

The Effect of Stearic Acid on Expanded Organoclay and Rheometric Properties of Natural Rubber/Expanded Organoclay Nanocomposites

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Abstract: The effect of stearic acid on expanded organoclay and rheometric properties of natural rubber (NR)/expanded organoclay (OCSA) was studied. The expanded organoclay was prepared by melting of stearic acid (SA) in an oven at 100 °C for 1 h. NR/expanded organoclay nanocomposites were prepared by melt intercalation technique using a laboratory open mill followed by compression molding. The characterizations were carried out by means of X-ray diffraction, field emission scanning electron microscopy (FESEM) and moving die rheometer. The results showed that the stearic acid intercalated in the gallery of organoclay (OC) Cloisite® 20A, so the *d*-spacing of organoclay increased with increasing of stearic acid concentration. The rheometric properties showed that the increasing concentration of stearic acid in NR compound improved the resistance to reversion but contrary for NR/OCSA compounds. The curing time of NR filled expanded organoclay compounds were faster than NR compounds. The increasing concentration of stearic acid reduced the size of aggeragate especially for ratio OC:SA = 1:1 which OCSA dispersed uniformly in NR matrix.

Key words: Stearic acid, expanded organoclay, natural rubber, nanocomposite, rheometric properties.

1. Introduction

Nowadays, the use of silicate as a reinforcing filler in elastomer is interesting to study, especially since Toyota group studied about preparation of Polyamide-6/organoclay nanocomposites [1]. Nanocomposite is a composite that contains inorganic filler dispersed in polymer matrix at nanoscale. Clay layer can intercalate or exfoliate in polymer matrix to clay/polymer produce nanocomposites. Nanocomposite material has good mechanical and thermal properties because of the dispersion of nanoscale filler with high aspect ratio [2].

Organoclay layer that exfoliate uniformly in matrix

polymer can increase mechanical properties, decrease swelling and permeability, increase thermal stability and flame retardant [2]. In order to increase the exfoliation of organoclay in elastomer matrix, stearic acid as an intercalant agent can be used [3].

Stearic acid can expand the gallery of organoclay, so the polymer can easily intercalate into the gallery of organoclay [4]. Stearic acid is used for activator in sulfur vulcanization system. Nowadays, stearic acid can be used to increase the intercalation/exfoliation of organoclay in nitrile rubber [3, 4]. When stearic acid melts, it can easily intercalate into layered silicate and reacts with hydroxyl group, so that it can increase the exfoliation and dispersion of organoclay in ethylene propylene terpolymer (EPDM), natural rubber (NR) and *cis*-1,4-polybutadiene (BR). It also can increase

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the mechanical properties of nanocomposites [3, 5]. However, the excess of stearic acid will effect to curing characteristic, mechanical and adhesion properties of natural rubber vulcanizates [6]. This research studied the effect of stearic acid on *d*-spacing of organoclay and rheometric properties of NR/expanded organoclay nanocomposites.

2. Experiments

2.1 Materials

Commercial organoclay (OC) Cloisite® 20A was obtained from Southern Clay Products. Inc. Rockwood additives. The organic modifier of Cloisite 20A: dimethyl dehydrogenated tallow quaternary ammonium, the particle size of the clays are 90% less than 13 μ m and the *d*-spacing of Cloisite® 20A was 2.42 nm.

Natural rubber (NR) grade thin pale crepe was supplied by PTPN 8, West Java, Indonesia. Zinc oxide (ZnO), stearic acid (SA), N-cyclohexylbenzhothiazole-2-sulfenamide (CBS), and sulfur were purchased from local suppliers.

2.2 Expanded Organoclay Preparation

The method to prepare the expanded organoclay was same with Ma et al, 2008 [7]. Organoclay Cloisite® 20 A and stearic acid were mixed together by using mortar with various weight ratio of organoclay:stearic acid (1:0.05, 1:0.1, 1:0.2, 1:0.5 and 1:1). The mix was put in an oven at 100 °C for about 1 h until stearic acid melt and reacted with organoclay

and intercalated into the gallery of organoclay. After cooling, the expanded organoclay can be obtained (OCSA).

