

Properties of Styrene Butadiene Rubber (SBR)/Recycled Acrylonitrile Butadiene Rubber (NBRr) Blends: The Effects of Carbon Black/Silica (CB/Sil) Hybrid Filler and Silane Coupling Agent, Si69

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ABSTRACT: The recycling or reuse of waste rubber by means of blending together with polymeric materials in addition of filler such as hybrid carbon black and silica (CB/Sil) to a polymer system can provides an opportunity to explore alternative product specifications. Therefore, in this work the investigation of recycled rubber blends based on styrene butadiene rubber/recycled acrylonitrile butadiene rubber (SBR/NBRr) blends reinforced with 50/0, 40/10, 30/20, 20/30, 40/10, 0/50 phr of carbon black/silica (CB/Sil) hybrid filler treated with and without silane coupling agent (Si69) were determined. Cure characteristics, tensile properties, and morphological behavior of selected SBR/NBRr blends at a fix 85/15 blend ratio were evaluated. Results showed that, cure time t_{90} , minimum torque (M_L), and maximum torque (M_H) of CB/Sil hybrid fillers filled SBR/NBRr blends with and without Si69 increased as silica content increased. However, t_{90} and M_L of SBR/NBRr blends with Si69 were lower than without

Si69 except for (M_H). The optimum scorch time (t_{s2}) of SBR/NBRr blends with and without Si69 was obtained at 30/20 phr of CB/Sil hybrid filler. However, t_{s2} of SBR/NBRr blends with Si69 were longer than SBR/NBRr blends without Si69. The incorporation of Si69 has improved the tensile properties [(tensile strength, elongation at break (E_b), stress at 100% elongation (M100), and stress at 300% elongation (M300)] of CB/Sil hybrid fillers filled SBR/NBRr blends. These properties were influenced by the degree of crosslinked density as the silica content is increased. Scanning electron microscopy (SEM) of the tensile fracture surfaces indicated that, with the addition of Si69 improved the dispersion of hybrid fillers and NBRr in SBR/NBRr matrix. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 19–27, 2012

Key words: SBR/NBRr blends; hybrid fillers; Si69; tensile properties; morphological properties

INTRODUCTION

The principle of reinforcement basically can be defined as the ability of fillers to increase the stiffness of unvulcanized rubber compounds and to improve a variety of vulcanizate properties, e.g., tensile strength, abrasion resistance, and tear resistance.^{1,2} Reinforcement is a measure for the strength of filler to keep its in-rubber structure to restrain the occluded rubber at increasing deformation.³ The mechanical properties of crosslinked rubber system can be improved by incorporating of particulate fillers, such as carbon black and silica.^{4,5}

It is well known that the mechanical properties of carbon black-filled rubber composites depend strongly on the degree of adhesion between the carbon black and the rubber.⁶ Carbon black has a relatively inactive surface toward the Si-H group;

therefore, more surface active fillers such as silica were used in combination with carbon black.⁷ Silica has been used as nonblack reinforcing filler in the rubber industry for a long time. Generally, silica contains a large amount of polar silanol group (Si-OH) on its surfaces, which includes strong particle-particle interaction via hydrogen bonds rise to a high tendency for filler agglomeration in the rubber matrix.⁸ Silica alone is assemble up a strong filler network and illustrates a low interaction with the polymer. Compared with carbon black, the use of silica is subject to many problem, especially poor silica dispersion and distribution. The factor such as crosslinked density of the rubber matrix, the size of agglomerates formed by the silica, and rubber/silica interactions will affect the stress-strain curves for silica filled rubber system, therefore, these effect can be controlled by the contents of curing agents, the number of silanol groups on silica particles and the introduction of coupling agent.⁹

Consequently, with increasing filler content, respectively, increasing filler activity, the viscosity of

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the mixture increases and makes the processing more difficult. Silane-based coupling agents are used to enhance both the dynamic and mechanical properties of silica-filled rubbers. The chemical linkages between the silica surface and polymer are formed using bifunctional silane. Meanwhile, for the carbon black linkages between the surface and polymer chains are formed only by physical adsorption. Silane coupling agents are reactive additives which modify the surface of inorganic fillers. It expected to deactivate silanol groups on silica surfaces and improve the distribution of silica in polymer blend. The effect of silanes on the physical properties of rubbers has been widely studied.^{10–15}

Today, the application in rubber-based industrialization has evolved into a versatile industrial raw material. It is used from the simplest elastic rubber band to massive tires for earth-movers. Malaysia is now a major producer of rubber goods, particularly those made from latex, and a major consumer of rubber, ranking sixth in the world. Malaysia continues to export large quantities of rubber products including general and industrial rubber goods and tires. Malaysia has a well-diversified market structure as it exports natural rubber to more than 60 countries. The major markets are the European Union, the Republic of Korea, the United States, Japan, and Singapore.¹⁶

Recycling of waste rubber has become an important global issue which can solve three major problems: wasting of valuable rubber, health, and environment pollution.¹⁷ As a fact recycled rubber waste does not decompose easily which owing to its crosslinked structure and presence of stabilizers and other additives. Compared with reclaimed rubber, recycled NBR rejects are lightly crosslinked and have the high quality nature of rubber hydrocarbon. Quantities of rejects are generate worldwide daily due to (a) use in many area; (b) does not meet processing and product specifications; (c) leftover rubber form manufacturing activities and also old and defective rubber products such as gloves, catheters, tubes, old tires, etc. In Malaysia, the output of nitrile rubber gloves (NBR) was found abundantly. Most of this material originates from medical, industrial as well as research activities. As a fact, nitrile rubber is widely use due to great oil resistance, heat and plasticizer, and low gas permeability, high shear strength for structural applications, and also its resilience makes NBR the perfect material for disposable lab, cleaning, and examination gloves. However, after a certain period of time these polymeric materials are not serviceable and mostly discarded.

