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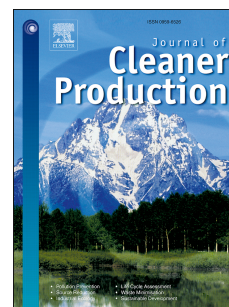
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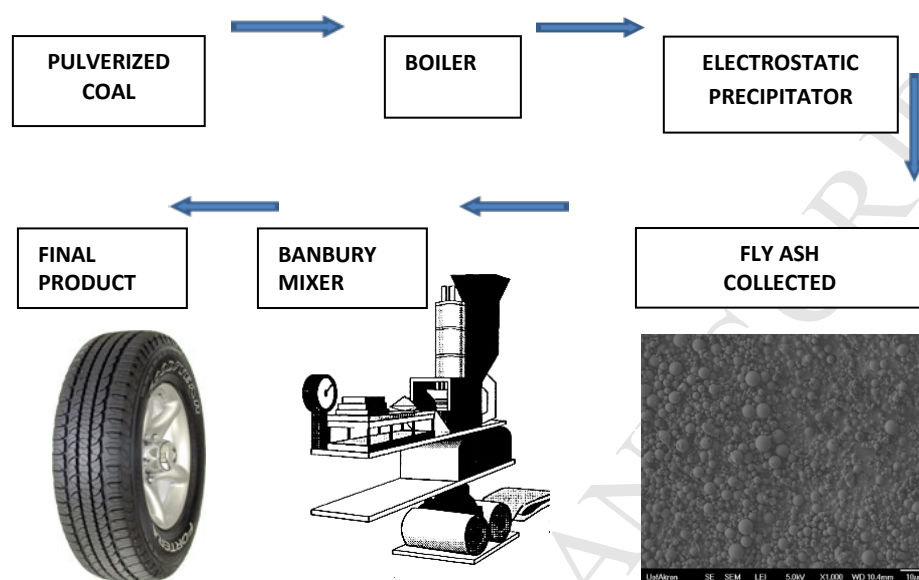
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Use of Fly Ash as Eco-friendly Filler in Synthetic Rubber for Tire Applications

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ABSTRACT

A byproduct of the power generation industries, fly ash can be used as a potential filler in many commercial products including rubber-based products. Reusing the fly ash in this manner is an efficient way to help prevent air pollution which occurs if such particles are released freely to the atmosphere. The reinforcement efficiency of fly ash for partial replacement of carbon black and silica fillers in styrene-butadiene rubber compounds was investigated in this work. The total content of fillers was held constant at 50 phr (weight ratio of filler to rubber was 0.5) when not using silica fillers at all, and 54 phr when using 4 phr carbon black only with silica fillers, while the content of fly ash increased from 0 to 10 phr. In the evaluation of the rubber compounds, the focus was the mechanical properties and adhesion of steel reinforcement cords to the styrene-butadiene rubber compounds. Adhesion between the compounds and steel wire reinforcement was measured for assessing efficacy of adding fly ash to the rubber compounds in tire applications. Ball mill treatment was used to reduce the size of the fly ash particles while also modifying their surface topography. The comparisons of untreated and ball mill treated fly ash filled rubber compounds and rubber compounds containing different fillers were accomplished subsequently. The results revealed that the partial addition of up to 10 phr fly ash to rubber compounds resulted in increases in elongation at break, adhesion to reinforcement steel cord, wet-grip, as well as lower rolling resistance as attributed to more effective filler dispersion and the reinforcing effect of silica

present in fly ash.

Key words: rubber compounds, fly ash, precipitated silica, carbon black, mechanical properties.

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1. Introduction

World-wide increase in demand for automotive ownership has resulted in an increasing market demand for pneumatic tires. The world vehicle production increased 25% during 2010 to 2017 (International Organization of Motor Vehicle Manufacturers, 2018a, 2018b). Pneumatic tires are composed of external surface, called tread, under which resides a reinforcement belt consisting of steel cords. Tread is the part which directly contacts the road surface, and thus, needs to be strong enough to avoid cracks or tears. In addition, reducing rolling resistance is very important for tread, because rolling resistance is related to fuel consumption with higher rolling resistance resulting in higher energy loss. Tread is made up of a rubber compound. There are two main types of rubber, synthetic rubber and natural rubber. Natural rubber is collected from mature rubber trees which must be planted in tropical areas (Salvucci et al., 2009). Therefore, the production of natural rubber is limited and cannot satisfy the overall market need; synthetic rubber was developed during World War II. Styrene Butadiene Rubber (SBR) is a synthetic rubber which is polymerized by using the monomers, styrene and butadiene (Baranwal and Stephens, 2001). SBR has become one of the most important synthetic rubbers in the world because of its huge production (Ciesielski, 1999). In tire applications, SBR rubber exhibits good abrasion resistance and stability, which is the reason why SBR rubber is usually used in tire tread (Zubov et al., 2012).

1.1 Carbon black fillers

Among all kinds of rubber fillers, carbon black (CB) is the most traditional and commonly used reinforcing filler. CB is produced from the carbon black oil furnace process (Lockwood and Niekerk, 1995). The production and use of CB increases the carbon footprint of rubber industry. Annually, the production of CB is about 10 million tons (Adams, 2007). Carbon dioxide is released into the atmosphere during the production of CB. For solving this problem, one direction involved a new process to replace the old method of producing CB.

Sustainable methods like solar methane dissociation were studied to produce CB (Rodat et al., 2011). Another direction is replacing the CB with other eco-friendly fillers. Partial replacement of CB by fly ash is discussed in this research.

1.2 Silica fillers

Silica is a widely used alternative to carbon black in rubber industry. It is produced through the acid precipitation of sodium silicate (Schlomach and Kind, 2004). Silica improves the mechanical properties of rubber composites, such as hardness, tensile strength and tearing energy (Ansarifar et al., 2005). In addition, silica has a great influence on the protection of the environment due to lower CO₂ emission during its production as well as in its capacity to reduce rolling resistance and to enhance wet and ice traction of epoxidized natural rubber composites in tires (Martin et al., 2015). Due to increasing environmental concerns, most of the tire companies are attempting to reduce rolling resistance and improve energy efficiency of tires. Silica also plays an important role in this research with mechanical and dynamic behaviors of silica rubber investigated as a potential filler in combination with carbon black as well as with fly ash.

1.3 Fly ash as reinforcement filler

Fly ash (FA) is a byproduct of the power generation industries neglected for many years as a potential filler in many different commercial products including rubber-based products. Nearly 41% of electricity is generated by coal combustion, which is predicted to reach 44% in 2030 (Chávez-Valdez et al., 2011). Fly ash is unavoidably produced as waste after combustion. About 750 million tons of fly ash are produced annually, but only 39% can be reused in U.S (Ranjbar and Kuenzel, 2017a). If fly ash is emitted to the environment by air and wind, a serious pollution problem would be created with the risk of pulmonary diseases. Reusing the fly ash is an efficient way to prevent such pollution. With this consideration, fly ash is often used to improve the durability of concrete in construction

industry. Fly ash can be used as a part of self-compacting concrete, which has good deformability and segregation resistance (Siddique et al., 2016). In self-compacting mortar, fly ash can hold the aggregates and increase the flowability of the fresh matrix (Behnia et al., 2017). Fly ash can be used in recyclable concrete pavement (Yoshitake et al., 2016). With proper heat treatment, the geopolymers produced by fly ash have improved mechanical properties and potential applications in construction industry (Ranjbar and Kuenzel, 2017b). Fly ash is also used as filler in rubber products. The main composition of the fly ash is silica. Like CB and precipitated silica, fly ash can also act as a reinforcing filler to improve the mechanical properties of rubber compounds. Palm based fly ash can be used to improve the mechanical properties of thermoplastic materials (Bahruddin et al., 2012). As the content of filler is relatively small in the rubber compounds, the reinforcing effect of fly ash without modification was similar to the reinforcing effect of silica (Sombatsompop et al., 2004). Silane coupling agents could be used to modify the surface of fly ash (Thongsang and Sombatsompop, 2006). Their results showed that silane treated fly ash would improve cure characteristics and mechanical properties. Fly ash was also studied as an alternative to carbon black. Nano-sized FA (148 nm) had superior reinforcing effect in comparison to CB, precipitated silica or unmilled FA (60-100 μm) in SBR composites, as revealed by higher modulus, tensile strength and hardness (Paul et al., 2009).

