation of unstrained fillers in the rubber matrix could stiffen the composite, consequently, increasing the tensile modulus. At comparable filler loading, as for tensile strength, the tensile modulus of CB filled composites are high. The reason is the greater rubber-filler interaction and the presence of unstrained fillers which perturbs the rubber chains movement occurring quickly at high strains, causing increased stress at the equivalent strain (Wampler *et al.* 2004). Meanwhile, the tensile modulus of NR/$CaCO_3$ (30 phr) composite is lower than that of NR/RP composite, and shows miniscule enhancement in tensile modulus with increasing the $CaCO_3$ loading.

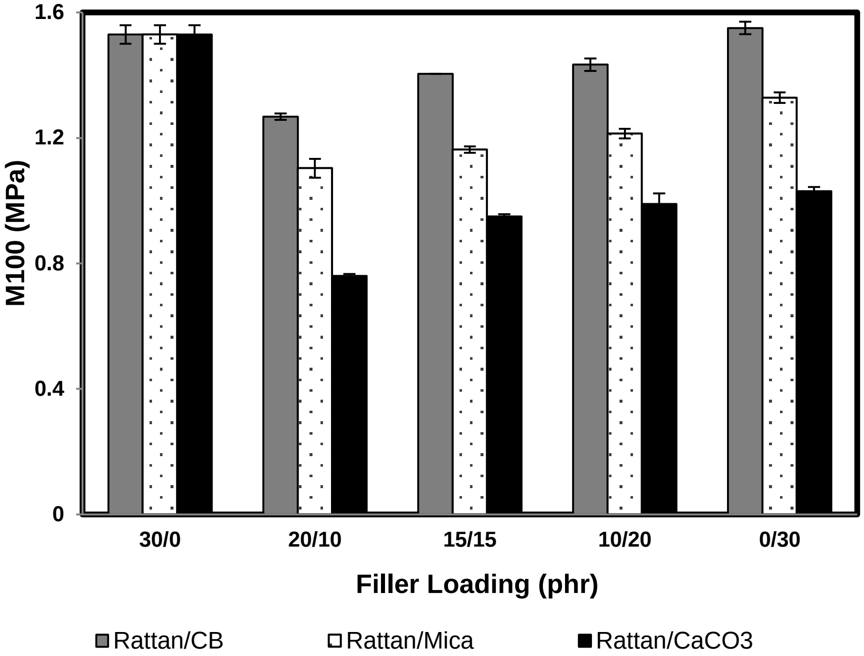

Fig. 7. Effect of partial replacement of rattan powder with commercial fillers on the stress at 100% elongation (M100) of natural rubber composites

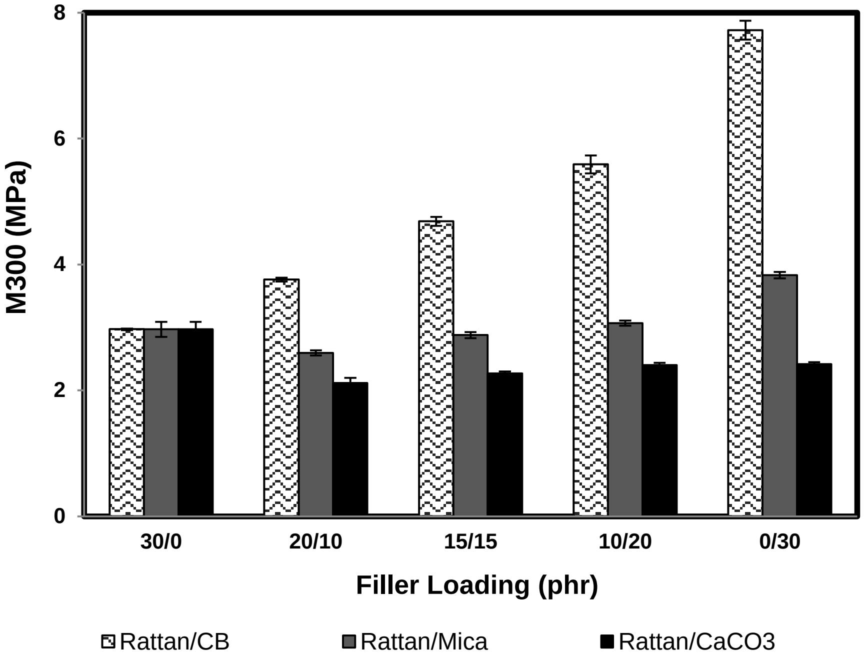

Fig. 8. Effect of partial replacement of rattan powder with commercial fillers on the stress at 300% elongation (M300) of natural rubber composites