Therefore, to solve this environmental issue, we have used a recycled NBR gloves (obtained from industrial productions reject) in effort to create a value added instead of being scrapped. Previously,

the authors¹⁸ reported the comparison properties of virgin NBR (NBRv) and recycled NBR (NBRr) of styrene butadiene rubber/acrylonitrile butadiene rubber (SBR/NBRr) blends. It revealed that most of SBR/NBRr blends properties such as tensile strength, fatigue, etc. showed a better value compared with SBR/NBRv (virgin) blends particularly up to 15 phr of NBRr and then decreased. Furthermore, the SBR/NBRr blends with smallest size of NBRr particles show better mechanical properties (tensile, elongation-at-break, M100, and fatigue) compared with all other blend ratios of bigger sizes of NBRr particles also has been investigated.¹⁹ The investigation of characterization of styrene butadiene rubber/recycled acrylonitrile-butadiene rubber (SBR/NBRr) blends: the effects of epoxidized natural rubber (ENR-50) as a compatibilizer also has been carried out.²⁰ The results indicated that the incorporation of ENR-50 improved the tensile strength, tensile modulus (M100, stress at 100% elongation), hardness, and crosslinked density of SBR/NBRr blends compared with controls without ENR-50 at all blend ratios. To best our knowledge, no work has been reported the detailed study of hybrid filler (CB/silica) principally involved with waste rubber blend. Therefore, in this work the effect of hybrid filler (CB/Sil) in blend ratio of 85/15 SBR/NBRr blends system was carried out. The cure characteristics, mechanical, physical, and morphological behavior of hybrid filler (CB/silica) in SBR/NBRr blends at selected blend ratio (85/15 phr/phr) were determined.

EXPERIMENTAL

Materials and preparation of blends

The materials used in this study were styrene butadiene rubber (SBR), recycled acrylonitrile-butadiene rubber (NBRr)—a recycled product from waste gloves with a range of sizes 117 to 334 μm , silica (vulcasil S), carbon black N330, Si69: silane coupling agent, *bis*(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT), *N*-cyclohexyl-2-benzothiazyl sulfenamide (CBS), zinc oxide, stearic acid, sulfur, and processing oil. Their characteristics are shown in Table I. The SBR/NBRr blends were formulated with blends ratio of 85/15 as given in Table II. The mixing procedure was carried using a two-roll mill at room temperature. First stage, mastication process—the mill nip were set at 0.20 mm wide then raw SBR is passed through the mill nip at two or three times without any stripping. This is important to soften the SBR before adding further ingredients. After mastication, the processing will be easier and the effectiveness of dispersion of compounding ingredients will increase (mastication time, around 1–2 min). Second stage—then, zinc oxides were added evenly into SBR (compounding time, about 2–4 min).

TABLE I
Characteristics of Materials

Materials	Description	Source
Styrene butadiene rubber (SBR)	1502	Bayer (M) Ltd
Recycled acrylonitrile-butadiene rubber (NBRr)	Size: 117–334 μm	Juara One Resources Sdn Bhd, Bukit Mertajam, Penang, Malaysia.
Silica (vulcasil S)		
Si69: Silane coupling agent; bis-3-(triethoxysilyl)-propyl)-tetrasulphide, (TESPT)		Bayer (M) Ltd.
Carbon black	N330	Malayan Carbon (M) Ltd.
N-cyclohexyl-2-benzothiazyl sulfenamide (CBS), zinc oxide, stearic acid, sulphur, and processing oil		Anchor Chemical Co (M) Ltd.

Next, the NBRr were added into SBR (compounding time, around 3–7 min). The CB/Sil (according to ratio) was incorporated into the blends with two major portions (the adding process gradually with small amount of filler). After half part of CB/Sil was added, the half of ingredient (CBS and stearic acid) will inserted together. This action followed with another half of CB/Sil and ingredient (compounding time, about 7–12 min). Lastly, the sulfur was gradually added into blend. Then, the rubber compounds were roll at opening mill nip (step by step) until thickness (6–9 mm). The final SBR/NBRr blend was done at the various shapes (similar to round shape at size A4 sheet) with thickness about 0.4–0.7 cm (4–6 min). The total mixing process was done approximately in 31 min. Cure characteristics were studied at 160°C using a Monsanto Moving Die Rheometer (MDR 2000) with about 4 g samples of the respective rubber blends. The rubber blends then were compression molded at 160°C using a hot press according to respective cure times, t_{90} . The dumbbell specimens were prepared using a die cutter.

Measurement of tensile properties

Dumb-bell shaped samples were cut from the molded sheets and the tensile testing procedure was done according to ASTM D 412-92. Tensile test was performed at a crosshead speed of 500 mm/min using an Instron 3366.

