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Using Stearyl Aromatic Esters as a Processing Aid in Natural Rubber Compounding: Effect on Curing, Mechanical and Aging Properties

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Abstract Four stearyl aromatic esters were synthesized and used as processing aids for natural rubber compounding. The structure of all esters, namely stearyl benzoate (SB), distearyl phthalate (SP), stearyl biphenyl-4-carboxylate (SBi) and stearyl naphthoate (SN) were characterized by spectroscopic techniques. Their effect on curing and mechanical properties of the natural rubber compounds were evaluated according to the standard of ASTM D3184. It was found that aromatic esters enhanced curing characteristics in a similar way to aromatic oil (AO) in the same rubber formula. Furthermore, the aromatic esters can slightly improve mechanical properties of natural rubber vulcanizates before aging. Although the mechanical properties in term of tear strength, compression set and thermal stability of the vulcanizates were deteriorated after aging, most useful properties were still comparable to that of the compound having added aromatic oil.

Key words aromatic oil, mechanical properties, processing aid, stearyl aromatic ester

Introduction

Natural rubber compounding is composed of various ingredients such as sulphur, accelerators, activators, antioxidants, carbon black and oil. The polycyclic aromatic hydrocarbon (PAH) or aromatic oil is generally added in the formula to improve processing properties, low temperature properties, dispersion of fillers and coat reduction. The report point at the ware of tire tread material and it being spread on the roadsides (Joseph *et al.*, 2004), introducing high amounts of PAH into environment. PAH, many of which are identified as suspected carcinogens. The EU defines in direction 67/548/EEC that the PAH oils have to be labeled R45, may cause cancer (Dasgupta *et al.,* 2007). The directive defines that the products with levels exceeding 3% by weight must be labeled.

Various natural oil were added to natural rubber compounding as plasticizers to improve dynamic properties, curing characteristics, reversion and fatigue life (Kukreja *et al.,* 2002). The hydrogenation reaction of various vegetable oil resulted in saturated long chain alcohol such as stearyl alcohol, a large natural resource and low coat material. The synthetic stearyl aromatic ester was selected to use as processing aid in natural rubber compounding.

The modification of stearyl aromatic esters that are composed of long chain hydrocarbon and aromatic part is the new trend of eco-friendly processing oil. The effect of ester as processing aid on curing characteristics and mechanical properties of rubber compounds were investigated.

Material & Methods

Synthesis of stearyl aromatic ester

To synthesize four stearyl aromatic esters; SB, SP, SBi and SN were synthesized by the esterification reaction between stearyl alcohol and benzoic acid, phthalic acid, biphenyl-4-carboxylic acid and 1-naphthoic acid respectively. Stearyl alcohol 1.0 mmol was first added in a round-bottom flask, equipped with a stirbar, reflux condenser, and set up the apparatus for heating on the oil bath with heater and stirrer. The flask has been heated until the alcohol was melted; aromatic oil (1.0 mmol) was then added to the melting alcohol. The temperature of oil bath was adjusted until the reaction mixture was completely melted (85–95 °C), 0.81 mL conc. sulfuric acid (15% w/w of acid) was then added dropwise. The stirring of mixture was continued under constant temperature. TLC was used to monitor the progress of reaction. After the reaction was complete, a crude stearyl aromatic ester product was cooled in an ice-bath and the product was collected by vacuum filtration. The white solid was transferred to the beaker having 20 mL of 10% aqueous solution of sodium hydrogen carbonate with slow stirring for a few minute. The mixture was cooled and then filtered by vacuum. The filter cake was rinsed by a few milliliter of water and dried in an oven at 60 °C.

The product was purified by quick column chromatography using silica gel 60 GF_{254} and 10% dichloromethane in hexane as eluting solvent. The obtained stearyl esters were characterized by IR and ^{1}H- NMR spectroscopy in comparison with the starting materials stearyl alcohol and corresponding aromatic acid.

Rubber compounding

Materials

Four types of stearyl aromatic esters (SB, SP, SBi and SN) were used as processing aids in natural rubber compounding, as compared with aromatic oil. The natural rubber compounds were prepared the formulations following by ASTM D 3184 as shown in Table 1.

