

Physical Properties and Cure Characteristics of Natural Rubber/Nanoclay Composites with Two Different Compatibilizers

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ABSTRACT: The effects of epoxidized natural rubber (ENR) and maleic anhydride-grafted polybutadiene (PB-g-MA) as compatibilizers to rubber formulations with and without organo-modified layered silicates are investigated. The physical properties and curing characteristics of composites are studied by moving die rheometer, rubber process analyzer, tensile, tear, and hardness testing. The state of organoclay intercalation was determined by X-ray diffraction method. The addition of compatibilizers, especially ENR 50, results in further intercalation or exfoliation of the organoclay that increased the clay dispersion in the rubber matrix. ENR 50 with organo-modified clay

improves the physical properties and changes the curing profile. The addition of PB-g-MA without organoclay increases the tensile strength (σ_{\max}) by increasing the stock viscosity of the rubber compound. Interestingly, simultaneous increase in hardness and σ_{\max} is achieved in the presence of both compatibilizers, a characteristic that is difficult to achieve and sometimes required in rubber processing. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 1530–1535, 2011

Key words: natural rubber; composites; compatibilizers; organoclay

INTRODUCTION

Natural rubber has many attractive properties and is widely used with reinforcing fillers such as silica and carbon black to give the required properties for specific applications. The addition of reinforcing fillers increases tear strength, modulus, tensile strength (σ_{\max}), and abrasion resistance of natural rubber-based composites. The state of filler dispersion determines the final properties of composites. Filler dispersion at nanometer size gives improved mechanical properties, flame retardancy, gas barrier properties, and thermal stability.^{1–3}

During compounding, polymer intercalation into silicate galleries is determined by entropic and enthalpic factors. To produce nanostructured natural rubber composites by melt compounding, it is necessary to use organo-modified layered silicates and compatibilizing agents because of the nonpolar charac-

ter of natural rubber. Organic modification of layered silicates increases the spacing between silicate layers, but it is not enough to intercalate polymeric chains into the silicate gallery. Polar interactions are required to produce exfoliated structure because of the Lewis acid-base character of polar silicates. It is therefore necessary to choose the right compatibilizing agents that are compatible and more polar than the polymer matrix.^{2,3}

Previous studies mainly investigated the effect of epoxidized natural rubber (ENR) either as compatibilizer or as matrix material in the presence of layered silicates without carbon black on the mechanical properties and curing characteristics of composites.^{4–12} Karger-Kocsis and coworkers¹² investigated two different grades of ENR with 25 and 50 mol % epoxidation as compatibilizer in natural rubber matrix. ENR with 50 mol % epoxidation (ENR 50) gives better results than the 25 mol % epoxidation with regards to clay dispersion and mechanical properties. In this study, ENR 50 and polybutadiene grafted maleic anhydride (PB-g-MA) are used with natural rubber with and without organo-modified clay in the presence of carbon black. The main purpose of this study is to investigate the effect of compatibilizing agents and organoclay on physical and cure characteristics of natural rubber composites.

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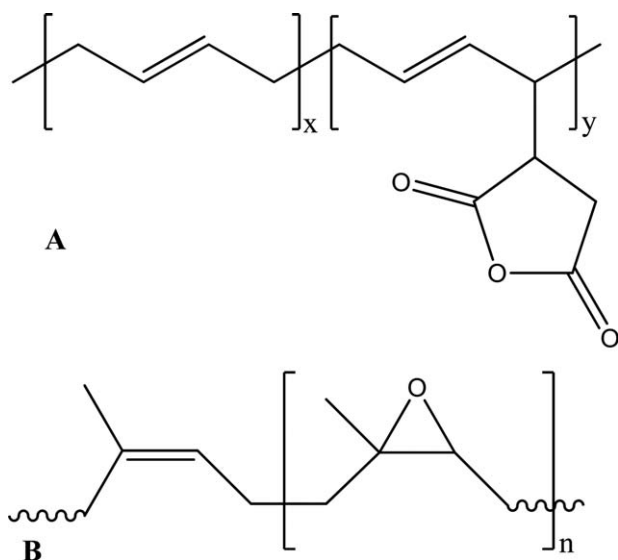


Figure 1 Chemical structures of compatibilizers. (a) PB-g-MA (x : 0.83, y : 0.17), (b) ENR 50 (n : 0.5).

