

Clay Nanolayer Reinforcement of *cis*-1,4-Polyisoprene and Epoxidized Natural Rubber

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ABSTRACT: Conditions were established for dispersing clay nanolayers into both *cis*-1,4-polyisoprene (synthetic) natural rubber (NR) and epoxidized natural rubbers (ENR) having 25 or 50 mol % epoxide. The clay was a sodium montmorillonite and was used as a pristine layered silicate or as organically modified layered silicates to make the galleries more hydrophobic and thus more compatible with the elastomers. The chemical modifications were carried out using an ion-exchange reaction with alkyl ammonium cations. Incorporation of the clays into the elastomers was achieved by mixing the components themselves in a standard internal blender or by mixing dispersions of them in toluene or methyl ethyl ketone. X-ray diffraction results indicated intercalation of NR and ENR into the silicate interlayers, followed by exfoliation of the silicate layers into the elastomer matrices. Of primary interest was the effect of the intercalated and exfoliated clays on the mechanical properties of the elastomers. The reinforcing effects obtained were found to depend strongly on the extent of the dispersion of the silicate layers into the rubber matrices. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1391–1403, 2001

Key words: elastomers; clay reinforcement; nanocomposites; modulus; tensile strength; elongation at break

INTRODUCTION

A variety of clays are now being used to obtain unusual nanocomposites, by exploiting the ability of the clay silicate layers to disperse into polymer matrices at the nanoscale level. The resulting clay polymer nanocomposites exhibit properties very different from their conventional counterparts. Some of the advantages of nanocomposites are improvements in the mechanical properties, heat

stability, flame retardance, gas-barrier properties, abrasion resistance, and solvent resistance. These improvements can be achieved at remarkably low clay contents.

The first such clay-based composites were synthesized by a Toyota research group^{1,2} and involved a polyamide as the polymeric phase. This work was expanded to the point that now there are numerous nanocomposites prepared using either clays or a variety of related layered materials. These include a wide variety of other polymers, including polystyrene,^{3–5} poly(ethylene oxide),^{4,6} polypropylene,^{5–11} polydimethylsiloxane,^{12,13} polycaprolactone,¹⁴ polyurethanes,^{15,16} methyl methacrylate copolymers,¹⁷ styrene–acrylonitrile copolymers,¹⁸ the polyisobuty-

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lene-bromomethylstyrene copolymer,¹⁹ unsaturated polyesters,²⁰ polyimides,^{21,22} epoxy resins,^{23–26} polyaniline,²⁷ polyhydroxybutyrate,²⁸ nitrile rubber,^{29,30} and a high-performance poly(biphenyl ether triphenylphosphate) polymer.³¹ There has also been interest in both theory and simulations addressing the preparation and properties of these materials.^{32–39}

The crystal structures of clays are unusually interesting in their own right.⁴⁰ For example, the clay montmorillonite consists of a dioctahedral aluminum sheet sandwiched between two silica tetrahedral sheets in a layer structure that is ~1 nm thick. Stacking of the layers leads to a regular van der Waal's space between the layers called an interlayer or gallery. The primary particles themselves consist of 10–20 layers in a coplanar orientation (usually referred to as the tactoid formation). Clay particles can associate through face-to-face, face-to-edge, and edge-to-edge bonding to form aggregates and agglomerates. Clay has the ability to undergo extensive interlayer expansion or swelling, exposing a large active surface area, permitting guest molecules to enter into the galleries. Interlayer cations such as Na⁺, Ca⁺⁺, and K⁺ exist on the internal surfaces, but can be exchanged with alkyl ammonium cations to give surfaces that are less ionic or polar.⁴⁰ Such organically modified galleries are more easily penetrated by polymers (either in the molten state or in solution) or by monomers that are subsequently polymerized *in situ*. These entering guest molecules can either simply increase the distances between the still-parallel layers in an "intercalation" process or randomly disperse the separate sheets entirely in an "exfoliation." Either type of dispersion occurs at the molecular level and the resulting materials are therefore justifiably called "nanocomposites."

