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Effects of Silica/Multiwall Carbon Nanotube Hybrid Fillers on the Properties of Natural Rubber Nanocomposites

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ABSTRACT: In this study, multiwalled carbon nanotubes (MWCNTs) and silica were used as hybrid fillers in natural rubber (NR) nanocomposites. The addition of MWCNTs and silica to NR was varied with the total filler loading fixed at 30 phr. The curing characteristics and mechanical, thermal, and morphological properties were investigated in this study. The results show that the scorch and curing time decreased as the MWCNT loading increased in the silica/MWCNT hybrid, but the maximum torque was increased by about 35%. The highest tensile strength was achieved at a loading ratio of 29 phr silica/1 phr MWCNTs. As the MWCNT loading increased in the silica/MWCNT hybrid, the tensile strength, elongation at break, and fatigue life decreased. However, the tensile modulus and rubber filler interaction increased. The scanning electron microscopy results show a good dispersion and better interaction between silica and the MWCNTs with the NR matrix at a 29/1 silica/MWCNT loading ratio. As the MWCNT loading ratio increased, the agglomeration of the MWCNTs became dominant and reduced the reinforcing effect of the MWCNTs. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

KEYWORDS: graphene and fullerenes; nanocomposites; nanotubes; silicas

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INTRODUCTION

Nowadays, rubber technology has become an important part in industry. Because of the remarkable properties of rubber, it is used extensively in industrial and societal fields. Because the essential modulus and strength of neat rubber is low, it is necessary to introduce an additional reinforcing phase to achieve optimum properties for practical purposes.[1–3] For most engineering applications, carbon black, calcium carbonate, zinc oxide, magnesium oxide, talc, mica, and silicates[4–6] are widely used as reinforcing fillers for rubber. However, the full reinforcing level cannot be achieved because of their large sizes and agglomeration.[3,7]

The use of nanomaterials for the reinforcement of natural rubber (NR) composites is a new technology that gives high expectations because it has shown enhancement in the composites, especially in its mechanical properties. A recent study[3] showed that carbon nanotubes (CNTs) treated with 3-aminopropyltriethoxysilane improved the mechanical properties by higher polymer–filler interaction between the CNTs and NR. It has been proven that CNTs are one of the most efficient reinforcing elements for NR.[2,3,7] The nature of the dispersion problem for CNTs is rather different from those of other conventional fillers, including spherical particles and carbon fibers, because CNTs characteristically have small diameters on the nanometer scale with a high aspect ratio (>1000) and, thus, an extremely large surface area. In addition, commercialized CNTs are supplied in the form of heavily entangled bundles; these cause inherent difficulties in dispersion.

On the basis of published articles[1–3,7,8] on the effect of CNT-filled elastomers, the major problem that they face is good distribution and dispersion of the CNTs in the elastomeric phase. They found that at low multiwalled carbon nanotube (MWCNT) loadings, the mechanical properties of NR (NR/MWCNT) nanocomposites are better than those with high loadings of MWCNTs in NR (NR/MWCNT) nanocomposites. This is due to a poor dispersion and high agglomeration of MWCNTs in the NR matrix phase. When mixed into rubber, the attractions of van der Waals forces between the outer planes of neighboring nanotubes result in the agglomeration of CNTs.

Furthermore, many researchers have reported the use of one or more fillers combined with CNT in rubber composites; these are commonly called hybrid systems. For instance, Bokobza[2] used this approach by introducing carbon black into a CNT/styrene butadiene rubber (SBR) composites system. The results show good improvement in the mechanical and electrical conductivity with a lower percolation threshold than that obtained with composites filled only with CNTs. Through a combination of the benefits of each type of filler, these hybrid composites could potentially exhibit improved characteristics with regard to single-filler materials. On the other hand, the dilution of expensive CNTs with a cheaper reinforcing component, without compromise of the mechanical properties of the resulting material, would have an economic impact as that would reduce the cost of nanotube-based composites.[2] The addition of silica in NR gives many benefits. These include a reduction in the heat buildup, an improvement in the tear strength, and an increase in compound adhesion in multicomponent products, such as tires. It is believed that the combination of both fillers could bring a synergistic effect to NR composites.[8]

This article presents the effects of the silica/MWCNT hybrid loading ratio on properties of NR/silica/MWCNT hybrid nanocomposites. The effects of the silica/MWCNT hybrid loading ratio on the curing characteristics, tensile properties, fatigue life, morphology, and rubber–filler interaction were investigated.