MATERIALS AND EXPERIMENTAL

Materials

Standard Malaysian Rubber was purchased from Pacidunia Sdn. Bhd. under the trade name SMR-10 CV (Mooney viscosity 60 (+7,−5)). Carbon black was purchased from Alexandria Carbon Black CO. S.A.E with trade name ACB5000. Organo-modified clay (Closite 30B) was purchased from Southern Clay Product. Low molecular weight (M_n : 5400) maleic anhydride grafted polybutadiene (Ricon 131 MA 17) was purchased from Sartomer. It is a copolymer of 83% butadiene and 17% maleic anhydride. Commercial-grade ENR having 50 mol % epoxy groups (ENR 50) was purchased from Guthrie Latex. The chemical structures of compatibilizing agents are shown in Figure 1.

Compounding and curing

Rubber compounds were prepared in a laboratory scale open two-roll mill at 60°C. The rotors operated at a speed ratio of 1 : 1.2. All compounds had the same composition, except for the amount of clay and the type and amount of compatibilizers. The recipes of the compounds are given in Table I. The standard rubber ingredients (stearic acid, zinc oxide, *N*-(1, 3-dimethylbutyl)-*N'*-phenyl-*p*-phenylenediamine (6PPD), *N*-*tert*-butyl-2-benzothiazole sulfonamide (TBBS), tetrabenzyl thiuram disulfide (TBZTD), sulfur) were used with a total of 16 phr.

First, natural rubber together with other ingredients except for accelerators and sulfur where these two substances were added towards the end of the mixing process were mixed. In case of recipe with compatibilizer, the natural rubber and the compati-

bilizer were first mixed before the addition of other ingredients. If recipe contains compatibilizer and clay, the natural rubber and compatibilizer were mixed earlier before the clay addition and mixed for 5 min. The mixing process was followed by similar additive inclusions as for the reference sample. All compounds were vulcanized to their optimum cure time, t_{90} , as determined by Alpha MDR B Moving Die Rheometer at 160°C in an electrically heated hydraulic press.

Characterization

Wide angle X-ray scattering (WAXS) was performed by Rigaku DMAX 2200 diffractometer in the reflection mode using an incident X-ray wavelength of 1.542 Å at a scan rate of 1°/min over the range of $2\theta = 1^\circ$ – 10° . X-ray analyses were performed at room temperature on disk shaped samples produced via compression molding. Cure characteristics of compounds were determined at 160°C with Alpha MDR B moving die rheometer (Alpha Technologies, Swindon, UK) according to DIN 53529. Dynamic mechanical analyses were carried out on the uncured compounds using an Alpha RPA 2000 Rubber Process Analyzer (Alpha Technologies, Swindon, UK). Compression molded sheet having a thickness of 2 ± 0.2 mm was used for tear and tensile testing. The measurements were carried out using Zwick/ROELL Z 010 with a cross-head speed of 500 ± 50 mm/min at room temperature. Tensile and tear properties of the specimens were measured according to ASTM D 412 and ASTM D 624, respectively. Five samples were tested in each experiment, and the average value is reported. Shore hardness was measured by using a Zwick/Roell Shore A tester according to ASTM D 2240.

RESULTS AND DISCUSSION

Morphology characterization by WAXS

Figure 2 shows the X-ray diffraction patterns for Closite 30B and Closite 30B containing composites. Closite 30B shows a peak at $2\theta = 4.9^\circ$, corresponding

TABLE I
Recipes of the Rubber Compounds

Ingredients (phr)	Samples						
	R^a	1	2	3	4	5	6
SMR-10 CV	100	100	96	96	90	95	90
C/B5000	50	50	50	50	50	50	50
Other ingredients ^b	16	16	16	16	16	16	16
Closite 30B	–	2	–	2	–	–	2
Ricon131 MA 17	–	–	4	4	–	–	–
ENR50	–	–	–	–	10	5	10

^a Reference sample.