1.4 Adhesion of steel reinforcement cord to filled rubber compounds

In general, the tire tread which consists of rubber compound must contact with the belt layer which is typically made up with steel cords in order to improve tire strength. Therefore, strong interaction or adhesion is required between the steel cord and the rubber compound. An early method which was used to improve adhesion involved physical attachments and bonding with ebonite. But, physical attachments were weak and ebonite began to fail even at moderate temperatures generated during tire operation. Then, the use of brass layer was invented as interface between rubber and steel cord to improve adhesion, and plating a layer

of brass on the steel cord was commercialized at the beginning of the last century (Darwish et al., 2013). During vulcanization, Cu_xS is formed and the rubber molecules crosslink with sulphur atoms in Cu_xS as a result. Thus, bonding between the rubber and the brass layer is created with rubber establishing physical and chemical interactions with the brass layer (Van Ooij, 1984). The filler in the rubber compounds also has a great influence on the adhesion between the rubber and brass plated steel cord. Silica can improve the adhesion between the steel cord and the rubber compounds due to changes in the interfacial layer between the cord and rubber (Vanooij et al., 2009).

1.5 Ball milling

Ball milling is commonly used as a method to improve the reinforcing effect of fillers. In general, ball mill treatment is used to reduce the particle size of filler and change the morphology of the filler particle (Molnár et al., 2014; Mucsi, 2016). Ball mill treated sago starch improved the mechanical properties of sago starch filled natural rubber latex as attributed to its dispersion and small particle size (Suki et al., 2016). Ball mill treatment improved the dispersion of attapulgite in natural rubber composites as indicated by smoother fracture surfaces and resulted in higher tensile strength and crosslink density of the resulting compound (Muttalib and Othman, 2016). As ball milling reduced fly ash size from macro (89 μm) to micro (12 μm), the tensile strength and modulus at 300% strain of Hevea natural rubber and guayule natural composites increased (Barrera and Cornish, 2016, 2015). However, the effect of ball mill treating fly ash to be used as hybrid filler with CB and silica in synthetic rubber composites have not been studied.

1.6 Hybrid fillers

From the above, we deduce that CB clearly plays an important role in reinforcing rubber compounds, while possibly causing environmental problems. Additionally, the use of silica fillers (SF) helps in reducing rolling resistance. However, silica without any surface treatment

cannot be used as the sole filler in rubber compounds because it produces poor mechanical properties. For example, the rubber compound containing untreated silica exhibited lower tensile strength and modulus at 100% strain when it was compared to the rubber compound which used silane treated silica as filler (Hashim et al., 1998). Thus, hybrid filler recipes combining several kinds of fillers are used in rubber compounds. The filler networking is weakened if a small amount of CB was replaced by silica (Feng et al., 2015). This is because filler-filler interactions are formed by hydrodynamic effect, with this effect being weaker on different fillers than on the same fillers. Under small dynamic strain, deconstruction of filler network contributes to the energy dissipation of rubber compounds. Weaker filler networks result in less energy loss. So, it is also found that lower rolling resistance can be achieved by partially replacing the carbon black with a small amount of silica. Silica treated by silane coupling agent was also investigated for the application involving hybrid fillers. Hybrid filler of CB and silane modified silica could reduce rolling resistance and maintain tensile strength when it was compared to the rubber compound which only used CB as filler (Rattanasom et al., 2007). To reduce rolling resistance and maintain mechanical properties of rubber compounds, carbon-silica dual phase filler (CSDPF) was thus proposed. CSDPF is produced through a co-fuming process, in which silicon and carbon black are mixed to produce this unique filler. CSDPF has higher rubber-filler interactions and lower filler-filler interactions than carbon black and silica (Wang et al., 2000). The hybrid filler of carbon black and fly ash (less than 30% in filler) reinforced guayule natural rubber composites had comparable tensile strength and modulus at 300% strain. The elongation at break and hardness number were also improved by replacing carbon black with fly ash in guayule natural rubber composites (Barrera and Cornish, 2016, 2015). CB, silica and fly ash all have reinforcing effect on rubber composites when used as single filler reinforcement even though their chemical structures and morphology are different. The combination of all three types of fillers may have synergetic effect, which results in better performance of rubber composites. In addition, unlike the synthetic fillers, such as CB and silica, fly ash with lower price and zero carbon

emission also reduces the cost and carbon footprint for rubber production. However, the interaction between fly ash and CB and silica has not been completely investigated. Therefore, in this research, fly ash was investigated as a secondary filler to be added with silica and/or CB for possible improvements in mechanical, adhesion, wet-grip and rolling resistance properties of rubber compounds.

1.7 Objective of this work

The purpose of this work is to determine the reinforcement efficiency of fly ash for partial replacement of carbon black and silica fillers in styrene-butadiene rubber compounds. To make this determination, the total content of fillers will be held constant at 50 phr (weight ratio of filler to rubber was 0.5) when not using silica fillers at all, and 54 phr when using 4 phr carbon black only with silica fillers, while the content of fly ash will be increased from 0 to 10 phr. Ball mill treatment will be used to reduce the size of the fly ash particles as well as changing their surface topography. The assessment of reinforcement efficiency will be done by using: 1) the mechanical properties of the compounds thus obtained; 2) the adhesion strength of steel reinforcement cords to these compounds; and, 3) by evaluating wet-grip and rolling resistance of the compounds using their damping capacity ($\tan \delta$) values.

2. Experimental

2.1. Materials

The experimental materials were rubber, fly ash, silica, carbon black and steel cord. Rubber used in this research is styrene butadiene rubber which was provided by the Lanxess Elastomers Company (Pittsburgh, PA), under the name BUNA VSL 5025-2 HM. The fly ash was Micron 3 provided by the Boral Co. (Canton, Georgia). It was a Class F fly ash, which is mainly composed of with 52% SiO_2 , 26% Al_2O_3 , 9% CaO and other metal

oxides (MgO , Fe_2O_3 , Na_2O and K_2O). Other than the fly ash, two additional kinds of fillers were also used; one is carbon black, N234, and the other is precipitated silica, Zeopol[®] 8745, provided by J.M. Huber Corporation (Edison, NJ). The steel cord (0.25+6+12x0.225HT) used in this research was provided by Bekaert Company (Kortrijk, Belgium). In steel cord specification, “0.25” means that the innermost layer contains only one strand and one filament, and the nominal diameter of filament is 0.25 mm. “6” means the intermediate layer contains one strand and six filaments. “12x0.225” means the out layer contains one strand and twelve filaments, and the nominal diameter of every filament is 0.225 mm. Two letters, “HT”, means this steel cord has high tensile strength.

2.2. Experimental methods

2.2.1. Ball mill treatment

The ball mill used in this research was Retsch PM 100 Planetary Ball Mill (Retsch, Haan, Germany). The fly ash was first added into the vial (a cylinder container) which had 21 balls (diameter 15 mm) for crushing and grinding the particles. The total time of ball mill treatment was 60 minutes and the rate of rotation was 400 rpm. The shape and particle size distribution of the fly ash particles were characterized by using a Scanning Electron Microscopy (SEM; Hitachi, Tokyo, Japan Model-S2150) and optical microscope (Leitz Laborlux-12-POL-S).

2.2.2. Rubber mastication and compounding

There were two steps for mastication and compounding of the rubber. The first step involved using an internal mixer (TYPE 808-1002-DTI, C.W. Brabender Instruments, Inc., South Hackensack, NJ) at 80°C to masticate SBR and then mixing it with fillers and other chemicals for vulcanization. The second step involved using a two-roll mill (NO: 5438, Reliable Rubber & Plastic Machinery Co., North Bergen, NJ) for further mixing and improving process ability of the rubber compound. There were two recipes of rubber

compounds containing CB/fly ash and silica/fly ash/CB: recipe A and recipe B, respectively.

