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Original Article

A comparative study of stearyl aromatic esters and aromatic oil as processing aids in natural rubber compounds

Charoen Pakhathirathien[1]* , Kulphanan Pearuang[2], Adisai Rungvichaniwat[2],
Azizon Kaesaman[2], and Charoen Nakason[3]

[1] *Department of Science,*

[2] *Department of Rubber and Polymer Technology, Faculty of Science and Technology,*
Prince of Songkla University, Pattani Campus, Mueang, Pattani, 94000 Thailand.

[3] *Faculty of Science and Industrial Technology,*
Prince of Songkla University, Surat Thani Campus, Mueang, Surat Thani, 84000 Thailand.

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Abstract

Synthesized stearyl aromatic esters, namely stearyl benzoate, distearyl phthalate, stearyl biphenyl-4-carboxylate, and stearyl naphthoate, were used as processing aids for natural rubber compounding formulations. Their effects on curing and mechanical properties of natural rubber compounds were evaluated according to ASTM D3184. It was found that the aromatic esters enhanced curing characteristics in a similar way to aromatic oil which has been typically used in otherwise similar rubber formulations. Furthermore, the aromatic esters can slightly improve mechanical properties of natural rubber vulcanizates before aging. Although the mechanical properties of the vulcanizates in terms of tear strength, compression set, and thermal stability, deteriorated with aging, most useful properties were still on levels comparable to compounds with aromatic oil. Overall, stearyl aromatic esters may potentially in the future provide environmentally friendly alternatives to the use of aromatic oil, as processing aids for the rubber industry.

Keywords: natural rubber, processing aids, stearyl aromatic esters, aromatic oil

1. Introduction

The functional role of processing aids and plasticizers is to reduce friction heating of the ingredients, during processing of natural rubber (NR) compounds. The processing aids also facilitate incorporation of filler, while plasticizers soften the compounds, reducing modulus and hardness, increasing elongation, and in some cases improving low temperature flexibility (Brentin and Sarnacke, 2010). It has been well recognized that aromatic processing oils contain a minimum 70% aromatic content, and are partly compatible with semipolar and polar elastomers. Highly aromatic oils are also referred to as distillate aromatic hydrocarbons (DAE), which contain a high concentration of polycyclic aromatic hydrocarbons (PAH) that are composed of two or more aromatic rings. The US Environmental Protection Agency (US-EPA, 1997) has fixed 16 PAH as priority pollutants due to their toxicity to mammals and aquatic organisms. Biological effects must be considered when PAH are distributed to the environment, whether in sediment or in the atmosphere. Canadian Soil Quality Guidelines for the protection of environmental and human health recommend the various concentration limits on PAH, based on their effects on human health (Canadian Council of Ministers of the Environment, 2010).

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* Corresponding author.
Email address: charoen.p@psu.ac.th

The replacement of highly aromatic oil by some non-carcinogenic oil could reduce the PAH emissions from rubber tire wear by more than 98% (Null, 1999). However, replacement of highly aromatic oils with safe process oils has by far not yet been fulfilled, partly due to the technical requirements for rubbers in terms of their physical, mechanical and dynamic properties. Various natural oils have been tested as plasticizers added to natural rubber compounding, to improve dynamic properties, curing characteristics, reversion and fatigue life (Kukreja *et al*., 2002; Dasgupta *et al*., 2007, 2008; Dasgupta *et al*., 2009) and the use of modified vegetable oils was also reported in prior work (Boontawee *et al*., 2012, 2013). Cardanol (cashew nut shell liquid) and aromatic oil in NR have been compared in a study (Alexander and Thachil, 2006). Various esters were produced, such as glyceryl esters, phosphate esters, and short chain aromatic esters, and reported as synthetic plasticizers (Klingender, 2007). The modification of stearyl aromatic esters, composed of long chain hydrocarbons and an aromatic part, is the new trend in seeking eco-friendly processing aids. The effects of esters and aromatic oil as processing aids, on the curing characteristics and mechanical properties of natural rubber compounds, were investigated in the current study.