There are essentially no reports on the use of nanolayered silicates in natural rubber (NR) itself or in its synthetic analog *cis*-1,4-polyisoprene. The effects of the clays on any properties of these rubber composites is unexplored, even though one effect could well be the reduction of air permeability in rubber tires. For these reasons, the present investigation involved introducing nanolayers of a montmorillonite clay into both nonpolar synthetic NR (*cis*-1,4 polyisoprene) and NR modified by epoxidation. The epoxidized natural rubber (ENR) has epoxy groups that are randomly distributed along the chain backbones, which gives it increased polarity and higher glass transition temperatures

(T_g 's). The increased polarity is of particular interest in the present context since it frequently facilitates reinforcement by fillers without the need for coupling agents.^{41–43} This investigation focused specifically on clay composites in which NR or ENR was introduced by mixing solutions of the elastomer with the organically modified clays, to obtain both intercalated and exfoliated materials.

EXPERIMENTAL

Materials

Synthetic NR, *cis*-1,4-polyisoprene (Natsyn 2200), was supplied by the Goodyear Tire and Rubber Co. (Akron, OH). Commercial-grade ENRs having 25 or 50 mol % epoxy groups (ENR25 and ENR50) were provided by Guthrie Latex, Inc. (Tuscon, AZ). A reference filler material, precipitated silica (Hi-Sil 233), was provided by the Harwick Co. (Akron, OH). The clay used in this work was sodium montmorillonite (Na-Mt), and both pristine samples and organically modified versions were supplied by Southern Clay Products (Gonzales, TX). The organic modifications were carried out using cation-exchange reactions between Na-Mt and the alkyl ammonium cations which are described in detail in Table I. The organically modified clays used in this work were bis(2-hydroxyethyl)methyl tallow ammonium montmorillonite (C1), dimethyl dihydrogenated tallow ammonium montmorillonite (C2), and dimethyl hydrogenated tallow (2-ethylhexyl)ammonium montmorillonite (C3). These organic modifications increased the interlayer distances of the layered silicates from the original value of 11 Å (as provided by the supplier) to 23 Å for C1 to the ranges 18.3–19.5 Å for C2 and 28.6–30.2 Å for C3.

Preparation of Samples

The clay loading used in polymer-clay composites is usually less than 10 wt %. In this investigation, the amounts of clay or organically modified clays were 10, 20, and 30 parts per hundred (phr) of rubber. Mixing of pristine clay (Na-Mt) or silica with rubbers was accomplished using a Brabender mixer at a temperature setting of 100°C. The mixing of the organically modified clays with ENR50 or Natsyn, however, was facilitated by the use of solvents. Specifically, ENR50 rubber was dissolved in methyl ethyl ketone (MEK) and synthetic NR (Natsyn) was dissolved in toluene. The

Table I Some Characteristics of the Clay and Its Modifications

The Clay and Its Organic Modifications	Organic Modifiers ^a	Losses on Ignition (%)
Na-Mt	—	6
C1	(CH ₃)N ⁺ (R)(CH ₂ CH ₂ OH) ₂	32
C2	(CH ₃) ₂ N ⁺ (R _h)CH(CH)(C ₄ H ₉)	34
C3	(CH ₃)N ⁺ (R _h) ₂ CH(CH)(C ₄ H ₉)	43

^a R represents the tallow (65% C18, 30% C16, and 5% C14), and R_h represents the same tallow after hydrogenation.

modified clays were swollen in toluene and then mixed with either of the elastomer solutions with vigorous stirring. The solvents in the resulting dispersions were then evaporated and the samples dried under a vacuum. The resulting clay or silica-filled rubbers were mixed with the additives and then with sulfur in a Brabender mixer at a temperature not exceeding 60°C. The formulations are described in detail in Table II. The vulcanizations were carried out in a standard hot press at 150°C for 30 min.

Characterization Techniques

Wide-angle X-ray diffraction (XRD) was used to study the nature and extent of the dispersions of the clays in the filled samples.⁴⁴ The XRD patterns were obtained using an X-pert diffractometer (Phillips), at the wave length CuK α = 1.54 Å, with the scattering shown as a function of the scattering angle. Dynamic mechanical analyses (DMA) were carried out on the uncured compounds using an RPA2000 mechanical spectrometer (Alpha Technologies, Akron, OH).⁴⁵ Tensile

properties were obtained using an Instron Tester (Instron, Acton, MA) on dog-bone-shaped samples having a length of 33 mm, a width of 5.7 mm, and a thickness of 2 mm. The strain rate was 500 mm/min.

All tests were repeated several times on different samples, using identical procedures to test for reproducibility. The results were essentially indistinguishable for the XRD and DMA tests, and none of the differences in the tensile properties exceeded 5%.

