The Role of Rubber Characteristics in Preparing Rubber/ Clay Nanocomposites by Melt Compounding

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ABSTRACT: Rubber/organic clay (OC) nanocomposites were produced by melt blending. Polar or unsaturated matrices (e.g., NBR and SBR) could easily enter into OC layers, whereas using nonpolar unsaturated rubber (EPDM), without other additives' help, intercalation structure could not be directly obtained. For the EPDM system, an intercalated structure was observed in presence of stearic acid (SA) for composites composed of SA and OC. Transmission electron microscopy observation showed that the dispersion of clay in nonpolar saturated rubber matrix was much poorer than that in polar or unsaturated matrix. The same effect of polar matrix was confirmed by comparison between IIR/OC and BIIR/OC systems. Moreover, using OC pretreated by SA (S-OC), the dispersion of clay was obviously improved in the investigated nanocompo-

INTRODUCTION

Since the researchers at Toyota Central Research Laboratories successfully prepared PA6/clay nanocomposites for the first time,¹ as a new kind of materials, polymer/clay nanocomposites have caught much attention through the world. This new class of materials is generally composed of layered silicates, as a reinforcing phase, dispersed in a polymer matrix on nano scale,^{2–7} and these nanocomposites exhibit markedly improved mechanical, thermal, barrier, and physicochemical properties compared with the starting polymers and conventional (microscale) composites.^{8–10}

The tradition methods to prepare polymer nanocomposites are to intercalate monomers¹¹ or polymers^{12–14} into swellable-layer silicate hosts, and especially for rubbers, there are mainly three kinds of methods for preparing the rubber matrix nanosites, due to the intercalation of SA into OC interlayers. Especially in the nonpolar saturated EPDM system, the intercalation structure could be easily observed. Relative to the corresponding nanocomposites using OC, tensile strengths and the stresses at low strain of NBR and SBR based nanocomposites with S-OC were significantly improved; while with EPDM nanocomposite, using S-OC, only tensile strengths were improved but the stresses at low strain were almost the same, which should be related to the different interfacial force between OC and different rubber matrices. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 1925–1934, 2008

Key words: organic clay; rubber; intercalation; nanocomposite

composites: latex,¹² solution,¹³ and melt compounding.¹⁴ Considering industrialization, melt intercalation is one of the feasible operations, in which polymer is directly intercalated into modified silicate layers (organoclay) in the molten state to prepare nanocomposites. The driving force of the intercalation is determined by physical and/or chemical interactions between polymers and modified silicate.

Using the method of melt intercalation to prepare rubber/clay nanocomposites, dispersion of clay layers is always a hotspot, and there are a few investigations focusing on the vulcanization additives, like accelerant zinc dimethyldithio carbamate (PZ)¹⁵ and zinc oxide (ZnO).^{16–18} However, only a few literatures discuss the effect of the characteristics of rubbers,^{19,20} and no literature investigates the combined effect of additives and characteristics of rubber matrix.

In this article, different rubbers were selected: the polar (acrylonitrile–butadiene rubber, NBR), the unsaturated (styrene–butadiene rubber, SBR), and the nonpolar saturated (ethylene–propylene–diene rubber, EPDM), to prepare rubber/clay nanocomposites by melt method. The effects of the characteristic of matrix, including polarity, saturation, and flexibility of chains on the dispersion of clay are investigated, and the effect of one of the ingredients, stearic acid (SA), is also discussed. According to the experimental

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results, polar or unsaturated macromolecule chain can easily enter into the interlayers, while nonpolar saturated macromolecule cannot. Moreover, SA can intercalate into the clay interlayer easily, and thus using organic clay (OC) pretreated with SA (S-OC), the dispersion and the tensile properties are obviously improved in the rubber matrices investigated in this article.