2. Experimentals

2.1 Materials

Ribbed smoked sheet 3 (RSS#3) were the natural rubber source used in this study, produced by Kokpho farmer group, Pattani, Thailand. The other ingredients of rubber formulation were commercial grade. Stearyl alcohol and aromatic acids for ester synthesis were analytical grade (Fluka Chemicals, Switzerland). An internal mixer (MX 500-D75L9, Charoen Tut, Thailand), a moving die rheometer (rheotesh MD$^+$, Tech Pro, USA), and a Mooney viscometer (TECH$^+$ VAR, Tech pro, U.S.A.) were used in this work.

2.2 Synthesis of stearyl aromatic esters

Four stearyl aromatic esters, namely stearyl benzoate (SB), distearyl phthalate (SP), stearyl biphenyl-4-carboxylate (SBC), and stearyl naphthoate (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 of 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 (2.5-3.0 hrs), 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} (TLC grade) and 10% dichloromethane in hexane as eluting solvent. The obtained stearyl esters were characterized by FTIR and ^{1}H-NMR spectroscopy, with comparisons to stearyl alcohol and the corresponding aromatic acids.

2.3 Compound mixing

The formulation of rubber compounding, that followed ASTM D3184, is shown in Table 1. Mastication was done in an internal mixer operated at a constant rotor speed of 60 rpm at 70°C. Firstly, natural rubber was mixed in the chamber for 1 min, added accelerator (TBBS) for 0.5 min, and added zinc oxide for 0.5 min. Then, the first half of stearic acid, processing aid, antioxidant and carbon black were added and mixed for 3 min, after which the remaining half of them were added and mixing continued for 3 min. The homogeneous mixture was further mixed with sulfur in a two-roll mill for about 2 min. Each batch was used to produce the tested sheets by compression molding technique.

Table 1. Formulation of rubber compounding.

Component	Quantities (phr)
Natural rubber (ribbed smoked sheet 3, RSS#3)	100
Accelerator, (*N*-*tert*-butyl-2-benzothiazylsulphenamide, TBBS)	0.7
Zinc oxide	5
Stearic acid	2
Processing aid 1 (aromatic oil, AO)	0, 5
Processing aid 2 (stearyl aromatic esters: SB, SP, SBC and SN)	0, 5
Carbon black (N330)	50
Antioxidant (*N*-(1,3-dimethylbutyl)-*N'*[-phenyl-*p*-phenylenediamine, 6PPD)	0, 1.5
Sulfur	2.25

2.4 Curing characteristics and dynamic properties

Curing characteristics of the compounds were measured with a rotorless rheometer according to ASTM 2240-93. Mooney viscosity and stress relaxation were determined with a Mooney viscometer using a large rotor, according to ASTM D1649-99. Curing and mechanical properties were tested according to ASTM D5289 and ASTM D412-06, respectively. Also, dynamic properties were investigated.

3. Results and Discussion

3.1 Stearyl aromatic esters

The optimized conditions for esterification of stearyl aromatic esters were first investigated and found at 1:1 molar ratio of alcohol:aromatic acid, 15 wt.% (by aromatic acid) of concentrated sulfuric acid catalyst, and reaction temperature of 85-95°C. Four stearyl aromatic esters (i.e., SB, SP, SBC and SN) were successfully synthesized from stearyl alcohol and aromatic acids, with 87, 89, 88, and 90% yields, respectively. The structures of stearyl aromatic esters were characterized by FTIR and ^{1}H-NMR as shown in Figure 1 and 2, respectively. In Figure 1, it can be seen that the IR absorption peaks at 1,711-1,721 cm^{-1} corresponded to the carbonyl of ester were observed. On the other hand, the ^{1}H-NMR spectra in Figure 2 revealed the presence of aromatic protons at δ 7.39-8.90 ppm, two oxymethylene protons at δ 4.30, 4.39 ppm, three methyl protons at δ 0.86 ppm, and an abundance of methylene protons at δ 1.20-1.81 ppm. Therefore, it is indicated that the synthesized esters were composed of an aromatic moiety and a long chain stearyl with an ester linkage. Stearyl benzoate as used in cosmetics has reported to be safe (Becker, 2012).

