A Comparative Study of the Cure Characteristics, Processability, Mechanical Properties, Ageing, and Morphology of Rice Husk Ash, Silica and Carbon Black Filled 75 : 25 NR/EPDM Blends

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ABSTRACT: The performance of rice husk ash (RHA), obtained by burning rice husks, as a filler for natural rubber (NR)/ethylene–propylene–diene monomer (EPDM) blends was investigated. For comparison purposes, two commercial reinforcing fillers, silica and carbon black were also used. A fixed 75 : 25 blend ratio (wt %) of NR and EPDM was prepared using a two-stage conventional mixing procedure. Filler loading was varied from 0 to 60 parts per hundred of resin (phr) at 15 phr intervals. The results indicated that RHA offers processing advantages over silica and carbon black. The use of RHA as an additional filler provided almost no improvement in the tensile strength and abrasion resistance of the 75 : 25 NR/EPDM blends. The ozone resistance of the blends was inferior to those obtained from the addition of RHA. However, RHA was better in resilience property than that of silica and carbon black. Scanning electron micrographs revealed that the dispersion of RHA filler in the rubber matrix is discontinuous, which in turn generates weak structure when compared with carbon black and silica. According to these observations, RHA could be used as a diluent filler for the 75 : 25 NR/EPDM blend, while silica and carbon black can be used as a reinforcing filler. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 932–941, 2008

Key words: natural rubber; EPDM; blend; rice husk ash; silica; carbon black; filler

INTRODUCTION

Natural rubber (NR) is a natural biosynthesis polymer having an attractive range of properties, possessing excellent mechanical properties, and good processing characteristics. However, NR is highly susceptible to degradation, due to the presence of double bonds in the main chain. Degradation of NR is accelerated mainly by heat, humidity, light, ozone, radiation etc. In general, improvement in the poor ozone resistance of NR can be achieved by blending it with low unsaturated rubbers such as ethylene–propylene–diene rubber (EPDM) obtained by polymerizing ethylene and propylene with a small amount of a nonconjugated diene, which imparts usually good ageing characteristics, good weathering oxidation, and chemical resistance.[1] Blending with EPDM has been reported to be effective in improving the ozone resistance of NR.[2] Polymers are rarely used without fillers in many applications. When NR is blended with EPDM, it is often found necessary to modify it with fillers to cater it to improve the modulus, failure properties (tensile and tear strength), and abrasion resistance and reduce unit manufacturing costs while maintaining a high level of product quality and performance. Introduction of fillers into polymers leads to a wide range of interactions arising at the polymer-filler interface. These dispersed fillers considerably influence the properties of the polymer composites, including their degradation and stability. Filler properties that have the most influence on rubber processing and vulcanizes are particle size, surface area and character, and structure. Among several fillers, carbon black, and silica are the main important reinforcing agents used in the compounding recipes.[3–15] In spite of being well known for their strong interaction with rubbers, these fillers are relatively expensive compared with natural fillers.

Recently, the application of fillers derived from agricultural wastes has attracted interest due to their low cost, renewable and environment friendly nature. Among different types of such fillers, while rice husk ash (RHA) which is obtained by burning rice husk for electrical power plants, mainly consists of amorphous silica and residual carbon black from incomplete combustion. The amount of silica and

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carbon black in the ash varies depending on the combustion conditions. Nowadays RHA is used in plastic, rubber, and thermoplastic elastomers because of various advantages, such as ease of processing, easy availability, economic considerations, environmental preservation, and an increased emphasis on the use of renewable resources. Fuad et al.[16] reported the application of RHA as a filler in polypropylene. They observed that the incorporation of RHA into polypropylene led to an increased flexural modulus of the composites while tensile strength, elongation at break and Izod impact strength showed a decrease. Sae-oui et al.[17] investigated the effects of filler loading on the properties of RHA filled NR materials when compared with commercial fillers. They found that both grades of RHA, low- and high-carbon contents, resulted in inferior mechanical properties (tensile strength, modulus, hardness, abrasion resistance, and tear strength) in comparison with reinforcing fillers such as silica and carbon black. Arayapranee et al.[18] reported that RHA-filled vulcanizates with 20 phr, gave the best results, providing physical properties slightly inferior to unfilled compounds. Da Costa et al.[19–23] have been reported some investigations about RHA influence in the vulcanization kinetics and mechanical properties of NR compounds. Siriwardena et al.[24–26] studied the effect of dynamic vulcanization and the influence of filler loading of white rice husk ash (WRHA)-filled ethylene–propylene–diene terpolymer/polypropylene blends. They reported that WRHA-filled blends could also be dynamically vulcanized to achieve enhanced properties in a similar manner to the unfilled blends. The influences of a compatibilizer, poly(propylene-ethylene acrylic acid) and a silane coupling agent, 3-aminopropyl-triethoxysilane-[CAS-No. 919-30-2] (3-APF), on mechanical properties of WRHA-filled polypropylene/NR blends was also investigated.[27] Ismail et al.[28] studied the use of WRHA as a filler for NR/linear low density polyethylene (LLDPE) blends. They reported that increasing WRHA loading in NR/LLDPE blends resulted in reduction of tensile strength, elongation at break and mass swell but increased tensile modulus and hardness. Filler dispersion also plays an important role in reinforcement. Filler properties that have the most influence on rubber processing and vulcanizes are particle size, surface area and character, and structure. Once an understanding of the particle characteristics is achieved, it is easier to correlate the compound mechanical properties with the microscopic particle properties. RHA has a large particle size, irregular-shaped particle (nonspherical shape with rough surface), and porous structure. A complex interdependence among the physical properties of filler and polymer determines the behavior of the compound. For example, larger particles give lower specific surface area, which influences the adsorption characteristics and negatively affects the filler-matrix interaction.[29] Actually, the bad adherence in the filler-matrix would give rise to the formation of voids in the interphase, which would decrease the mechanical properties of filled rubbers. However, no serious attempt has been made to evaluate the use of RHA as a reinforcing filler for rubber. Since RHA is readily available at extremely low cost as an unwanted by-product of rice mills, the finding of useful applications for the RHA will certainly help to alleviate the problems related to the disposal of the waste husks.