EXPERIMENTAL

Materials

EPDM (J2080, 67% ethylene and 6% ethylidene norbornene content) and SBR (1502, 23.5% styrene) were purchased from Jilin Chemical Industrial Co. (China). NBR (220S, 41% AN) was purchased from Japan Synthetic Rubber Co. (Japan). IIR (Polysar301, 1.6% degree of unsaturation) was produced by Polysar Co. (Canada); bromobutyl rubber (2030, 2.1% saltformer) (BIIR) was purchased from Bayer AG (German). OC, montmorillonite modified by dimethyl dialkyl (C14–18) ammonium (Nanomer I.44P), was supplied by Nanocor, USA. Other compounding ingredients, including zinc oxide (ZnO), SA, tetramethyl thiuram disulfide, dibenzothiazyl disulfine, diphenyl guanidine (D), 2-mercapto benzothiazole (M), N-phenyl- α -naphthylamine (A), N-isopropyl-N'-phenyl-p-phenylene-diamine (4010NA), and sulfur (S), were commercial grade products. Basic formulas of composites are shown in Table I.

Preparation of rubber/OC nanocomposites

Rubbers and OC were mixed in an open two-roll mill for about 10 min, and then other compounding ingredients, for example, ZnO, SA, antioxidants, accelerators, S, were added in usual order. The compounds were vulcanized in a standard mold for optimum cure time (t_{90}) under the pressure of 15 MPa at 150°C for the SBR system and at 160°C for the EPDM, NBR, and IIR systems. Oscillating disk rheometer P355B2 produced by Beijing Huanfeng Chemical Industry Machine Experiment Factory (China) was used to measure optimum cure time (t_{90}), according to ASTM D 2084-01, and kinetics of vulcanization were recorded at the same time.

Preparation of S-OC powder and rubber/S-OC nanocomposites

The process of OC pretreated with SA is described as following: SA and OC (ratio between SA and OC is 2 : 10) were mixed in homomixer for about 1 min at room temperature. The mix was put in an oven at 100° C (the melting point of SA is nearly 70°C) for about 1 h to ensure that melted SA reacted with OC

		1	0					
	Loadings (phr ^a)							
	NBR	SBR	EPDM	IIR	BIIR			
Rubber	100	100	100	100	100			
OC	10	10	10	10	10			
ZnO	5.0	5.0	5.0	5.0	5.0			
SA	2.0	2.0	2.0	2.0	2.0			
Accelerator								
TMTD	-	0.2	1.0	1.0	1.0			
D	_	0.5	_	_	_			
DM	_	0.5	_	_	_			
М	1.5	_	_	0.5	0.5			
S	1.5	2.0	1.5	2.0	2.0			
Antioxidant								
4010NA	2.0	1.0	_	_	_			
А	_	_	_	1.0	1.0			

^a phr: weight parts per 100 weight parts of rubber.

and intercalated into the interlayers of OC. After cooling, the pretreated OC with SA can be obtained, which was denoted as S-OC.

S-OC was mixed with matrices and then additives were added. These compounds were vulcanized at the same conditions as rubber/OC nanocomposites to prepare rubber/S-OC nanocomposites. Since SA had been added to S-OC, the basic formulas of composites, which are shown in Table II, are little different from the systems using OC.

Characterization

X-ray diffraction (XRD) was carried out using a diffractometer (D/Max-III C, Rigaku, Japan) with CuK α radiation operating at 40 kV and 200 mA. Basal spacing between silicate layers of OC and rubber/ OC(S-OC) nanocomposites was observed from 0.5° to 10° (2 θ) at a scan rate of 1°/min.

Transmission electron microscopy (TEM) observations were performed on the ultrathin sections with an H-800 TEM (Hitachi, Japan) at an acceleration voltage of 200 kV at room temperature, and the ultrathin sections were prepared with a cryoultramicrotome under liquid nitrogen cooling.

Differential scanning calorimetry (DSC) measurements were performed with a DSC 204F1 calorimeter (Netzsch Company, Germany) to obtain the glasstransition temperature of relative matrices.

Fourier transform infrared spectroscopic (FTIR) measurements were also used to investigate the possible interaction between SA and OC. FTIR on the films was performed at a resolution of 4 cm⁻¹ by using a Hitachi 270-30 spectrometer (Hitachi, Japan). OC, S-OC, and SA were pressed with KBr powder, respectively, for FTIR measurements in the transmission mode.

