Effect of Montmorrilonite on the Chloroprene/Natural Rubber Blend

Pengaruh Montmorillonite pada Campuran Chloroprene/Karet Alam

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Abstract— The effect of montmorillonite on chloroprene (CR)/ natural rubber (NR) blend was studied in this research. Montmorillonite was used as a compatibilizer with the various amounts (0, 2.5, 5, 7.5, 10 phr). The compounds were done by the two-roll mill and hydraulic press. The cure characteristics, mechanical properties, morphology, and thermal characteristics had been investigated by rheometer, tensile strength tester, scanning electron microscope (SEM), and differential scanning calorimetry (DSC). The montmorillonite resulted in longer scorch time and lower activation energy. Analysis of the blends by SEM and DSC showed that montmorillonite resulted in a compatible blend. The 2.5 phr montmorillonite gave the best curing characteristics with the lowest optimum time, the highest constant rate, and the lowest activation energy. It also gave the best tensile strength, elongation, and tear strength. The 2.5 phr montmorillonite was the proper compatibilizer for CR/NR blend.

Keywords: Chloroprene rubber, natural rubber, montmorillonite, compatibilizer

Abstrak— Pengaruh montmorillonit pada campuran chloroprene (CR)/karet alam (NR) dipelajari dalam penelitian ini. Montmorillonite digunakan sebagai compatibilizer dengan jumlah yang bervariasi (0, 2.5, 5, 7.5, 10 phr). Pembuatan kompon dilakukan dengan two-roll mill dan hydraulic press. Karakteristik curing, sifat mekanik, morfologi, dan karakteristik termal telah diteliti dengan rheometer, tensile strength tester, scanning electron microscope (SEM), dan differential scanning calorimetry (DSC). Montmorillonit menghasilkan waktu hangus yang lebih lama dan energi aktivasi yang lebih rendah. Analisis campuran dengan SEM dan DSC menunjukkan bahwa montmorillonit menghasilkan campuran yang kompatibel. Montmorillonit 2,5 phr memberikan karakteristik curing terbaik dengan waktu optimum terendah, laju konstan tertinggi, dan energi aktivasi terendah. Ini juga memberikan kekuatan tarik, perpanjangan, dan kekuatan sobek terbaik. Montmorillonit 2,5 phr adalah kompatibilitas yang tepat untuk campuran CR/NR.

Kata kunci: Karet chloroprene rubber, karet alam, montmorillonit, kompatibiliser

I. INTRODUCTION

Nowadays, the material needs in the industry are increasing with the increase of human needs. The pure elastomers often do not have all the desired properties. So the blending material is an interesting topic for the researcher because the blending materials give more excellent properties than single material. The blending materials such as rubber blends can be applied in large industries and have economic advantages [1].

Chloroprene rubber is a synthetic rubber that has excellent oil, ozone resistance, and thermal stability. However, CR is expensive and hard to disperse when being milled [2]. Natural rubber (NR) is well known as an excellent mechanical rubber. It has high tensile, elasticity and good dynamic properties. But NR is sensitive to heat and ozone attack because of its reactive double bonds on its backbone. It also has low resistance to oil. To improve the low properties of the rubber, the rubber blending is the alternative [3]. The blending with CR can improve the solvent resistance and the blending with NR can improve the processability of synthetic rubber.

In rubber blending, there are some aspects need more attention. The difference in polarity could bring high interfacial tension, affect the mechanical properties, and could make an incompatible blend, such as blending of CR/ NR [1,4]. Thus, the blending of two or more rubber sometimes needs compatibilizer to make the compatible blend [3]. There are some compatibilizers used by the previous researchers such as maleic anhydrate [5], silica [6,7], and bentonite[8].

