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Study on Utilization of Palm Oil Fly Ash as a Filler for Thermoset Natural Rubber

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Abstract. Palm oil fly ash (POFA) as solid waste produced from crude palm oil industries consist of quite high of silica (more than 50% w/w). This study aimed to compare the properties and morphology of thermoset natural rubber (TNR) with POFA, silica, carbon black (CB), and mixture of POFA-CB fillers. The filler content used is 30 phr (per hundred rubbers). The process of making the compound was conducted by using a roll mill at room temperature and a maximum roll rotational speed of 20 rpm. Zinc oxide 5 phr, stearic acid 2 phr, mercaptodibenzothiazyldisulfide (MBTS) 0.6 phr, and Sulfur of 3 phr were used as curative agents. Trimethylquinone (TMQ) 1 phr was used as an antioxidant. Commercial minarex 2.5 phr was used as a plasticizer. Vulcanization process was carried out at a temperature of 150 °C and a pressure of 50 kg/cm^2 using a hot press. Morphology was observed using a scanning electron microscope (SEM). Measurement of tensile properties was carried out using universal testing machine (UTM) according to ASTM D412-06a standard. The results indicated that the use of POFA as a filler could potentially produce TNR with quite good morphology, tensile properties and water absorption properties. A mixture of POFA-CB with a mass ratio of 50/50 (w/w) produced the thermoset with the value of 18.5 MPa of tensile strength, 1600% of elongation at break, and 1.2 MPa of elastic modulus.

Introduction

Mechanical properties improvement of thermoset rubber could be performed by the addition of filler into the rubber material. Commonly fillers are such as carbon black, silica, calcium carbonate, calcium silicate, and clay[1]. Palm oil fly ash (POFA) is one of the solid wastes generated in the combustion process of palm fruit fiber and palm shell in boiler unit at palm oil mills. This material contains a lot of silica, which is about 59% (w/w) [2]. Silicahas known as commercial filler for thermoset rubber as filler to increase the tensile strength, hardness, tear strength and abrasion resistance of the rubber [3]. One POFA production centers in Indonesia is Riau Province, where there are currently around 146 unit palm oil mills [4]. Riau province is estimated produces POFA at least 100,000 tons per year [5]. A highly silica contents in POFA making it potentially be used as a alternative to commercial silica filler in rubber industries. The material is also availability of sufficiently large and sustainability production. The main purpose of the research is the utilization of materials of solid waste of palm oil industries as substituting for common fillers in the industries of natural rubber (NR). It is potentially economical valuable and environmental friendly.

Materials and Method

Materials. Materials used in this study were POFA as a filler obtained from local mills (Riau, Indonesia), natural rubber (SIR-20 with a 70 Mooney viscosity at 100 °C), obtained from local rubber processing industry (Riau, Indonesia). Silica-sized commercial of ≥ 30 μm and N330 type of carbon black with an average particle diameter of 31 nm were also used as filler, purchased from local distributors. Some additives including Sulfur, Mercaptodibenzo-thiazoledisulfide (MBTS), ZnO, Stearic Acid, Trimethylquinone (TMQ) type Flectol TMQ, Minarex as plasticizer, Maleated polypropylene (MA-g-PP) type Epolene E-43 Polymer, purchased from local distributors.

Filler Preparation. The POFA of 200 mesh was kept in the oven at 110 °C for 3.5 hours to reduce its moisture. For silica and carbon black fillers were not done special treatment. The ratio of POFA and carbon black used was 50/50 (w/w) as hybrid filler.

Compound Preparation and Vulcanization. Compound was prepared using roll mill (speed control Thosiba UF-S9 400 volt, 3.7 kw; Teco 1440 rpm motors, 5 hp; roll diameter of 10 cm and 35 cm long roll) performed at room temperature. The roll speed was kept very low (maximum of 20 rpm) to prevent increasing temperature compound. Rubber compound is a mixture consisting of SIR-20, plasticizer minarex, filler, ZnO, stearic acid, TMQ, MBTS, and sulfur. The following is a sequence of the mixing process shown in Table 1.Vulcanization process was carried out at a temperature of 150 °C and a setting load of 50 kg/cm^2 using a hot press.