EXPERIMENTAL

Materials, Formulation, and Mixing Method

Standard Malaysian Rubber Light (SMR L)-grade NR was purchased from the Rubber Research Institute of Malaysia (Selangor, Malaysia). MWCNTs were supplied by Sun Nanotech Co, Ltd. (Jiangxi, China). The average diameter of the MWCNTs was between 10 and 30 nm, and the average length was between 1 and 10 μm. Other compounding ingredients, such as silica (Vulcasil c), zinc oxide, stearic acid, sulfur, *N*-cyclohexyl-2-benzothiazole sulfonamide (CBS), and *N*-isopropyl-*N*′-phenyl paraphenylenediamine (IPPD) were all purchased from Bayer (M), Ltd. (Penang, Malaysia). The formulation used is shown in Table I.

The NR was preblended, and the mixing procedure was carried out in accordance with ASTM D 3184 with a laboratory-sized two-roll mill (model XK-160, 160 × 320 mm^2) maintained at 70 ± 5°C. The various rubber additives were added to the masticated NR before the addition of the CNTs, and finally, the sulfur was added. Five NR nanocomposites were produced and tested. On the basis of our experience, it is too hard to handle MWCNT levels of more than 5 phr; therefore, the blend ratio of the MWCNTs to silica for this study was fixed at 30 phr.

Measurement of the Curing Characteristics

The curing characteristics of the NR nanocomposites were studied with a Monsanto moving die rheometer (MDR 2000) according to ISO 3417 at 150°C. The respective curing times, scorch times, maximum torque, minimum torque, and so on, were determined from the rheograph. The NR nanocomposites were then compression-molded at 150°C for the respective curing times.

Measurement of the Tensile Properties

Dumbbell-shaped samples were cut from the molded sheets, and tensile tests were performed at a crosshead speed of 500 mm/min with a Monsanto tensometer M500 according to ISO 37. The tests were performed at a temperature of 25°C. Five specimens were used, and the average was calculated in each case. The tensile strength, moduli at 100 and 300% (M_{100} and M_{300}), and elongation at break (EB) readings were recorded directly from the digital displays at the end of each test.

Table I. Formulation of the NR Nanocomposites with Different Silica/MWCNT Hybrid Loading Ratios

Material	Compound (phr)
SMR L	100
Sulfur	1.6
Zinc oxide	1.5
Stearic acid	1.5
CBS	1.9
IPPD	2.0
Silica/MWCNT	30/0, 29.5/0.5, 29/1, 27/3, 25/5

Scanning Electron Microscopy (SEM) of the Tensile Fracture Surfaces

The fracture surfaces of the NR nanocomposites were investigated with a Zeiss Supra 55VP PGT/HKL scanning electron microscope. The fracture ends of the specimens were mounted on aluminum stubs and sputter-coated with a thin layer of gold to prevent electrostatic charging during examination.

Measurement of the Rubber–Filler Interaction

Cured samples with dimensions of 30 × 5 × 2 mm^3 were swollen in toluene in a dark environment until equilibrium swelling was achieved, which normally took 48 h at 25°C. The samples were dried in an oven at 60°C until a constant weight was reached. The Lorenz and Park[9] equation [eq. (1)] was applied to study the rubber–filler interactions:

$$Q_f/Q_g = ae^{-z} + b \qquad (1)$$

where the subscripts *f* and *g* of refer to filled and gum vulcanizates, respectively; *z* is the ratio by weight of the filler to the rubber hydrocarbon in the vulcanizates; and *a* and *b* are constants. The higher the Q_f/Q_g values are, the lower the extent of interaction will be between the filler and the matrix. For this study, the weight of toluene uptake per gram of rubber hydrocarbon (Q) was determined by eq. (2):