Montmorillonite is the kind of silica clay that belongs to the family of phyllosilicates 2:1 which consists of two layers of tetrahedral silica sandwiching octahedral alumina. Montmorillonite has unique properties that often used in polymer nanocomposites preparation [9][4]. Montmorillonite is one of compatibilizer that can make a compatible blend. The montmorillonite also could improve the mechanical properties of the rubber [10,11]. Sun *et al.* found that organic montmorillonite could improve the vulcanization reaction, reduced the cure time, and raised the production efficiency in CR composite [12], Nik Ismail *et al.* found that montmorillonite could improve heat aging and thermal properties of silicone rubber [9], Shen *et al.* also found that montmorillonite could improve the mechanical properties of the rubber-modified phenolic on fiberglass [13].

Nowadays, there are some researches about CR/NR blend. Azizli *et al.* studied the effect of nanoclay cloisite on CR/NR blend [4], Azar and Sen studied the effect of the accelerator on CR/NR blend [14], Salleh et al studied the effect of virgin and recycled CR on CR/NR blend [1]. However, only a few research that studied the effect of montmorillonite in CR/NR blend. In this work, CR and NR were blended together with montmorillonite at various ratios. The curing characteristics, mechanical properties, morphology, and thermal properties were studied by rheometer, tensile strength tester, scanning electron microscopy (SEM) and differential scanning calorimetry (DSC). The blending of CR and NR could give cheaper materials with excellent resistance to ozone, thermal aging, and oil with good processability and mechanical properties.

II. MATERIALS AND METHODS

All of the material used in this work was supplied by commercial sources. The CR/NR blends were prepared by the two-roll mill with the formulations shown in Table 1. The rubber materials used were chloroprene (Baypren 2020) and natural rubber (RSS1, PTPN). The filler used was carbon black high-abrasion furnace type N330 (Multicitra), the compatibilizer was montmorillonite (Sigma Aldrich). Zinc oxide (ZnO, Indoxide) and stearic acid (Aflux 42 M Rhein Chemie) were used as an activator. Paraffinic wax (Antilux 654A) and N-(1,3- dimethylbutyl)-N'-phenyl-p-phenylendiamine (6PPD) (Starchem) were used as antioxidant. The softener was paraffinic oil (Indrasari), the accelerator was mercaptobenzothiazole (MBT) (Bayer), and the vulcanization agent was sulfur (Miwon). The tools used in this study are two-roll mill, MDR (moving die rheometer) Gotech 3000 A, hydraulic press Toyoseiki A-652 200 500, tensile strength tester Kao Tieh, SEM SNE 3200 M, and DSC Mettler Toledo.

Table 1. The formulation of CR/NR blend

Materials	CNM0	CNM25	CNM5	CNM75	CNM10
CR	25	25	25	25	25
NR	75	75	75	75	75
Montmorillonite	0	2.50	5	7.50	10
Zinc Oxide	5	5	5	5	5
Stearic acid	3	3	3	3	3
CB N330	50	50	50	50	50
Paraffinic oil	5	5	5	5	5
Paraffinic wax	0.5	0.5	0.5	0.5	0.5
6 PPD	5	5	5	5	5
MBT	2	2	2	2	2
Sulfur	2	2	2	2	2

*phr: part per hundred resin (primary matrix, CR and NR)

The materials shown in Table 1 were mixed by two-roll mill. CR and NR were mixed first, then the other materials were added with the sequence as shown in Table 1. The compound rubber then tested by the rheometer at 140. 150, and 160 ºC to study the curing characteristics and got the cure time. The CR/NR compound blends then were cured at 160 ºC by the hydraulic press with the time according to the rheometer test under pressure 150 kg/cm^2.

A. *Curing characteristics*

The cure characteristics can be studied using MDR. The scorch time (ts_2) and optimum curing time (t_{90}) can be found. The cure kinetics of CR/NR blend can be calculated from the torque-time curves taken from experiments performed at 140, 150 and 160 °C by the MDR. The data can be used to predict the curing kinetics using a kinetic model. General chemical reactions can be modeled in Equation (1).

$$\frac{d\alpha}{dt} = k(T).f(\alpha) \quad (1)$$

The degree of conversion (α) from the time dependency of torque values is defined from rheometer using the following Equation (2).