Crosslink density measurements

Cure test pieces of dimension 30 × 5 × 2 mm were weighed using an electrical balance and each test piece was immersed in a glass vessel containing toluene (30 mL) at 25°C. The vessel was kept in the dark to prevent oxidation. The sample from glass vessels and excess toluene was removed by lens blotting paper. The samples were then kept in a closed vessel to prevent toluene evaporation and the weights of the swollen samples were determined. The sample was then reimmersed in the toluene and the process was repeated until a constant swollen weight could be obtained. The sample was de-dried in a vacuum

at room temperature to a constant weight for volume fraction of swollen rubber. The swelling data (three readings each) were utilized to calculate the molecular weight between two crosslink (M_c) by applying the Flory-Rehner equation.²¹

$$M_c = \frac{-\rho_p V_s V_r^{1/3}}{\ln(1 - V_r) + V_r + \chi V_r^2}, \tag{1}$$

$$V_r = 1/(1 + Q_m), \tag{2}$$

Where ρ is the density of the rubbers, V_s is the molar volume of the solvent (toluene), V_r is the volume fraction of the swollen rubber, χ is the interaction parameter of the rubber, and Q_m is the weight swell of the SBR/NBR blends in toluene. The degree of crosslinking density (v) is given by;

$$V = 1/(2M_c). \tag{3}$$

The following constant values were used to determine the degree of crosslinking density of SBR/NBR.

$$\begin{aligned} \rho (\text{SBR}) &= 0.933 \text{ g/cm}^3, \quad \rho (\text{NBR}) = 1.17 \text{ g/cm}^3 \\ \chi (\text{SBR}) &= 0.446, \quad \chi (\text{NBR}) = 0.390, \\ V_s (\text{toluene}) &= 106.35 \text{ cm}^3/\text{mol} \end{aligned}$$

TABLE II
Formulation for SBR/NBR Blends with and Without Si69

Ingredients (phr)	Blend ratio (85/15)	
	Without Si69	With Si69
SBR	85	85
NBRr	15	15
Si69	–	3
Zinc oxide	5	5
Stearic acid	2	2
Sulfur	2	2
CBS	1	1
Processing oil	5	5
Carbon black (N330)/silica (Vulcasil S)	50/0, 40/10, 30/20, 20/30, 10/40, 0/50	50/0, 40/10, 30/20, 20/30, 10/40, 0/50

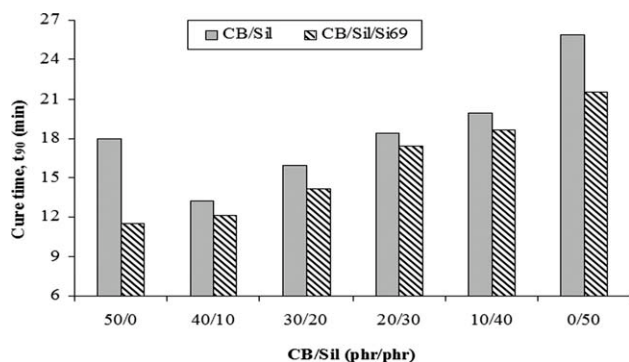


Figure 1 The effects of cure time (t_{90}) of CB/Sil hybrid fillers filled SBR/NBRr blends with and without Si69.

Fourier transform infrared (FT-IR) spectroscopy

The spectrum was obtained using Perkin-Elmer Spectrum One Series equipment and attenuated total reflection (ATR) technique was adopted. The FT-IR test was done with 64 numbers of scans at 4 cm^{-1} spectrum resolution and within wave number range of 4000 to 600 cm^{-1} , respectively.

Scanning electron microscopy (SEM)

Scanning electron microscopy (VPFESEM), model Zeiss SUPRA 35VP was used to analyze the surface aspects concerning the quality of bonding, and to detect the presence of microdefect if any. The surfaces of the samples were mounted on aluminum stubs and sputter coated with a thin layer of gold about 20 nm thickness before avoiding electrostatics charging and poor resolution during examination.

RESULTS AND DISCUSSION

Cure characteristics

The cure characteristics of CB/Sil hybrid fillers filled SBR/NBRr blends with and without Si69 are shown in Figures 1 to 4, respectively. It can be seen that

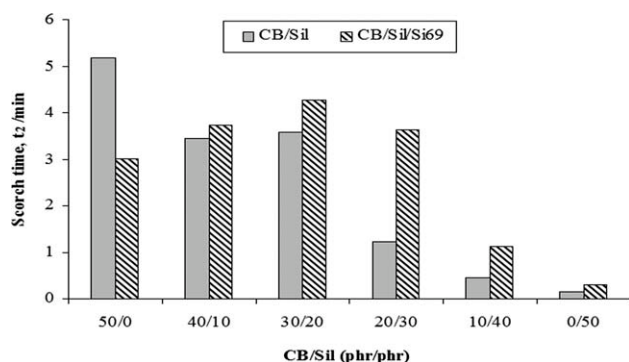


Figure 2 The effects of scorch time (t_2) of CB/Sil hybrid fillers filled SBR/NBRr blends with and without Si69.

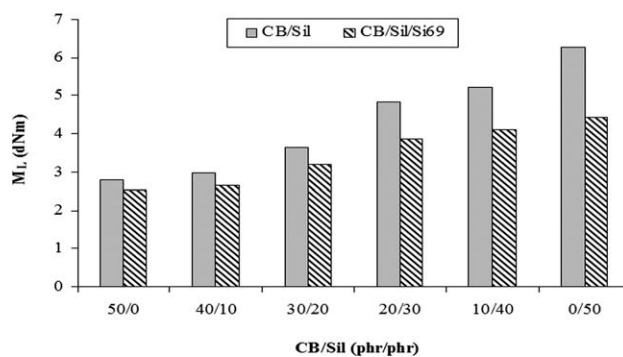


Figure 3 The effects of minimum torque (M_L) of CB/Sil hybrid fillers filled SBR/NBRr blends with and without Si69.

cure time t_{90} of both blends increased as silica content increased (Fig. 1). The increment of t_{90} was due to the present of the silanol group as the silica content increased.²² The silanol groups can cause the adsorption of accelerator resulting in the delay of vulcanization reaction and, thus, the reduction of crosslinked density in sulfur-cured rubbers. In this situation, the retardation effect of silica plays a more dominant role. In addition, the surfaces of silica are polar and hydrophilic and there is a strong tendency to absorb moisture, which adversely influences cure and properties of rubber vulcanizates.²³ However, at similar blend ratio, with incorporation of Si69 in SBR/NBRr blends filled CB/Sil, the t_{90} are shorter than without Si69. According to Yan et al.²⁴ with the presence of silane coupling agent, the silanol groups of silica decreases, resulting less hydrophilic behavior thus t_{90} become faster.