In the present study, a NR/EPDM weight ratio corresponding to 75 : 25 has been chosen because at this composition, it is possible to maintain the good mechanical properties of NR while improving the ageing resistance of the rubber material. RHA was introduced into 75 : 25 NR/EPDM blends and the effects of filler loading compared to that of the commercial fillers, silica, and carbon black, were investigated. This study evaluated the processability, mechanical properties, effect of heat ageing on tensile properties, abrasion and ozone resistance, and morphology studies of the tensile fracture surfaces of filler-filled 75 : 25 NR/EPDM blends.

EXPERIMENTAL

Materials

Details of blending ingredients and rubber formulas used are shown in Table I. RHA was sieved on a 325-mesh sieve. The particle size distribution was measured by using a particle size analyzer (Mastersizer-S, Malvern Instruments Ltd., England). The surface area of the fillers was determined by the Brunauer-Emmett-Teller method using an ASAP 2000 surface area analyzer (Micromeritics Instrument Corp., Norcross, GA 30093-1877).

When rice husk is burnt about 20 wt % of the husk remains as ash. The majority of the substance in RHA is silicon dioxide (=78.33%) together with an amount of residual carbon (=17.05%) and other oxides such as Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O, K_2O, and P_2O_5 in small amounts (=4.62%). The particles show an irregular form with a minimum size of 0.49 μm and a maximum size of 45 μm. The particle average size of RHA was 36.6 μm as shown in Table II. The physical properties of RHA, silica, and carbon black are presented in Table II.

Preparation of NR/EPDM blends

Formulations of the blends are provided in Table I. NR/EPDM (75 : 25 wt %) blends were prepared in an internal mixer using conventional mixing procedures

TABLE I
Ingredients Used in the Present Study

Ingredient	Amount phr[a]	Grade/Supplier
NR	75	STR XL/Thailand
EPDM	25	DuPont's Nordel® IP 4570/DuPont Dow Elastomers L.L.C./Wilmington, DE, USA
Paraffin oil	4	Flexon 845/Exxon Co., Ltd., Thailand
Zinc oxide (ZnO)	2.0	Commercial/Gradmann, Thailand
Stearic acid	2.0	Commercial/P. T. Cisadaneraya Chemical, Indonesia
Tetramethylthiuram bisulfide-[CAS-No. 137-26-8] (TMTD)	0.15	Flexsys Co. Ltd., Germany
Mercaptobenzothiazole disulfide-[CAS-No. 120-78-5] (MBTS)	1	Flexsys Co. Ltd., Belgium
Sulfur	2	Commercial/Chemmin Co. Ltd., Thailand
Filler: Carbon Black	Variable (0–60)	N330/Thai Carbon Product Co., Ltd., Thailand
Silica	Variable (0–60)	Hi-Sil 233s/PPG-Siam Silica Co., Ltd., Thailand
Rice husk ash (RHA)	Variable (0-60)	Ooncharoensap Rice Mill Ltd., Part., Thailand

[a] phr, parts per hundred of rubber.

involving two stages. In the first stage, the blends were prepared in a dispersion kneader machine (Kneader Machinery Co., Tainan Shiann, Taiwan) with a fill factor of 0.7, at a chamber temperature of 75°C and a rotor speed of 40 rpm. NR was initially masticated in the mixer for 3 min and blended with the EPDM component, followed by the other ingredients in this order: plasticizer (paraffin oil), activators (ZnO and stearic acid), filler and accelerators (MBTS and TMTD). In the second stage, complete vulcanized compounds were prepared by the addition of sulfur using a laboratory-sized two-roll mill (Kodaira Seisakusho Co., Tokyo, Japan) at 70°C for 3 min.

Cure characteristics

Cure characteristics were studied using a rheometer, accurate to ±1% of the report value, (TECH-PRO, Cuyahoga Falls, Ohio) according to ISO 3414 for 30 min at 150°C. The Mooney viscosity (ML_{1+4} at 100°C) was determined by using a Mooney viscometer, accurate to ±1% of the report value, (TECH-PRO, Cuyahoga Falls, Ohio). The testing procedure was conducted according to the method described in ISO 289-1.

Vulcanization process

A conventional vulcanization system was used for curing. NR is highly unsaturated, it is chemically reactive. EPDM, on the other hand, is highly saturated and thus nonreactive. Because of such difference in chemical reactivity, during vulcanization, NR possesses a higher crosslinking rate while the EPDM phase is poorly crosslinked. The vulcanization using a combination of TMTD and MBTS accelerators as the conventional curative system could improve the cure compatibility of the blend. Sae-oui et al.[30] reported that MBTS gave a relatively long optimum curing time (13.3 min), compared to TMTD (2.8 min). When the combination of TMTD and MBTS accelerator is employed, the EPDM phase in the blend has a sufficiently long time to cure. All blends were compression molded at 150°C with a force of 17.5 MPa using a hydraulic hot press (Power Drive System Co., Thailand) according to their respective cure time, $t_{90,}$ determined with a TECH-PRO instrument.

TABLE II
Physical Properties of the RHA, Silica, and Carbon Black

Filler	Mean particle size (μm)	Surface area (m^2/g)
RHA	36.6	17
Silica	18	165
Carbon Black	20.2	84

Mechanical properties

Tensile properties were determined on an Instron Testing (Model 1011; Norwood, MA) using C-type Dumbbell-specimen, according to ASTM D 412. Resilience was studied using a Wallace Dunlop Tripsometer (England) according to B.S. 903 Part A8. An abrasion test was carried out according to B.S. 903 Part A9 on a Wallace Test Equipment (England), accurate to ±5%.

Ozone ageing

Ozone ageing studies under static conditions were conducted according to ISO 1431/1-1980 (E) in a Hampden (Northampton, England) Model 703 ozone test chamber at 40°C. Ozone concentration in the chamber was adjusted to 50 parts per hundred million (pphm). The ozonised oxygen generated in the ozoniser by ultra violet quartz lamp was collected in

a separate chamber where the two specimens having 20% strain were exposed.