^b Standard rubber additives.

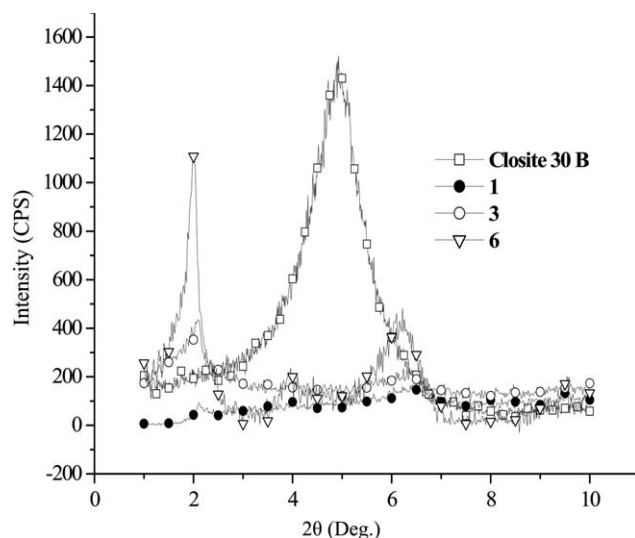


Figure 2 XRD graphs of clay and clay containing composites.

to basal spacing of 17.9 Å. The clay containing compound without any of the compatibilizer (Recipe 1) shows two peaks at $2\theta = 2.1^\circ$ and 6.4° corresponding to basal spacings of 42.4 and 13.8 Å, respectively. This curious result indicates that mechanical mixing facilitates the intercalation and collapse of clay layers to take place at the same time without the presence compatibilizer.⁴ More evidences are demonstrated by tensile results that will be discussed later. Clay-containing composite with PB-g-MA showed two peaks at $2\theta = 2.06^\circ$ and 6.24° corresponding to basal spacings of 42.8 and 14.2 Å (Recipe 3), respectively. Both peaks have similar intensities suggesting similar amounts of two types of intercalation. Clay containing compound with ENR showed two peaks at $2\theta = 2.0^\circ$ and 6.4° corresponding to basal spacing of 44.8 and 13.9 Å. The relatively higher peak intensity at $2\theta = 2.0^\circ$ for composite with ENR-50 compared to that of composite without the compatibilizer at $2\theta = 2.1^\circ$ indicates that a larger fraction of clay particles is involved in intercalation within the former. The polar character of compatibilizers determines the degree of intercalation.^{4-6,13} Arroyo et al.⁵ proposed that the hydroxyl groups present in the structure of Cloisite 30B are able to react with the epoxy groups of ENR 50, which favors the dispersion and intercalation. The higher reactivity of epoxy groups compared to maleic anhydride group, especially at medium temperature may give rise to more intercalated structure. Without TEM data, it will be speculative to discuss the amount of intercalation or exfoliation regarding ENR-50 and PB-g-MA.

Cure characteristics

Cure characteristics of composites were determined at 160°C with Alpha MDR B moving die rheometer.

The scorch time, t_{90} (time for 90% cure) and torque values are given in Table II. S_{\min} (minimum torque) gives information about the stock viscosity of a compound. Delta torque ($\Delta S = S_{\max} - S_{\min}$) gives information about the crosslink density of cured compounds. The larger the ΔS the higher is the crosslink density.^{4,5,12}