Meanwhile, scorch time t_2 of the CB/Sil hybrid fillers filled SBR/NBRr blends with and without Si69 increased with increasing silica content up to 20 phr indicated an increase in scorch protection of the compound (Fig. 2). Choi²⁵ reported that the adsorption of curatives by silica results in delay of the scorch time and reduction of the delta torque of a silica-filled rubber compound. It can be seen that the

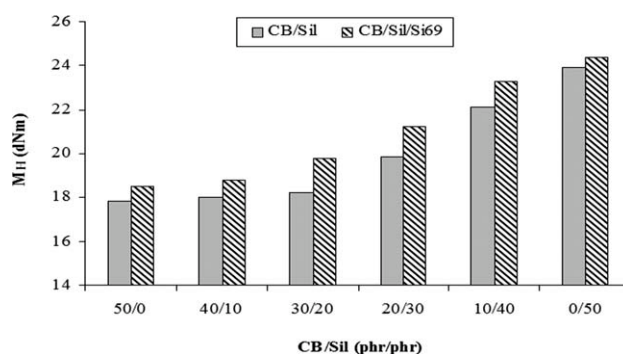


Figure 4 The effects of maximum torque (M_H) of CB/Sil hybrid fillers filled SBR/NBRr blends with and without Si69.

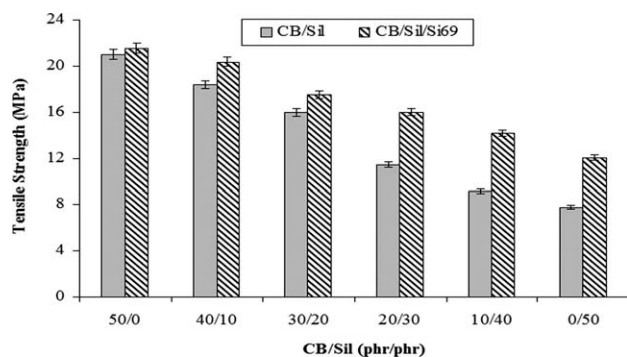


Figure 5 The effects of tensile strength of CB/Sil hybrid fillers filled SBR/NBR blends with and without Si69.

blends with Si69 show growth of scorch time compared with blend without Si69. It is believed that, the amount of Si69 used in this work may not be enough when the silica content is high (as the SBR, NBR, and Si69 are constant except for silica content). This resulted less reaction between silica-Si69-NBR. For the blends without Si69, the NBR tend to adsorbed on the silica surface and prevents the silica from adsorbing the accelerator thus lower scorch time. When silica content is dominant particularly more than 30 phr, the t_2 gradually decreased. It is believed that with the existence of crosslinked precursors and unreacted curatives in the recycled rubber together with the effect of Si69 on silica surface will accelerate the vulcanization process. According to Rattanasom et al.,²⁶ the gradual decrease in scorch time when silica content is more than 30 phr might be because these compounds have experienced greater thermal history during mixing.

The minimum torque, M_L , of SBR/NBR blends of CB/Sil hybrid filler with and without Si69 increased with increasing silica content, respectively (Fig. 3). This is probably due to the presence of crosslinked precursors and unreacted curative in NBR and other additives together with CB/Sil hybrid filler, therefore increasing the M_L of the vulcanizates. However, at all blend ratios, the blends with Si69 exhibited lower M_L compared without Si69, thus indicates a better processability.

It can be seen that the maximum torque, M_H , of both SBR/NBR blends of CB/Sil hybrid with and without Si69 increased gradually as silica content increased (Fig. 4). The presence of both filler (CB/silica) would reduce the mobility of the macromolecular chains in the blends hence increased the M_H . However, at similar blend ratio, CB/Sil hybrid fillers filled SBR/NBR blends with Si69 exhibited higher value of M_H compared without Si69. The improvement in M_H can be explained due to the increased interaction between filler and rubber matrix particularly with presence of Si69.

Tensile properties

Figure 5 presents the relationship between tensile strength of CB/Sil hybrid fillers filled SBR/NBR blends with and without Si69. It can be seen, both blends showed the same trend, where the tensile strength decreased as silica content increased. These observations are mainly attributed to incompatibility of the blends.^{18,19,20,27,28} It is well known that physico-mechanical properties of SBR and NBR will drop due to the fact that NBR has greater polarity than SBR.²⁹ It appears that the tensile strength notably change with increasing the silica content. The deterioration of tensile strength at higher silica content was due to increase silica-silica interaction and consequently a weak interaction between filler-rubber was formed. In fact, silica dispersion is worsening than carbon black dispersion in rubber blends. Silica forms a strong hydrogen bond with basic materials due its surface is acidic, as a consequence it would increase agglomeration. However, with the incorporation of Si69 in CB/Sil hybrid fillers filled SBR/NBR blends, the tensile strength was improved. It can be seen at a similar blend ratio of hybrid filler, the tensile strength of the CB/Sil hybrid fillers filled SBR/NBR blends with Si69 is higher than without Si69 particularly when more silica was added. When using Si69, a stable Si-O-Si bond is formed between the silane and the filler particle surface. Meanwhile, the nitrile group will make a hydrogen bond with the silanol group of silica. All can be explained due to a better interaction of CB-silica-NBR in the SBR matrix with the presence of Si69; hence better dispersion occurred thus improving the interfacial adhesion of CB/Sil hybrid fillers filled SBR/NBR blends by reducing the interfacial energy between phases as discussed later in morphological studies.