$$\alpha = \frac{M_t - M_L}{M_H - M_L} \quad (2)$$

where Mt is the torque at a given time t, ML and MH are the minimum and maximum torque. M values between 25 and 45% of torque change were chosen to estimate the rate constants in this work. The torque change from 25 to 45% considered representing the kinetic character of rubber blend [15]. The curing reaction is assumed to follow the first-order reaction and expresses as the uncrosslinked sample, (1 – α). The kinetic expression of rubber curing can be shown in equation (3).

$$\ln\frac{M_H - M_L}{M_H - M_t} = kt \quad (3)$$

Rearrangement equation

$$\ln(M_H - M_t) = \ln\ (M_H - M_L) - kt \quad (4)$$

The slope of the straight line of $\ln(M_H - M_L)$ against the time, t, can be used to obtain the rate constant, k.

The activation energy of the blend also can be calculated from the rheometer data using the Arrhenius equation. The equation (3) was combined with equation (5).

$$k = A\ exp(\frac{E_\alpha}{RT}) \quad (5)$$

Or

$$\ln k = \ln A - (\frac{E_\alpha}{R}\frac{1}{T}) \quad (6)$$

Where T is the temperature in K, E_α is the activation energy, R is the gas constant, and A is the constant factor. The activation energy was plotted according to the data from MDR.

The activation energy was determined from the slope of the straight line.

B. *Mechanical properties*

The mechanical properties of the CR/NR blends were carried out by Kao-Tieh tensile strength tester. The tensile strength and elongation at break were tested according to ISO 37. The tear strength was tested according to ISO 34.

C. *Morphological properties*

The scanning electron microscope (SEM) of the tensile fractured surfaces of the CR/NR blend was observed using SEM Zeiss EVO MA 10. The dried samples were sputter-coated by the conductive gold layer before SEM analysis.

D. *Thermal properties*

The thermal properties was made on differential scanning calorimetry (DSC) Mettler Toledo. The heating rates were set at 5 ºC/ min. under the nitrogen atmosphere from ambient temperature to 400ºC.

III. RESULTS AND DISCUSSION

A. *Curing characteristics*

The curing characteristic is the one aspect that important to be studied to get an efficient process. The rheometer test gave some important information such as the scorch time, optimum curing time, and activation energy. The scorch time (ts_2) could be seen in Figure 1 and the optimum curing time (t_{90}) could be seen in Figure 2. Figures 1 and 2 shows that the higher curing temperature gives faster scorch time and optimum curing time. The scorch time showed the safety time of processing of the rubber products. The longer the scorch time, the safer the rubber processing. The addition of montmorillonite in 2.5 and 7.5 phr could increase the scorch time.

The optimum curing time was considered as optimum cure time and related to production efficiency. Optimum cure time shows the time used for the rubber to reach the crosslinking. Before the t_{90}, the blend is still uncured, but at the time above t_{90}, the rubber compound can be degraded. This happens because there is a heat attack rubber blend even at storage condition [3]. From Figure 2, it can be observed that the optimum curing time is achieved by 2.5 phr montmorillonite at curing temperatures 150 and 160ºC. At higher compatibilizer loading, the curing time is increasing. It shows that montmorillonite at a suitable amount could make good interaction in the rubber matrix. The shorter cure time indicates fast formations of crosslink in CR/NR blend, hence it can reduce the consumption of electric energy [3]. The increase in cure time may be due to the intercalation of the montmorillonite by the polymer chains, thus inhibiting the curing reaction and make the time to achieve optimum crosslink is higher.