Rubber-filler Interaction

Figure 9 shows the effect of partial replacement of rattan powder (RP) with commercial fillers such as carbon black (CB), mica, and calcium carbonate ($CaCO_3$) in natural rubber (NR) on the rubber-filler interaction (Q_f/Q_g). Q_f/Q_g signifies the extent of the rubber-filler interaction in the filled composites. It is known that the lower the Q_f/Q_g value, the higher the extent of interaction between the filler and the matrix (Ismail 2001).

From the result, it can be concluded that the partial or complete replacement of RP by commercial fillers caused reduction in Q_f/Q_g value, meaning the value of Q_f/Q_g continuously decreased with increasing the load of commercial fillers. This revealed that the commercial fillers have brought a better rubber-filler interaction, consequently have reinforced the composites compared to the rattan powder filled composite (NR/RP). This affirms the result obtained with the tensile properties discussed previously.

The NR/RP/$CaCO_3$ hybrid composites exhibit higher Q_f/Q_g value among the other two composites. The higher Q_f/Q_g value indicates that the NR/RP/$CaCO_3$ hybrid composites have allowed more toluene uptake which shows the poor rubber-filler interaction in the composites. Meanwhile, NR/RP/CB gave a lower Q_f/Q_g value, confirming a greater interaction between the rubber and the filler that is a factor for its good reinforcement in the NR/RP/CB hybrid composites.

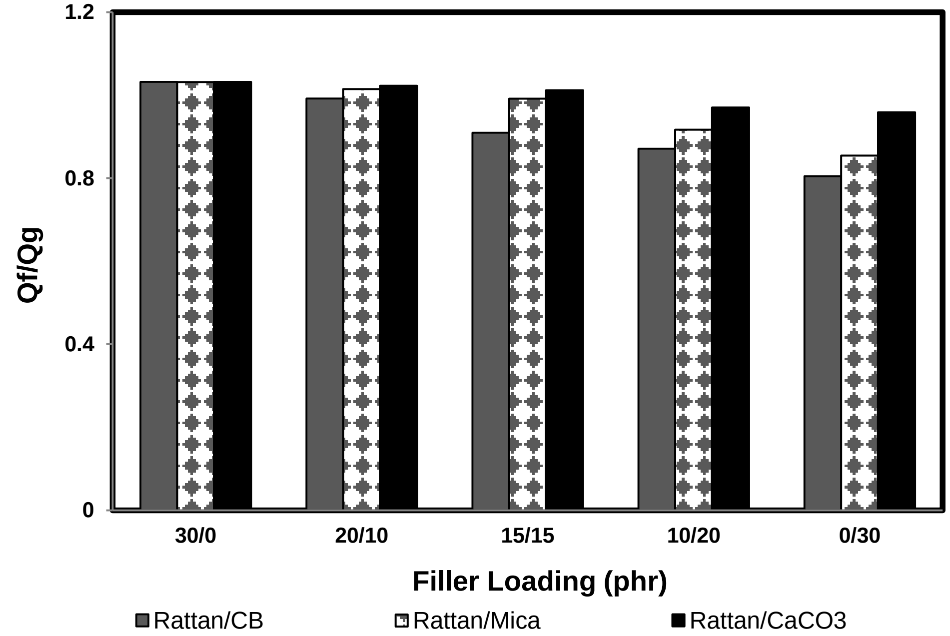

Fig. 9. Effect of partial replacement of rattan powder with commercial fillers on the rubber-filler interaction of natural rubber composites

Scanning Electron Microscopy (SEM)

The morphology of tensile fractured surfaces of NR/RP, NR/RP/CB, NR/RP/mica, and NR/RP/$CaCO_3$ are illustrated in Figs. 10 and 11. The SEM micrograph of 30 phr RP filled composites (Fig. 9) shows poor filler dispersion in rubber matrix and poor interfacial adhesion with more filler pullouts and more voids, which resulted in the lowest tensile strength of the composites.