Table 1 Compounds' formulations.

Ingredients	**phr****
NR	100
Accelerator	0.7
ZnO	5
Stearic acid	2
Processing aids*	5
Carbon black (N330)	50
sulphur	2.25

* Processing aids are aromatic oil (AO), stearyl benzoate (SB), distearyl phthalate (SP), stearyl biphenyl-4-carboxylate (SBi) and stearyl naphthoate (SN)

** Per hundred parts of rubber

Natural rubber that used in this experiment is in a form of a ribbed smoked sheet 3 (RSS3), carbon black is N330. Other ingredients are commercial grade that are generally used in rubber industry.

Compounding

The mastication was done on the internal mixer (brabender plasticorder) which was operated at a constant rotor speed of 60 rpm at 70°C. The process was followed by mixing a natural rubber in the chamber for 1 min, accelerator (TBBS) for 0.5 min. and ZnO for 0.5 min, respectively. A half of stearic acid, processing aid and carbon black were added and mixed for 3 min, then the remaining of them were added and continued mixing for 3 min.

The homogeneous mixture was further mixed with the amount of sulphur on the two-roll mill for about 2 min. Each batch was rolled to produce the tested sheets.

Curing Characterization

Curing characteristics of the compounds were measured on rotorless rheometer (rheoTECH MD+, Tech Pro, Inc., Cuyahoya Falls, USA) according to ASTM 2240-93 and pressing cured at 150°C.

Processing properties

- Mooney viscosity and stress relaxation

Mooney viscosity, ML (1+4) at 100 °C and stress relaxation were determined on a Mooney viscometer (TECH+VAR from Tech Pro, Inc., Cuyahoya Falls, USA) using a large rotor, according to ISO 289-1. For the stress relaxation, it was running on 1 min for preheating time, 4 min for testing time and last 4 min for decaying time, respectively.

Testing

- Mechanical and ageing properties

Determination of mechanical and ageing properties, tensile testing were determined on a Hounsfield tensometer, model H 10 KS (Hounsfield Test Equipment Co., Ltd., UK) with a crosshead speed of 500 mm/min according to ASTM D412 at 25°C using the dumbbell-shaped specimens. Hot air ageing conditions was done at 100°C for 22 h.

- Tear strength

Tear strength was determined on a Hounsfield tensometer with a crosshead speed at 500 mm/min according to ASTM D624.

- Hardness

The hardness was tested on digital hardness tester (Toyo Seiki Seisaku-sho, Tokyo, Japan) according to ASTM D2240.

- Compression set

The compression set was measured on a UTM according to ASTM D395.

- Abrasion loss

The abrasion loss was measured on a UTM according to B.S. 903: Part A 9:1957, Method C- Akron machine.

Results & Discussion

Four stearyl aromatic esters SB, SP, SBi and SN were successfully synthesized from stearyl alcohol and aromatic acids using sulfuric acid as a catalyst by the general esterification reaction. The 80-90 percentage yield were surprisingly determined from equilibrium esterification reaction by 1:1 molar ratio of alcohol:aromatic acid and 15% by weight of catalyst. The esterification ran on the melting of reaction mixture at 85-95°C. High products yield was obtained due to the evaporation of water from the mixture during the reaction of which the temperature was as high as 95°C that shifted the equilibrium to the ester product.

The structure of stearyl aromatic esters was characterized by IR and ^{1}H-NMR. The IR absorption peaks exhibited at 1760-1770 cm^{-1} signals corresponding to the carbonyl of ester, while ^{1}H-NMR spectra revealed the presence of the aromatic protons at δ 7.20-8.90 ppm, two oxymethylene protons at δ 4.25 ppm, three methyl protons at δ 0.9 ppm and abundance of methylene protons at δ 1.2-2.3 ppm. These indicated that esters composed of aromatic part and long chain stearyl by ester linkage.