The addition of organo-modified clay and compatibilizers varies the cure characteristics of reference recipe. The addition of organo-modified clay (Recipe 1) reduces both the scorch time and t_{90} with respect to the reference sample and compatibilizer-containing composites. This is due to the ammonium groups of organic-cations that facilitate the curing reaction of natural rubber. These modifiers are believed to take part in amine complexation reaction that behaves as an accelerator during natural rubber vulcanization.^{12,14-17} The addition of ENR50 (Recipes 4 and 5) has negligible effect on the scorch time compared to the reference material. The t_{90} value of reference composite (R) increases when ENR 50 is added and increases even further as the ENR50 content is increased in the recipe. The increase of t_{90} is possibly due to the interaction between epoxy group in the ENR 50 and amine compound that is functioning as an accelerator in the composites. The addition of PB-g-MA (Recipe 2) increases both the scorch time and t_{90} with respect to the reference sample due to the grafted maleic anhydride group. From previous studies, organic acids and their anhydrides are known as potential vulcanization inhibitors since sulfur vulcanization is driven by alkaline media. They are typically used to increase the induction time or scorch safety in rubber compounds.^{18,19} When organo-modified clay is used with compatibilizers (Recipes 3 and 6), the t_{90} value decreases with respect to the compatibilizer containing recipes.

The addition of organo-modified clay and ENR 50 increases the S_{\max} and ΔS value of composite. The increase in ΔS indicates that both organo-modified clay and ENR 50 increases the crosslink density of the compounds. In addition, the delta torque progressively increases as the ENR 50 content in the blend increases.¹⁷ The addition of PB-g-MA lowers the ΔS value of composite. The lower delta torque is an indication of lower crosslink density that may

TABLE II
Cure Characteristics of the Compounds

Compound	R	1	2	3	4	5	6
Scorch Time (min)	1.8	0.9	2.1	1.6	1.8	1.9	1.2
t_{90} (min)	3.7	2.3	5.1	3.4	4.2	4.0	2.6
S_{\max} (dN m)	13.5	19.6	12.3	13.7	16.1	15.0	17.2
S_{\min} (dN m)	1.0	0.5	1.5	1.3	1.3	0.8	1.7
ΔS (dN m)	12.5	19.1	10.7	12.3	14.8	14.2	15.5

TABLE III
Dynamic Mechanical Properties of Uncured Composites

Compound	G' 1% (KPa)	G' 10% (KPa)	G' 15% (KPa)	G' 50% (KPa)	$\tan \delta$ (%10)
R	1090	980	940	820	0.068
1	1340	1070	1010	870	0.070
2	1240	975	920	765	0.083
3	1400	1080	1020	840	0.082
4	1770	1260	1180	980	0.097
5	1445	1100	1040	900	0.081
6	1850	1340	1250	1030	0.096

arise from the retardation effect of maleic anhydride groups on sulfur curing pathway.

Dynamic mechanical properties

The dynamic mechanical properties of uncured compounds are given in Table III, where the percentages indicate the strain values. The dynamic mechanical properties of uncured compounds are influenced by polymer–filler and filler–filler interactions.⁶ From Table III, the addition of organo-modified clay increases the elastic modulus (G') of the uncured compounds at all strain values. Previously, the XRD diffractogram of natural rubber clay composites with compatibilizer showed the intercalation of polymeric chains into clay gallery. The intercalated chains are immobilized due to polymer–clay adhesion and occlusion that increased the effective volume of filler and the G' . When compatibilizers are used without clay, the G' of uncured compound increases compared to reference sample, but it is comparatively smaller than that of samples with organoclay. This effect could be due to strong interactions between carbon black, organoclay and polar components of the compatibilizers.

Tan δ is the ratio of loss modulus (G'') to elastic modulus (G'). When dynamic strains are applied to the rubber, certain amount of energy is converted into heat (G'') while the remaining energy used to recover the sample into initial state.¹ The most important factor that governs tan δ of uncured rubber products is the filler networking effect.^{6,8,9} The increase tan δ value of composites as compatibilizers are added is caused by polar component in the compatibilizer molecules (Fig. 1). Carbon black particles has some small amount of polar components on their surfaces such as hydroxyl, carboxyl, etc.²⁰ The interaction between these polar components and polar groups in the compatibilizers reduces the interaction among the carbon black particles which increases the polymer–filler interaction that contributes to increase tan δ .⁶ When natural rubber is cured normally, the formation of chemical crosslinks during curing reaction will reduce the loss modulus G'' and tan δ .