These recipes are shown in Tables 1 and 2, with the only difference being the type of fillers.

Table 1 Recipe A for the CB/fly ash rubber compound.

Function	Item-grad	phr
Rubber	Buna VSL 5025-2 HM	100
Reinforcing filler	Carbon black N234 and fly ash	50
Activator	Zinc oxide	3
Accelerator (CBTS)	N-cyclohexyl-2-benzothiazole	1.6
Vulcanizer	Sulphur	1.4
Accelerator	Stearic acid	2
Antioxidant and antiozonant	6-PPD	1
Sum		159

Table 2 Recipe B for the CB/silica/fly ash rubber compound.

Function	Item-grad	phr
Rubber	Buna VSL 5025-2 HM	100
Reinforcing filler	Silica Zeopol® 8745 and fly ash Micron 3	50
Reinforcing filler	Carbon black N234	4
Activator	Zinc oxide	3
Accelerator (CBTS)	N-cyclohexyl-2-benzothiazole	1.6
Vulcanizer	Sulphur	1.4
Accelerator	Stearic acid	2
Antioxidant and antiozonant	6-PPD	1
sum		163

The purpose of using the recipe A was to investigate the effect of different concentration and types of fly ash on the mechanical properties of CB filled rubber compound. In recipe A, the total content of filler was fixed at 50 phr. The differences within recipe A involves fly ash content as shown in Table 3.

Table 3 Content of fillers in recipe A.

Fillers	phr				
Carbon black	50	47.5	45	42.5	40
Fly ash	0	2.5	5	7.5	10
Total filler	50	50	50	50	50

The purpose of adopting the recipe B was to investigate if there were any synergistic effects related to the rubber compounds containing precipitated silica, fly ash and CB at the same time in hybrid form. The filler content in recipe B added up to 54 phr in the rubber compound used, in which the content of carbon was fixed at 4 phr and the content of fly ash and silica fillers changed with different specimens prepared. The details of such filler content changes for recipe B are shown in Table 4.

Table 4 Content of fillers in recipe B.

Fillers	phr				
Silica	50	47.5	45	42.5	40
Fly ash	0	2.5	5	7.5	10
Carbon black	4	4	4	4	4
Total filler	54	54	54	54	54

A moving die rheometer (MDR 2000, Alpha Technologies, Akron, Ohio, USA) was used for measuring the cure time of the rubber compounds. 5 g of the sample was placed between two dies and its temperature was maintained at 160°C for 30 min. By measuring the maximum value of torque, the machine would calculate the time when the torque reach 90% of its maximum value. This procedure determined the 90% cure time designated as T90. Thus, the cure time was calculated using Eq. (1).

$$\frac{T_{90}}{0.9} = \text{cure time} \quad (1)$$

During the compression molding, the temperature was set at 160°C and pressure was set at 18.6 kPa (2.7 psi). The rubber compound was then cut into dumbbell shaped samples. The sample width was 4.00 mm and the sample thickness was about 1.50 mm.

2.2.3. Swelling tests

The crosslink density of the rubber compounds was measured by Soxhlet extraction method. The sample weight was measured after 48 hours of swelling test and the sample was taken out and weighted immediately. The swollen sample was then placed into an oven where the temperature was 100°C. In order to make sure that the sample was completely dried, it was kept in the oven for 48 hours, after which, the weight of the dried sample was measured. The crosslink density was calculated by the Flory-Rehner equation (Eq. (2)): (Flory and Rehner, 1943; Sperling, 2001)

$$-\ln(1 - V_r) - V_r - \chi V_r^2 = V_s \eta_{swell} \left(V_r^{\frac{1}{3}} - \frac{V_r}{2} \right) \quad (2)$$

where, V_r is the volume fraction of the rubber in swollen gel, and χ is the polymer-solvent interaction parameter. For SBR-toluene, χ is 0.31 (Marzocca, 2007). η_{swell} is crosslink density of rubber (kmol/m³). V_s is the molar volume of toluene (in this research, 106.27 cm³/mol).

In order to calculate the crosslink density, V_r was calculated using Eq. (3):

$$V_r = \frac{V_{rubber}}{V_{solvent} + V_{rubber}} = \left(\frac{m_3 - m_1 \times f}{\rho_{rubber}} \right) \div \left[\frac{m_2 - m_3}{\rho_{solvent}} + \left(\frac{m_3 - m_1 \times f}{\rho_{rubber}} \right) \right] \quad (3)$$

In Eq. (3), m_1, m_2, m_3 are the weights of the sample: m_1 was measured before swelling, m_2 was measured after swelling and m_3 was measured after drying. $\rho_{rubber}, \rho_{solvent}$ are the density of SBR and toluene. As for BUNA VSL 5025-2 HM and toluene, ρ_{rubber} was 0.94 g/cm³ and $\rho_{solvent}$ was 0.867 g/cm³. f is the weight fraction of non-rubber components in rubber compounds. According to the Tables 1 and 2, in recipe A, f was 0.371, and in recipe B, f was 0.387.

2.2.4. Tensile tests for the mechanical properties

The tensile strength, elongation at break and moduli were measured by the tensile tester (Model 5567 56P4494, Instron, Norwood, MA). The load cell used was 1 kN and the specimens were tested using 500 mm/min crosshead rate. The tensile strength and elongation

at break were obtained directly from the results. The tensile strength represents the maximum value of stress during the tensile tests. The elongation at break refers to the fracture strain of the sample. The modulus at 2% strain and the modulus at 100% were calculated from the results. This is because in practical applications, the deformation of tires is small and modulus at 2% strain is used. At small strain (0.5%-2%), there is a linear relation between the stress and the strain allowing the slope to be used to represent the modulus at 2% strain. On the other hand, modulus at 100% strain is often used to represent the modulus of the rubber compound at large deformations.

2.2.5. Measurement of dynamic properties

As mentioned earlier, rolling resistance is related to the energy loss during the usage of tire products. Wet grip is used to describe the ability of tire to prevent sliding during rotation. The Rolling resistance and wet grip of the rubber compounds were measured by a dynamic mechanical analyzer (Model RSA3, TA Instruments), which was operated in the temperature ramp/ frequency sweep mode. Temperature was set from -50 °C to 90 °C, using a ramp rate of 3°C/min. Dynamic strain was 0.1% and frequency was 1 Hz. The loss modulus (G''), storage modulus (G') and glass transition temperature were obtained from the results. In order to calculate wet grip, rolling resistance and glass transition temperature, the damping capacity ($\tan \delta$) was calculated using Eq. (4).

$$\frac{G''}{G'} = \tan \delta \quad (4)$$

In general, $\tan \delta$ at 0°C and 60°C are used to describe the wet grip and rolling resistance behaviors, respectively (Wu et al., 2015; Zafarmehrabian et al., 2012).

2.2.6. Hardness tests

The hardness of the rubber compounds was measured using Shore Durometer Type “A-2” and represented in units of Shore type A-2.

2.2.7. Adhesion tests

Pull-out tests were carried out to measure adhesion between the rubber compounds and the steel cords. In this test, a special mold was used for shaping and curing the pull-out adhesion sample shown in Fig. 1. There were three parts of this mold, the lid, slotted middle part and the base. Before curing, 5.5 g of rubber was placed in each mold slot (middle part) and steel cord (0.25+6+12x0.225HT) was vertically inserted into the sample on both slots of the mold to produce the sample shown in Fig. 1. Then the mold was placed between two panels of the compression mold. The temperature was set at 160°C and time was set to the cure time which was measured using the moving die rheometer. After molding, the sample for the adhesion tests was obtained. The picture of the sample is shown in Fig. 1. The right sample in Fig. 1 was cured but not subjected to adhesion tests. The left sample in Fig. 1 shows the result of a pull-out test with the steel cord already pulled out from the sample.