Table 1. Material mixing sequence for rubber compounds using roll mill

Activites	Quantity (phr)	Mixing time (minutes)
Mastication of rubber	100	15
The addition of plasticizer	2,5	5
The addition of filler	30	20
The addition of ZnO	5	15
The addition of stearic acid	3	5
TMQ addition	1	3
The addition of MBTS	0,6	2
The addition of sulfur	3	3
Termination	-	5

Samples Testing. The testing include tensile properties by using universal testing machine (UTM) according to ASTM D412-06a standard; morphologyby using scanning electron microscope (SEM); and water absorption according to ref [6].

Results and Discussion

Morphology. Morphology of thermoset natural rubber with various fillers are shown in Figure 1. The distribution of POFA filler and hybrid filler of POFA/CB less evenly if compared with thermoset rubber which using CB filler. This happens because the particle size of carbon black which is smaller than the POFA causing the surface area of carbon black larger so that the contact or interaction becoming better between CB and rubber [11]. However distribution of POFA filler and hybrid filler of POFA/CB be still better if compared with thermoset rubber which using silica filler. Silica cluster tend to binds each other to form agglomeration, so that the interaction between filler and rubber become weak [7, 8].

Tensile Properties. Comparison of tensile properties of thermoset rubber with various types of filler can be seen in Figure 2. Tensile strength of thermoset rubber with POFA filler (particle size 200 mesh) obtained is 15 MPa. While the use of filler hybrid POFA/CB on the mass ratio of 50/50 (w/w), the tensile strength of thermoset rubber acquired 18.5 MPa. This result is lower than when compared to thermoset rubber using commercial carbon black filler, which reached 20.7 MPa. The thermoset rubber using silica filler has a value 6.5 MPa tensile strength. It is much lower tensile strength compare with that of thermoset rubber with POFA filler. Thermoset rubber tensile strength produced inversely proportional to the obtained its elongation at break. The use of POFA filler tends to increase the elongation at break. The elongation at break obtained using POFA filler reach

2040%. This value is higher than that using a thermoset rubber filler silica, carbon black, and POFA/CB. Elastic modulus thermoset rubber with POFA filler reaches 1.3 MPa. The elastic modulus is smaller than the elastic modulus of thermoset rubber with silica filler of 2.5 MPa. But greater than that using the premises thermoset rubber carbon black filler (1.05 MPa) and hybrid filler POFA/CB (1.2 MPa).

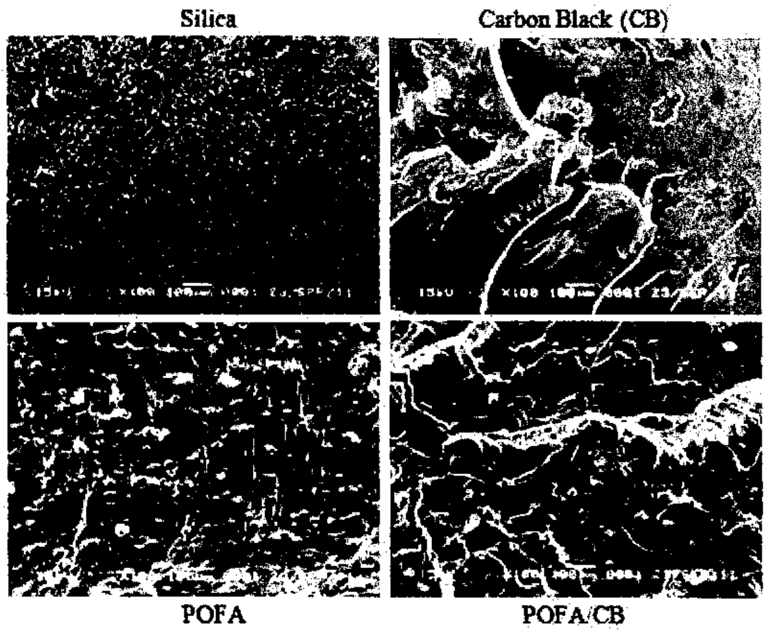

Fig1. Morphology of thermoset rubber with various types of fillers.