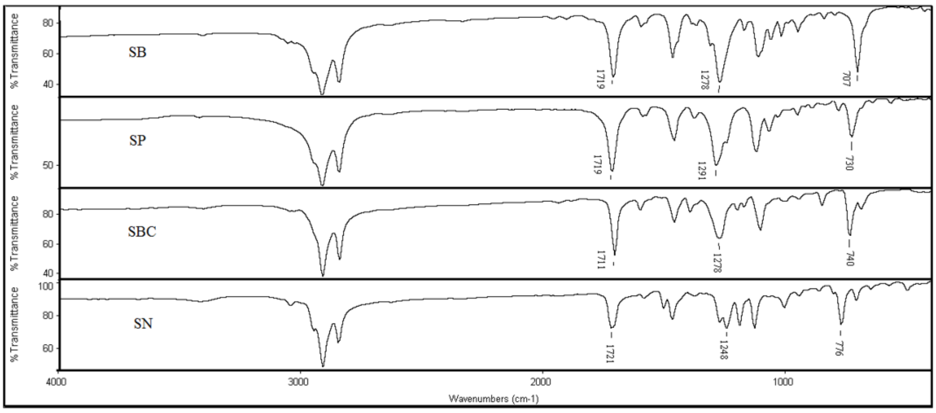

Figure 1. FTIR spectra of stearyl benzoate (SB), distearyl phthalate (SP), stearyl biphenyl-4-carboxylate (SBC), and stearyl naphthoate (SN).

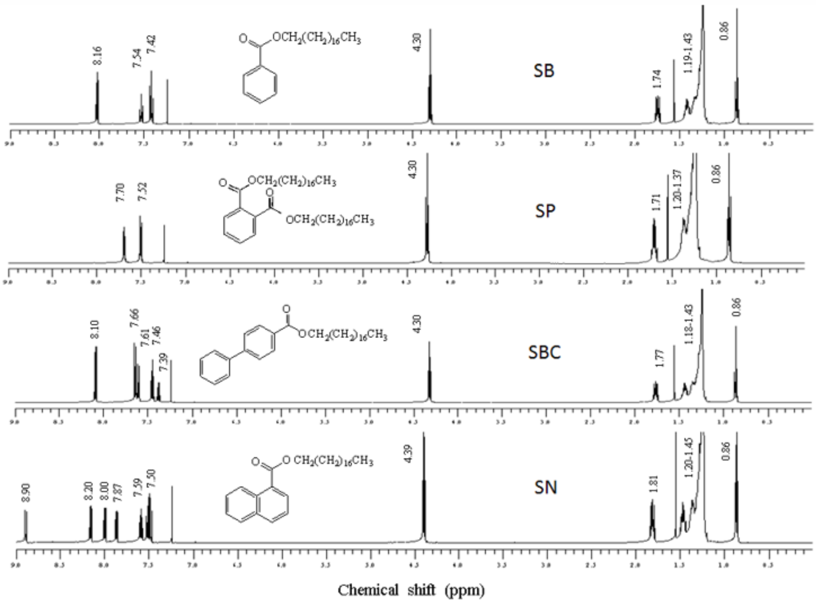

Figure 2. ^{1}H-NMR spectra and structures of stearyl benzoate (SB), distearyl phthalate (SP), stearyl biphenyl-4-carboxylate (SBC), and stearyl naphthoate (SN).

3.2 Process properties of rubber compounds

The rubber compounds, the stearyl aromatic esters and aromatic oil, as processing aids should help disperse carbon black and other ingredients, but should not affect vulcanization. The stearyl aromatic esters were composed of an aromatic part joined with saturated long side chain hydrocarbons (18 carbons atom) by an ester linkage. They were in solid state at room temperature, but melted in the steps performed for compound mixing.

The effects of synthetic stearyl aromatic esters on the mixing energy, Mooney viscosity, dump temperature, and stress relaxation of natural rubber compounds, are shown in Table 2. The compounds with aromatic esters showed low values for mixing energy, Mooney viscosity, and dump temperature, similar to compounds with aromatic oil as processing aid, and unlike processing without such aid (without oil, WO). This indicated that the esters improved the processability of natural rubber compounds, with a good dispersion of the mixture components in the rubber matrix. Stress relaxation slope was closely similar to that observed with aromatic oil, indicating similar elastic properties, while compounds without processing aids were less elastic.

The effect of esters and aromatic oil on scorch time and cure time are shown in Table 3. It can be seen that the compounds with process aids cured slower than compounds without oil, as indicated by higher cure rate index (CRI). The curing properties were similar for compounds with esters and that with aromatic oil. The torque difference (M_H-M_L) indicated that the degree of crosslinking in vulcanizates was decreased by the processing aids.