TABLE II Basic Formulas of Composites Using S-OC As Fillers							
		Loadings (phr ^a))				
	NBR	SBR	EPDM				
Rubber	100	100	100				
S-OC ^a	12	12	12				
ZnO	5.0	5.0	5.0				
Accelerator							
TMTD	_	0.2	1.0				
D	_	0.5	_				
DM	_	0.5	_				
М	1.5	_	_				
S	1.5	2.0	1.5				
Antioxidant							
4010NA	2.0	1.0	_				
А	-	-	-				

^a SA : OC is 2 : 10 (wt) in S-OC, and no free SA was added in systems.

Mechanical properties tests were carried out on CMT4104 electric tensile tester (SANS, Shenzhen China) at a crosshead speed of 500 mm min⁻¹ and 23°C according to ASTM D 412-87 method, and the stress–strain curves were drawn simultaneously. The measurements were done as ASTM D 624-81 for tear strength at a crosshead speed of 500 mm min⁻¹. The hardness (Shore A) of the samples was measured by using a Durometer (Yingkou Material Experiment Factory, China) according to ASTM 2240-86.

RESULTS AND DISCUSSION

Microstructure analysis of rubber/OC system

XRD spectrograms of OC, rubber/OC mixes, rubber/OC/SA mixes, and rubber/OC nanocomposites are shown in Figure 1.

The interlayer distance of OC is 2.6 nm, which is related to the modifier (dimethyl dialkyl ammonium) expanding it, from Figure 1(A). Just adding OC to SBR or NBR (rubber/OC mix), the interlayer distance of clay is further expanded from 2.6 nm of OC to 3.6/3.8 nm. Adding other additives and vulcanization (rubber/OC nanocomposites), the distance of clay interlayers is expanded little, for example, from 3.8 to 3.9 nm in SBR system, and from 3.6 to 3.7 nm in NBR system. Obviously, SBR or NBR macromolecule chains can easily intercalate into OC during the mixing process. This should be attributed to strong interactions between polar nitrile groups of NBR or benzene side groups of SBR and amine groups of modifier on surface clay layers.²¹

Although the effects of additives, for example, ZnO and S^{15–19,22} and vulcanization²³ were widely researched in EPDM and IIR systems, they are not so obvious in above systems for adding other additives and vulcanization, the distance of clay interlayers is further expanded little.

Additionally, small peaks at about 4.4° (marked as *) are observed for rubbers/OC mixes or vulcanizates, which are considered as secondary diffraction peaks

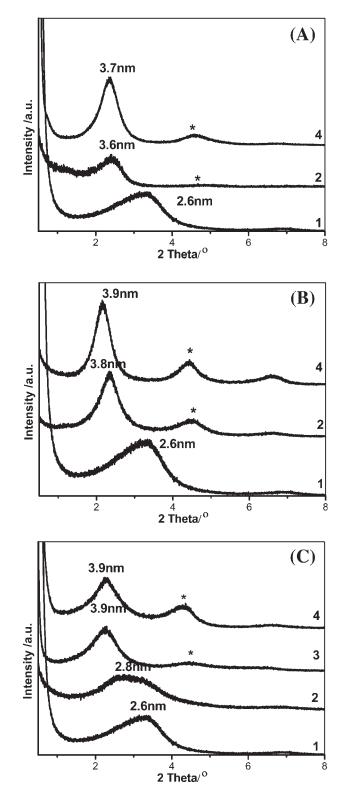


Figure 1 XRD spectrograms of OC, and rubber/OC systems in NBR (A), SBR (B), EPDM (C) matrix: 1, OC powder; 2, rubber/OC mix; 3, rubber/OC/SA mix; 4, OC/rubber nanocomposites.

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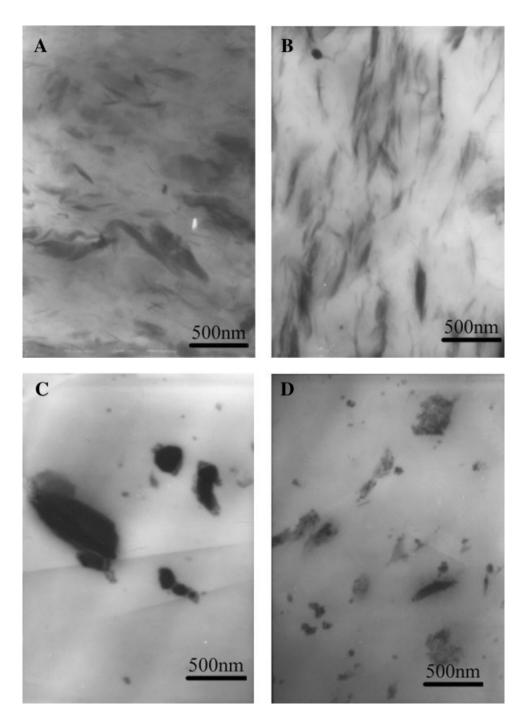