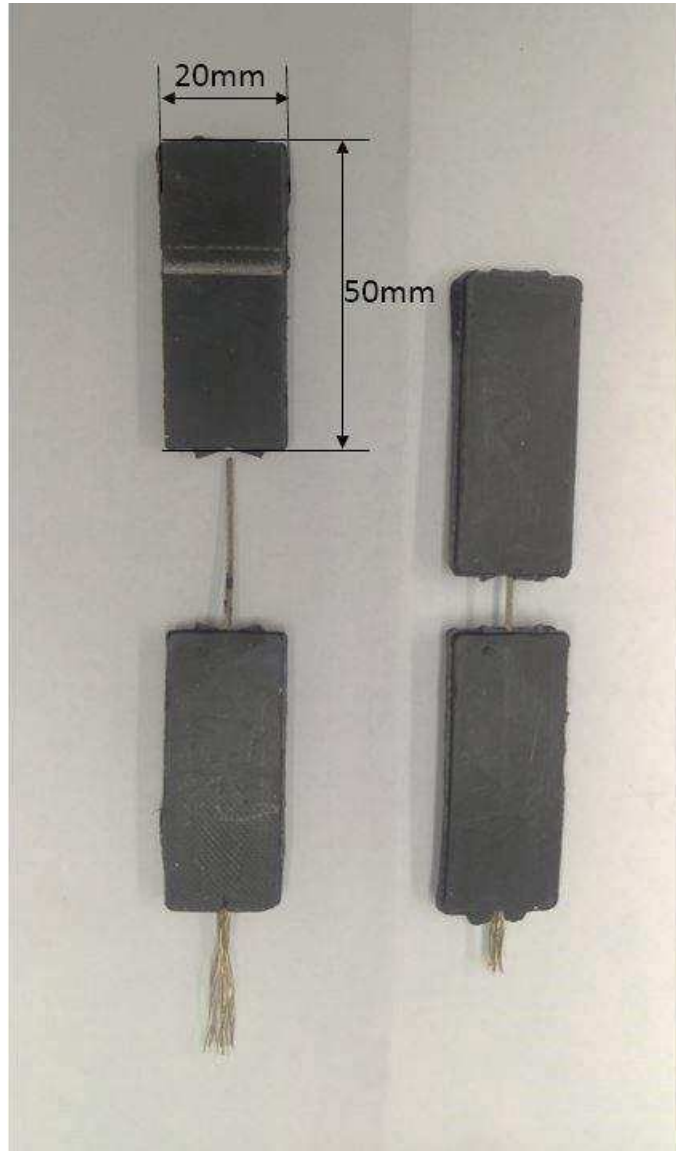


Fig. 1. Pull-out (adhesion) test sample.

For the adhesion tests, the two sides of the sample were clamped on the tensile tester (Model 5567 56P4494, Instron, Norwood, MA). The load cell was 1 kN and the crosshead rate used was 50 mm/min. When the experiment started, the steel cord which connected to the upper part of the sample was pulled out from the remaining part. The tensile tester would record the tension during the experiment. After the experiment, the maximum force (F_{\max}) was obtained from the results and the adhesion ratio was calculated using Eq. (5):

$$\frac{F_{max}}{L} = \textit{Adhesion ratio} \quad (5)$$

where, L is the embedded length of the steel cord.

3. Results and discussion

3.1. Morphology of fly ash

The particles of Micron 3 fly ash were spherical before the ball mill treatment (Fig. 2). By direct measurement, the mean size of the particles was determined as $1.62\ \mu\text{m}$ (Fig. 3). After the ball mill treatment, the mean size of the fly ash particles was reduced to $1.16\ \mu\text{m}$ calculated using the SEM pictures. After ball mill treatment, the shapes of most fly ash particles were changed from regular sphere to irregular (Fig. 2).

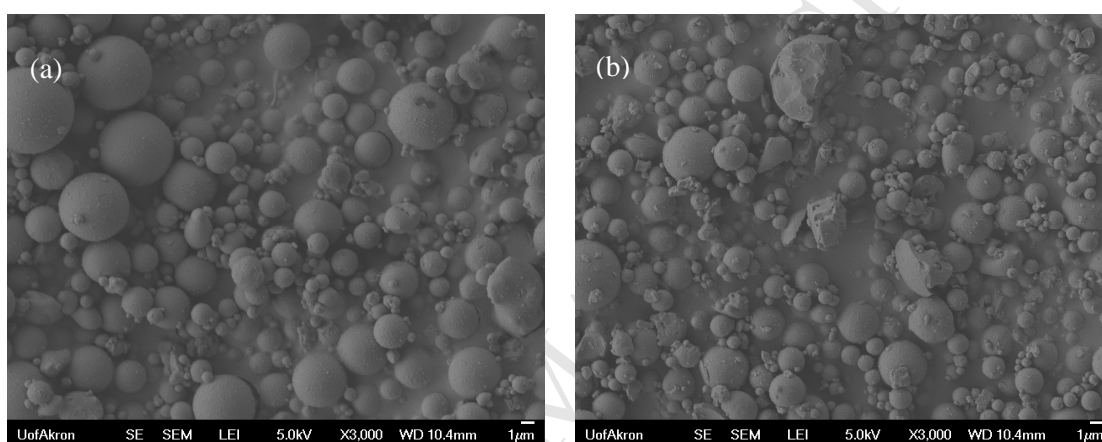


Fig. 2. SEM microphotographs of fly ash: (a) untreated fly ash; (b) ball milled fly ash.

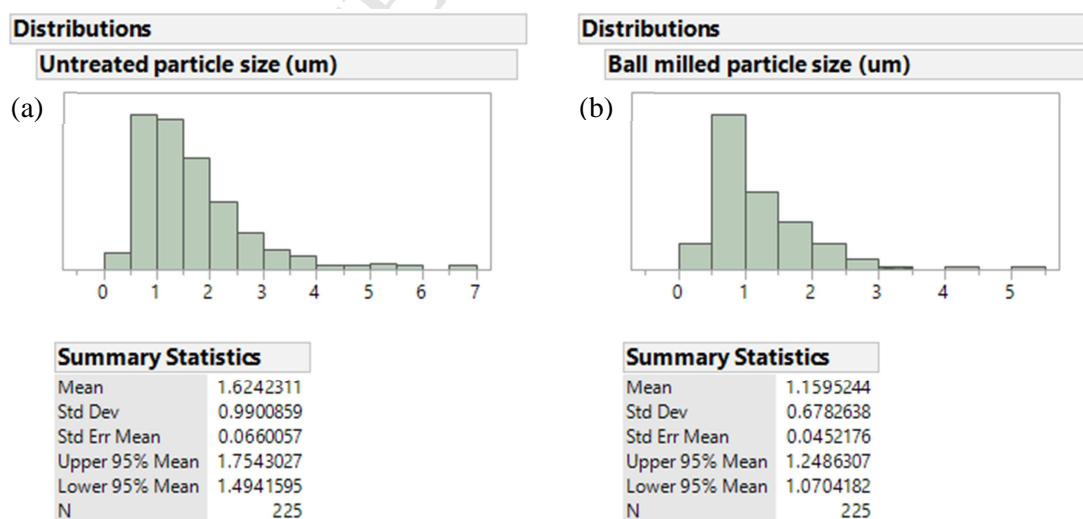


Fig. 3. Particle size distribution of fly ash: (a) untreated fly ash; (b) ball milled fly ash.

3.2. Cure characterizations

In Fig. 4, “50Si, FA UNT+4CB” and “50Si, FA ball+4CB” refer to the rubber which involves recipe B, “50CB+FA UNT” and “50CB+FA ball” refer to the rubber which involved recipe A. “UNT” refers to untreated fly ash and “ball” refers to ball mill treated fly ash. For CB and fly ash filled rubber (recipe A), curing time increased from 9 min to 12 min when carbon black was replaced by up to 10 phr (Fig. 4). This is attributed to the characteristic of CB which acts as a catalyst in the vulcanization of rubber (Baranwal and Stephens, 2001; Wampler and Gerspacher, 1994). Thus, depletion of carbon black resulted in increased cure time. Furthermore, we note that the main composition of fly ash is silica, and during vulcanization, silica reacts with zinc oxide to produce zinc sulfid (Awagon, 1996; Baranwal and Stephens, 2001; Laning et al., 1959). Zinc oxide reacts with the sulfur accelerator system to result in higher vulcanization rate (Baranwal and Stephens, 2001). Thus, the introduction of silica into the compound by fly ash resulted in reduction in the amount of zinc oxide causing an increase in cure time. For the silica and fly ash filled rubber (recipe B), however, the curing time did not change much and just fluctuated when fly ash was added up to 10 phr (Fig. 4). The reason is again the fact that silica causes retardation of vulcanization as explained above. Silica fillers were added in recipe B in rather large amounts (40 to 50 phr, see Table 4), thus inducing retardation in vulcanization. Therefore, compared with the rubber compound recipe A, the cure time of the rubber compound recipe B was higher (Fig. 4).