Photographs were taken using an optical microscope Carl Zeiss Stemi 2000 C (Werk Göttingen, Germany) with magnification of 50.

Heat ageing

Tensile specimens were aged at 100°C for 72 h in an air-circulating ageing oven and the tensile properties of the aged samples were determined according to ASTM D573 (1994). Tensile test (ASTM D 412-99) was carried out on a tensile dumbbell test specimen before and after ageing to estimate ageing resistance.

Scanning electron microscopy

Scanning electron microscopic studies of the compounds' tensile fracture surfaces were carried out on gold-coated samples using a Joel Microscope (model JSM 5600 LV; Tokyo, Japan) at a magnification of 3000.

RESULTS AND DISCUSSION

Cure characteristics and processability of 75 : 25 NR/EPDM blends

Various fillers were incorporated with loading ranging from 0 to 60 phr (parts per hundred of rubber) at 15 phr intervals in 75 : 25 NR/EPDM blends to study the effect of filler loading on the cure properties of the blends as shown in Figure 1. The blends were vulcanized for their optimum cure time. For the optimum cure time, it can be observed the compared with unfilled blend, with increase in loading of carbon black and RHA decreased optimum curing time. However, at a similar filler loading, carbon black-filled 75 : 25 NR/EPDM blends exhibit the shortest t_{90} followed by RHA-filled 75 : 25 NR/EPDM blends. For carbon black the reduction of t_{90} is due to the role of carbon black, which accelerates the vulcanization process. With silica, there is a different trend in cure characteristics. The curing time tends to increase with increasing silica content. The retardation effect found in the silica vulcanizated can be attributed to a silica-accelerator system interaction. This filler reacts with ZnO and subsequently reduces the zinc available, thus slowing down the vulcanization process. Other researchers[17,20] observed a similar trend in other RHA-filled NR compounds.

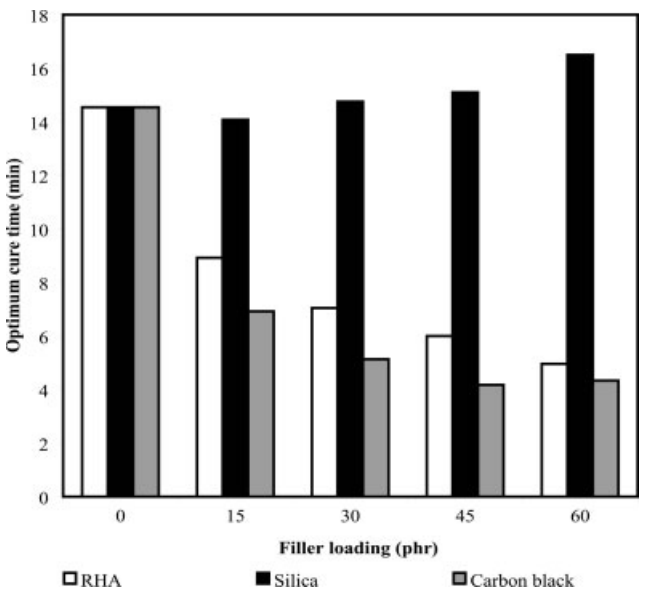

Figure 1 Relationship between filler loading and optimum cure time (ML_{1+4} at 100°C) of 75 : 25 NR/EPDM blends filled with various fillers.

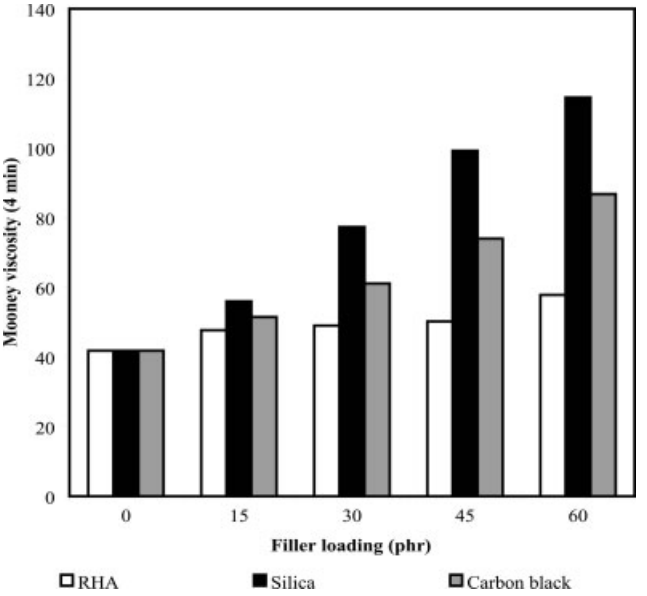

Figure 2 Relationship between filler loading and Mooney viscosity of 75 : 25 NR/EPDM blends filled with various fillers.

The effect of filler loading on the Mooney viscosity of the blends is shown in Figure 2. It can be seen that for silica and carbon black, Mooney viscosity increases significantly with an increase in filler loading. However, for RHA, the change of this property with filler loading is only small. Silica-filled 75 : 25 NR/EPDM blends have the highest Mooney viscosity followed by carbon black and RHA-filled 75 : 25 NR/EPDM blends. In the mixing state, large particle size (Table II) and low interaction between the fillers and rubber gave rise to lower viscosity, as compared to blend filled with reinforcing fillers. Polymer-filler interaction leads to immobilization of chain segments on the filler surface whose mobility is reduced with regard to that of the polymer matrix. The presence of reinforcing fillers in the rubber matrix