Figure 2 TEM photos of OC/rubber systems: (A) NBR/OC mix; (B) SBR/OC mix; (C) EPDM/OC mix; (D) added SA into sample C.

and related to reflections at higher order.²⁴ If X-ray reflects from the third layers of clay, the parameter *n* in Bragg Law ($n\lambda = 2d \sin \theta$) should be 2, and distance of the peak is the same as the first peak. In fact, scarce of adequate orientation of clay layers, secondary diffraction peaks are not so obvious, for example, OC powder.

In EPDM system [Fig. 1(C)], mixing OC with EPDM, layer distance is expanded only from 2.6 nm

of OC to 2.8 nm, and the full-width-at-half-maximum increases, which is completely different from NBR and SBR systems. OC is the powder that clay particles and layers are blanketed by nonpolar alkyl chains of organic modifier, and there are many aliphatic chains between the interlayer, which have compatibility with nonpolar EPDM macromolecule chains, but the interaction between EPDM and OC (London force) is much weaker than NBR/OC and

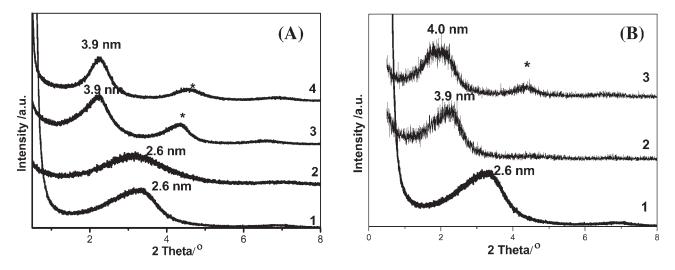


Figure 3 XRD spectrogram of OC, and rubber/OC system in IIR (A), BIIR (B) matrices: 1, OC powder; 2, rubber/OC mix; 3, OC/matrix/SA mix; 4, nanocomposites.

SBR/OC systems. Under shearing force, only few EPDM chains can only enter into the edge of interlayers and expand the parallel arrayed layers to wedge-shaped structure, and thus the array order of interacted structure is poor, leading to the little shift of diffraction peak to low angle and wide full-widthat-half-maximum.

Besides the polarity of macromolecules, flexibility of chains is another factor that influences the efficiency of intercalation.²⁵ Comparing to methyl side groups of EPDM, benzene pendant groups of SBR or nitrile groups of NBR dramatically reduce the flexibility of SBR and NBR, which can be estimated from the glass-transition temperature order of three rubbers: -55.2° C of EPDM $< -52.5^{\circ}$ C of SBR < -16.6° C of NBR (measured by DSC). EPDM macromolecules can coil more easily, and it must overcome more conformational entropy for EPDM when intercalating into the narrow clearance between clay layers. In the meantime, absence of strong interaction with OC, flexible EPDM chains have difficulties in the formation of intercalation structure.

Additionally, if there are enough driving forces for flexible chains to intercalate into interlayers of clay, the interlayer distance should be wider.²⁴ The reason is that the flexible chains entering into interlayers of clay tend to coil to decrease the loss of conformational entropy, and thus further expand the interlayer distance. This can be supported by the XRD results of SBR and NBR systems. Compared to the polar NBR, the unsaturated SBR is more flexible and the interlayer distance of OC (3.8 nm) is larger. On

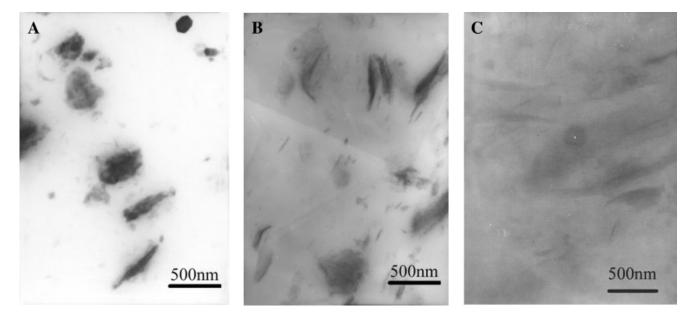


Figure 4 TEM photos of IIR/OC and BIIR/OC systems: (A) IIR/OC mix; (B) IIR/SA/OC mix; (C) BIIR/OC mix.