RESULTS AND DISCUSSION

Morphologies from the XRD Results

These XRD results bear on the regular arrangements of silicate layers in both pristine or intercalated forms and the irregular arrangements in the case of complete exfoliation of the layers.⁴⁰ Figure 1 shows the X-ray diffraction patterns for the melt-blended compounds of epoxidized rubbers and pristine clay (Na-Mt).⁴⁴ As usual, the 2θ values along the abscissa can be converted to layer spacing values d through the Bragg relationship ($l = 2d \sin \theta$, where l is the wavelength of the radiation). In both the ENR25- and ENR50-filled elastomers, peaks were observed in the two angular ranges corresponding to spacings of 30–32 Å and 12–14 Å, respectively. This indicates that mechanical mixing above the melt facilitated the intercalation of ENR into the galleries of the clay. When the Na-Mt loading was small (10 phr), the interlayer distances in ENR25 and ENR50 were around 31.7 and 14.0 Å and 32.7 and 13.0 Å, respectively. For 30 phr clay Na-Mt loading, the interlayer distances for ENR25 and ENR50 were 30.8 and 11.3 Å and 31.9 and 11.9 Å, respectively.

Table II Compound Formulations

Ingredient	I	II	III
ENR25	100	—	—
ENR50	—	100	—
Natsyn	—	—	100
Sulfur	1	1	1
Stearic acid	2	2	2
Zinc oxide	5	5	5
Calcium stearate	2	2	—
MBT ^a	—	—	1
CBS ^b	1	1	—
Fillers ^c	—	—	—

^a Mercaptobenzothiazole.

^b *N*-Cyclohexyl-2-benzothiazolesulfenamide.

^c Various fillers were employed, as described in the text.

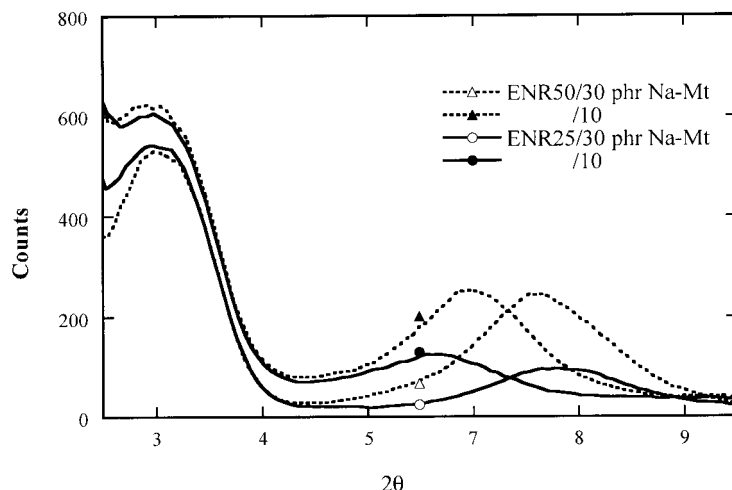


Figure 1 X-ray diffraction patterns for compounds of ENR with Na-Mt prepared by blending the components in a Banbury mixer. Here and throughout, the first number in the designation specifies the mol percent epoxy groups in the elastomer, and the second number specifies the parts per hundred (phr) of the dispersed phase.

The extent of intercalation depends on the polymer transport processes through the agglomerate micropores, the agglomerate size, the diffusion of the elastomer chains within the silicate galleries, and the nature of the elastomer itself. For example, more intercalation occurs in the case of ENR50, which has a higher polarity. This intercalation of ENRs into the clay galleries occurred for a portion of the clay filler where the rubbery polymer was exposed to the silicate layers, and this increased the interlayer distance from 11 to 30–32 Å. Some additional swelling occurred in other regions, but this ap-

parently increased the interlayer distance by only 1 or 2 Å. Although the extent of intercalation is thought to be independent of the filler concentration, in most cases, usually less than 10% w/w, increased clay loadings from 10 to 30 phr led to less intercalation of the polymer into the galleries of the silicate layers, which means smaller interlayer distances.