Mechanical properties

The tensile properties of composites are given in Table IV. The mechanical properties of organoclay containing polymeric materials are primarily determined by the degree of dispersion of clay in the polymer matrix. The highest dispersion state (exfoliated structure) gives much better mechanical properties than the lowest dispersion state (micro structure).^{21–24} The incorporation organo-modified clay without compatibilizer reduced both σ_{\max} and elongation at break values (ϵ_{\max}) of the composites. There are two possible explanations of this phenomenon. The breakage depends on the amount of weak spots or inhomogeneties in the vulcanized rubber.²⁵ Without using any compatibilizer, organo-modified clay tends to agglomerate and forms weak points in the natural rubber matrix and reduces σ_{\max} . The second reason is the reduction of S_{\min} value, giving information about the stock viscosity of the compound, that is caused by the organic components in the modified clay.⁵ The low S_{\min} indicates the reduced shear force during mixing, which tends to reduce carbon black dispersion and form agglomerates that turn into weak points. The reduction in ϵ_{\max} therefore is believed to be due to the increased agglomeration of clay and carbon black particles. In the presence of ENR 50, the addition of organo-modified clay into the composites increases their σ_{\max} due to increase of filler dispersion and the formation of intercalated structure. When the amount of ENR 50 is increased from 5 to 10 phr the tensile strength is slightly increased in case of composite without clay addition. This is due to the fact that the epoxidized groups in ENR50 reduced the ability for strain induced crystallization of the natural rubber.¹² The highest tensile strength is obtained when the organoclay is added in the presence of 10 phr of ENR 50. However, it shows insignificant difference compared to that of composite with 5 phr ENR 50 and clay content. The addition of ENR 50 caused the increase in ϵ_{\max} values with respect to the reference sample (R). The low degree of strain induced crystallization increases the mobility

TABLE IV
Tensile Properties of Compounds

Compound	R	1	2	3	4	5	6
E 50% (MPa)	1.4	2.1	1.9	1.8	1.4	1.3	1.5
E 100% (MPa)	2.8	4.1	3.7	3.6	2.8	2.5	2.8
E 200% (MPa)	7.5	8.5	8.6	8.0	–	6.3	7.1
E 300% (MPa)	12.8	12.7	13.0	12.2	11.5	10.9	12.2
σ_{\max} (Mpa)	19.1	13.3	20.6	15.9	19.7	20.3	20.5
ϵ_{\max} (%)	420	310	460	394	492	495	483

E: Youngs' modulus.

of rubber molecules that subsequently increases the ϵ_{\max} values. The addition of PB-g-MA increases the σ_{\max} with respect to reference sample (R) and composite containing organoclay without compatibilizer (Recipe 1). The addition of PB-g-MA increases the σ_{\max} of the compound without increasing the crosslink density. From Table II, S_{\min} value increases with the addition of PB-g-MA, which improves the carbon black dispersion that increases the σ_{\max} . When the compatibilizer, PB-g-MA is used with clay in Recipe 3, the tensile strength of this composite shows significant decreases compared to that of compound from Recipe 2. The same effect is observed in case of composites without the addition of compatibilizer. Although the PB-g-MA facilitates the intercalation of clay because of its polar character, some amount of clay remains unintercalated as inferred from the peak at $2\theta = 6.24^\circ$ (Fig. 2). These unintercalated organo clays form weak spots and inhomogeneities leading to the reduced tensile strength, σ_{\max} .

The tear strengths of the compounds are given in Figure 3. The tear characteristic of a compound is related to the crosslink density, filler type, and filler dispersion.^{1,12} The tear strengths of all compounds are higher than that of the reference sample. The addition of organo-modified clay slightly increases the tear strength of the natural rubber composites. Although the organo-modified clay increases crosslink density of the composites, the slightly increase of tear strength is caused by the poor clay dispersion within the composites. The addition of ENR 50 increases the crosslinking density and filler dispersion that help to increase the tear strength. Similarly, the inclusion of PB-g-MA improved the carbon black dispersion that contributes to increase the tear strength with respect to the reference sample. High tear strength is a desired property in natural rubber elastomers.