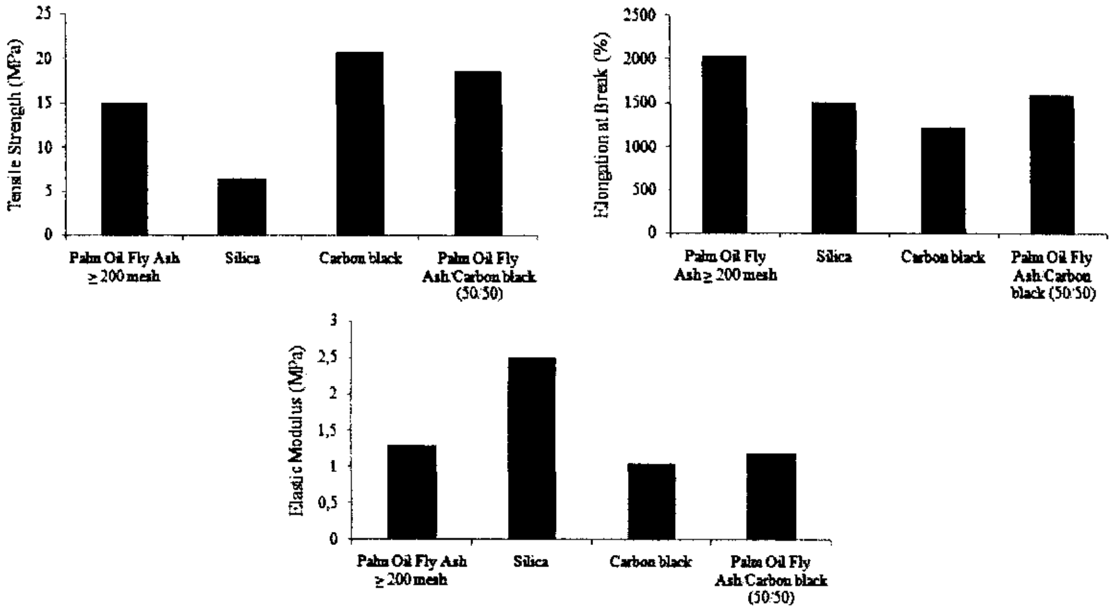

Fig2. Effect of filler types on the tensile properties of the thermoset rubbers

According to Morton [9], physical and chemical properties that affect the strengthening of vulcanized rubber is particle size, surface area, structure and surface activity. The smaller the particle size of the filler allows it to be properly and evenly dispersed in the rubber compound. If the filler is evenly spread, there will be interaction with physics and chemistry is better any way. Carbon black has a high surface energy derived from unsaturated polyaromatic structure and its functional groups. This structure makes carbon black particles can adsorb strongly polymer chains. Without fillers, the thermoset rubber has a tensile properties that only comes from crosslinking by sulfur atoms. However, the presence of fillers, the tensile properties becomes greater because it is supported by the interaction between the polymer chains with fillers. An increase in temperature due to friction roll mill that occurred between the rotor and the compound also has an effect on the properties. Temperature rising roll mill on the addition of POFA or silica filler can cause vulcanization process took place before filler and additive spread/distributed evenly, thus resulting in a crosslink bond will be formed in early (too fast it was formed) and end the process further crosslink bond formation. Consequently, it can reduce the elasticity of vulcanized affecting the elongation at break [8]. However, an increase in the elastic modulus tends to occur at low filler concentration [10]. In addition to the type of filler used, the increase in bond crosslink density resulting from the vulcanization process and the conversion of polysulfide bonds into mono and disulfide bonds also affects the resulting elastic modulus. This can happen if the thermoset rubber duration of vulcanization process is too long [11].