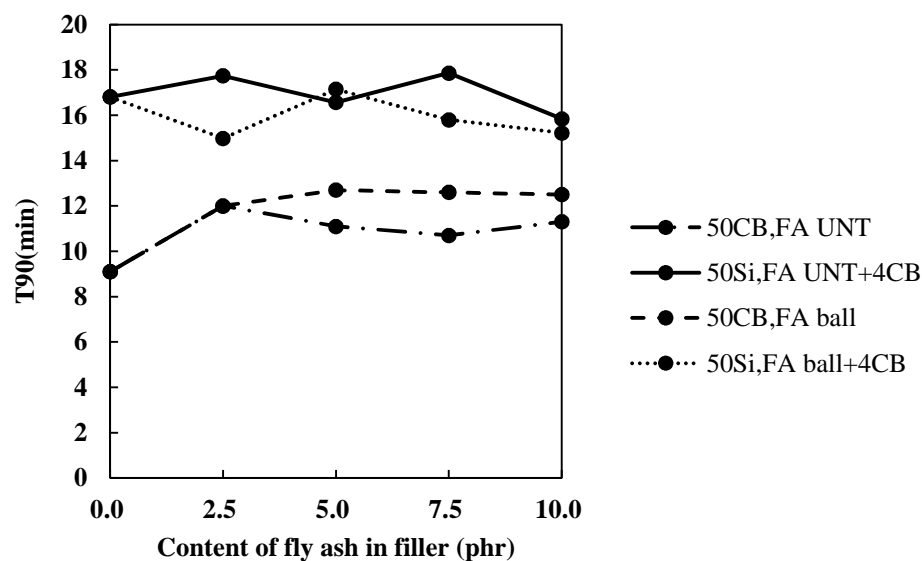


Fig. 4. T90 (time to 90% cure) of SBR compounds with various fly ash loadings.

3.3. Crosslink density of silica/CB/fly ash rubber

Increasing amount of fly ash below the 10 phr level did not have significant effect on the crosslink density of rubber composites. The results in crosslink density can be explained by the synergic effects of the hybrid filler used (fly ash, silica and CB). When a small amount of fly ash was added into the filler system, the dispersion of all of the fillers likely improved. On the other hand, the crosslink density declined at higher contents of fly ash when using either untreated or ball mill treated fly ash, as the fly ash particles would aggregate with silica and other fly ash particles, and the forming of crosslinking network was affected by such aggregated structures.

3.4. Tensile properties

Fig. 5 shows the tensile strengths of the rubber compound recipes A and B containing untreated and ball-milled fly ash fillers. Except for the 50CB+FA ball compound with 10 phr fly ash, addition of fly ash increases or preserves most of the tensile strength values observed in comparison to no-fly ash compounds. The slight initial decrease with 50CB+FA UNT compound is recovered to 0 phr tensile level at 10 phr FA. Fly ash particles may

improve the dispersion of CB and silica by reducing CB-CB or silica-silica interactions, which enhance the stress transferred from the rubber matrix to the filler. Compared with the CB/fly ash rubber compounds (treated and untreated), the silica/fly ash/CB rubber compounds exhibit higher tensile strength, especially for the compound which contained untreated fly ash. Noting that Micron 3 induces a synergic effect observed with the CB/fly ash rubber results, it maintains such synergic effect on further improving the tensile strength of the silica/fly ash/CB rubber compounds. We note that, for the CB/fly ash rubber, ball mill treatment improves the tensile strength as shown in Fig. 4. For the silica/fly ash/CB rubber, however, ball mill treatment reduces the tensile strength. This behavior can be attributed to the distinct characteristics of fillers; in CB/fly ash rubber compound, the CB-fly ash interaction is weak because of different polarity. The main composition on the surface of CB is carbon and a small fraction of the surface consists of hydrocarbon and oxygen-containing groups, while the surface of silica is mainly covered by silanol groups (Baranwal and Stephens, 2001). In addition, the quasi-graphitic crystallites form the aggregation structure of CB and the unit structure is a graphite-like hexagon (Göritz et al., 1999; Wang, 1998). Thus, different chemical components on the surface result in the weak interaction between the CB and fly ash particles. However, in silica/fly ash/CB rubber, the fly ash-silica interaction is strong because the main composition of the fly ash is silica, and silica particles prefer to form strong filler-filler interactions with adjacent silica particles (Ansarifar et al., 2005; Baranwal and Stephens, 2001; Sombatsompop et al., 2004). Therefore, silica particles tend to aggregate with ball mill treated fly ash particles.

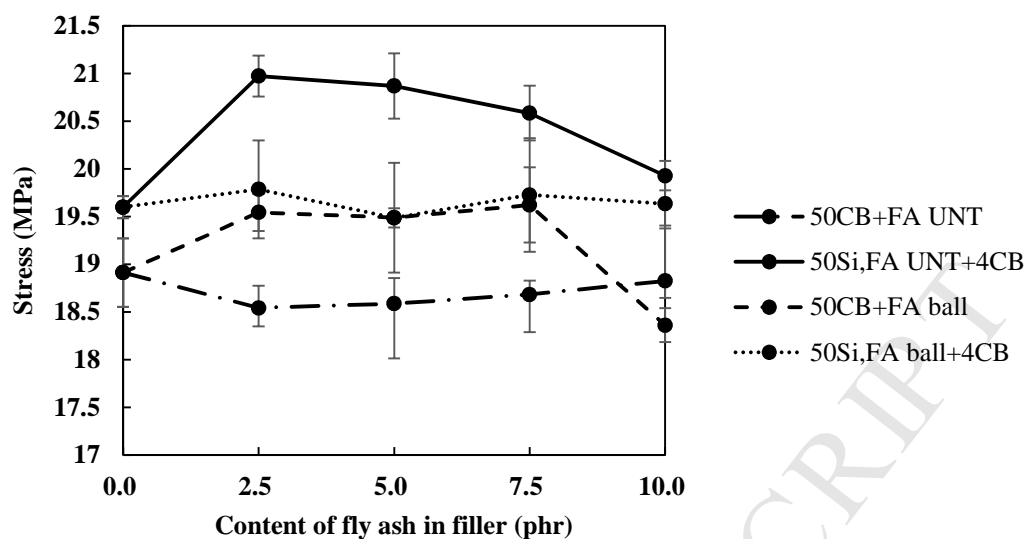


Fig. 5. Tensile strength of rubber compounds with various fly ash loadings.