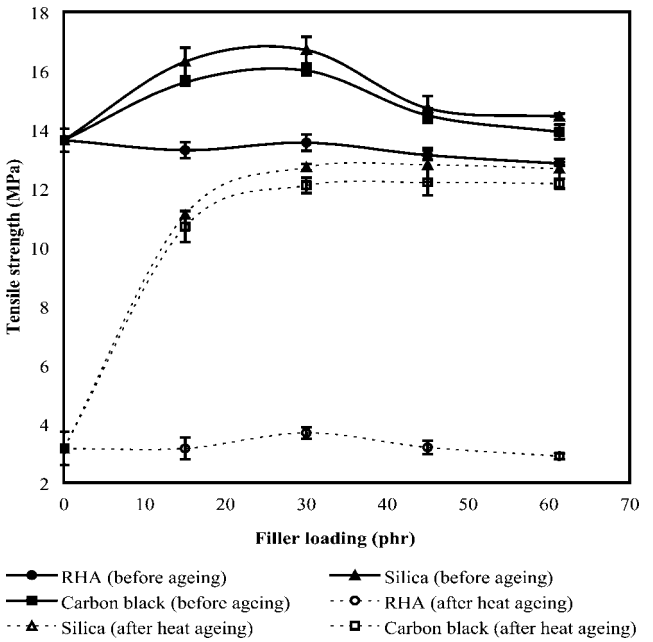

Figure 3 The effect of filler loading on tensile strength of RHA, silica, and carbon black filled 75 : 25 NR/EPDM blends before and after heat ageing.

reduced the mobility of the rubber's macromolecular chains. The lowest Mooney viscosity of RHA indicated that it could be processed more easily than silica and carbon black-filled 75 : 25 NR/EPDM blends.

Mechanical properties of 75 : 25 NR/EPDM blends

Tensile properties before heat ageing

Tensile strength is an important characteristic of polymeric materials because it indicates the limit of final stress in most applications. Various fillers were incorporated at different ratios up to 60 phr in 75 : 25 NR/EPDM blends to study the effect of filler loading on the mechanical properties of the filled 75 : 25 NR/EPDM blends. Figure 3 shows the tensile strength of unaged and thermally aged 75 : 25 NR/EPDM blends as a function of filler loadings. The effect of filler loading on tensile strength of unaged 75 : 25 NR/EPDM blends may increase or decrease with the incorporation of filler. It can be seen that at a similar filler loading, silica-filled 75 : 25 NR/EPDM blends gave the highest tensile strength, followed by carbon black and then RHA filled 75 : 25 NR/EPDM blends. Both silica and carbon black-filled 75 : 25 NR/EPDM blends exhibited similar trends; tensile strength of the filled 75 : 25 NR/EPDM blends increased with filler loading until a maximum level was reached (at $\sim$ 30 phr) and then the property started to decrease with an increase in filler loading. Rigbi[31] reported that the reinforcing filler increases the tensile strength up to maximum filler loading of the elastomer, after which a detrimental effect on tensile strength at high loadings may be attributed to the dilution effect or agglomeration of filler. On the other hand, a negative effect on the tensile strength was observed for RHA-filled 75 : 25 NR/EPDM blends. Tensile strength of the filled 75 : 25 NR/EPDM blends slightly decreased with an increase in RHA loading because of the inability of the filler to support stresses transferred from the rubber matrix. RHA-filled 75 : 25 NR/EPDM blends exhibited the highest tensile strength with the loading being 30 phr RHA compared with the other loadings investigated, as shown in Figure 3, considering the best formulation (30 phr) and lower strength values compared with unfilled 75 : 25 NR/EPDM blends. It is believed that a smaller particle size (Table II) and uniform dispersion of both silica and carbon black in the rubber blends contributes to better tensile strength. In addition, for irregular-shaped fillers such as RHA, their capability to support stress transmitted from the rubber matrix is rather poor. Thus, the strength enhancement in the RHA-filled blends is, in general, much lower than that of reinforcing filler-filled blends.

Modulus is an indication of the relative stiffness of the material. Fillers are known to increase modulus provided the modulus of the filler is higher than that of the polymer matrix. The most important contribution to the elastic modulus arises from polymer-filler interactions, which can be increased if a good dispersion of the filler is characteristic of the particles and also on the chemical nature of the polymer. Figure 4 shows the effect of filler loading on

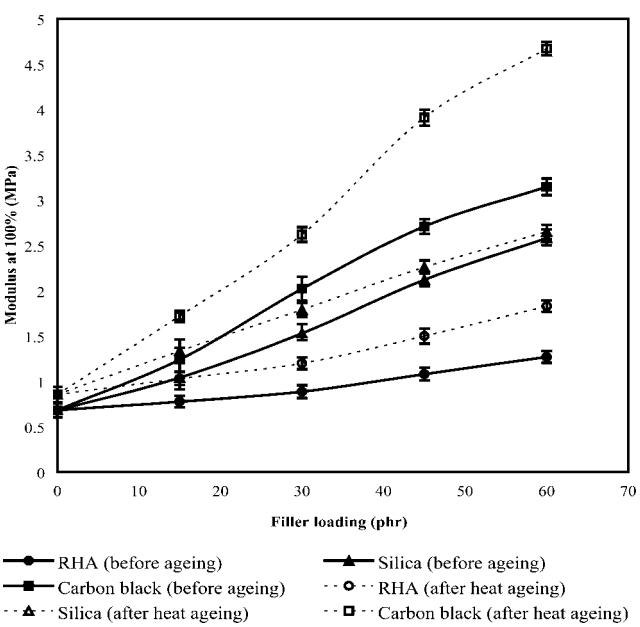

Figure 4 The effect of filler loading on modulus values at 100% of RHA, silica, and carbon black filled 75 : 25 NR/EPDM blends before and after heat ageing.

modulus at 100% elongation of the rubber blends, which is an indication of material stiffness for filler filled 75 : 25 NR/EPDM blends. Modulus of the filled blends increased with an increase in filler loading. It can be seen that carbon black improved the stiffness of the rubber blends, followed by silica, whereas RHA showed a small increase in this property. Ismail et al.[28] who worked on WRHA-filled NR and LLDPE blends, has reported that incorporation of WRHA increased the modulus of NR/LLDPE blends. The sharp increasing trend for carbon black may be attributed to the good rubber-filler interaction of this filler. As more filler particles are introduced into the rubber, the elasticity of the rubber chains is reduced, resulting in higher stiffness properties. It can be observed that, at any particular loading, the silica-filled compound had higher tensile strength, whereas its modulus was much lower than carbon black-filled rubber blends. Sae-oui et al.[17] also reported that surface area is the most important factor controlling the tensile strength, whereas the surface activity controls the modulus.