More pronounced intercalation was achieved by using solutions for the mixing of the elastomers and clays. The organically modified clay is able to swell in organic solvents due to its long alkyl chain modification. In the case of the

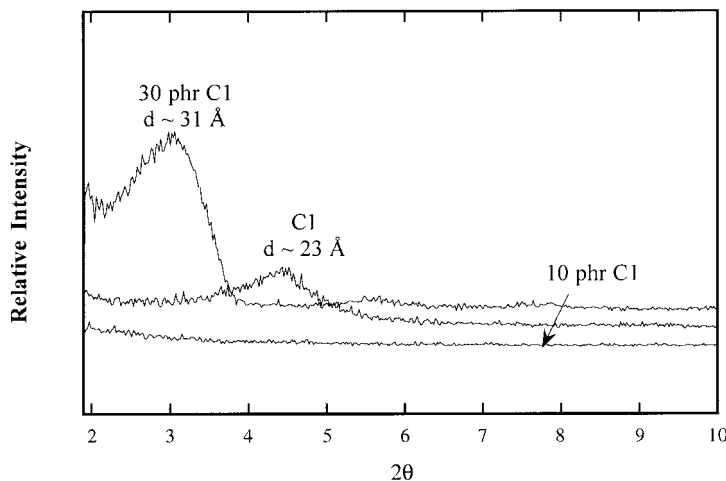


Figure 2 X-ray diffraction patterns for compounds of ENR50 with organo-modified clay prepared by solution mixing.

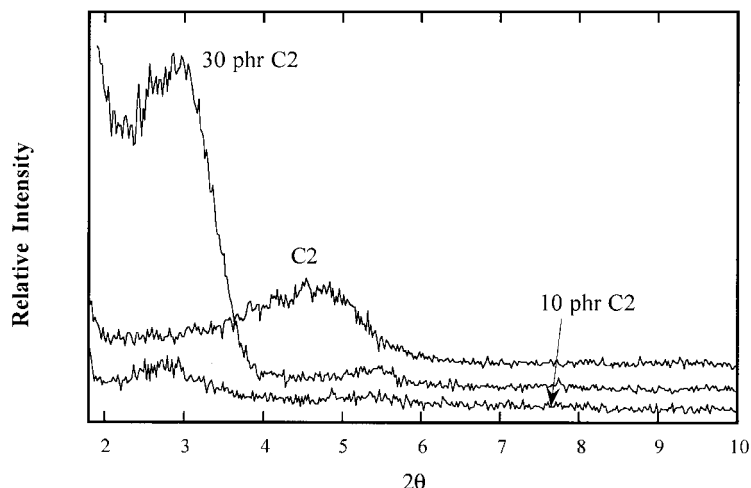


Figure 3 X-ray diffraction patterns for compounds of ENR50 with organo-modified clay C2.

ENR50 compounds with 10 phr organically modified clays, no peaks were observed in its XRD pattern for the C1 compound, as shown in Figure 2. This indicates that sufficient rubbery polymer was introduced into these galleries so that the layers were exfoliated (dispersed into random arrangements). For the compound with 10 phr C2, the interlayer distance was increased by 12 Å, specifically from 18.3–19.5 to 30–32 Å, as shown in Figure 3. The difference in filler dispersion of the two clays presumably resulted from the different organic modifiers. Organically modified clay C1 would be expected to have better compatibility with ENR50 than

does C2, since the alkyl ammonium chains of C1 contain polar groups.

Clays with long alkyl-chain modifications (C2 and C3) were chosen for reinforcement of synthetic NR (Natsyn). The interlayer distance of organically modified clay C3 was in a range 28.6–30.2 Å, as shown in Figure 4. A broad peak around 35.0–36.0 Å was observed in the XRD patterns for the compound with 10 phr C3. This indicates that the intercalation of Natsyn into the organically modified clay was pronounced, with some of the clay possibly being exfoliated into the elastomer matrix. Extensive intercalation was also observed for the C2 compound at

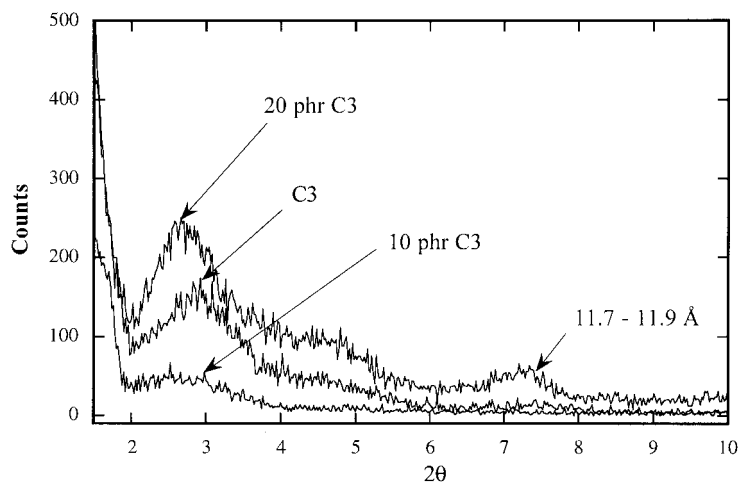


Figure 4 X-ray diffraction patterns for compounds of synthetic NR, Natsyn, with organo-modified clay C3.