$$Q = (W_s - W_d)/(W_i \times 100/\text{Formula weight}) \qquad (2)$$

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

Determination of the Fatigue Life

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

$$\text{JIS average} = 0.5A + 0.3B + 0.1(C + D) \qquad (3)$$

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

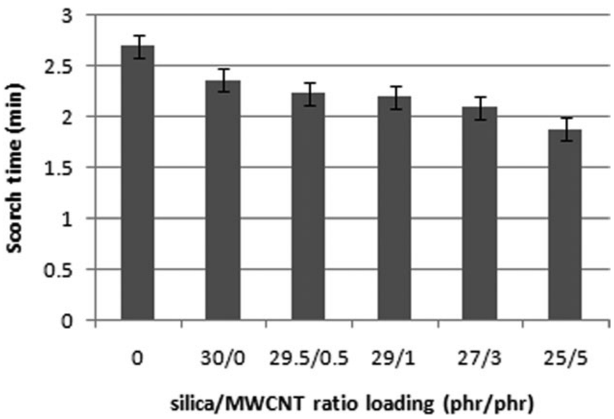

Figure 1. Effect of the silica/MWCNT hybrid loading ratio on the scorch time of the NR/silica/MWCNT hybrid nanocomposites.

RESULTS AND DISCUSSION

Figures 1 and 2 show the effects of the silica/MWCNT hybrid loading ratio on the NR/silica/MWCNT hybrid nanocomposites. Both the scorch and curing times showed a decreasing trend as the MWCNT loading ratio increased in the silica/MWCNT hybrid. It is believed that carbon can activate the vulcanizing process through the promotion of hydrogen sulfide formation and the rupture of S—N linkages when it is heated with sulfenamides in rubber in the presence or absence of other compounding ingredients.[10]

Figure 3 displays the increasing trend of maximum torque with increasing MWCNT loading in the NR/silica/MWCNT hybrid nanocomposites. The increase in maximum torque (M_H) was attributed to the smaller sized (high aspect ratio) MWCNTs, which created a great restriction in the molecular motion of the NR macromolecular chain. In other words, the addition of fillers with smaller sizes, especially MWCNTs, tends to impose extra resistance to flow.[11] As the MWCNT loading increases, the agglomeration also increases. These agglomerations become more dominant and restrict the movement of the NR chain. It causes the maximum torque to increase.[3]

Rubber–Filler Interaction

The effect of the silica/MWCNT hybrid loading ratio on the rubber–filler interaction in the NR/silica/MWCNT hybrid nanocomposites is shown in Figure 4. It is well known that silica has strong filler–filler interactions;[12] therefore, as shown in Figure 4, there was a higher value of Q_f/Q_g at a 30/0 silica/MWCNT loading ratio, and this indicated poor rubber–filler interactions. As the silica/MWCNT loading ratio increased in the silica/MWCNT hybrid, the Q_f/Q_g value decreased until it reached 29/1. This hybrid ratio gave the lowest Q_f/Q_g value, which indicated good rubber–filler interaction. However, as the MWCNT loading ratio increased, Q_f/Q_g also increased. This was due to the low dispersion and high agglomeration of the MWCNTs; this limited the high specific area for interaction with the NR matrix, as shown later in the SEM study.

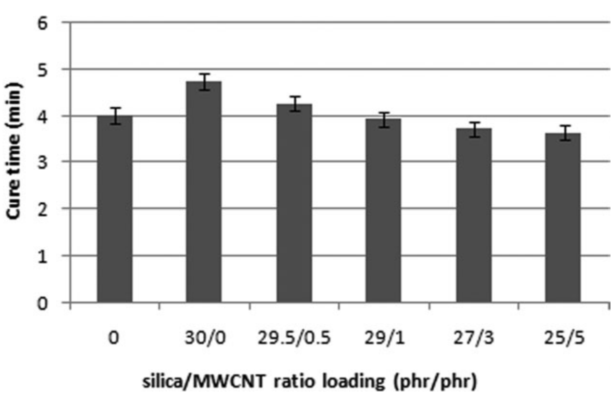

Figure 2. Effect of the silica/MWCNT hybrid loading ratio on the curing time of the NR/silica/MWCNT hybrid nanocomposites.

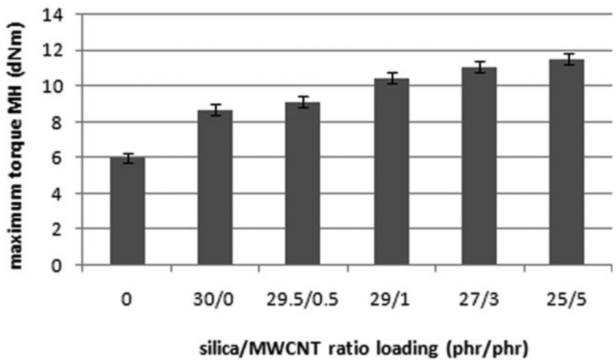

Figure 3. Effect of the silica/MWCNT hybrid loading ratio on the maximum torque of the NR/silica/MWCNT hybrid nanocomposites.