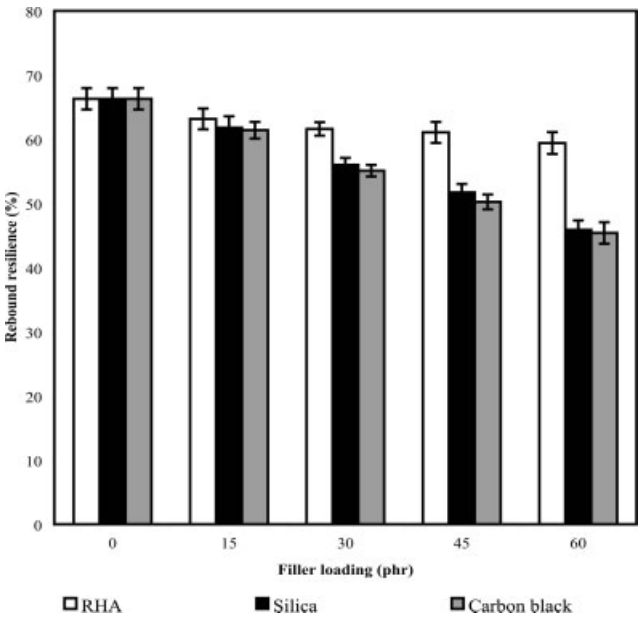

Figure 5 The effect of filler loading on resilience of RHA, silica, and carbon black filled 75 : 25 NR/EPDM blends.

Tensile properties after heat ageing

The thermal resistance of the blends was studied by ageing for 22 h at 100°C, then measuring the retention in tensile strength. Ageing of polymers normally reduces its useful properties. Figure 3 also shows all of the blends after ageing showed a reduction in tensile strength, as compared to before ageing, indicating thermal degradation of matrices in the blends. Among different fillers silica showed the highest retained tensile strength, followed by carbon black, with the lowest retained strength observed for a RHA-filled blend. The superiority of reinforcing filler filled blends over the RHA-filled blends, with respect to tensile was obvious. The function of silica and carbon black, in addition to reinforcement, was envisaged as a thermal antioxidant to control the ageing of the blends to some extent. It can be seen that for silica and carbon black, the retention in tensile strength increased with an increase in filler loading. This is believed to be due to the small amount of matrices degrade compare to other compositions that have more amount of matrix. The tensile strength of unfilled samples after thermal ageing supported this fact. However, in the case of RHA, with an increase in filler content in NR/EPDM blends, the retention in tensile strength showed no significant change with increased loading.

The effect of heat ageing on Young's modulus is illustrated in Figure 4. Young's modulus for all of the blends filled with different fillers at a given loading shifted to a higher value after ageing. These increases are generally attributed to increase in the stiffness of the rubber matrix brought about by a reduction in the number of double bonds. On comparing these results, it is observed that the blends filled with carbon black mostly showed the highest 100% Young modulus, followed by silica, with the lowest modulus observed for a RHA-filled blend. As mentioned earlier, the elasticity of the rubber chains is reduced with the incorporation of filler, thus enhancing stiffness properties.

Rebound resilience

The effect of various filler loading on resilience of the rubber blends is shown in Figure 5. It can be seen that at a similar filler loading, RHA-filled 75 : 25 NR/EPDM blends gave the highest resilience, followed by silica and then carbon black-filled 75 : 25 NR/EPDM blends. All of the filler-filled 75 : 25 NR/EPDM blends exhibited similar trends; rebound resilience of the filled blends decreased with filler loading. For silica and carbon black, the resilience of the rubber blends decreases drastically with an increase in filler loading. However, for RHA, the reduction of this property with filler loading is small. This observation may be attributed to a poorer rubber-filler interaction of RHA. On the contrary, the sharp decreasing trend for silica and carbon black may be attributed to better rubber-filler interaction of these fillers. As more filler particles are introduced into the rubber, the elasticity of the rubber chains is reduced, resulting in lower resilience properties. The surface activity is an important factor, indicating the extent of rubber-filler interaction.

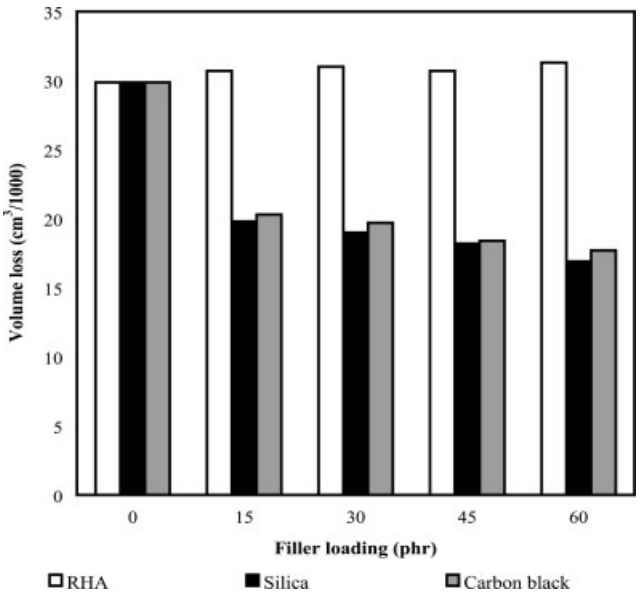

Figure 6 The effect of filler loading on abrasion resistance of RHA, silica, and carbon black filled 75 : 25 NR/EPDM blends.

According to Jacques[32] the incorporation of most of the particulate fillers into rubber leads to an increase in hardness and a reduction in resilience, particularly with more reinforcing filler.