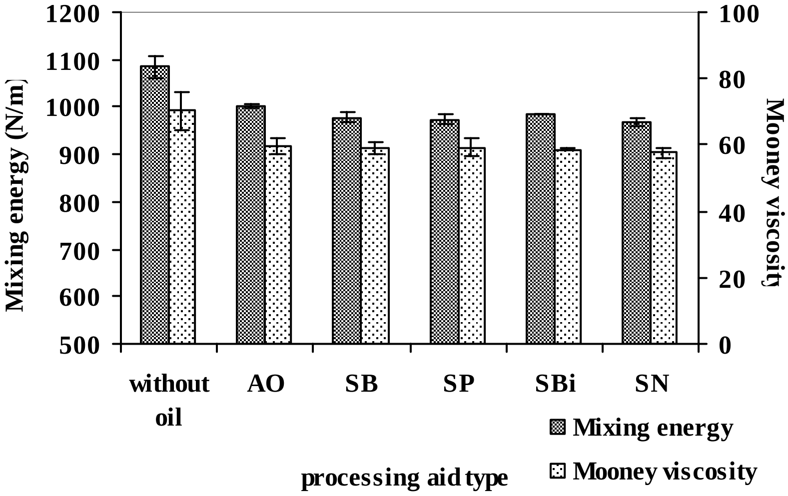

Figure 1 Bar diagram of the mixing energy and Mooney viscosity for the rubber compounds at various processing aids.

The effects of synthetic stearyl aromatic esters on the mixing energy and Mooney viscosity of natural compounds are shown in Fig. 1. Compounds with aromatic esters showed lower mixing energy and Mooney viscosity, similar to that of the aromatic oil, but different from that processed without processing aid. This indicated that ester processing aid improved the processability of the rubber compounds, due to a good dispersion of matrix.

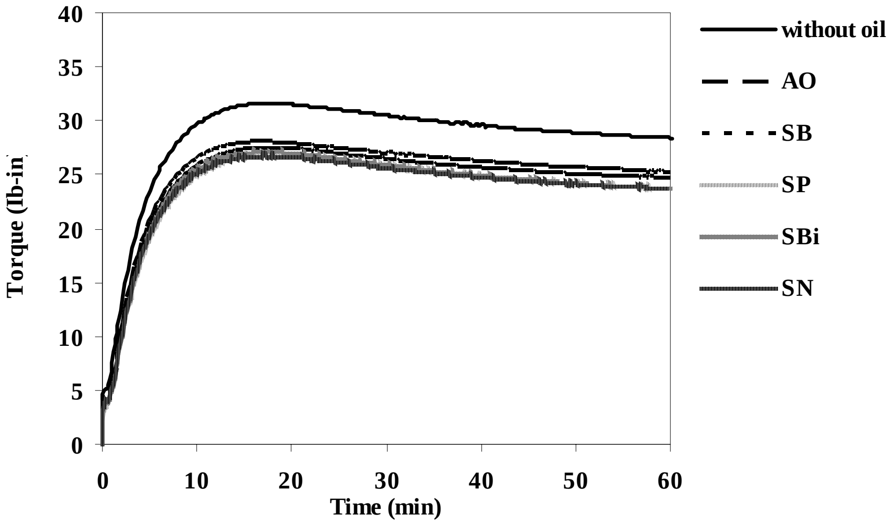

Figure 2 Curing characteristics of rubber compounds of various processing aids.

To demonstrate the differences of curing properties on rubber compounds, the curing curves of processing aid types in natural rubber compounds were done at 150°C. Rubber compounds having aromatic esters showed longer scorch time and shorter curing time similar to that of the compound having added aromatic oil as shown in Fig. 2.