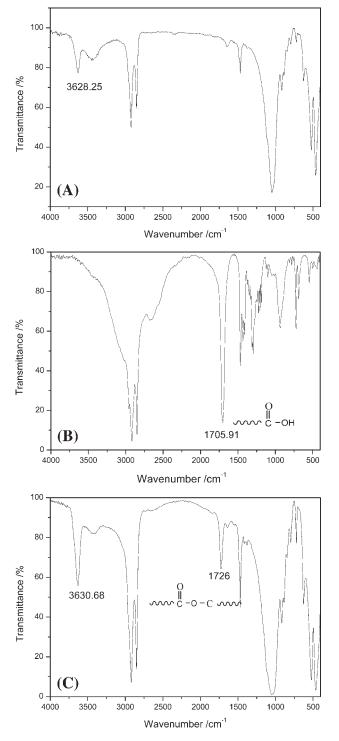


Figure 5 FTIR spectrogram of OC, SA, and SA/OC mixed powders: (A) OC; (B) SA; (C), SA: OC = 2 : 10.

the basis of the above results, the polarity of rubber plays a more important role than flexibility in formation of intercalated structure.

Adding SA to EPDM/OC system on the two-roll mill [Fig. 1(C)] (rubber/OC/SA mix), interlayer distance can be efficiently expanded. As a kind of surfactants, SA has good compatibility with clay, modi-

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fier, and macromolecule. It can not only entangle with macromolecule chain, but also be absorbed on or reacted with the surface structure of silicate

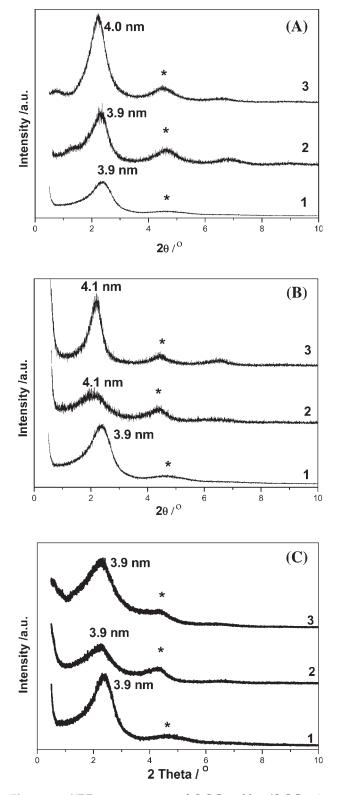


Figure 6 XRD spectrograms of S-OC, rubber/S-OC mix, and rubber/OC vulcanizates in NBR (A), SBR (B), EPDM (C) matrices: 1, S-OC powder; 2, rubber/S-OC mix; 3, vulcanizate of samples with other ingredients except SA added.

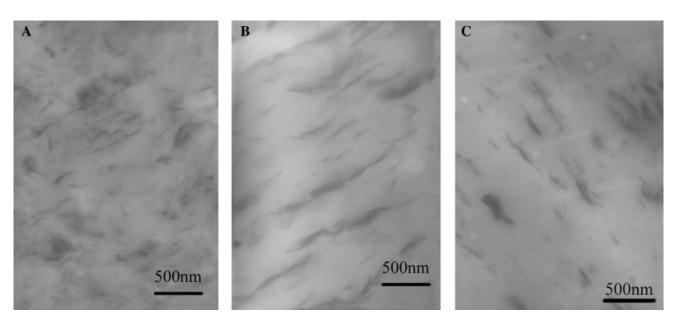


Figure 7 TEM photos of (A) NBR/S-OC mix; (B) SBR/S-OC mix; (C) EPDM/S-OC mix.