Figures 6 to 8 show the relationship between modulus M100, modulus M300 and elongation at break (E_b) of CB/Sil hybrid fillers filled SBR/NBR blends with and without Si69, respectively. Both modulus

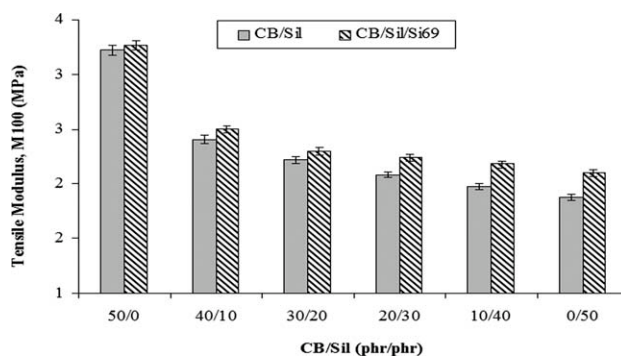


Figure 6 The effects of tensile modulus (M100) of CB/Sil hybrid fillers filled SBR/NBR blends with and without Si69.

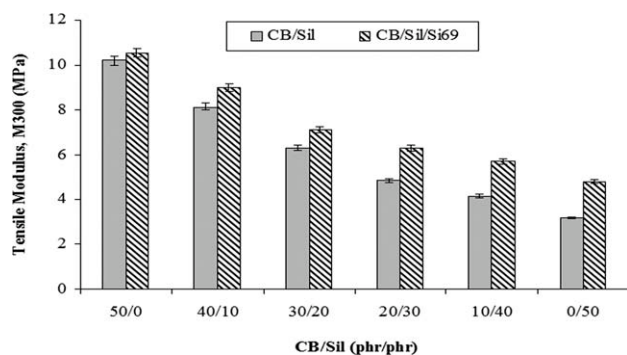


Figure 7 The effects of tensile modulus (M300) of CB/Sil hybrid fillers filled SBR/NBRr blends with and without Si69.

tend to decrease and E_b increases as silica content increased correspondingly. This was due to decrease in crosslinked density as illustrated later in Figure 9. The increases in silica content will lead to decrease in filler-rubber interaction (increases in silica-silica interaction) and consequently it will affect the cross-linked density value.²⁵ However, at similar blend ratio, the tensile modulus of CB/Sil hybrid fillers filled SBR/NBRr blends with Si69 exhibit higher value than without Si69. This is simply due to improved filler dispersion and increased crosslinked density in the presence of Si69. The Si69 noticeably reduced the filler-filler interaction thus improved rubber-filler interaction which contributed to better filler dispersion. With corresponding to the cross-linked density results (Fig. 9), the E_b of both CB/Sil hybrid fillers filled SBR/NBRr blends with and without Si69 is continuously increased with increasing silica content. However, with the incorporation of Si69, E_b values tend to increased as silica content increased. This was probably due to the chemical bonding between the filler and matrix which facilitated by the Si69 thus improved the E_b values.³⁰ For notes, the chemical bonding between SBR and NBRr was formed via sulfur crosslinking between unsaturated bonds in both SBR and NBRr as illustrated in Figure 10.

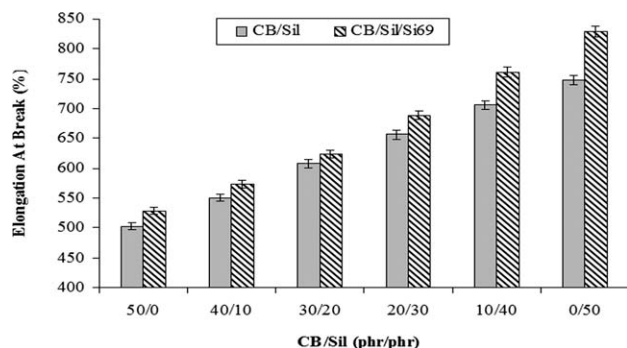


Figure 8 The effects of elongation at break (E_b) of CB/Sil hybrid fillers filled SBR/NBRr blends with and without Si69.

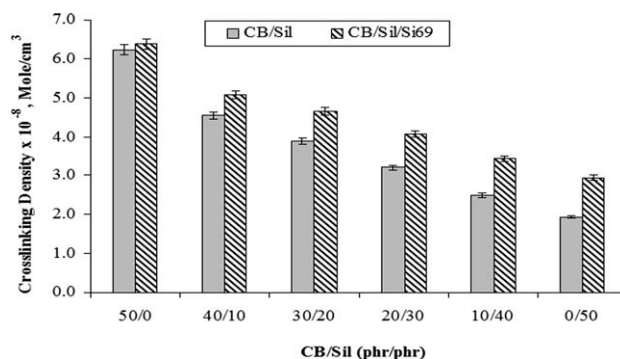


Figure 9 The effects of crosslinked density of CB/Sil hybrid fillers filled SBR/NBRr blends with and without Si69.