Hardness is essentially a measure of modulus. It is the resistance to very limited deformation when a force is applied by a rigid indenter to a cured compound.¹ The hardness values of all compounds are

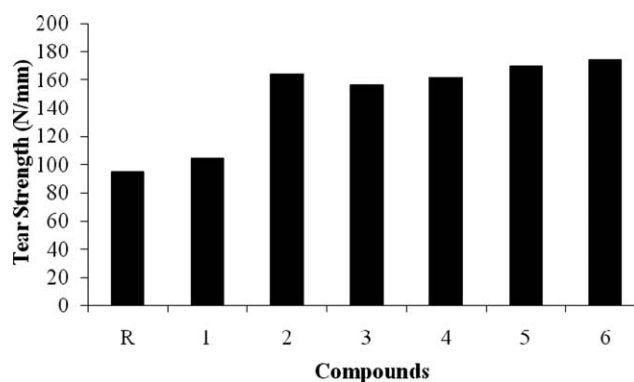


Figure 3 Tear strength of compounds.

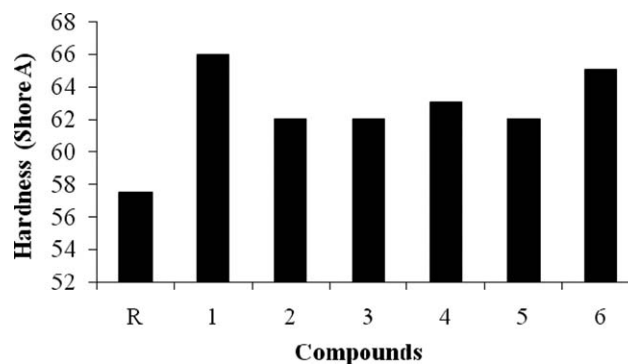


Figure 4 Hardness of compounds.

shown in Figure 4. The hardness values of all composites are higher than that of the reference sample and the clay containing composite (Recipe 1) having the highest value (66 Shore A). The hardness of rubber compounds increases generally with the addition of widely used fillers (carbon black and silica). When the filler exceeds a certain amount, it tends to agglomerate that leads to a reduction in σ_{\max} value of the natural rubber composite.¹⁰ ENR 50 and PB-g-MA can be good candidates to increase the hardness of the material without reducing the σ_{\max} value of the compounds.

CONCLUSIONS

Two types of compatibilizers (ENR 50 and PB-g-MA) with different polar character are added to a standard natural rubber composition. These compatibilizers are used to produce samples with and without organo-modified clay. An increase in the intercalation amount of the clay is observed both for ENR 50 and PB-g-MA, but, ENR 50 is found to impart more desirable properties overall compared to PB-g-MA that may be due to higher reactivity of epoxy groups compared to maleic anhydride group, especially at ambient temperatures.

The addition of organoclay with compatibilizers changes both physical and curing characteristics of the rubber compound. With no compatibilizer, addition of organoclay reduces the σ_{\max} , increases the hardness, and slightly increased the tear strength. Organoclay acts as an accelerator during curing and increases the crosslink density of the final product. The addition of PB-g-MA increases the σ_{\max} , tear strength and hardness of the compound when used without organoclay by increasing the stock viscosity of the compound. PB-g-MA acts as retarder during curing because of the maleic anhydride group, which reduced the crosslink density. With ENR 50, the σ_{\max} , tear strength and hardness of the compound increased with and without organoclay addition, which is most probably due to the intercalation of organoclay and increase in crosslinking density of

the composition. The most important finding of the study is the increase of hardness with compatibilizers with parallel increase in the σ_{\max} . Usually hardness in standard natural rubber compositions can be increased by more carbon black addition that reduces the mechanical strength.

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