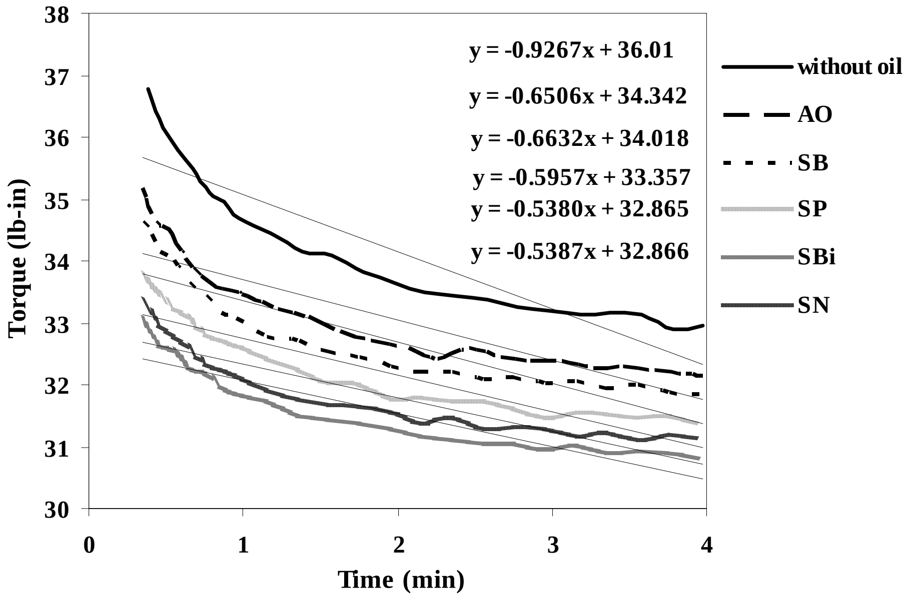

Figure 3 Stress relaxation of rubber compounds having various processing aid.

From the curing curve (Fig. 3), all of the rubber compounds containing either esters or aromatic oil showed lower stress relaxation than the compound without processing aid. However, this result indicated the elastic properties of all compounds.

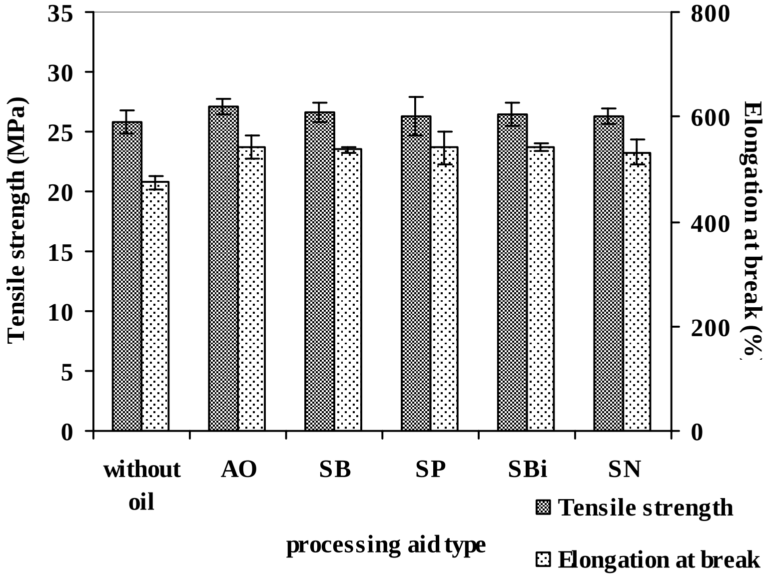

Figure 4 Bar diagram of the tensile strength (MPa) and elongation at break (%) for the rubber compounds having various processing aids.

The tensile strength (MPa) and elongation at break (%) of compounds are illustrated in Fig. 4. The tensile strength seemed to be not different among all of test compounds. This might be from the result of small content of added processing aid and good mixing. The elongation at break was comparable to that of the compound with aromatic oil having the same rubber formula. This might be due to the structure similarity of esters in comparison with the aromatic oil.