Fourier transform infrared (FT-IR) analysis

The FT-IR spectra of CB/silica at ratios 50/0, 40/10, 30/20, and 0/50 show hydroxyl absorption at 3266, 3265, 3263, and 3393 cm^{-1} , respectively (Fig. 11). These hydroxyl groups represent the reactive surface of the silica. Addition of Si69 improved the dispersion of CB and silica fillers in SBR and NBR blends because it provides chemical bonds between both fillers and polymers. Even though SBR and NBR are incompatible due to the differences of polarities but the chemical interaction such as sulfur vulcanization or reaction with coupling agents can take place at double bond of both rubbers. The chemical interaction of SBR or NBR with Si69 is preferable to occurs at primary carbon compared with tertiary carbon of propyl group in Si69. This is because removal of hydrogen from primary carbon is easily to take place than tertiary carbon. By incorporating silane coupling agent, the hydroxyl groups were eliminated at all ratios. It is explained by hydrolytic condensation process which binds the silica filler at its OH reactive site with ethoxy groups of silane coupling agents as shown in Figure 12. Therefore, each of the silica particles binds to the silane coupling agents and reduced silica aggregation in the

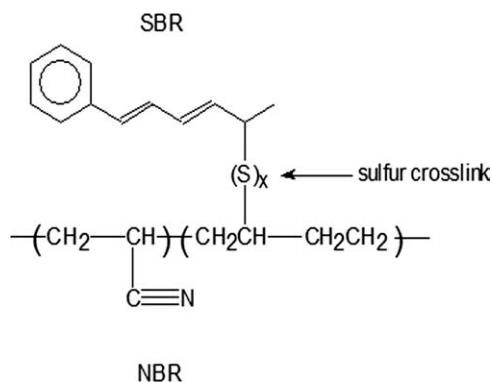


Figure 10 The proposed interaction of SBR/NBRr blends.

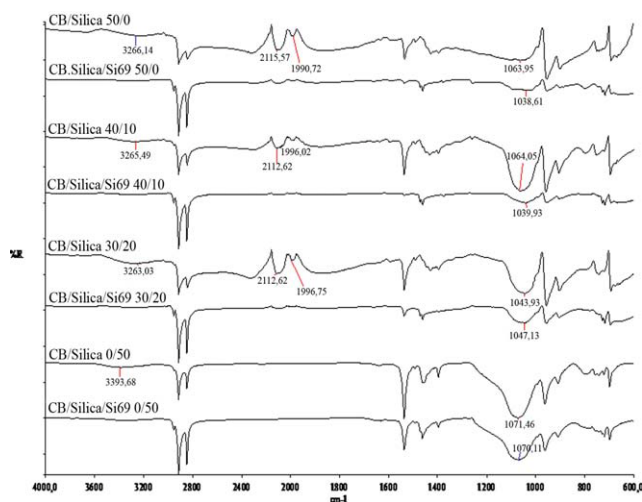


Figure 11 FT-IR analysis of CB/Silica hybrid fillers filled SBR/NBRr blends with and without Si69. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

blends. This is correlates with recorded Si-O-Si absorption in range 1100 to 1000 cm^{-1} at 1039, 1047, and 1070 cm^{-1} for ratios 40/10, 30/20, and 0/50 with silica loading. Without silica loading (i.e., ratio 50/0) the bond formation between carbon black and silane coupling cannot be determine based on Si-O-C bond. Therefore the successful in binding carbon black with silane coupling agents is judge based on elimination of trapped CO_2 onto carbon black surface area after incorporating silane coupling agents. The trapped CO_2 were shown at 2115 to 2112 cm^{-1} and 1996 to 1990 cm^{-1} for ratios 50/0, 40/10, and 30/20.

Morphological properties

Figure 13 shows the schematic effect on distribution of CB/Sil hybrid fillers filled SBR/NBRr blends. Figure 13(a) shows the CB particles form secondary aggregates and the space between them is filled with rubber matrix. CB tends to form low aggregates

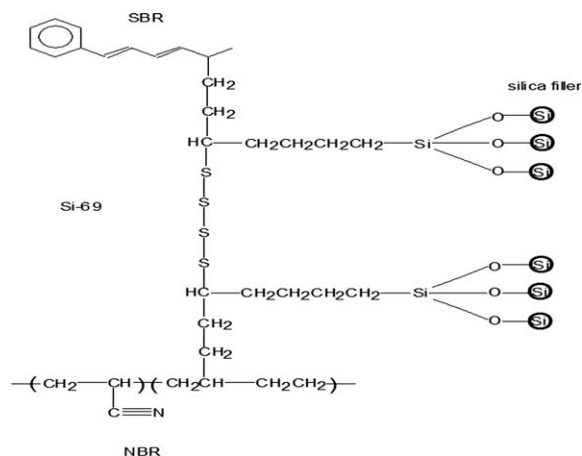


Figure 12 The proposed interactions of CB/Sil hybrid fillers filled SBR/NBRr blends with and without Si69.

structure as the silica particles occupied the space between them at low silica content [Fig. 13(b)]. When CB content is low, most CB particles will undersized and spread networks among the silica in the system due to the distribution effect of silica as shown in Figure 13(c). Figure 13(d) shows the CB aggregates is blocked-up by the continuous silica phase at high silica content. A partial network of silica tends to form agglomeration which contributed to poor dispersion between CB-silica in rubber matrix.