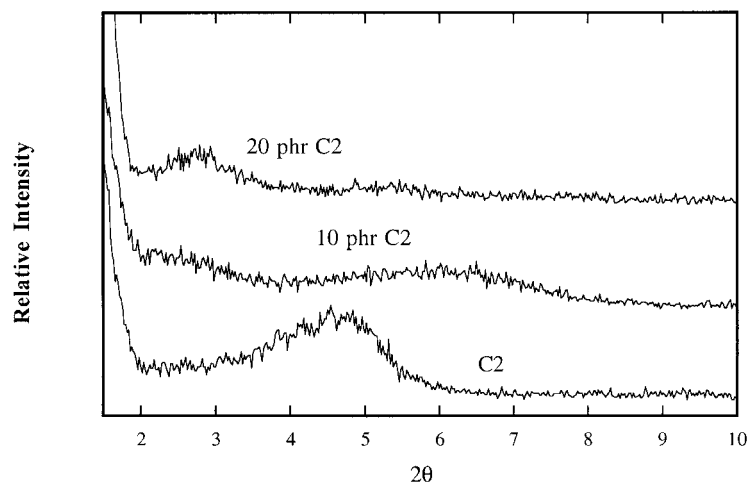


Figure 5 X-ray diffraction patterns for compounds of synthetic NR, Natsyn, with organo-modified clay C2.

10 phr, as can be seen in Figure 5. When the organically modified clays were present to the extent of 20 phr in the Natsyn elastomer, the interlayer distance was 33.2–34.2 Å for the C3 compound. The peak corresponding to 11.7–11.9 Å may be attributed to an unmodified part of the C3. For organically modified clay C2, Natsyn increased the interlayer distance from 18.3–19.5 to 30.1–31.6 Å, as shown in Figure 5, indicating that the amount of the intercalated polymer is greater for C2 than that for C3.

Thus, there is intercalation of rubber (ENR or Natsyn) into the interlayers of either the pristine clay or the organically modified clays, by mixing above the melt or by solvent, with corresponding increases in the interlayer distances. Extensive intercalation was obtained for the ENR50 and Natsyn compounds at 10 phr loading of organo-modified clays.

Dynamic Mechanical Properties

Relationship to the Morphologies of the Materials

These results focus on the strain dependence of the elastic storage modulus G' and $\tan \delta$ (which is the ratio of loss modulus G'' to G'). Since the dynamic tests were run on uncured compounds, the storage modulus is determined by polymer-to-filler interactions, hydrodynamic reinforcement, and filler secondary structures.^{46,47} For a conventional particulate filler such as silica or carbon black, the interactions between the elastomer and the filler occur on the surfaces of the fillers, as illustrated in Figure 6(a). “Bound rubber” is made up of elastomeric chains adsorbed onto the surface to the extent that they cannot be extracted by a solvent and can exhibit significantly elevated glass transition temperatures (T_g 's). This is one aspect of filler–elastomer behavior that indicates

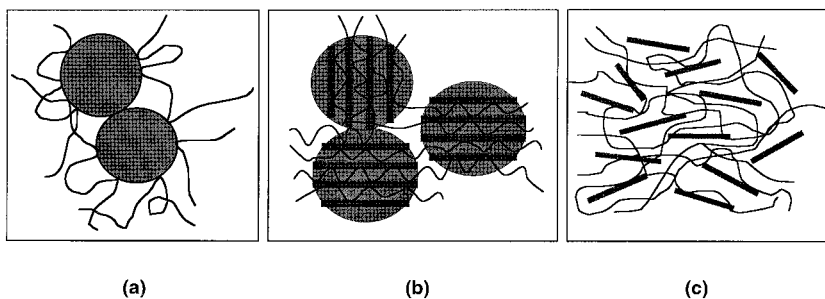


Figure 6 Schematic showing (a) adsorption of polymer onto conventional fillers (bound rubber), (b) intercalation of polymer into silicate layers, and (c) extensive intercalation or exfoliation of silicate nanolayers into a rubber matrix, giving a very large surface area from a small amount of the clay filler.