2.3 NR/Expanded Organoclay Nanocomposite Preparation

rubber/expanded Natural organoclay nanocomposites were prepared on two roll mill with speed of slow roll (24 rpm) and friction ratio (1.4) maintained at 65 ± 5 °C. Firstly, natural rubber was masticated for 2 minutes, then zinc oxide and stearic acid were blended as long as 2 min. The expanded organoclays were blended in natural rubber for 10 minute. Finally, the accelerator N-cyclohexylbenzhothiazole-2-sulfenamide (CBS) and curatives (sulfur) were added continuously for 2 min. The rubber nanocomposite compounds were conditioned at room temperature for minimum 16 h. The formulations of the compounds are compiled in Tables 1 and 2.

2.4 Characterization

The dispersion of expanded organoclay in the NR matrix was studied by X-ray diffraction (XRD) Rigaku, Japan in transmission mode using CuK α radiation ($\lambda = 0.1542$ nm) X-ray diffractometer (40 kV, 30 mA). X-ray diffraction data were obtained from 2° to 10° (20) at a scanning rate of 1° min⁻¹. Bragg's law, defined as $\lambda = 2$ dsin θ , was used to measure the crystallographic spacing (*d*) for organoclay that was expanded by using stearic acid.

Table 1 Formulations (in phr) of the NR/expanded organoclay compounds.

Sampel	NROCSA0	NROCSA0.05	NROCSA0.1	NROCSA0.2	NROCSA0.5	NROCSA1	
Materials	phr (Part Hundred Rubber)						
NR	100	100	100	100	100	100	
OCSA							
Organoclay	5	5	5	5	5	5	
Stearic acid	0	0.25	0.5	1	1.5	5	
ZnO	5	5	5	5	5	5	
Stearic acid	1	1	1	1	1	1	
CBS ^a	1.5	1.5	1.5	1.5	1.5	1.5	
Sulfur	2.5	2.5	2.5	2.5	2.5	2.5	

^a N-cyclohexylbnezhothiazole-2-sulfenamide.

Sampel	NRSA1	NRSA1.25	NRSA1.5	NRSA2	NRSA3.5	NRSA6	
Materials	phr (Part Hundred Rubber)						
NR	100	100	100	100	100	100	
ZnO	5	5	5	5	5	5	
Stearic acid	1	1.25	1.5	2	3.5	6	
CBS ^a	1.5	1.5	1.5	1.5	1.5	1.5	
Sulfur	2.5	2.5	2.5	2.5	2.5	2.5	

 Table 2
 Formulations (in phr) of the NR compounds.

^a N-cyclohexylbnezhothiazole-2-sulfenamide.

The interaction between stearic acid and organoclay Cloisite® 20A was studied by attenuated total reflectance infra red (ATR-IR) Thermo Scientific Nicolet iS5. The dispersion of expanded organoclay in the NR matrix was also studied by ATR-IR and analyzed using OMNIC Software. ATR-IR spectrum was measured between 600-4,000 cm⁻¹ at a resolution of 4 cm⁻¹.

The cure characteristics of the rubber compounds were determined using a Moving Die Rheometer (MDR 2000) at 150 °C according to ISO 6502. The compounds were then compression moulded at electrically heated hydraulic press, at 150 °C with the respective cure time (t_{90}), previously determined from MDR 2000. The samples thickness of 2 mm sheets was molded.

Microstructure of NR/expanded organoclay was studied by field emission scanning electron microscopy (FESEM) INSPECT F50. Fractured surfaces of the vulcanizates NR/expanded nanocomposites were obtained by tensile test. The surfaces were coated by gold/palladium to prevent electrostatic charging during examination.