It can be seen from the SEM micrographs that the partial addition of commercial fillers improved the rattan filler dispersion in the rubber matrix. Basically, the dispersion of fillers is one of most important factors that can contribute to reinforcement of composites. If agglomeration and low degree of dispersion occurs, then the reinforcing effect cannot be attained completely. Moreover, fewer filler pullouts and voids are observed in the NR/RP/CB (Fig. 11a), NR/RP/mica (Fig. 11b), and NR/RP/$CaCO_3$ (Fig. 11c) as compared RP filled composite (Fig. 10). Apart from that, broken rattan fillers were also detected in the composites that were partially replaced by CB and mica, as shown in Fig. 11a and Fig. 11b, respectively. It can be deduced that more strength was needed to bear the stress transferred from the matrix to the filler, ultimately breaking the rattan. This proved the existence of better rubber-filler interaction imparted by the two fillers.

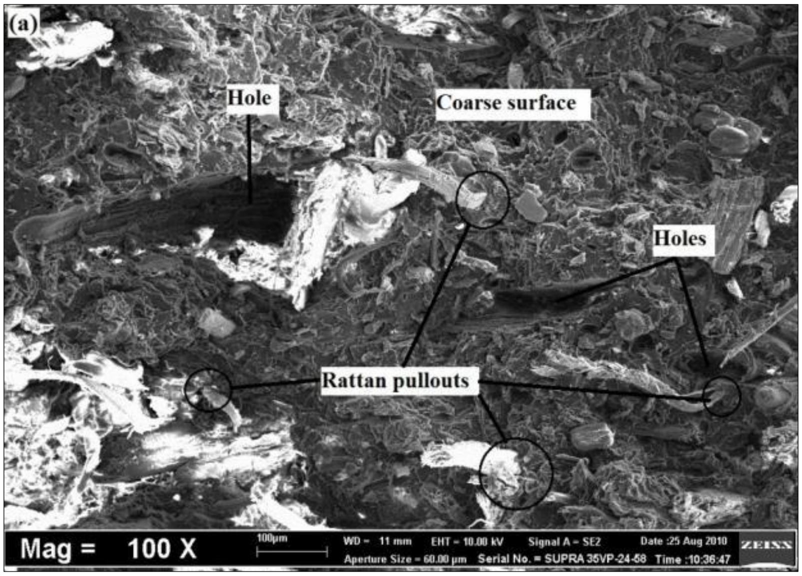

Fig. 10. Scanning electron micrograph of tensile fractured surface of 30 phr rattan powder-filled natural rubber composite at magnification of 100×

The SEM micrograph of 30 phr CB filled composite (Fig. 12a) exhibits a more uniform and smooth surface fracture. Deeper matrix tearing lines are noticed, indicating that high stress was needed to cause the composite to fail. These observations revealed the ability of the smaller sized CB to disperse homogeneously in rubber matrix without any agglomerates and create a greater rubber-filler interaction. The CB fillers are not visible at the surface of fracture as compare to mica, $CaCO_3$, and RP, proving that the CB is smaller in particle size. Thus, the CB filled composite showed highest tensile strength.

Figure 12b displays the SEM micrograph of 30 phr $CaCO_3$ filled NR composite. The particle size of $CaCO_3$ is bigger with irregular spherical shape, leading to lower rubber-filler interaction. There are many voids found in the fracture surface that resulted from easy debonding of the filler from the matrix. Thus, lower stress is transferred from matrix to the filler, which is the cause of the decrease in tensile strength. So, less matrix tearing is observed.

On the other hand, mica-filled composite (Fig. 12c) showed the combination properties of both CB and $CaCO_3$. The tensile fracture surface of mica shows that the mica adhesion to the rubber matrix was low, resulting in debonding of the filler from the matrix and leaving microvoids. However, as the mica has a platy shape, it is well oriented, and the adhesion of the filler to rubber is higher than the $CaCO_3$; thus, it exhibited deeper matrix tearing as CB. This observation is in accordance to the results of tensile properties.