Tensile Properties

The tensile strength and EB values of the NR/silica/MWCNT hybrid nanocomposites are shown in Figures 5 and 6, respectively. From the figures, it can be seen that the tensile strength and EB displayed an increased trend up to a 29/1 silica/MWCNT hybrid loading ratio and then decreased gradually. The increasing trend was possibly caused by the higher surface area, together with the aspect ratio of MWCNTs compared to silica. It is well known that the larger the surface area of the filler is, the greater the interaction between the filler and rubber matrix is. Besides that, the dispersion and the agglomeration of silica and MWCNTs also affected the mechanical properties of the nanocomposites. The hybrid loading ratio at a 29/1 silica/MWCNT ratio gave the highest tensile strength and EB because

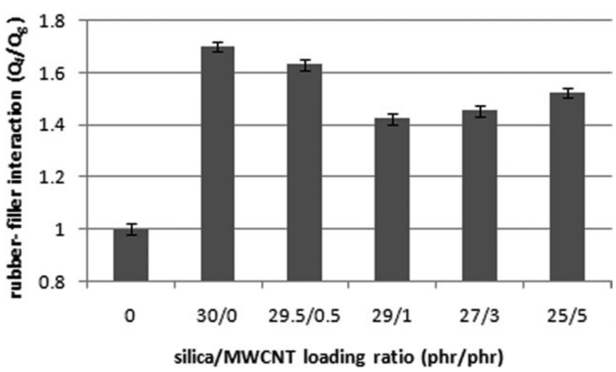

Figure 4. Effect of the silica/MWCNT hybrid loading ratio on the rubber–filler interaction of the NR/silica/MWCNT hybrid nanocomposites.

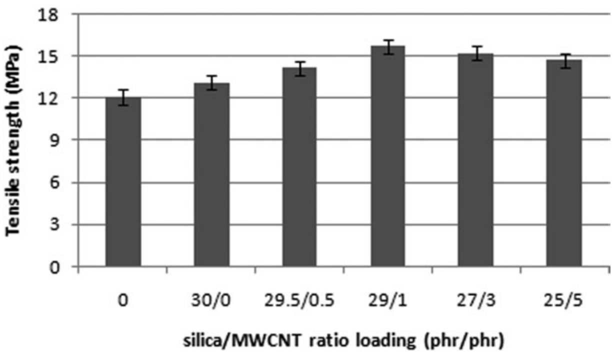

Figure 5. Effect of the silica/MWCNT hybrid loading ratio on the tensile strength of the NR/silica/MWCNT hybrid nanocomposites.

of the good dispersion and lower agglomeration of both fillers. As the MWCNT loading ratio increased in the silica/MWCNT hybrid, the MWCNTs tended to agglomerate and form a domain that acted like a foreign body; this weakened the filler–rubber interaction. This created a reduction in the tensile strength and EB.

Figures 7 and 8 show the effect of the silica/MWCNT hybrid loading ratio on the stress at M_{100} and M_{300} of the NR/silica/MWCNT hybrid nanocomposites. Both figures show that M_{100} and M_{300} increased steadily as the MWCNT loading ratio increased in the silica/MWCNT hybrid. This observation indicates that the addition of MWCNTs improved the stiffness of the nanocomposites. As stated earlier, the high aspect ratio and larger surface area of the MWCNTs gave better rubber–filler interaction at low MWCNT loading. Apart from that, Shanmugharaj et al.[13] also stated that the nanoparticle fillers, which had a large aspect ratio, could provide an additional source of entanglement or physical crosslinks in the NR matrix. As the MWCNT loading increased, the agglomeration also increased. These agglomerations became more dominant and restricted the movement of the NR chain. It caused the composites to become more rigid.