3.3 Mechanical and dynamic properties of rubber compounds

Comparative data on the tensile strength, elongation at break, modulus at 300% elongation, shore A hardness, and tear strength, are shown in Table 4 for the rubber vulcanizates. It is seen that the vulcanizates without processing aid

Table 2. Processing properties of compounds.

Processing aids	Mixing Energy (kJ)	Mooney Viscosity (ML 1+4, 100°C)	Dump Temperature (°C)	Slope of Stress Relaxation
WO	65.14±1.37	70.3±5.6	113±3	-0.135
AO	60.18±0.19	59.7±2.4	108±1	-0.102
SB	58.77±0.66	59.1±2.0	104±2	-0.109
DP	58.49±0.67	59.3±2.5	105±1	-0.100
SBC	58.69±0.55	58.6±0.2	104±2	-0.101
SN	58.45±0.77	57.5±1.3	105±1	-0.101

Table 3. Curing properties of compounds.

Processing aids	Scorch time (min)	Cure time (min)	Cure Rate index (min^{-1})	M_H-M_L (dN.m)
WO	0.86±0.04	9.39±0.40	11.65±0.64	25.89±0.50
AO	0.96±0.04	9.43±0.85	12.48±0.12	23.97±0.06
SB	0.96±0.03	8.86±0.22	12.67±0.27	23.40±0.44
DP	0.94±0.09	9.24±0.26	12.85±0.53	23.53±0.30
SBC	1.01±0.07	8.99±0.21	12.54±0.21	23.66±0.18
SN	1.01±0.44	8.50±0.71	12.78±0.30	22.32±0.64

Table 4. Mechanical properties of vulcanizates.

Processing aids	Tensile strength (MPa)	Elongation at break (%)	300% modulus (MPa)	Shore A hardness (degree)	Tear strength (N/mm)
WO	25.87±0.97	475±13	13.67±0.12	58.7±0.6	88.47±6.52
AO	27.13±0.60	542±23	11.73±0.30	56.5±0.5	104.25±3.18
SB	26.60±0.83	537±05	11.86±0.06	55.5±0.5	91.09±0.62
DP	26.26±1.65	541±32	11.47±0.29	55.2±0.3	92.03±1.14
SBC	26.45±0.96	541±08	11.40±0.24	56.3±0.6	92.12±0.83
SN	26.71±0.64	547±24	11.52±0.39	55.3±0.6	93.10±1.56

showed the highest 300% modulus and hardness, whereas the compounds with esters and aromatic oil showed lower values similar to each other. The decrease of modulus and hardness by incorporating of the processing aids was due to increasing mobility of polymer chains, and decrease in the entanglement of rubber molecules, due to lubricating effects that were comparable for both esters and aromatic oil. Furthermore, the esters and aromatic oil in compounds improved tensile strength and elongation at break, but the tear strength deteriorated after aging. In general, tearing of rubber involves crack propagation, initiated at a stress concentration at the rubber-carbon black interface. The aromatic oil contains higher aromatic rings than the stearyl aromatic esters, and gave a good distribution of carbon-black in the rubber by its action as a compatibility agent between rubber and carbon black. This leads to an increased tear strength.

Table 5 shows data on tensile strength and elongation at break after aging. It is seen that the rubber compounds with aromatic oil showed the best aging properties, as indicated by the highest retention of tensile strength and elongation at break. This might be attributed to the highest aromatic content in aromatic oil improving the rubber-filler interaction and increasing the thermal stability of compounds. In Table 5, it is also seen that the abrasion resistance of rubber vulcanizates with stearyl aromatic esters was good, due to low friction coefficients. The aging properties of compounds and vulcanizates could be improved by adding of 1.5 phr of antioxidant (6PPD), as the mechanical properties shown in Table 6. It is seen that the mechanical properties of SB added compound were comparable to that with aromatic oil. In this work, the dynamic mechanical properties in term of relationship between storage modulus and temperature as well as tan δ and temperature were studied, as results shown in Figure 3 and 4, respectively. The tan δ peaks in Figure 4 are representative glass transition temperatures (T_g) of rubber vulcanizates, which are summarized in Table 5. It is seen that the rubber vulcanizates with AO, SB, SCB and SN showed lower glass transition temperatures (T_g) than the compounds without oil or with DP. This indicates that aromatic esters affected dynamic properties of the compounds by reducing

Table 5. Mechanical properties after aging and glass transition temperature of rubber vulcanizates.