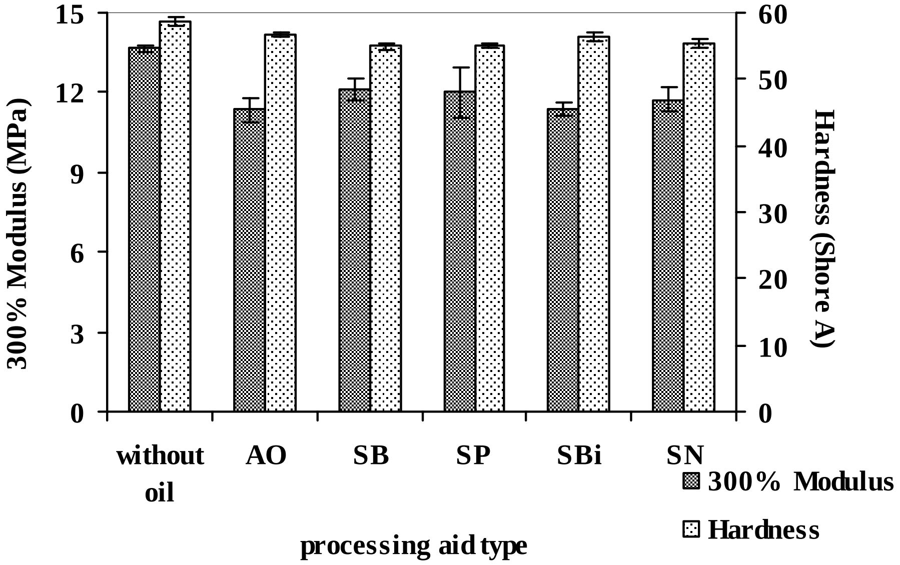

Figure 5 Bar diagram of the hardness (shore A) and modulus at 300% elongation (MPa) for the rubber compounds having various processing aids.

Comparative bar diagrams of the modulus at 300% elongation (MPa) and hardness (shore A) for rubber compounds are shown in Fig. 5. It was found that the compound without processing aid exhibited the highest 300% modulus and hardness, whereas the compounds with esters and aromatic oil showed lower values which are not much different from one another. The decreasing of modulus and hardness of compounds with processing aid were explained by increasing mobility of polymer chains and decreasing of entanglement of rubber molecules due to lubricating effect of processing aid.

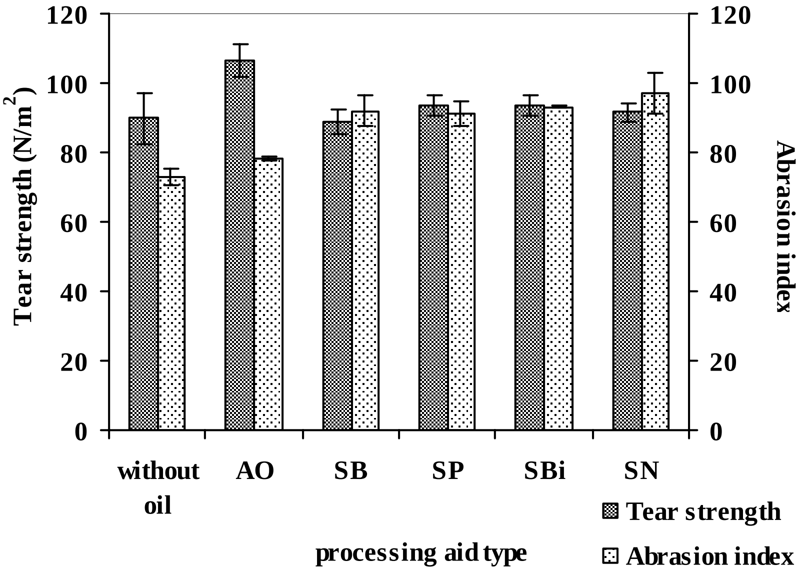

Figure 6 Bar diagram of the tear strength (N/m) and abrasion loss (wt %) for the rubber compounds having various processing aids.

Comparative bar diagrams of the tear strength and abrasion loss of rubber compounds are shown in Fig. 6. The diagram displayed the highest tear strength of compound with aromatic oil, but the tear strength of the other compounds was quite similar. In general, tearing of rubber occurs due to the propagation of cracks initiated of the stress point through the wearing of rubber molecules at the rubber-carbon black interfaces. In the case of compound with aromatic oil, which had higher aromatic rings than stearyl aromatic ester, the good distribution of carbon-black in rubber was obtained. This is because the action of aromatic oil as compatibilizer between rubber molecules and carbon black particles led to increase in tear strength. The abrasion resistance of compounds having stearyl aromatic esters indicated better property caused by lower friction coefficient of those compounds.