(which will be discussed below), forming strong interaction and expanding interlayer distance.

To further make sure of the OC dispersion in the above system, TEM observations were performed. The results are shown in Figure 2. In the photos, the light areas are the rubber matrix, while dark lines are clay layers.

From the TEM photos, clay layers disperse as many thin layers or single platelets in NBR and SBR systems. For the EPDM/OC mix, clay layers stack and flocculate to form large aggregates [dark block in Fig. 2(C)]. When SA is added, the aggregates disperse to many smaller blocks, or even disperse to some thin layers, which are shown in Figure 2(D). These results are consistent with those of XRD.

To further testify the influence of the polar matrix, the similar tests are done in IIR and BIIR matrices.

The interlayer distance of clay in IIR/OC mix is only 2.6 nm. Adding SA can expand it, as Figure 3 A-3, while the interlayer distance of clay in BIIR/OC mix is expanded to 3.9 nm and the distance is further expanded to 4.0 nm when adding all ingredients and curing.

IIR is a kind of saturated nonpolar rubber with flexible chains. Using it as matrix, the intercalation structure should be difficult to form, which is the same as EPDM matrix: interlayer distance in rubber/OC mix is not expanded unless adding SA.

If Br—C structure is introduced to partly replace H—C structure in macromolecules, the polarity of macromolecule increases, and the flexibility of chains decreases, simultaneously. So BIIR can easily intercalate into the interlayers of clay, like that in SBR and NBR systems. The phenomenon that distance is further expanded to 4.0 nm in Figure 3 B-3 should be

attributed to the effect of additives, for example, addition of SA.

Analyzing TEM photos (Fig. 4), the similar conclusion can be drawn that in the nonpolar saturated IIR system, the clay layers form some smaller agglomerates, while, adding SA, the layers' dispersion is improved; in BIIR system, just mixing OC with matrix, the clay layers disperse as thin slice. The phenomena prove that the polarity of matrix has a strong effect on the intercalation structure of clay. In fact, the similar phenomena was reported by Tsou and Measmer,²⁰ when they used different isobutylene-based elastomers to prepare the elastomers/OC nanocomposites.

FTIR analysis

In nonpolar saturated matrix, adding SA can promote the formation of intercalation structure. To find out the interaction between OC and SA, FTIR test is carried on.

FTIR spectrums of OC, SA, and S-OC at the ratio 2 : 10 of SA to OC are shown in Figure 5. According to Figure 5(A), there are no peaks corresponding to C=O structures, which is consistent with the structure of OC. The negative peak at 1706 cm⁻¹ in Figure 5(B) refers to the C=O structure of carboxylic groups in SA. With S-OC, the corresponding negative peak is shifted to 1726 cm⁻¹, which means that carboxylic groups are esterified by hydroxy groups of OC layers [Fig. 4(C)]. This esterification between SA and OC can be the driving force for SA intercalating into OC to expand the spacing of OC.

Referring to XRD spectrograms, adding SA to nonpolar rubber/OC mix can efficiently expand the interlayer distance of clay, the reason is SA molecules themselves can intercalate into interlayers of clay. Dimethyl dialkyl ammonium molecule between the clay layers can expand the interlayer distance from 1.0–1.2 nm to 2.6 nm, but without enough driving force, the distance is still too small for nonpolar macromolecules to intercalate into. In EPDM or IIR/ OC system, the parallelly arrayed layers are just expanded to wedge-shaped structure, and macromolecular chains could stay at the edge of interlayers. When SA is added into the system, esterification between SA and hydroxy group helps SA entering into the interlayers and expanding the distance, and the interaction between clay layers is weakened. Under the shearing force, some clay can be exfoliated to smaller aggregates while the small aggregates can agglomerate to form incompact agglomerates, and EPDM chains between exfoliated single layers are also kept between the interlayers.

The effect of SA on microstructure of rubber/OC systems

To further clarify the effect of SA, S-OC is added to three rubbers: NBR and SBR as polar and unsaturated matrices and EPDM as nonpolar one. IIR is not investigated further, for IIR and EPDM are both nonpolar saturated rubber and the above results of them are so similar.