Processing aids	Akron abrasion index (%)	Decrease in tensile strength (%)	Decrease in elongation at break (%)	T_g (°C)
WO	72.89±2.29	32.82±1.80	31±3.1	-40.3
AO	78.19±0.55	20.78±0.84	24±1.2	-44.4
SB	93.76±4.77	33.76±2.14	33±2.0	-45.7
DP	92.50±4.29	32.29±2.38	31±2.1	-40.3
SBC	93.04±0.32	31.01±2.86	33±2.2	-44.4
SN	93.87±1.53	34.66±0.23	33±1.3	-45.7

Table 6. Mechanical properties of compounds having antioxidant (6PPD).

Processing aids	Tear strength (N/mm)	Shore A hardness (degree)	300% modulus (MPa)	Decrease in tensile strength (%)	Decrease in elongation at break (%)
WO	82.99±6.45	57.3±0.6	13.02±0.68	11.51±1.78	12±2
AO	99.60±1.56	56.0±0.4	10.83±0.60	8.78±1.96	10±2
SB	87.37±6.42	55.2±0.4	10.96±0.59	10.38±0.71	14±1

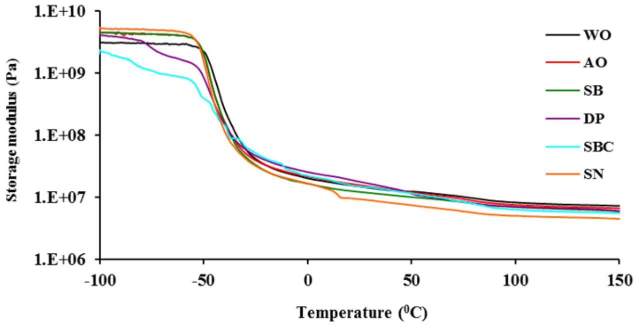

Figure 3. Storage modulus of compounds having various process aids

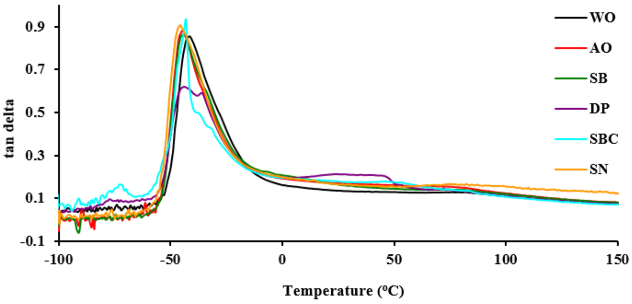

Figure 4. Tan delta of compounds having various process aids.

hysteresis, except for the DP that is composed of distearyl side chain and has the lowest aromatic content. With DP also storage modulus and tan differed from the other esters, as indicated in Figures 3 and 4. However, compounds with SB and SN had similar trends of storage modulus and tan δ as compounds with aromatic oil. The use of stearyl aromatic esters and aromatic oil was limited to 5 phr in this study, and the compounds had generally similar properties despite different aromatic characters of the esters. Therefore, SB ester could be further studied, due to its lowest cost of synthesis.

4. Conclusions

Four stearyl aromatic esters, namely stearyl benzoate, distearyl phthalate, stearyl biphenyl-4- carboxylate, and stearyl naphthoate, were synthesized from stearyl alcohol and corresponding aromatic acids. The structures of these stearyl aromatic esters were characterized by FTIR and ^{1}HNMR spectroscopy. The effects of esters as processing aids in natural rubber compounds, on the curing properties and mechanical properties, was studied and compared to effects of aromatic oil. The aromatic esters enhanced curing characteristics in a similar fashion to the aromatic oil, in otherwise similar rubber formulations. Moreover, the aromatic esters can slightly enhance mechanical properties of the vulcanizates before aging. While after aging the vulcanizates with aromatic esters had inferior properties in terms of tear strength, compression set, and thermal stability, their most important properties were still on levels comparable to those achieved with aromatic oil. Thus, stearyl aromatic esters might provide potentially alternative eco-friendly processing aids for the rubber industry.

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