SEM

The SEM micrographs of the NR/silica/MWCNT hybrid nanocomposites are shown in Figures 9 and 10, respectively. Figure 9(a–c) shows the tensile fractured surfaces at 30/0, 29/1, and 25/5 silica/MWCNT loading ratio of the NR/silica/MWCNT hybrid nanocomposites. Figure 9 reveals that as the MWCNT loading ratio increased, the tensile fractured surface roughness of the NR/silica/MWCNT hybrid nanocomposites increased. This observation explained the increased M_{100} and M_{300} of the NR/silica/MWCNT hybrid nanocomposites with increasing MWCNT loading ratio.

Figure 10(a–c) shows the fractured surfaces of the NR/silica/MWCNT hybrid nanocomposites at higher magnification (10,000×). The micrographs show the dispersion of the fillers in the NR matrix. The dispersion of the fillers was one of most important factors that contributed to the strengthening of the nanocomposites. If a lot of agglomeration and a low degree of dispersion occurred, the reinforcing effect could not be attained completely. For the MWCNT/silica/NR hybrid nanocomposites with a 30/0 silica/MWCNT loading ratio, the agglomerations of silica [Figure 10(a)] occurred in the fracture surface, whereas those with a 29/1 silica/MWCNT loading ratio, a good dispersion of MWCNTs and silica [Figure 10(b)] could be seen. Therefore, it gave a high reinforcing effect to the nanocomposites. However, at a 25/5 silica/MWCNT loading ratio, the agglomeration of MWCNTs was dominant [Figure 10(c)], thus limiting the reinforcing effect of the MWCNTs.

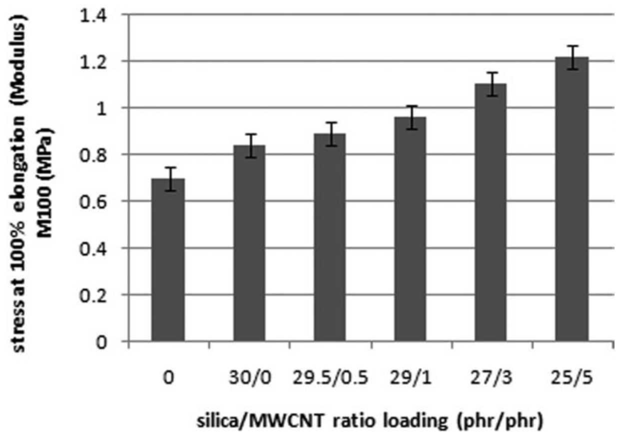

Figure 7. Effect of the silica/MWCNT hybrid loading ratio on the modulus (M_{100}) of the NR/CB/MWCNT hybrid nanocomposites.

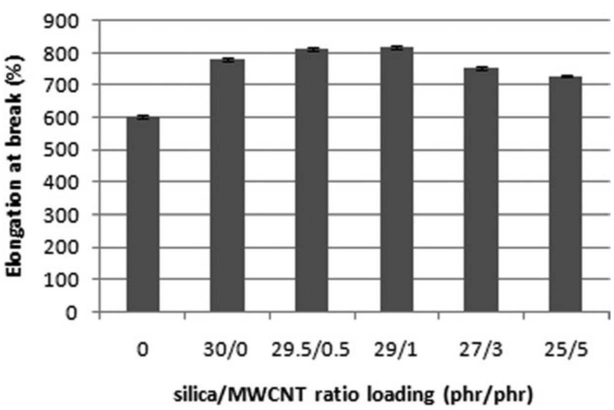

Figure 6. Effect of the silica/NWCNT hybrid loading ratio on the EB of the NR/silica/MWCNT hybrid nanocomposites.

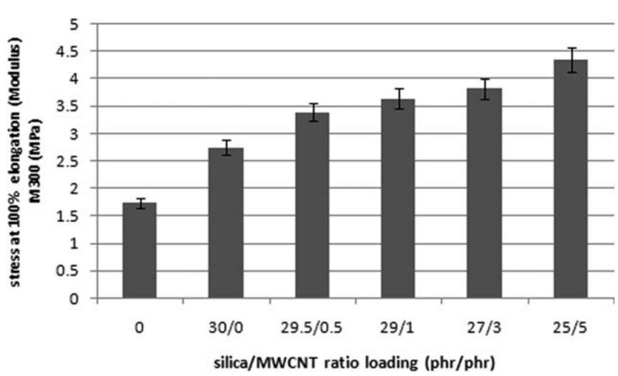

Figure 8. Effect of the silica/NWCNT hybrid loading ratio on the modulus (M_{300}) of the NR/silica/MWCNT hybrid nanocomposites.