Figures 14 to 16 show the SEM micrograph of tensile fracture surfaces of CB/Sil hybrid fillers filled SBR/NBRr blends with and without Si69 at 40/10, 20/30, and 0/50 blend ratio. As can be seen from Figure 14(a), the tensile fracture surfaces is characterized by rougher surface with many tear line mean more energy needed to break the sample compared with Figure 14(b) which appeared broader tearing line. This could be explained by the good interaction between the CB and silica with SBR and NBRr in the presence of Si69. The uniformly dispersed of hybrid CB/Sil in SBR/NBRr matrix has alter the crack path which leads to more resistance for crack

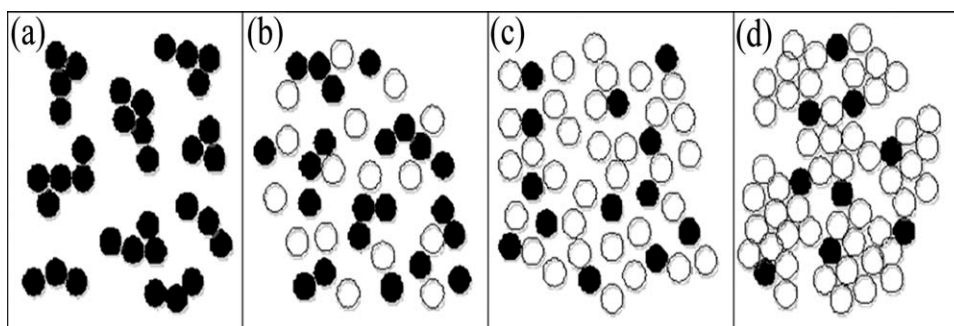


Figure 13 The schematic effects on distribution of CB/Sil hybrid fillers filled SBR/NBRr [CB (●), Silica (○)].

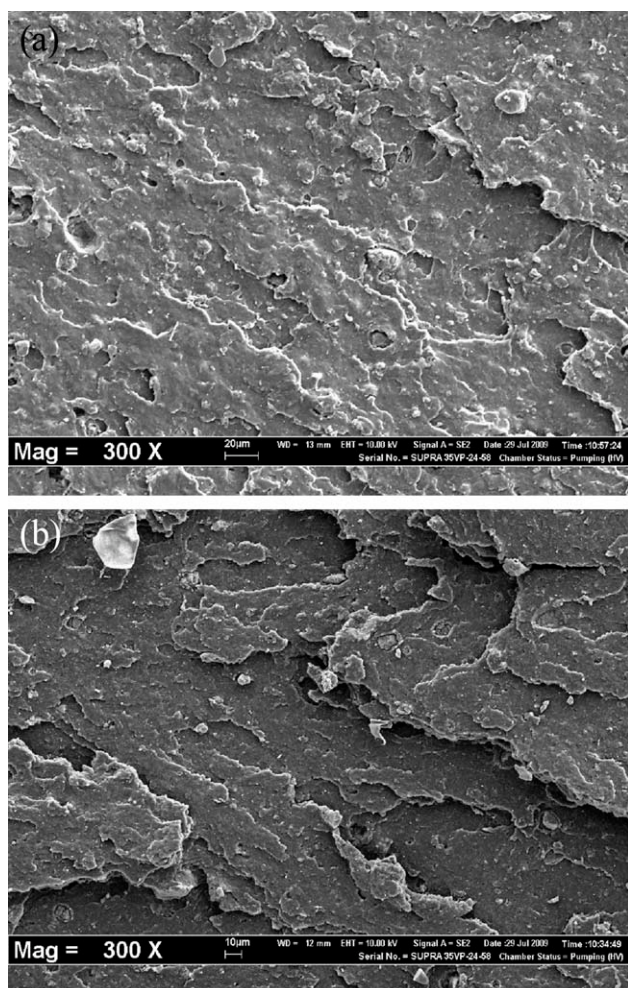


Figure 14 The tensile fracture surfaces of CB/Sil hybrid fillers filled SBR/NBR blends (a) with Si69 at 40/10 blend ratio, $\times 300$ magnification. The tensile fracture surfaces of CB/Sil hybrid fillers filled SBR/NBR blends (b) without Si69 at 40/10 blend ratio, $\times 300$ magnification.

propagation and hence better tensile strength. The addition of Si69 provides a better filler dispersion, reduced the filler-filler interface thus improved the filler-rubber interactions.

Figure 15 displays the tensile fracture surfaces of CB/Sil hybrid fillers filled SBR/NBR (a) with Si69, (b) without Si69 at 20/30 blend ratio. It can be seen that, Figure 15(b) shows a coarse and poor distribution of CB/Sil hybrid filler and NBR in SBR matrix. This shows low adhesion between phases and contributed to poor stress transfer across the interface. However, the surface of CB/Sil hybrid fillers filled SBR/NBR with Si69 [Fig. 15(a)] illustrates better adhesion between CB/Sil hybrid filler and NBR in SBR matrix.

Figure 16 illustrates the tensile fracture surfaces of CB/Sil hybrid fillers filled SBR/NBR (a) with Si69 and (b) without Si69 at 0/50 blend ratio. As can be seen in Figure 16(a), at high concentration of silica,

the agglomeration and detachment of silica and NBR is minor. It strongly support that, with the present of Si69 in CB/Sil hybrid fillers filled SBR/NBR, the dispersion of filler is better, resulting in reduction silica-silica and NBR interaction and lead better dispersion in SBR/NBR blends. The poor distribution of NBR at higher silica content can be clearly seen in Figure 16(b).