3. Experimental Results

3.1 d-Spacing of Expanded Organoclay

Organoclay Closite® 20A was expanded by stearic acid in order to increase the d-spacing of organoclay. The d-spacing of expanded organoclays were determined by X-ray diffraction. Fig. 1 shows the diffraction pattern of organoclay, stearic acid and expanded organoclay with various concentration of stearic acid. Diffraction peak of stearic acid at $2\theta = 4.5^{\circ}$ (*) shows in the organoclay that was mixed with stearic acid. The increasing of stearic acid concentration, the diffraction peak I of organoclay at $2\theta = 3.50^{\circ}$ (d = 2.52 nm) shift or decreased. At ratio between organoclay:stearic acid = 1:0.05 (OCSA0.05), the diffraction peak of organoclay shift to 3.02° (d = 2.92 nm), at ratio = 1:0.1 (OCSA0.1) shift to 2.52° (d = 3.50 nm) and at ratio 1:0.2 (OCSA0.2) shift to 2.30° (d = 3.83 nm). At ratio 1:0.5 and 1:1 the diffraction peak of organoclay disappear, may be it shift lower than 2° . The shift of 2θ could increase the d-spacing of organoclay according to Bragg's law.

3.2 Interaction between Organoclay and Stearic Acid

Fig. 2 shows ATR-IR spectrum of stearic acid, organoclay and OCSA with various concentration of



Fig. 1 X-ray diffraction pattern of organoclay, stearic acid and expanded organoclay with various concentration of stearic acid.



Fig. 2 The ATR-IR spectrum of SA, OC and OCSA with various concentration of SA.

stearic acid. The analysis of interaction between organoclay and stearic acid was showed at wavenumber of 1,550-1,900 cm⁻¹. In organoclay structure, there was no peaks of C=O structure. The negative peak at 1,700 cm⁻¹ referred to the C=O structure of carboxylic groups in stearic acid. After adding stearic acid until OC:SA = 1:0.2, the negative peak is shifted to 1,723 cm⁻¹, which meant that carboxylic groups were esterified by hydroxyl groups of organoclay. The negative peak appeared at OC:SA = 1:0.5 and 1:1, because the excess of stearic acid that didn't react with hydroxyl groups in OC. The esterification between SA and OC could be the driving force for SA intercalating into OC gallery to expand the spacing of OC [7].

3.3 Curing Characteristic of NR/Expanded Organoclay and NR Compound

The curing characteristics NR/expanded of organoclay and NR with various concentration of SA are graphically represented in Figs. 3 and 4. respectively. The curing characteristics of NR/expanded organoclay and NR compounds, expressed in terms of the scorch time (ts₂), optimum cure time (t₉₀), the maximum and minimum values of the torque (S_{max} and S_{min}), respectively, and delta torque ΔS ($\Delta S = S_{max} - S_{min}$), are compiled in Table 3.

The increasing concentration of stearic acid in NR compound would improve the resistance to reversion.

It is due to the zinc stearate formation in hydrocarbon caused faster desulphuration of cross-linking and most of crosslinking formed was mono and disulphidic [8]. This results was different with Fig. 3, the increasing of SA would improve the reversion, because the stearic acid reacted with OC and no excess of zinc stearate in the NR/expanded organoclay compounds.

The increasing of stearic acid in rubber compounds and NR/expanded organoclay compounds would increase the curing time (t₉₀) of compounds and contrary for CRI. The excess of stearic acid would inhibit the vulcanization and the zinc stearate would cover the ZnO activation [6]. The curing time of NR filled expanded organoclay compounds faster than NR



Fig. 3 Vulcanization curves of the NR/expanded organoclay at 150 °C.



Fig. 4 Vulcanization curves of the NR at 150 °C.