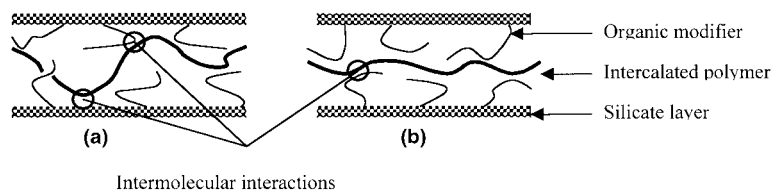


Figure 7 (a) Polymer–filler interactions for an intercalated polar elastomer–organo-modified clay system; (b) polymer–filler interactions for an intercalated nonpolar elastomer–organo-modified clay system.

particularly strong interactions.^{48–50} In the present context, elastomer chains intercalated into the layered structures, as illustrated in Figure 6(b), could be considered bound rubber, with analogous changes in the T_g . Polymer–filler interactions also include (i) interactions of intercalated polymer chains with surface layers of pristine clay filler in the case of Na–Mt and (ii) secondary interactions with the long alkyl groups in the case of the organically modified clays. This is illustrated in Figure 7.

Hydrodynamic reinforcement is frequently present in the case of conventional particulates, and arises from increase in the viscosity in the case of a liquid or increase in the modulus in the case of a polymer matrix, upon introduction of a filler. Hydrodynamic reinforcement is a function of the filler-volume fraction and the shape factor of the filler particles.^{47,48,51,52} The shape factor, as described by Guth,⁵¹ is the ratio of the longest dimension of the particle to the shortest. Thus, the shape factor would be very large for those silicate layers exfoliated into a polymer matrix. An effective volume

fraction (instead of theoretical volume fraction) which takes into account the polymer chains immobilized by adhesion and occlusion has been used to describe the effect of an active filler on elastomer properties.⁵³ The effective immobilization of these chains is thought to make them more a part of the filler rather than of the polymer. Thus, hydrodynamic reinforcement is largely dependent on the filler surface area, surface energy, and aggregate structures.^{47,48,51,52,54} The intercalation of a polymer into silicate interlayers increases the active surface area of the filler. In addition, polymer layers confined between silicate layers are immobilized; thus, intercalation also increases the effective volume. The increased effective volume of modified clays includes the modifier and the amount of the intercalated polymer.

The effect of the filler secondary structure, or the filler-networking effect, arises from the tendency of filler aggregates to form agglomerates or chainlike filler networks, especially at high filler-volume fractions. Such interparticulate networks are usually broken down under applied dynamic strains. The

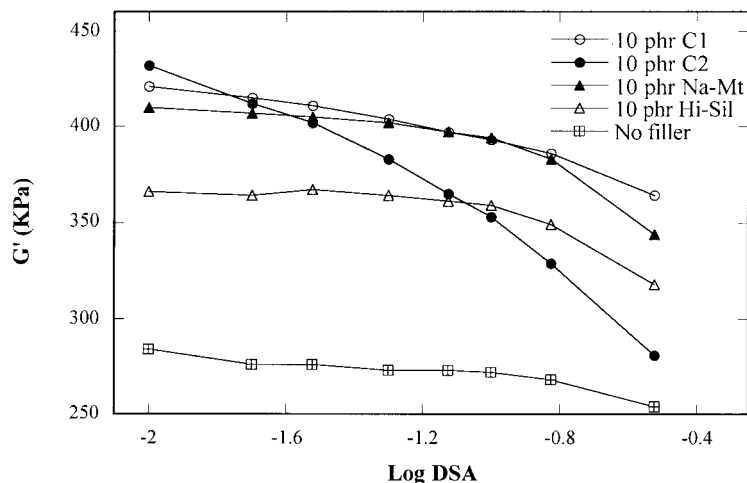


Figure 8 Strain dependence of G' at 50°C and 5 Hz for ENR50 compounds with 10 phr of various fillers. DSA is the dynamic strain amplitude.