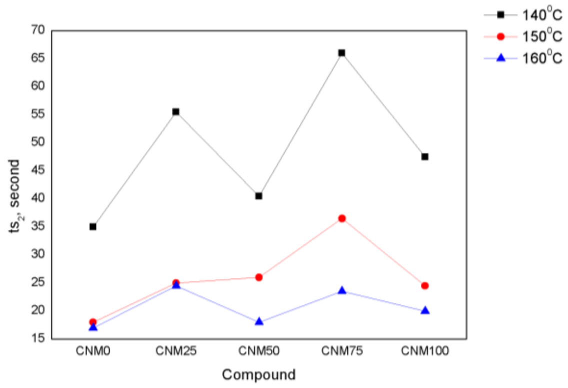


Figure 1. The scorch time (ts_2) of CR/NR blends

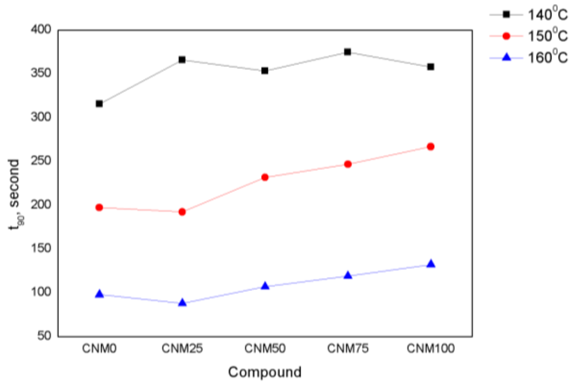


Figure 2. The optimum curing time (t_{90}) of CR/NR blends

The cure kinetics of CR/NR blend could be obtained from the Equation (4) and (6). The rate constant (k) and the activation energy (E_α) can be seen in Table 2. The rate constant shows the rate of the reaction. A higher constant rate means the faster the reaction. Table 2 shows that the higher curing temperature results in a higher constant rate. This phenomenon is suitable with the result of scorch time and optimum curing time. The higher temperature makes the heat easier to flow through the rubber molecules, so the reaction becomes faster.

Table 2 shows that at a certain amount of montmorillonite, the activation energy needed is lower than blend without montmorillonite. This research gives the same results as the previous researcher [16]. The activation energy is the required energy that needs within the curing process. The required activation energy for curing decreased about 0.5 until 31 kJ/mol in the presence of montmorillonite. It may happen because of the improvement of heat transfer within the system. The heat transfer increased with the enhancement of montmorillonite with the rubber matrix. It means that montmorillonite could be a good compatibilizer for CR/NR blends. The 2.5 phr montmorillonite gives the lowest activation energy. But at higher filler loading, the required activation energy is increasing. The increase in activation energy might be caused by the restriction of CR, NR, and montmorillonite. The higher amount of montmorillonite needs more time to cure hence needs more energy.

Table 2. The rate constant (k) and the activation energy (E_α) of curing process of the CR/NR blend

Blend	Constant rate, k (sec^{-1})			E_α (kJ/mol)
	140ºC	*150ºC*	*160ºC*	
CNM0	0.0067	0.0111	0.0257	87.25
CNM25	0.0103	0.0156	0.0220	56.45
CNM50	0.0064	0.0108	0.0207	87.17
CNM75	0.0075	0.0110	0.0236	81.79
CNM100	0.0060	0.0095	0.0193	86.69

B. *Mechanical properties*

Figures 3 to 5 show the relationship between the mechanical properties of CR/NR blends with the addition of montmorillonite. Mechanical properties of the composites depend on some factors such as particle size, filler content, and degree of the dispersion of filler on the matrix [17].

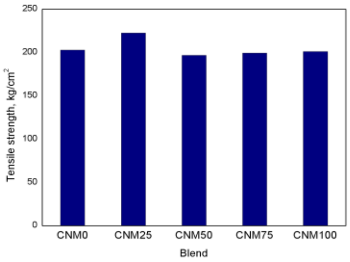


Figure 3. Tensile strength of CR/NR blends

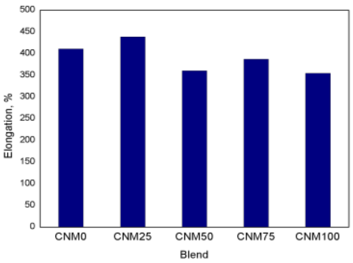


Figure 4. Elongation of CR/NR blends

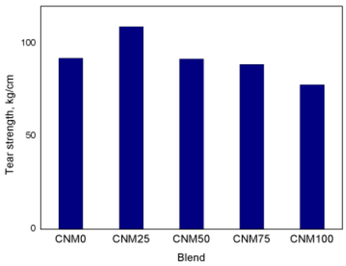
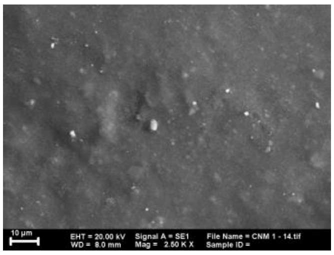