Water Absorption. The percentage of water absorption in each sample thermoset rubber with different filler can be seen in Figure 3. Water absorption test aims to examine the extent to which the filler affects the water absorption of the material thermoset rubber. The higher the water absorption of the material is expected to be able causing the useful life will be shorter due to the rapidly changing its properties. The thermoset rubber with POFA filler has a percentage of water absorption of 2.2% (w/w), it is the highest among that using other fillers. The thermoset rubber with hybrid filler of POFA/CB (50/50 w/w) has the percentage of water absorption of 1.7% (w/w). It is still higher when compared with that using silica and carbon black fillers. This fact is attributable to the nature of the POFA contains many hygroscopic ingredients, such as calcium and magnesium which can react with water. According to the previous study [11], silica in rubber is also hygroscopic. However, POFA in thermoset rubber demonstrates more hygroscopic than that of silica.

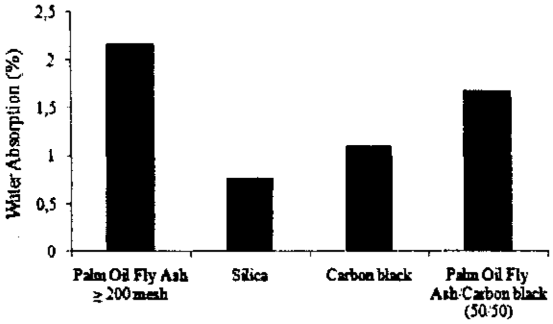

Fig3. Effects of filler type on water absorption of the thermoset rubber

Summary

The use of POFA as filler can produce thermoset natural rubber with morphology, tensile properties and water absorption properties are quite good, although still lower than when using carbon black. The presence of carbon black having particle size smaller than the POFA in mixed POFA/ CB filler influence in improving the tensile properties of the thermoset rubber. Tensile properties of thermoset rubber with hybrid filler of POFA/CB with a mass ratio of 50/50 (w/w) are the tensile strength of 18.5 MPa, the break elongation of 1600%, and the elastic modulus of 1.2 MPa. These results indicate that the potential of POFA used as filler for the thermoset rubber. However, the use of POFA in excessive amounts can increase the percentage of water absorption of thermoset rubber.

References

[1] D. Moonchai, N. Moryadee, N. Poosodsang, Comparative Properties of Natural Rubber Vulcanizates Filled with Defatted Rice Bran, Clay, and Calcium Carbonate, Maejo International Journal of Science and Technology 6 (2012) 249-258.

[2] Bahruddin, Adrianto Ahmad, AdhyPrayitno, Morphology and Mechanical Properties of Palm Based Fly Ash Reinforced Dynamically Vulcanized Natural Rubber/Polypropylene Blends, Procedia Chemistry 4(2012) 146-153.

[3] Siswanto, M. Hamzah, A. Mahendra,Fausiah, Engineering of Nanosilika made of Local Silica as Filler Compound Rubber of Air Bag Rubber of Ship Yard Launching, In Proceedings of SINas (2012) 56-59.

[4] Information on http://www.almasdi.staff.unri.ac.id/2012/09/06/potential-development-industrial-oil-palm /

[5] Information on http://www.isroi.com/2008/03/12/-utilization of by-products-coconut-palm-as-source-alternative-renewable-energy /

[6] Ismail, H. Salmah, M. Nasir. 2001. Dynamic Vulcanization of Rubberwood Filled Polypropylene/Natural Rubber Blend, *Polymer Testing*,Vol. 20: 819-823.

[7] M.J. Wang, P. Zhang, K. Mahmud, Carbon Silica Dual Phase Filler, A New Generation Reinforcing Agent for Rubber, Wilson Applied Science and Technology. 74 (2001) 124-128.

[8] P. Ghosh, S. Katare, P. Patkar, J.M. Caruthers, V. Venkatasubramanian, Sulfur Vulcanization of Natural Rubber For Benzothiazole Accelerated Formulations: From Reaction Mechanisms to A Rational Kinetic Model, Rubber Chemistry and Technology. 76 (2003) 592.

[9] M. Morton, Rubber Technology, third ed., Van Nostrand Reinhold, New York, 1987.

[10] S. Nago, Y. Mizutani, Microporous Polypropylene Fibers Containing CaCO3 Fillers, J. Appl. Polym. Sci. 62 (1996) 6-81

[11] T. Saowapark, "Reinforcement of Natural Rubber with Silica/Carbon Black Hybrid Filler", Ph.D Thesis, Mahidol University, 2005, pp 20.

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