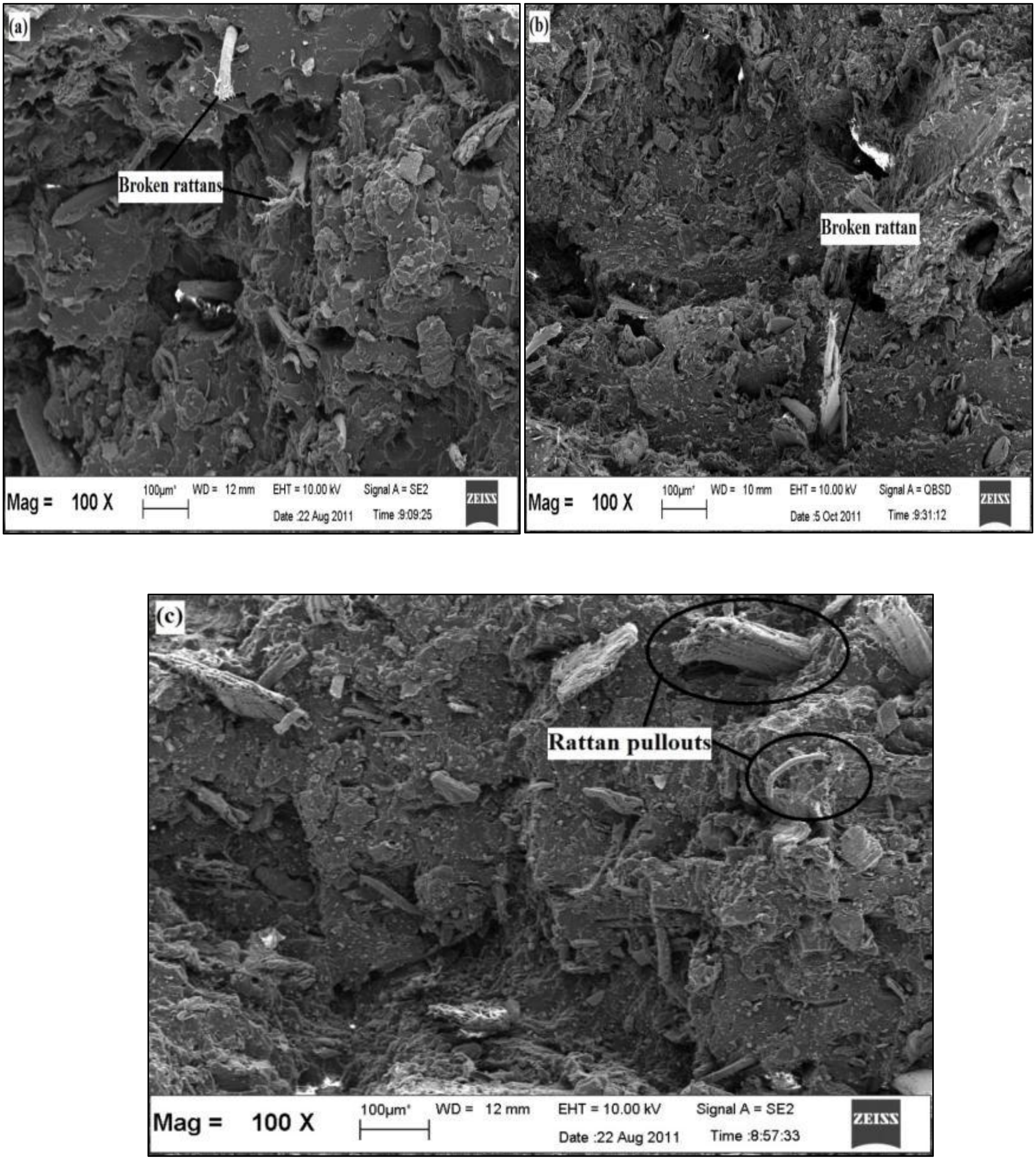

Fig. 11. Scanning electron micrograph of tensile fractured surfaces of partially replaced (15/15: rattan powder/commercial filler phr) rattan powder filled natural rubber composite at magnification of 100× (a) carbon black, (b) mica, and (c) calcium carbonate