Figure 5. Tear strength of CR/NR blend

Figure 3 shows the tensile strength of the CR/NR blends. Tensile strength indicates the maximum stress of the product. The montmorillonite on the CR/NR blends gives the fluctuated result. The 2.5 phr montmorillonite can improve the mechanical properties of the blend, but above 2.5 phr montmorillonite give the lower mechanical properties than CR/NR without compatibilizer. This may be due to excess montmorillonite, which leading to the aggregation of montmorillonite in the blend and weak interaction of bonding between particles. This synergism effect is associated with the optimum tensile strength The increase in mechanical properties because of excess montmorillonite also found by the previous researchers [10][18]. Figure 4 and Figure 5 show that the elongation and tear strength of CR/NR blends also give almost similar pattern as that shown in tensile strength. The degree of exfoliation of the layered silica in montmorillonite could be related to the improvement of mechanical properties. The alkyl ammonium ions on the layered silica may plasticize the blend that could increase the elongation. But at a higher amount of montmorillonite, the non-exfoliated montmorillonite aggregates make the blend more brittle [18]. The suitable amount of compatibilizer can improve mechanical properties

C. *Morphological properties*

The micrograph of the CR/NR blends was observed by SEM with magnification x2500. The morphology of the blends depends on the blend composition, the blend processing, and the characteristic of individual components. Figure 6 shows that all of the blends are homogeneous. It shows that montmorillonite is well dispersed and make a compatible blend.



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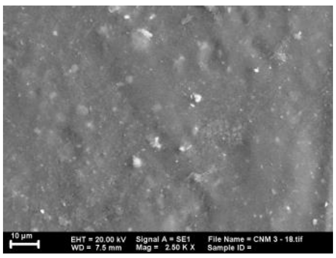

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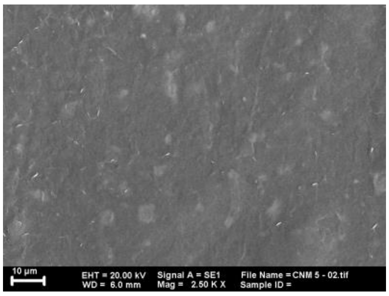
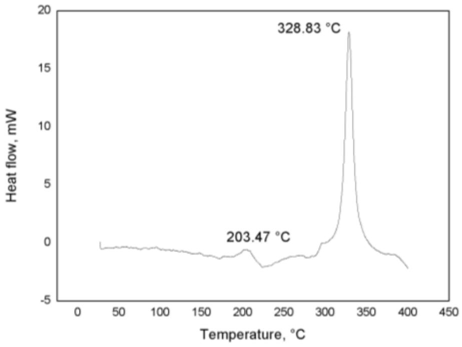


(c)

Figure 6. The morphology of CR/NR blends (a) CNM0, (b) CNM50, (c) CNM100

D. *Thermal properties*

DSC is used to characterize the thermo-physical properties of the blends such as melting temperature (T_m), the heat of melting, and phase of transition. The thermal stability was influenced by the component of the blend. Figure 7 shows that the blend without montmorillonite has two phases with slow peak at 203 ºC. The blends with montmorillonite have one phase that means the blend is miscible. The DSC result of all blend showed that the thermal transition is exotherm with melting temperature (T_m) remained almost unaltered, around 327-329 ºC with peak value 18.18 to 20.76 mW. The melting temperature of CR/NR blends is shown in Table 3. The melting temperature (T_m) show the peak temperature and the onset melting temperature ($T_{m\ onset}$) show the starting temperature of the melting process. The montmorillonite give T_0 higher than the blend without montmorillonite, especially 2.5 phr montmorillonite. The higher starting melting temperature, the longer time before melting process start. This pehenomenon is called by a thermal delay effect [19]. The montmorillonite also give a smoother graph than a blend without montmorillonite. It shows that montmorillonite has a good interaction with CR/NR blend and being good compatibilizer for CR/NR blend.