Abrasion resistance

The abrasion resistance of a solid body is defined as its ability to withstand the progressive removal of material from it surface, as the result of mechanical action of a rubbing, scraping, or erosive nature. The incorporation of silica and carbon black reduced the abrasion loss of the 75 : 25 NR/EPDM blends notably, whereas RHA showed less effect with filler loading, as show in Figure 6. As far as this property is concerned, the ashes gave similar effect to non-reinforcement fillers. The abrasion loss showed a small increase with increase in loading. An inverse effect is found in the systems filled with silica and carbon black in which, the abrasion loss is found to decrease sharply with an increase of the filler loading up 15 phr and then the abrasion loss decreased marginally. Reinforcing fillers, silica and carbon black, interact preferentially with the rubber phase, as shown by the higher reduction of abrasion loss in the blends. This improvement is probably due to the greater surface area and better filler-rubber interfacial adhesion resulting in an improved abrasion resistance. Fine particles actually reflect their greater interface between the filler and the rubber matrix and, hence, provide a better abrasion resistance and adhesion than the coarse ones. Similar results were also reported by Sae-oui et al.[17]

Ozone ageing

The interaction of rubber with ozone is best noted when the rubber is stressed or stretched in use. To assess the ozone resistance of the filler-filled blends, test samples having 20% strain were exposed to ozonized air of 50 pphm ozone concentration for 72 h at 40°C in the dark. However, the nature and intensity of cracks due to ozone attack are different for various fillers.

Optical photographs of the surfaces of the unfilled and filled blends of ozone exposed samples are presented in Figure 7. The photographs clearly show that the unfilled NR/EPDM blend showed fine cracks represented by the horizontal lines [Fig. 7(a)] while highest level of cracking with wider and deeper is observed for samples containing RHA [Fig. 7(b)]. Compared with the silica and carbon black-filled NR rubber blends, all showed no cracks as seen in Figure 7(c,d). However, silica-filled blends showed a smoother surface than carbon black-filled blends, which confirms that crack growths were stopped more effectively by finely dispersed filler particles in the rubber matrix. This shows that the ozone resistance of the blends containing reinforcing fillers is superior to the blends containing unfilled and RHA-filled blends. Results revealed that when the reinforcing filler is added to a blend, it goes more into the polymer phase which has a higher affinity. That is, more finely dispersed filler particles prohibit the growth of ozone cracks initiated in the rubber matrix before the cracks grow over the critical length for failure. Thus, the ozone resistance of the silica- and carbon-filled blends improved remarkably. In the case of RHA-filled blends, the ozone resistance of the blends was inferior to those obtained. This may due to the poor adhesion and nonuniform dispersion of the discrete phase in the matrix.

Morphology

The morphology of unfilled and filler-filled 75 : 25 NR/EPDM blends at 30 phr filler loading after tensile fracture is shown in Figure 8. The surface of the unfilled 75 : 25 NR/EPDM blends is smooth [Fig. 8(a)]. For the fracture surface of RHA-filled 75 : 25 NR/EPDM blends [Fig. 8(b)], the dispersion of RHA in the rubber matrix was not continuous where the formation of filler agglomeration started due to the interfacial interaction between filler and matrix, which led to void formation. The presence of many holes on the fracture surface may be due to the weak interfacial interaction resulting in the deterioration of blend properties such as tensile strength when compared with unfilled 75 : 25 NR/EPDM blends. Silica and carbon black-filled 75 : 25 NR/

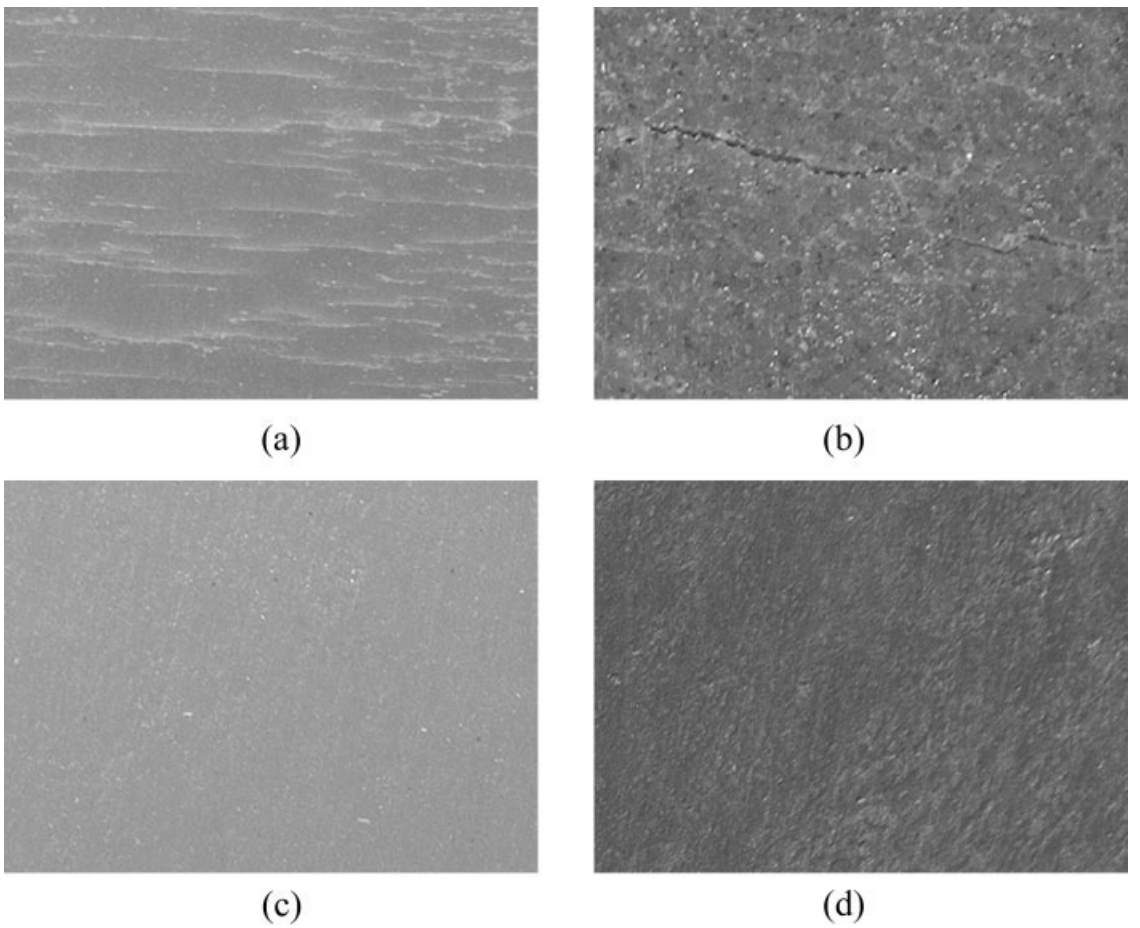

Figure 7 Optical photographs of exposed (a) unfilled 75 : 25 NR/EPDM blends and (b) RHA, (c) silica, and (d) carbon black filled 75 : 25 NR/EPDM blends after tensile fracture at 30 phr filler loading (×50).