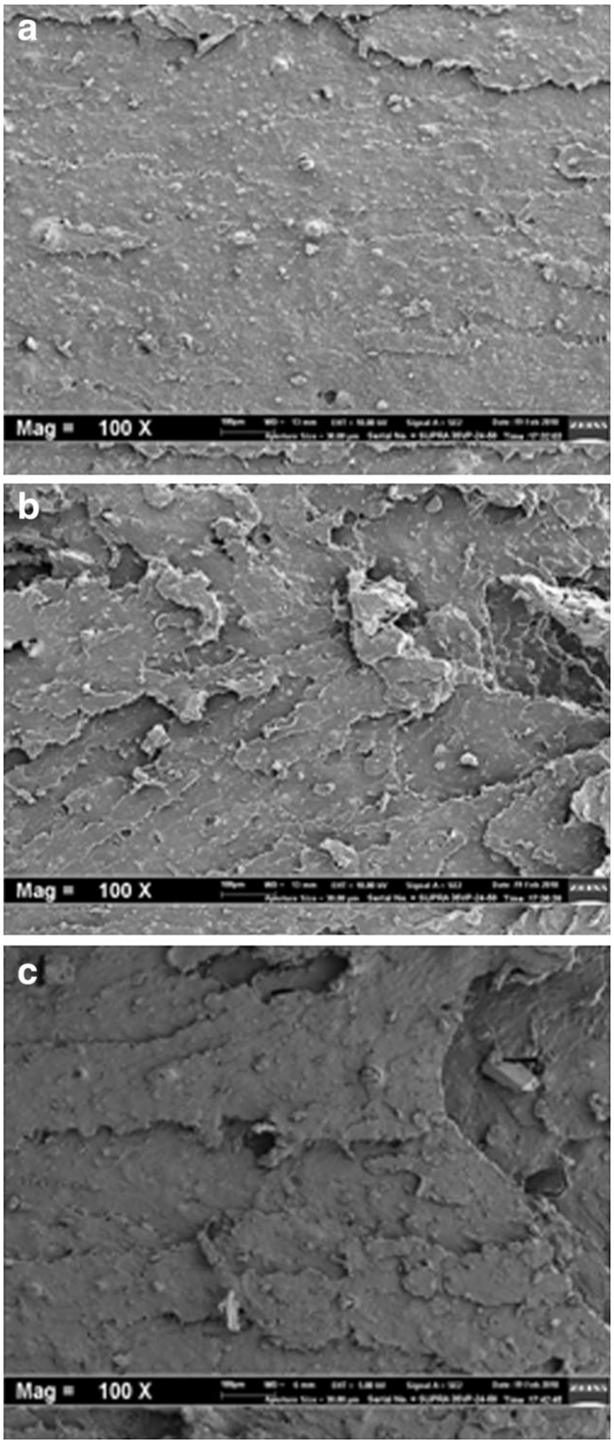

Figure 9. SEM micrographs of the NR/silica/MWCNT hybrid nanocomposites after they were tensile fractured with different silica/MWCNT loading ratios (phr/phr): (a) 30/0, (b) 29/1, and (c) 25/5 (magnification = 100×).

Fatigue Life

Figure 11 shows the fatigue life of the NR/silica/MWCNT hybrid nanocomposites. The fatigue life increased at a 29/1 phr loading and then decreased with increasing filler loading. It was almost similar with the tensile strength and EB results. Again, this observation was attributed to the better dispersion of both fillers in the NR matrix. With a high MWCNT loading ratio, the MWCNTs were not well dispersed and were wetted efficiently by the rubber matrix and agglomerated [Figure 10(c)].