Since the temperature is higher than the melting point of SA, the matter, as the liquid state, has better mobility and better activity. According to the FTIR result, SA can esterify with hydroxyl groups, and S-OC can be regarded as OC intercalated by SA. This intercalated structure can be observed in Figure 6.

XRD spectrogram clearly shows that the S-OC is the structure of SA intercalation into OC, and the interlayer distance is 3.9 nm, nearly the same distance as that in EPDM/OC mix, indicating that the matter between interlayers of clay is SA instead of EPDM, and for EPDM it is difficult to form intercalated structure. If adding S-OC to polar or unsaturated matrix, the diffraction peak is shifted to the lower angle, indicating that even for the intercalated OC by SA, macromolecule chains can enter into and further expand the clearance.

TEM is used to observe the microstructure of relative mixes, and the photos are shown in Figure 7.

Comparing the photos in Figure 2, dispersions of S-OC in all kinds of matrices (polar, unsaturated, and nonpolar saturated rubbers) are all much better, because crowded SA molecules have packed all the surface of clay layers in S-OC to promote the compatibility between rubber and clay.

At the same time, it should be noticed that the interlayer distance of clay in SBR is larger than in NBR, but the dispersion of clay in the latter is better.

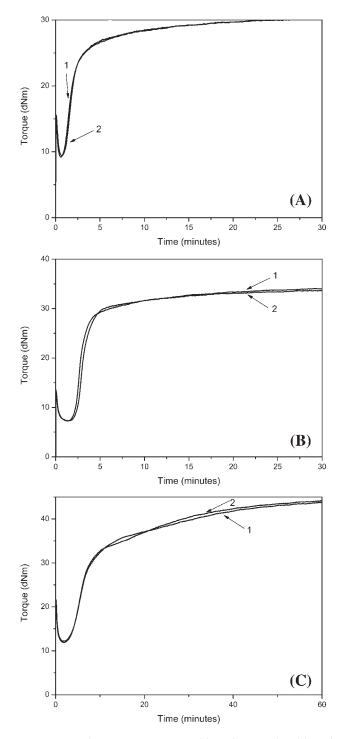


Figure 8 Vulcanization curve rubbers/OC and rubbers/ S-OC nanocomposites in (A) NBR, (B) SBR, (C) EPDM matrices: 1, rubber/OC nanocomposites; 2, rubber/S-OC nanocomposites.

As mentioned earlier, the interaction between OC and matrix is the polar (NBR)>the unsaturated (SBR)>the nonpolar and saturated (EPDM). The larger the interaction is, the more the intercalating chains is, and the better the dispersion is. However, the flexibility of macromolecules determines the

	Mechanical Properties of OC(S-OC)/Rubbers Nanocomposites							
	NBR/OC	NBR/S-OC	SBR/OC	SBR/S-OC	EPDM/OC	EP/S-OC		
Shore A hardness	56	57	59	60	59	60		
Stress at 100% (MPa)	1.4	1.4	1.5	1.6	1.3	1.4		
Stress at 300% (MPa)	3.0	3.7	2.7	3.5	2.0	1.9		
Tensile strength (MPa)	7.8	9.4	7.3	12.8	3.4	4.2		
Elongation at break (%)	589	570	452	475	419	444		
Permanent set (%)	14	14	10	12	8	12		
Tear strength (kN/m)	27.4	28.1	20.5	21.7	15.5	15.5		

TABLE III Aechanical Properties of OC(S-OC)/Rubbers Nanocomposites

interlayer distance, so the order of interlayer distance of clay in different matrix should be EPDM>SBR>NBR. Obviously, from TEM and XRD results, EPDM can not form intercalated structure, but can expand part of clay layers to single layers (exfoliate structure) because of the coil of flexible chains decreasing the loss of conformational entropy, which should be further investigated.

As described earlier, using macromolecules with nonpolar and flexible chains, the matrix chains are difficult to intercalate into interlayers of clay, and the intercalation structure is caused only by SA. Using polar macromolecules as matrix, polymer chains can easily intercalate into the interlayers of layer, and effect of SA is not excluded.

For NBR and SBR systems, macromolecules intercalate into clay to prepare intercalated nanocomposites, while for EPDM system, the genuine structure should be: single layers and smaller aggregates of SA/OC intercalated structure dispersed in matrix.