EPDM blends are shown in Figure 8(c) and (d); it can be seen that the fracture surface of reinforcing filler shows a more homogenous phase dispersion, resulting its higher tensile strength. Figure 8(c) shows a scanning electron microscope (SEM) photomicrograph of the fracture surface of silica-filled 75 : 25 NR/EPDM blends. The rough surface with stress whitening is a typical feature of ductile failure; which indicates the higher tensile strength of the silica-filled 75 : 25 NR/EPDM blends. From the fracture surface in Figure 8(d) [compare to Fig. 8(c)], the incorporation of the carbon black does not alter the ductile mode of failure of the materials, which resulted in the brittle failure, hence the enhancement in the stiffness. The SEM photomicrographs shown in Figure 8 confirm that smaller particle size of the filler provides a larger surface area for a better filler dispersion and interfacial bond between filler and rubber matrix.

CONCLUSIONS

We studied binary blends of NR and EPDM with a fixed 75 : 25 blend ratio (wt %) to investigate the effects of three different types of fillers on the processability and mechanical and ageing properties. Silica, carbon black, and RHA were used as filler. The incorporation of fillers in 75 : 25 NR/EPDM blends decreased the cure time t_{90} with an increase in RHA and carbon black loading whereas silica showed a different trend in cure time tending to increase with increasing silica loading. At a similar filler loading, carbon black showed the shortest t_{90} followed by RHA and silica. Mooney viscosity increased with an increase in silica and carbon black loading, whereas RHA showed a small change in this property. At a similar filler loading, RHA showed the lowest viscosity followed by carbon black and silica. Filler loading and filler type influence the processability of the rubber blends in RHA, offering better processing advantage over silica and carbon black. The change (positive or negative) in tensile properties, resilience, and abrasion loss was quite significant with increasing loading of silica and carbon black in NR/EPDM blends. Addition of reinforcing fillers (silica and carbon black) gave rise to marked improvements in the tensile strength and abrasion resistance of 75 : 25 NR and EPDM blends.

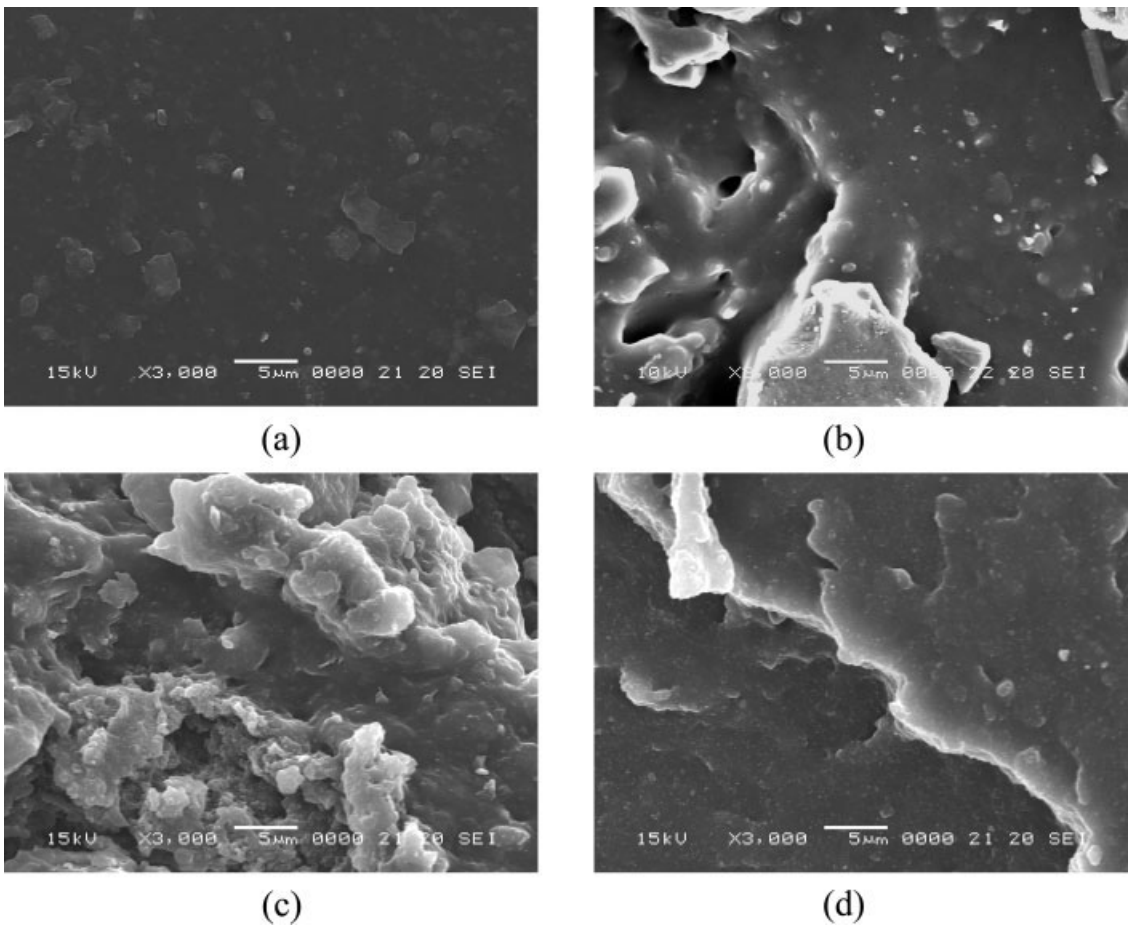

Figure 8 SEM micrographs of (a) unfilled 75 : 25 NR/EPDM blends and (b) RHA, (c) silica, and (d) carbon black filled 75 : 25 NR/EPDM blends after tensile fracture at 30 phr filler loading (×3000).