CONCLUSIONS

The following conclusions can be drawn from this study;

1. The cure time, t_{90} of CB/Sil hybrid fillers filled SBR/NBR blends with Si69 are shorter than without Si69 due to the reduction of curative adsorption on silica surface. The CB/Sil hybrid

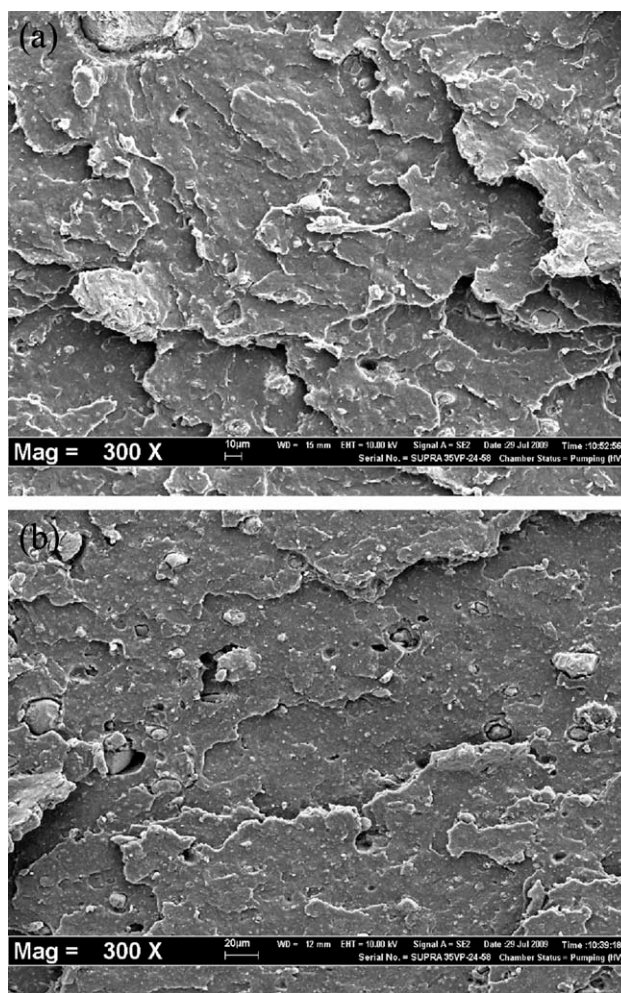


Figure 15 The tensile fracture surfaces of CB/Sil hybrid fillers filled SBR/NBR blends (a) with Si69 at 20/30 blend ratio, $\times 300$ magnification. The tensile fracture surfaces of CB/Sil hybrid fillers filled SBR/NBR blends (b) without Si69 at 20/30 blend ratio, $\times 300$ magnification.

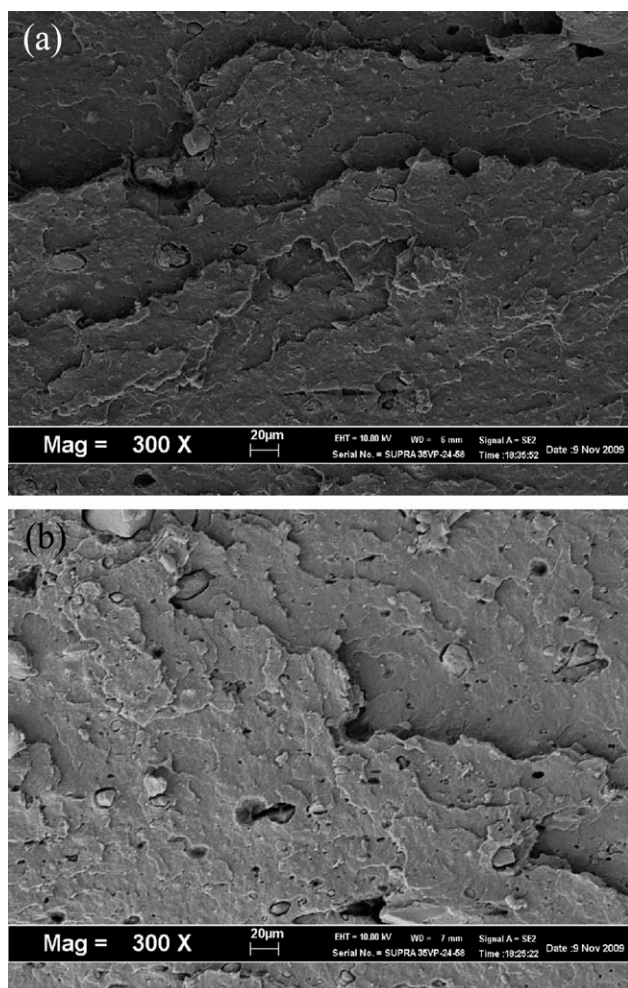


Figure 16 The tensile fracture surfaces of CB/Sil hybrid fillers filled SBR/NBRr blends (a) with Si69 at 0/50 blend ratio, $\times 300$ magnification. The tensile fracture surfaces of CB/Sil hybrid fillers filled SBR/NBRr blends (b) without Si69 at 0/50 blend ratio, $\times 300$ magnification.

fillers filled SBR/NBRr blends with Si69 had better scorch time, t_2 compared blends without Si69 at all blend ratio except at 50/0 blend ratio (CB dominant).

- The minimum torque, M_L , of CB/Sil hybrid fillers filled SBR/NBRr blends with and without Si69 increased with increasing silica content. The CB/Sil hybrid fillers filled SBR/NBRr blends with Si69 exhibited lower M_L compared without Si69, thus indicates a better processability. The maximum torque, M_H , of both CB/Sil hybrid fillers filled SBR/NBRr blends with and without Si69 increased gradually as silica content increased.
- The tensile strength, tensile modulus (M_{100} and M_{300}), and (E_b) of CB/Sil hybrid fillers filled SBR/NBRr blends with Si69 were higher than blends without Si69. This observation was due to the better rubber-filler interaction with the presence of Si69.

- SEM micrographs results show that the presence of Si69 in CB/Sil hybrid fillers filled SBR/NBRr blends, improved the dispersion of hybrid fillers in SBR/NBRr matrix.

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