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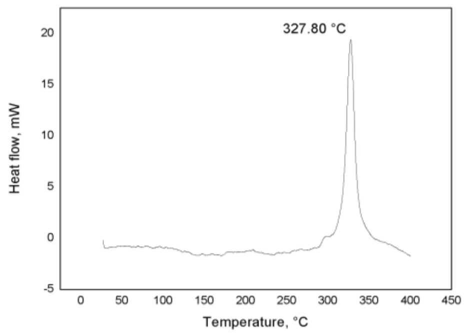

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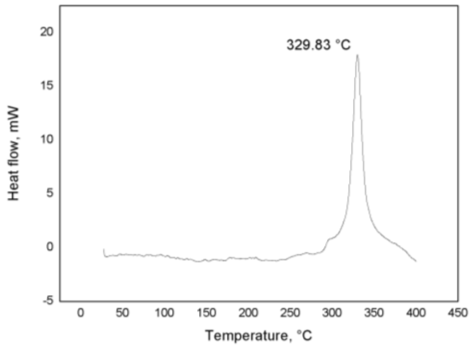

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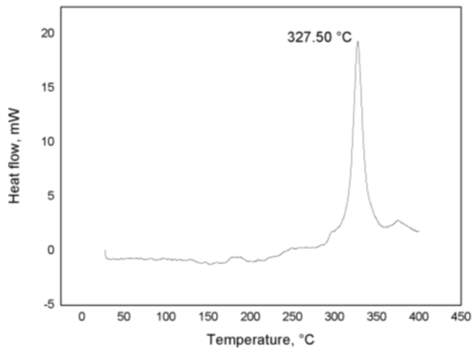

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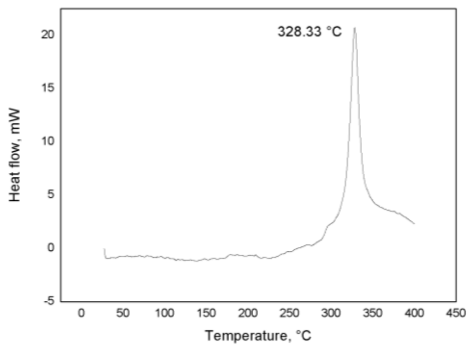

(e)

Figure 7. The DSC result of CR/NR blends

Table 3. The melting temperature of CR/NR blends

Blend	Peak value, mW	$T_{m\ onset}$, ºC	T_m, ºC
CNM0	18.18	319.88	328.83
CNM25	19.42	344.54	327.80
CNM50	17.96	329.52	329.83
CNM75	19.32	321.99	327.50
CNM100	20.76	325.83	328.33

IV. CONCLUSION

Montmorillonite is the effective compatibilizer for the CR/NR blends. This research demonstrated that the incorporation of 2.5 phr montmorillonite into CR/NR blend could improve the curing characteristic, mechanical properties, and thermal properties. The 2.5 phr montmorillonite gave the fastest optimum curing time at 150 ºC (88 s) and 160 ºC (193 s), the lowest activation energy (56.45 kJ/mol), the highest tensile strength (222 kg/cm^2), the highest elongation (439%), and the highest tear strength (109 kg/cm). SEM analysis showed that the montmorillonite is well dispersed on CR/NR blend. The DSC results showed that all of the blends have almost the same temperature melting, but montmorillonite gave a higher melting temperature than a blend without montmorillonite. The blends with montmorillonite have one phase that means the blend is miscible. It could be concluded that the 2.5 phr montmorillonite is the proper compatibilizer for CR/NR blends.

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