Vulcanization properties analysis

As described earlier, the processes of adding the additives in the rubber/OC and rubber/S-OC system are different: for the former, SA was directly added to the rubber/OC mix on the two-roll mill; while for the latter, SA was mixed with OC in homomixer and then was added to rubber on the two-roll mill. However, all the components, including the sorts and loadings, are the same, so the vulcanization should not be affected. To make sure about this, the vulcanization curves are analyzed.

From Figure 8, the curves clearly show that the vulcanization is not affected by the different processes of adding those additives, as the estimation above: the curves of rubber/OC composites and the ones of rubber/S-OC composites are nearly superposed. According to the curves, the curing structures of these are nearly the same.

Mechanical properties analysis

To further clarify the effect of SA on dispersion of clay layers, mechanical properties of rubbers/OC/

(S-OC) nanocomposites are carried on. The results are shown in Table III.

From Table III, parts of the mechanical properties, like hardness and tear strength, are insignificantly different, which can be explained by the similar crosslinking structures.

But the tensile properties are the different: rubber/S-OC have better tensile strengths and larger stresses at low strain, which is more clearly displayed in Figure 9.

From Figure 9, replacing the filler OC with S-OC, the tensile strengths of the nanocomposites are enhanced in different degrees (7.8–9.4 MPa for NBR, 7.3–12.8 MPa for SBR, and 3.4–4.2 MPa for EPDM). This is related to the dispersion of clay. During the tensile process, the silicate layers will be arrayed to improve the orientation of macromolecules, and better tensile properties of nanocomposites can be obtained.²⁶ Obviously, in those systems, there are more single clay layers or thin layer aggregates, and the tensile strengths are better.

For nonpolar saturated EPDM, the stresses at low strains of those samples using OC or S-OC are not obviously different and the curves are almost the same. However, for polar NBR or unsaturated SBR,

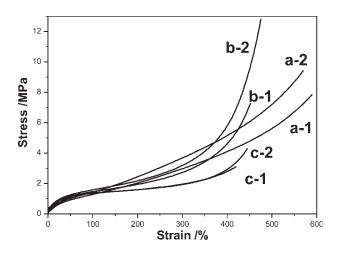


Figure 9 Stress–strain curves of rubbers/OC and rubbers/S-OC nanocomposites in NBR (a), SBR (b), EPDM (c) matrices: 1, rubber/OC nanocomposites; 2, rubber/S-OC nanocomposites.

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the stresses at low strains are different, and curves of samples using S-OC are obviously higher at the same strains. It is still related to the characteristic of macromolecules: the interfacial interaction between OC and EPDM matrix is mainly physical, and adding SA can increase the dispersion of OC, but can not strengthen the interfacial interaction; the interaction between OC and NBR or SBR is much higher and adding SA can increase the dispersion of OC and increase the area of interface to further strengthen the interfacial interaction.

The permanent sets of rubber/S-OC nanocomposites are larger, because the orientation of macromolecules is more obvious, as described earlier, which confines the restoration of the strains after the samples are broken and the tension is removed.

CONCLUSIONS

Polar or unsaturated matrices (e.g., NBR, SBR, and BIIR) can easily enter into OC layers, but nonpolar and flexible macromolecules (e.g., EPDM and IIR) can not. For the latter, the intercalation structure in final composite is composed of SA and OC. TEM observation shows that the dispersion morphology of NBR and SBR systems are much better than that of EPDM systems. Comparing IIR and BIIR, the same conclusion can be drawn that clay disperses better in polar matrix. When using S-OC as fillers, XRD spectrograms and TEM photos show in NBR and SBR systems, macromolecules and SA can both intercalate into clay to prepare intercalated nanocomposites, while in EPDM system, the genuine structure should be: single layers and smaller aggregates of SA intercalating into OC dispersed in matrix, and EPDM can not form the real stable intercalated structure. The esterification between SA and hydroxy group on clay layer is the driving force.

Changing the fillers from OC to S-OC, tensile strengths are all improved in these systems, which are related to the better dispersion of clay. However, the stresses at low strain of those samples are nearly the same in EPDM systems, but are improved in NBR and SBR systems, which are related to the different interfacial force between OC and macromolecules.

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