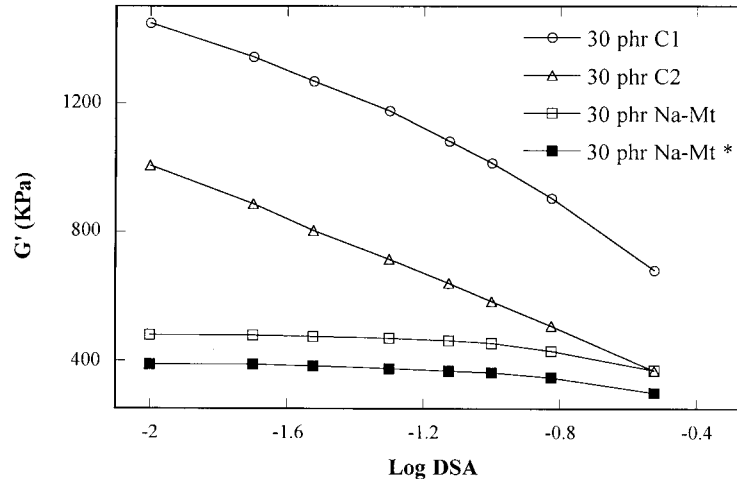


Figure 9 Strain dependence of G' at 50°C and 5 Hz for ENR50 and (*) ENR25 compounds with 30 phr filler.

breakdown of the filler network caused by increasing the strain amplitude leads to a decrease in the modulus, generally termed the “Payne effect.”⁵⁵ The filler-networking effect depends on filler–filler interactions, aggregate spacings, and filler–polymer interactions.^{47,54,56} Silica has a strong Payne effect due to its significant filler–filler interactions and weak polymer–filler interactions.^{47,54–57} The organic modification and the intercalation change the chemistry and structure of the clay particles. Thus, these changes have effects on the filler secondary structure.

Storage Moduli

The present results were put into context by some results on the silica (Hi-Sil) reference material.

Figure 8 shows the effect of the dynamic strain amplitude (DSA) on the storage modulus for compounds of ENR50 at 10 phr filler loading. Although the change in storage modulus values was not profound at this small filler loading, some effects of the filler structures and morphologies on the storage modulus were observed. The higher storage modulus of the compound ENR50 with Na–Mt in comparison to that of compound with Hi-Sil possibly results from a greater hydrodynamic reinforcement due to the intercalation of the polymer into the galleries of the Na–Mt. With an identical Na–Mt loading, the storage modulus of ENR50 was greater than that of ENR25.⁴⁴ This result can be attributed to stronger polymer–filler interactions in the more polar ENR50. The stor-

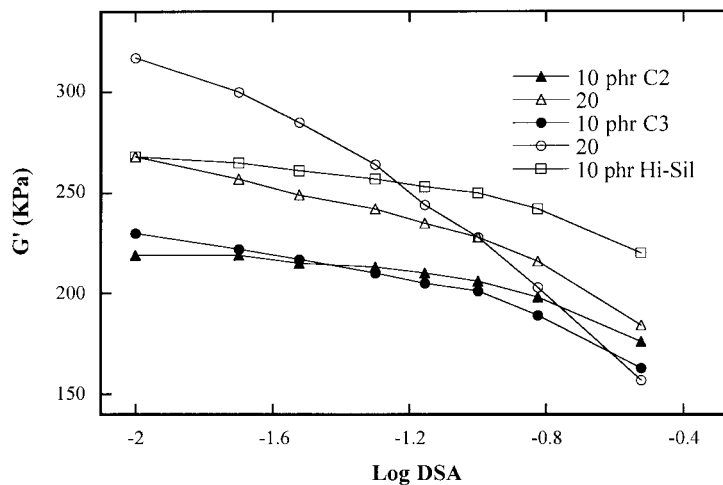


Figure 10 Strain dependence of G' at 50°C and 5 Hz for NR compounds with different organo-modified clays.

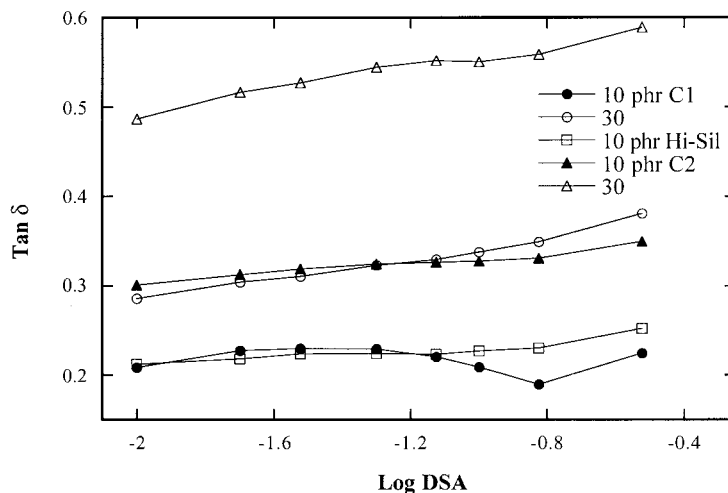


Figure 11 Effect of organo-modified clay loading on the strain dependence of $\tan \delta$ at 50°C and 10 Hz for ENR50 compounds.