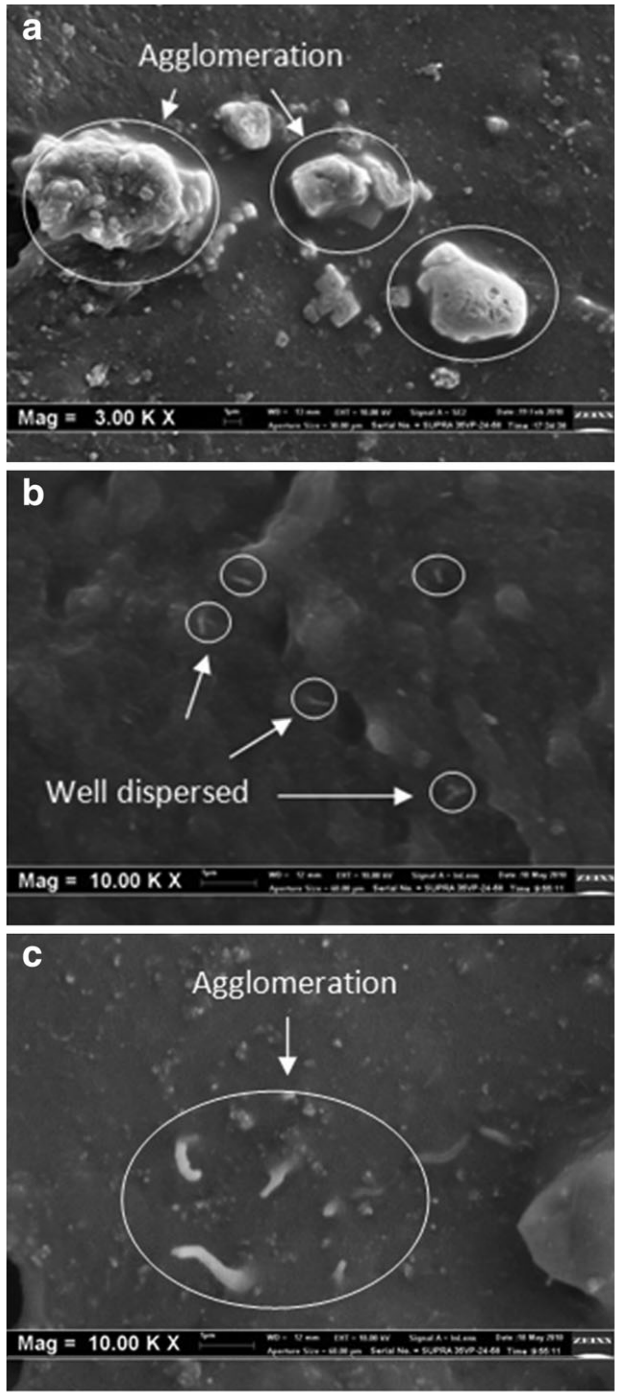

Figure 10. SEM micrographs of the NR/silica/MWCNT hybrid nanocomposites after they were tensile fractured with different silica/MWCNT loading ratios (phr/phr): (a) 30/0, (b) 29/1, and (c) 25/5 (magnification = 3000× and 10,000×).

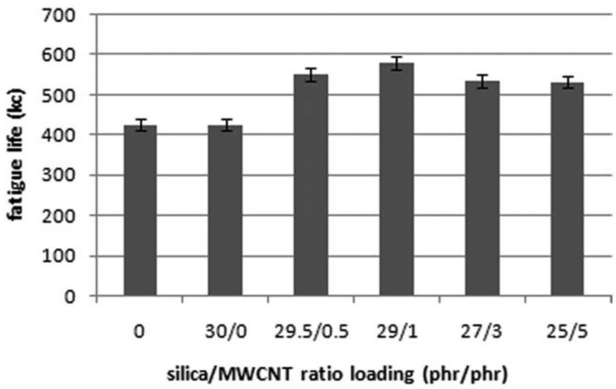

Figure 11. Effect of the silica/MWCNT hybrid loading ratio on the fatigue life of the NR/silica/MWCNT hybrid nanocomposites.

This created a stress concentration or starting point for the crack to occur, consequently led to catastrophic failure, and thus shortened the fatigue life of the composite.[14–17]

CONCLUSIONS

The addition of MWCNTs to the NR/silica hybrid nanocomposites decreased the scorch and curing times of nanocomposites, but the maximum torque exhibited the opposite trend. Furthermore, the tensile strength, EB, and fatigue also increased up to a certain blending ratio and then decreased because of the agglomeration of both fillers. The dispersion and agglomerations of silica and MWCNTs are shown in the SEM micrograph. As the MWCNT loading ratio increased, the agglomeration of MWCNTs became dominant and reduced the reinforcing effect of the MWCNTs. These results imply that the 29/1 silica/MWCNT hybrid presented better properties and created a synergistic effect for the nanocomposites.

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