Elongation at break and modulus at 100% strain for rubber compounds with various fly ash loadings are shown in Fig. 6 and Fig. 7. Above 2.5 phr fly ash loading, elongation at break generally increased and modulus at 100% strain generally decreased as the content of fly ash increased for all the rubber compounds. This behavior is attributed to the crosslink density of the rubber compounds (see Section 3.3). As the content of fly ash increased above 2.5 phr, the crosslink density decreased, so that elongation at break increased and the modulus at 100% strain decreased. At these higher fly ash loading levels, not much difference exists between the rubber compound with untreated fly ash and the rubber compound with ball mill treated fly ash, while more sensitivity is observed below 2.5 phr FA loading level

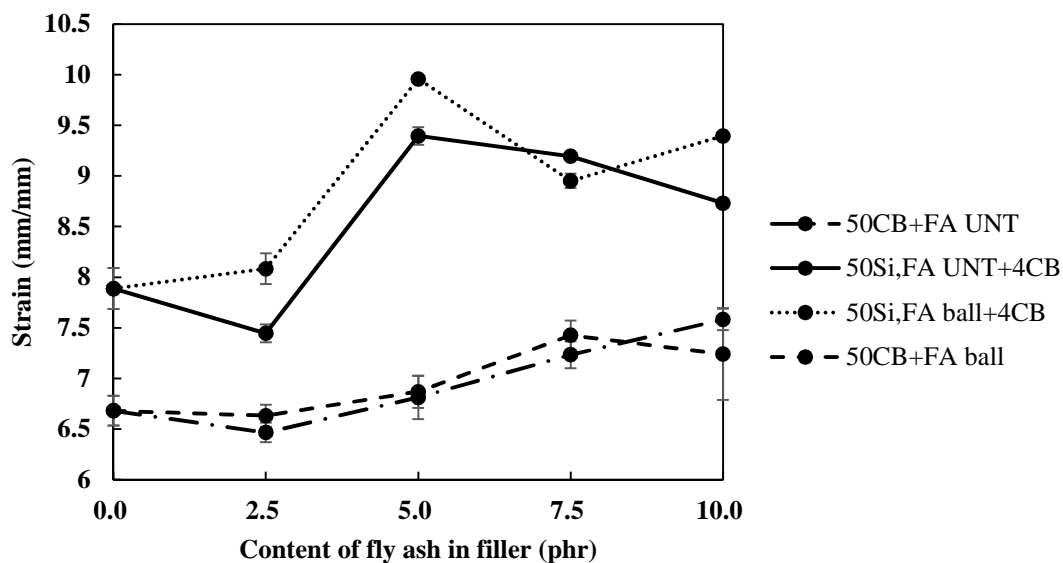


Fig. 6. Elongation at break of rubber compounds with various fly ash loadings.

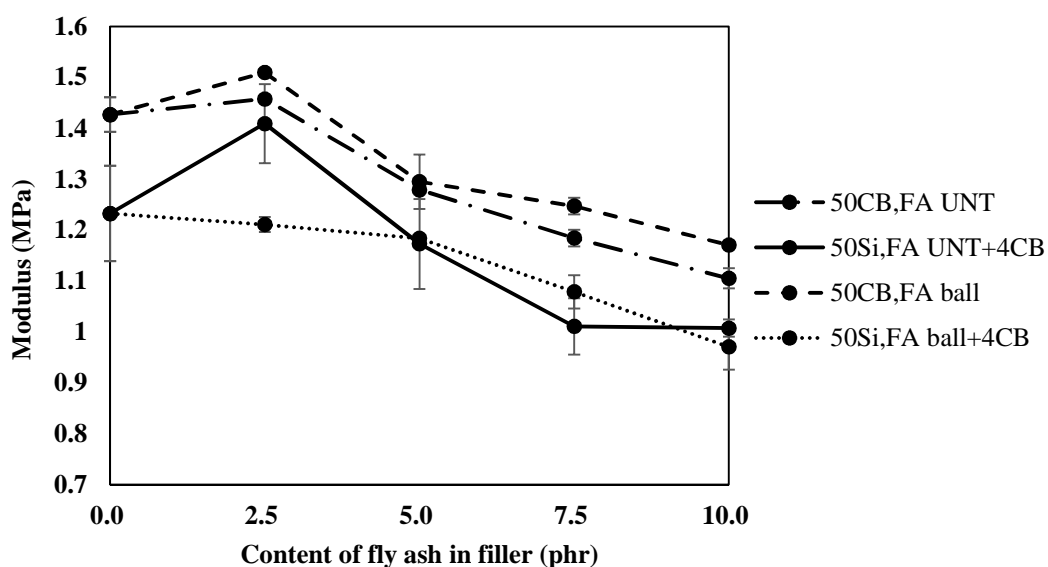


Fig. 7. Modulus at 100% strain of rubber compounds with various fly ash loadings.

The modulus at 2% strain is shown in Fig. 8. The modulus of the silica/fly ash/CB rubber is higher than that for the CB/fly ash rubber, which can be explained by the Payne effect. It is well known that silica forms filler-filler networks in rubber compounds, so that the filler-filler interactions are stronger in the silica/fly ash/CB rubber compound. The influence

of fly ash particles on the filler networks is shown Fig. 9 (real particle size is different from the particles shown in Fig. 9). As the fly ash content increases, the filler network is interrupted and filler-filler interactions are reduced contributing to the decrease in modulus at small strain levels. When used at small concentration, increasing ball mill treated fly ash results in the decline of the modulus at 2% strain. This phenomenon indicates that the addition of ball mill treated fly ash interrupts the silica network and initiates weak filler-filler interactions with silica.

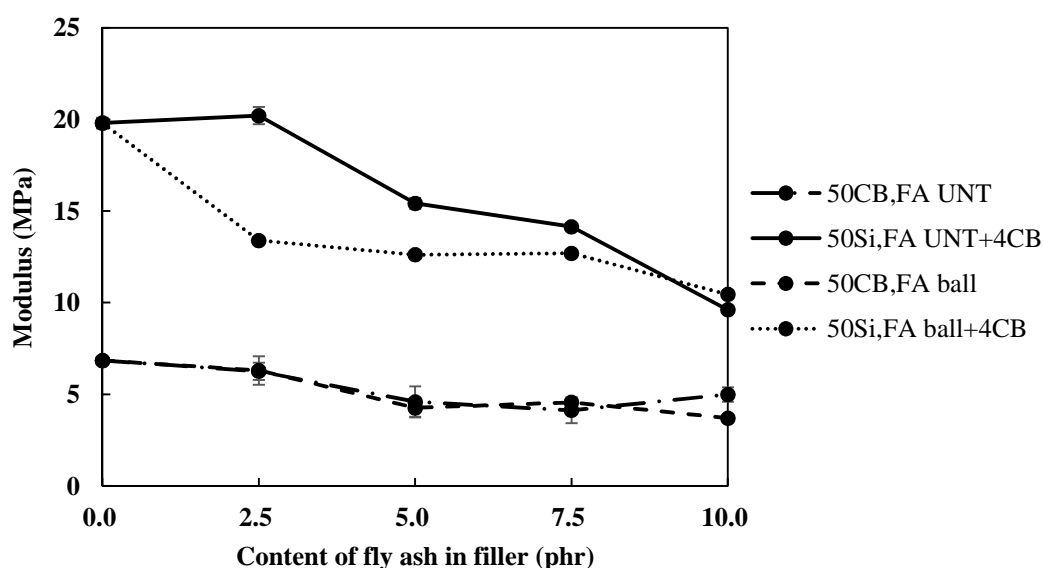
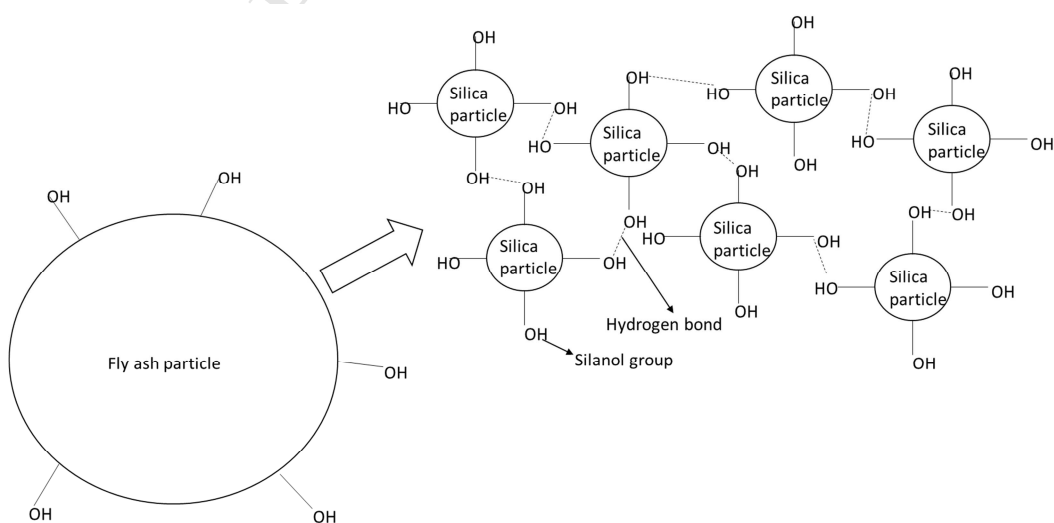


Fig. 8. Modulus at 2% strain of rubber compounds with various fly ash loadings.