Tensile strength and abrasion resistance of the materials slightly reduced with increasing RHA loading, whereas the Young's modulus of the compounds slightly increased. Young's modulus increased with increasing filler loading while resilience is often reduced. At a similar filler loading, RHA showed the highest resilience followed by silica and carbon black. Heat ageing had increased the Young modulus of filled NR/EPDM blends but reduced the tensile strength. However, the best improvement in the heat ageing of the NR/EPDM with additional fillers was also achieved when filled with the silica and carbon black, whereas the use of RHA as additional filler provided almost no improvement in this property. Optical photographs of ozone exposed samples showed that in the case of unfilled 75 : 25 NR/EPDM blends the cracks are small whereas wide, deep, and intense cracks were observed in the RHA-filled rubber blends, while no cracks were found in all of the silica and carbon black-filled blends. The ozone resistance of the blends improved significantly with the addition of silica and carbon black fillers while this property of the blends was inferior to those obtained from the addition of RHA filler. Silica and carbon black provide better mechanical properties than the RHA, mainly because of their high surface area (small particle size) and surface activity. It was found that RHA provided inferior mechanical properties in comparison with reinforcing fillers such as silica and carbon black. Scanning electron microscopy on fracture surfaces shows poor filler dispersion and weak filler-matrix interaction with the RHA-filled NR/EPDM blends. This explains the reduction of tensile strength with RHA-filled NR/EPDM blends. The results reveal that the mechanical properties of the 75 : 25 NR/EPDM blends filled with RHA are comparable to silica and carbon black with inert filler.

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References

1. Botros, S. H. Polym Plast Technol Eng 2002, 41, 341.

2. Ghosh, A. K.; Debnath, S. C.; Naskar, N.; Basu, D. K. J Appl Polym Sci 2001, 81, 800.
3. Choi, S. S. Polym Int 2001, 50, 524.
4. Choi, S. S. J Appl Polym Sci 2001, 79, 1127.
5. Choi, S. S. J Appl Polym Sci 2002, 85, 385.
6. Choi, S. S. J Polym Sci Part B: Polym Phys 2001, 39, 439.
7. Suzuki, N.; Yatsuyanagi, F.; Ito, M.; Kaidou, H. J Appl Polym Sci 2002, 86, 1622.
8. Thammathadanukul, V.; O'Haver, J. H.; Harwell, J. H.; Osuwan, S.; Na-Ranong, N.; Waddell, W. H. J Appl Polym Sci 1996, 59, 1741.
9. Ono, S.; Kiuchi, Y.; Sawanoburi, J.; Ito, M. Polym Int 1999, 48, 1035.
10. Manna, A. K.; De, P. P.; Tripathy, D. K.; De, S. K.; Peiffer, D. G. J Appl Polym Sci 1999, 74, 389.
11. George, K. M.; Varkey, J. K.; Thomas, K. T.; Mathew, N. M. J Appl Polym Sci 2002, 85, 292.
12. Wang, M. J.; Lu, S. X.; Mahmud, K. J Polym Sci Part B: Polym Phys 2000, 38, 1240.
13. Chiu, H. T.; Chiu, W.-M. J Appl Polym Sci 1996, 61, 607.
14. Nakajima, N.; Yamaguchi, Y. J Appl Polym Sci 1997, 66, 1445.
15. Nasir, M.; Poh, B. T.; Ng, P. S. Eur Polym Mater 1988, 24, 961.
16. Fuad, M. Y. A.; Ismail, Z.; Ishak, Z. A. M.; Omar, A. K. M.; Eur Polym Mater 1995, 31, 885.
17. Sae-oui, P.; Rakdee, C.; Thanmathorn, P. J Appl Polym Sci 2002, 83, 2485.
18. Arayapranee, W.; Na-Ranong, N.; Rempel, G. L. J Appl Polym Sci 2005, 98, 34.
19. Da Costa, H. M.; Visconte, L. L. Y.; Nunes, R. C. R.; Furtado, C. R. G. J Appl Polym Sci 2000, 76, 1019.
20. Da Costa, H. M.; Visconte, L. L. Y.; Nunes, R. C. R.; Furtado, C. R. G. J Appl Polym Sci 2002, 83, 2331.
21. Da Costa, H. M.; Visconte, L. L. Y.; Nunes, R. C. R.; Furtado, C. R. G. J Appl Polym Sci 2003, 87, 1194.
22. Da Costa, H. M.; Visconte, L. L. Y.; Nunes, R. C. R.; Furtado, C. R. G. J Appl Polym Sci 2003, 87, 1405.
23. Da Costa, H. M.; Visconte, L. L. Y.; Nunes, R. C. R.; Furtado, C. R. G. J Appl Polym Sci 2003, 90, 1519.
24. Siriwardena, S.; Ismail, H.; Ishiaku, U. S. Polym-Plast Technol Eng 2001, 40, 519.
25. Siriwardena, S.; Ismail, H.; Ishiaku, U. S. Polym-Plast Technol Eng 2002, 41, 419.
26. Siriwardena, S.; Ismail, H.; Ishiaku, U. S.; Perera, M. C. S. J Appl Polym Sci 2002, 85, 438.
27. Ismail, H.; Mega, L. Polym-Plast Technol Eng 2001, 40, 463.
28. Ismail, H.; Nizam, J. M.; Abdul Khalil, H. P. S. Polym Test 2000, 20, 125.
29. Chaudhary, D. S.; Jollands, M. C.; Cser, F. Silicon Chem 2002, 1, 281.
30. Sae-Oui, P.; Sirisinha, C.; Thepsuwan, U.; Thapthong, P. Polym Test 2007, 26, 1062.
31. Rigbi, Z. Rubber Chem Technol 1982, 55, 1180.
32. Jacques, J. E. In Rubber Compounding, Rubber Technology and Manufacture, 2nd ed.; Blow, C. M.; Hepburn, C., Eds.; Butterworths: UK, 1985; pp 386–387.