Samples	S'_{max} (dN·m)	S'_{\min} (dN·m)	ts_2 (min)	<i>t</i> ₉₀ (min)	$\Delta S'^* (dN \cdot m)$	CRI* (min ⁻¹)
NROCSA0	8.89	0.21	1.35	4.01	8.68	37.59
NROCSA0.05	8.86	0.22	1.10	3.37	8.64	44.05
NROCSA0.1	8.33	0.29	1.19	3.42	8.04	44.84
NROCSA0.2	8.38	0.18	1.19	3.53	8.20	42.74
NROCSA0.5	8.03	0.22	1.27	4.15	7.81	34.72
NROCSA1	7.51	0.08	2.19	5.36	7.43	31.55
NRSA1	7.97	0.22	5.29	8.19	7.75	34.48
NRSA1.25	7.80	0.24	5.58	9.27	7.56	27.10
NRSA1.5	8.11	0.31	7.00	10.28	7.80	30.49
NRSA2	7.95	0.20	6.02	9.55	7.75	28.33
NRSA3.5	7.96	0.22	7.01	11.38	7.74	22.88
NRSA6	7.59	0.17	6.37	12.14	7.42	17.33

Table 3 Curing characteristic of NR/expanded organoclay compounds and NR compounds.

* $\Delta S' = S'_{max} - S'_{min}$.

 $*CRI = Cure rate index = 100/t_{90} - t_{s2}$).

compounds. Because organoclay contained amine group that can act as accelerator for sulfur vulcanization system [9] and it was a synergy between CBS accelerator and amine group that can accelerate the vulcanization [10]. The increasing of stearic acid would reduce the $\Delta S'$ NR and NR/expanded organoclay compounds. The excess of stearic acid could act as plasticizer at temperature of 150 °C.

The ratio between $\Delta S'$ to NR filled expanded organoclay and NR compound is proportional with concentration of filler. This ratio could produce the slope that indicates the distance between aggregate of filler, according to equation [11]:

$$\frac{S'_{\max} - S'_{\min}}{S'_{\max}^0 - S'_{\min}^0} - 1 = \alpha_f \frac{m_f}{m_p} \tag{1}$$

where, $S'_{max} - S'_{min}$ was delta torsion of NR/expanded organoclay compound, $S'^{0}_{max} - S'^{0}_{min}$ was delta torsion of NR compound, m_f and m_p is weight of filler (expanded organoclay) and polymer in the compound, respectively.

Fig. 5 shows the value of α_f at various concentration of stearic acid. The increasing concentration of stearic acid would reduce the value of α_f . The decreasing α_f indicated that decreasing the distance between aggregate in NR matrix.

The decreasing distance between aggeragate could be proven with the FESEM results. Fig. 6 shows that the increasing concentration of stearic acid will reduce the size of aggeragate especially for ratio OC:SA = 1:1 (Fig. 6f). OCSA dispersed uniformly in NR matrix.

4. Conclusions

The effect of stearic acid on expanded organoclay and rheometric properties of NR/expanded organoclay had been investigated. The stearic acid intercalated in the gallery of organoclay Cloisite® 20A, so could increase the *d*-spacing of organoclay with increasing the concentration of stearic acid. The increasing of *d*-spacing was due to the esterification. The esterification between SA and OC can be the driving force for SA intercalating into OC gallery to expand the spacing of OC.

The rheometric properties showed that the increasing 3.5 $_{\top}$



Fig. 5 α_f value at various stearic acid concentrations.

The Effect of Stearic Acid on Expanded Organoclay and Rheometric Properties of Natural Rubber/Expanded Organoclay Nanocomposites



(e) (f) Fig. 6 Microstructure of NR/OCSA nanocomposites: (a) NROCSA0, (b) NROCSA0.05, (c) NROCSA0.1, (d) NROCSA0.2, (e) NROCSA0.5 and (f) NROCSA1 with magnification 10,000×.

concentration of stearic acid in NR compound will improve the resistance to reversion but contrary for NR/OCSA compounds. The curing time of NR filled expanded organoclay compounds faster than NR compounds. The increasing of stearic acid in rubber compounds and NR/expanded organoclay compounds will increase the curing time (t_{90}) of compounds. The increasing concentration of stearic acid will reduce the size of aggeragate especially for ratio OC:SA = 1:1 and OCSA dispersed uniformly in NR matrix.

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