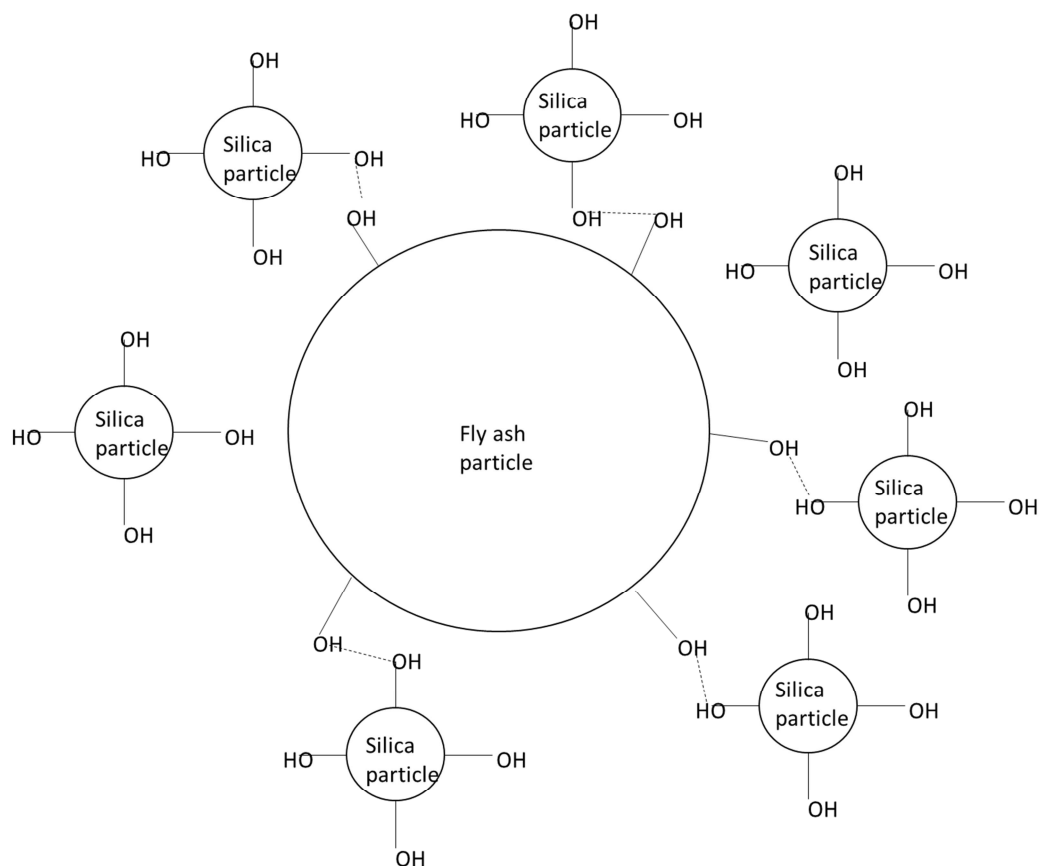


Fig. 9. Schematic representation of silica/fly ash filler networks.

3.5. Dynamic mechanical properties

As mentioned earlier, Tan delta ($\tan \delta$) values at 0°C and 60°C are correlated to wet grip and rolling resistance. Our measurements for the rolling resistance and wet grip behavior of the rubber compounds are shown in Fig. 10 and Fig. 11. Compared with the CB/fly ash rubber, both rolling resistance and wet grip are reduced when silica/fly ash/CB rubber compounds are used, including the cases of 0 phr fly ash. This indicates that silica has an influence on reducing the rolling resistance and wet grip. As the content of the fly ash increased in the

CB/fly ash rubber compound, the rolling resistance decreased, as attributed to increased silica by fly ash usage (Fig. 10). In silica/fly ash/CB rubber, rolling resistance was independent of the fly ash content, as silica was already present as a main component of the rubber compound (Fig. 10). As for the wet grip, the addition of fly ash improved wet grip due to the fact that the addition of fly ash interfered with the filler network, so that the rubber molecules were flexible at 0°C, and wet grip increased (Fig. 11).

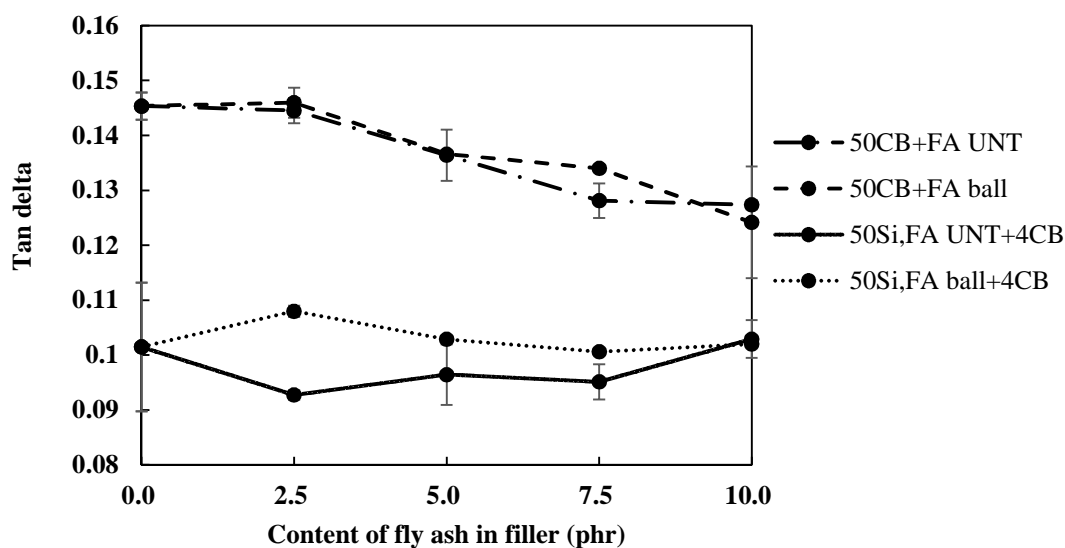


Fig. 10. $\tan \delta$ at 60°C with various fly ash loadings revealing changes in the rolling resistance.

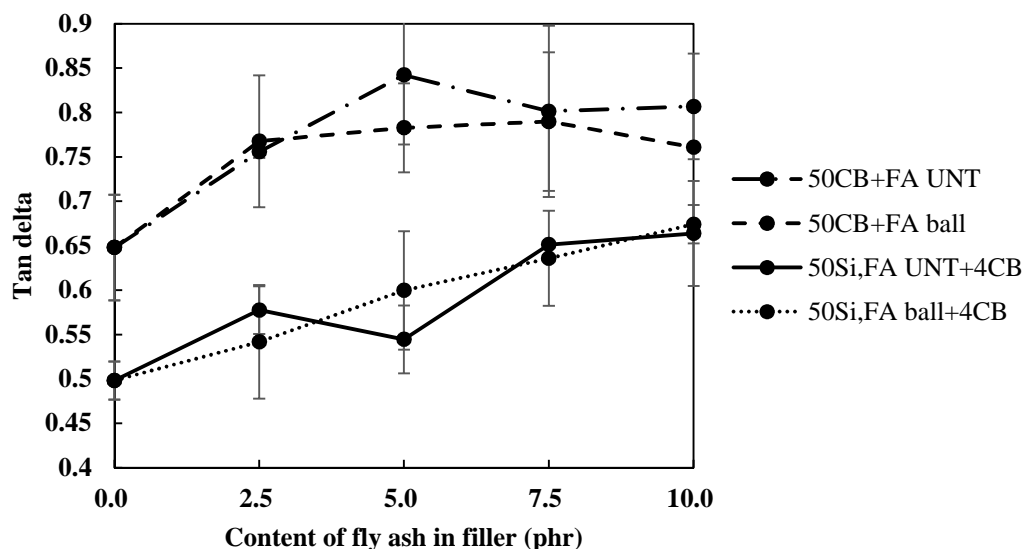


Fig. 11. $\tan \delta$ at 0°C with various fly ash loadings revealing changes in the wet grip behavior.