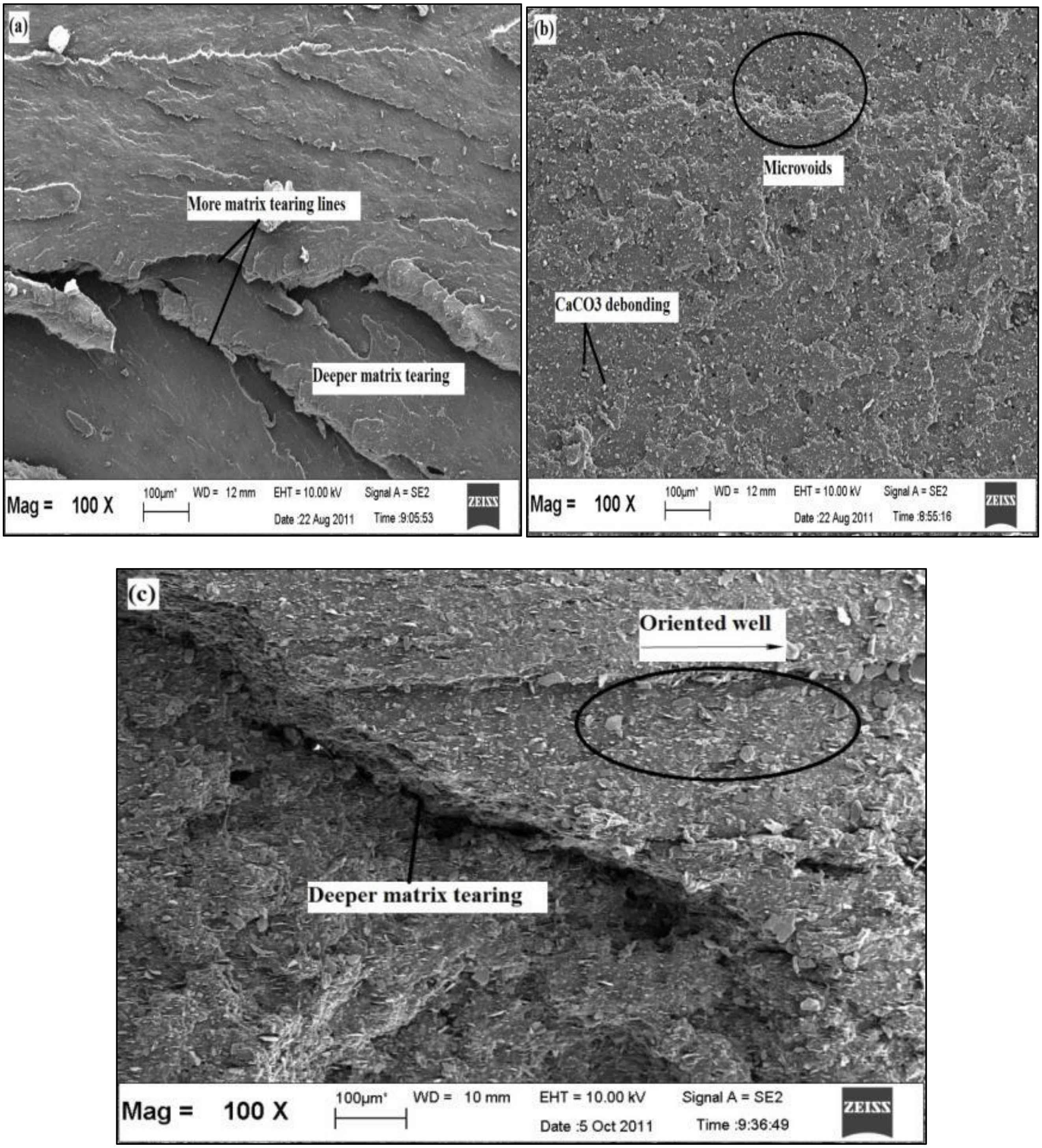

Fig. 12. Scanning electron micrograph of tensile fractured surface of 30 phr (a) carbon black, (b) calcium carbonate, and (c) mica filled natural rubber composite at magnification of 100×

CONCLUSIONS

The partial replacement of rattan powder (RP) with carbon black (CB), mica, and calcium carbonate ($CaCO_3$) improved the properties of the NR/RP composites. The scorch time and cure time of NR/RP/CB composites decreased as the ratio of CB loading was raised, whereas, t_{s2} and t_{90} of NR/RP/mica and NR/RP/$CaCO_3$ composites increased as mica and $CaCO_3$ loading ratio were increased, respectively. The maximum torque, tensile strength, elongation at break, stress at 100% elongation, and stress at 300% elongation increased with increasing commercial filler loading. This observation was due to the reinforcing effect imparted by commercial fillers compared to the RP filler, which is non-reinforcing. The commercial fillers imparted better rubber-filler interaction, which maximized the filler dispersion and provided reinforcement, thus enhancing the properties of the composites. The CB provided the greatest reinforcement followed by mica and $CaCO_3$. Whilst, the RP filled NR composite showed superior tensile modulus compared to mica and $CaCO_3$.

ACKNOWLEDGMENT

One of the authors (Komethi Muniandy) gratefully acknowledges the Fellowship Scheme of Universiti Sains Malaysia.

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Article submitted: May 28, 2012; Peer review completed: July 11, 2012; Revised version received: July 26, 2012; Accepted: August 4, 2012; Published: August 8, 2012.