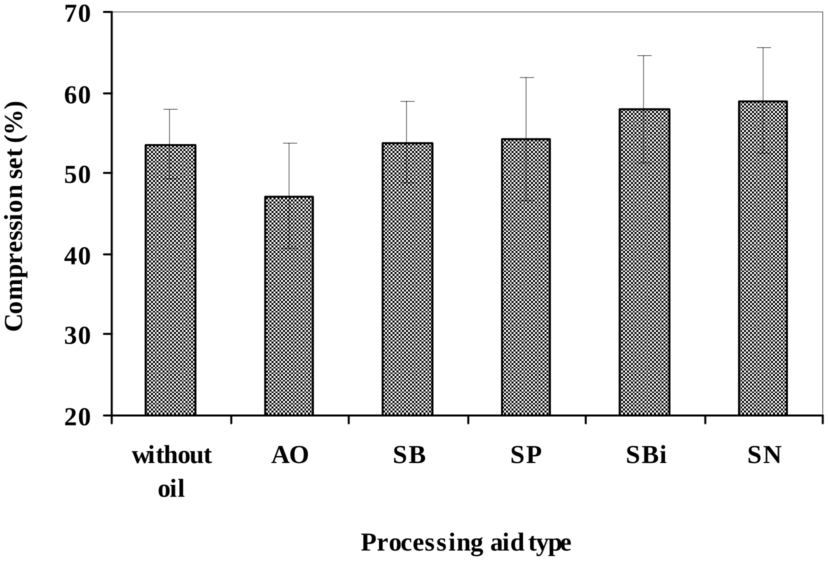

Figure 7 Bar diagram of the compression set for the rubber compounds having various processing aids.

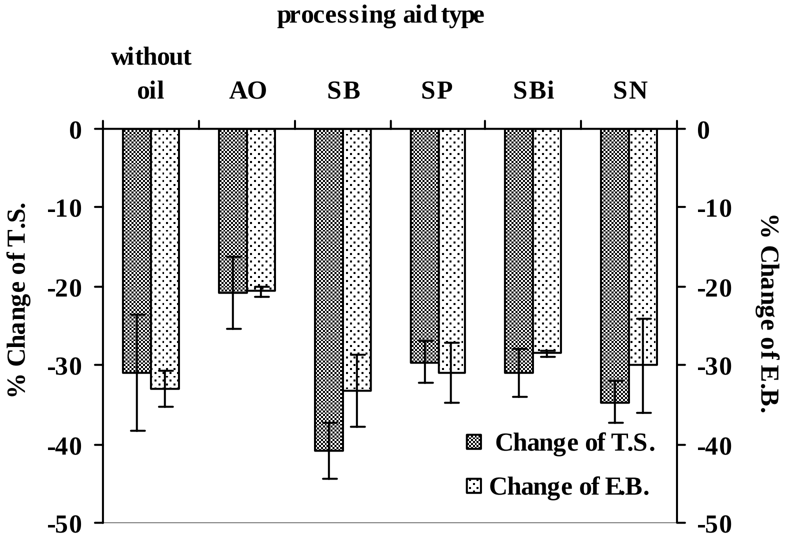

Figure 8 Change of tensile strength and elongation at break after aging of rubber compounds having various processing aids.

Figures 7 and 8 show the compression set, change of tensile strength and elongation at break after aging. It was found that rubber compounds having aromatic oil showed the best aging properties. This was the highest retention of tensile strength and elongation at break due to aromatic oil with the highest aromatic content contributed in rubber resulting in improvement of rubber-filler interaction and increasing of thermal stability of compounds.

Conclusions

Four stearyl aromatic esters; stearyl benzoate, distearyl phthalate, stearyl biphenyl-4-carboxylate and stearyl naphthoate were synthesized from stearyl alcohol and corresponding aromatic acids. The structures of stearyl aromatic esters were characterized by IR and ^{1}H-NMR spectroscopy. The effect of esters as processing aids in natural rubber compounds on the curing properties and mechanical properties has been studied and compared with that of the aromatic oil. The result showed that aromatic esters enhanced curing characteristics in a similar fashion to the aromatic oil having the same rubber formula. Moreover, aromatic esters can slightly enhance mechanical properties of the vulcanizates before aging. Although, the vulcanizates after aging showed interior properties in term of tear strength, compression set and thermal stability most useful properties were still comparable to the compounds having added aromatic oil. Thus, stearyl aromatic esters can be used as alternative eco-friendly processing aids in rubber industry.

Acknowledgements

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