The rubber compounds which involve recipe B exhibit lower glass transition temperature, compared with recipe A, which can be explained by the similar reason for the higher elongation at break of recipe B. The poor silica-rubber interaction results in the flexible rubber molecules, so the glass transition temperature decreases. As the fly ash content increases, glass transition temperature does not change much, and ball mill treatment also has no obvious effect on glass transition temperature.

3.6. Hardness

The hardness of the rubber compound recipes A and B are shown in Fig. 12. At smaller concentrations of fly ash, as well as with 0 phr fly ash, the hardness of silica/fly ash/CB filled compounds is higher than the CB/fly ash filled compounds, as attributed to the Payne effect; in other words, strong filler-filler interaction of silica result in high hardness. Such filler-filler interactions are reduced with increasing fly ash, and the hardness is reduced. As for the CB/fly ash rubber compound, the hardness is practically independent of the fly ash content, which can be explained by the fact that, while fly ash interrupts the interaction between

carbon black particles, and it forms new filler-filler interactions among its own particles.

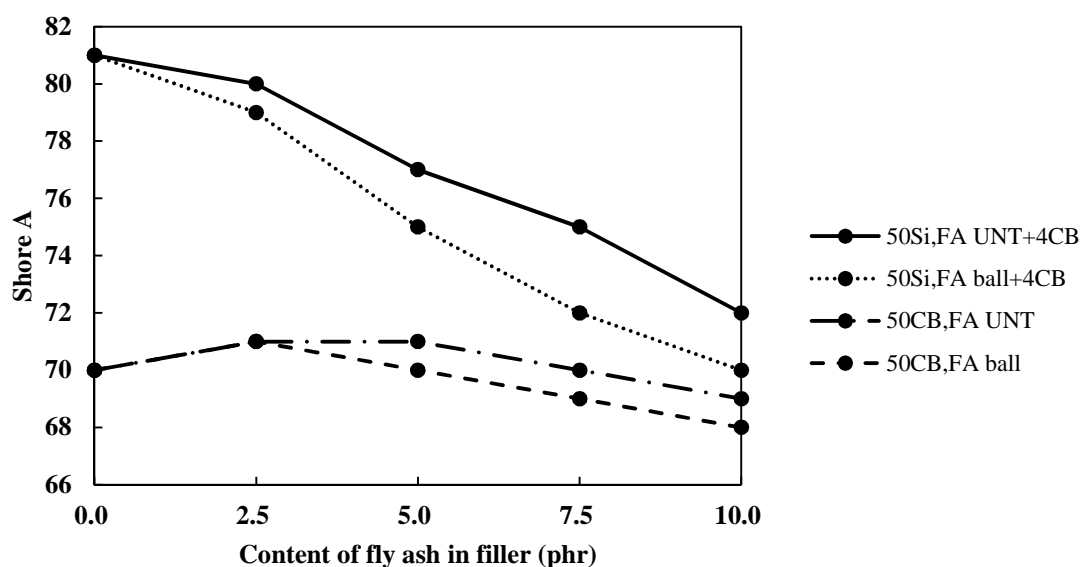


Fig. 12. Hardness of rubber compounds with various fly ash loadings.

3.7. Adhesion

Fig. 13 shows the adhesion ratios (Eq. (5)) of the rubber compounds. Compared with recipe A rubber compound, the silica/fly ash/carbon black rubber compound exhibits higher adhesion ratio, including the 0 phr fly ash compound, which indicates that silica has an influence on improving the adhesion between the rubber and the brass-coated steel cord. The ball mill treatment has a similar effect on adhesion when it is compared with the tensile results, indicating that ball mill treatment would improve the dispersion of filler in the CB/fly ash rubber. However, in the silica/fly ash/CB rubber compound ball mill treatment has the reverse influence on adhesion, due to the fact that ball mill treated fly ash absorbs more silica and tends to form larger aggregation structures. As the content of fly ash increases, adhesion ratio decreases, because the particle size of the fly ash is larger than silica. As for the CB/fly ash rubber, at small concentrations of fly ash, the adhesion is slightly improved by the ball mill treated fly ash, but adhesion decreases with increasing content of fly ash. At high fly ash loading, the influence of the silica in fly ash is blocked by flaws which may be created in the rubber compound caused by the aggregation structure.

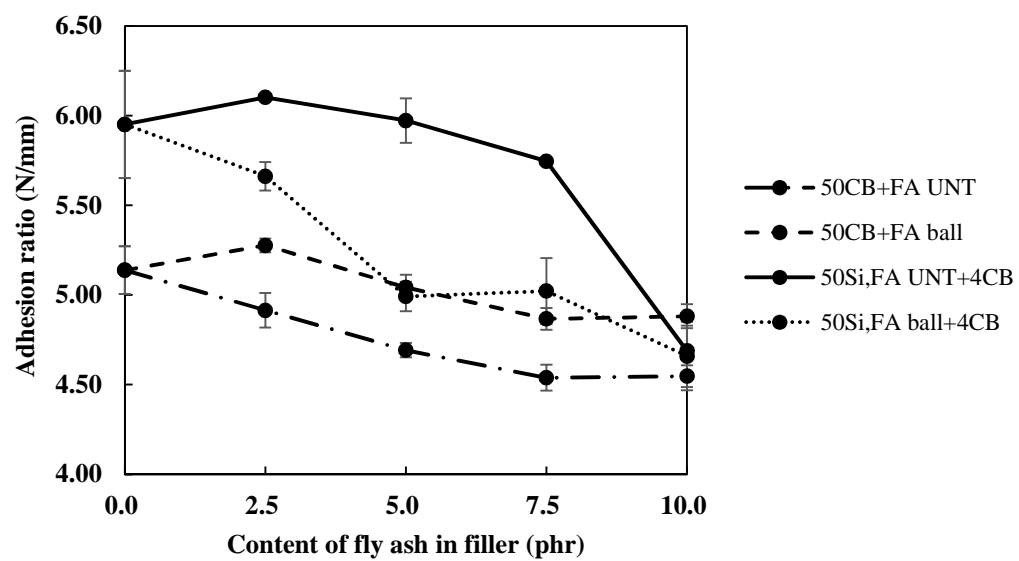


Fig. 13. Adhesion ratio of rubber compounds with various fly ash loadings.

4. Conclusions

Adhesion between brass coated steel cord and rubber was improved by using silica as the main part of fillers in rubber compounds. When the main filler was CB, partial replacement of the CB with ball mill-treated fly ash (up to 5 phr) improved or matched the adhesion strength as related to the anionic character of silica in fly ash. However, high fly ash content resulted in decreased adhesion because of the big particle size and aggregated structure of fillers. The ball mill treatment improved the mechanical properties of the CB/fly ash rubber compound due to changes in morphology of the fly ash. The fly ash particles changed from regular balls to irregular particles by ball mill treatment. Strain at break was improved as fly ash partially replaced the carbon black, due to the synergic effect of silica in fly ash, and the tensile strength increased slightly or remained about the same. The silica/fly ash /CB rubber also exhibited higher elongation at break and higher (with untreated fly ash) or the same tensile strength (with ball milled fly ash). Modulus at 2% strain and hardness remained approximately the same when partially replacing the carbon black with fly ash. While fly ash interrupted the interaction between carbon black particles, it formed new filler-filler interactions among its own particles. As the content of the fly ash increased in the CB/fly ash rubber compound, the rolling resistance decreased, as attributed to increased silica by fly ash usage. As for the wet grip, the addition of fly ash improved wet grip due to the fact that the addition of fly ash interfered with the filler network, so that the rubber molecules were flexible, and wet grip increased. Thus, the potential of fly ash as filler in tire applications has been demonstrated. The future studies may focus on the aging properties of fly ash filled SBR or natural rubber compounds.

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HIGHLIGHTS

- Fly ash is a byproduct of the fossil fuel power generation industries;
- Fly ash can be an alternative to carbon black and silica in rubber products.
- Fly ash reinforces styrene-butadiene rubber compounds.
- Tensile, dynamic mechanical and adhesive properties are improved by addition of fly ash.