age modulus also shows the expected increase with increasing clay-filler loading.⁴⁴

In the case of the organically modified clays, it should be noted that the filler loadings cited include the organic modification layers. Their relative contributions can be gauged from the ignition losses given in Table I. Although the filler-networking effect (decrease of G' with increasing DSA) was not strong at 10 phr loading, some filler network may still exist, especially for the C2 compound. The intercalation of the rubbery polymer into the galleries of C2 expanded the clay particles. The expansion of the filler particles increased the filler volume so that more filler networking occurred. However, at the same filler loading, the storage modulus of the compound with C1 was rather constant with increasing DSA. This indicates that a filler-networking effect did not exist. As seen in the XRD pattern of the 10 phr C1 compound (Fig. 2), the elastomer was extensively intercalated and it disrupted the regular stacked-layer structure of the clay. When the primary clay particles were dispersed into individual layers as illustrated in Figure 6(c), the aggregates and agglomerates that were formed from the primary particles disappeared. The extensive intercalation or exfoliation of C1 increased the filler active surface while it broke up the filler secondary structure. In addition, the storage modulus of the 10 phr C1 compound at large-strain deformations is higher than that obtained using silica, because of a greater hydrodynamic reinforcement from an increase in the filler surface area due to exfoliation. The fact that C1

gave a higher storage modulus than did C2 was due to its larger active surface area and also to the stronger polymer-filler interactions arising from the two OH groups in its organic chains. For such organically modified clay fillers, the interactions depend on the nature of the elastomer matrix and on the chain length and structure of the organic modifiers. Besides interacting with the silicate layers themselves, a polymer would interact with the organic modifiers and a polar polymer can have stronger interactions with a modifier that has polar groups. This stronger polymer-filler effect was more evident at higher loadings as can be seen in Figure 9. The storage modulus of the compound with C1 was larger than that of the compound with C2 over the range of the dynamic strains investigated.

With increase of the filler loading from 10 to 30 phr, a strong Payne effect was observed for both organically modified clays C1 and C2, but not with compounds ENR50 or ENR25/Na-Mt, as shown in Figure 9. This indicates different filler-networking effects, which result from different effective volume fractions. As previously mentioned, the intercalated polymer ENR50 confined within silicate layers was immobilized and acted as a part of the filler, increasing the volume of the clay particles and the extent of the filler networking. While more intensive intercalation was achieved by solvent mixing (the solvent expands the polymer and expands the galleries of the silicate layers, facilitating the intercalation), it is possible that only a small portion of the Na-Mt

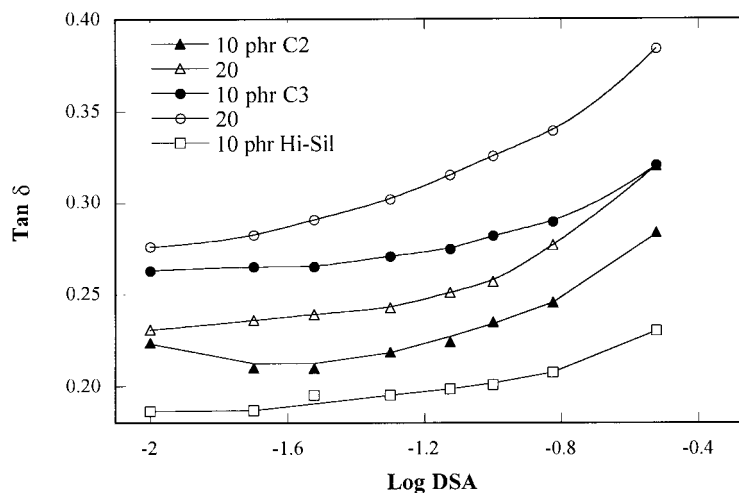


Figure 12 Strain dependence of $\tan \delta$ at 50°C and 10 Hz for NR compounds with various organically modified clays.

filler was intercalated upon being mixed in the elastomer melt.

Figure 10 shows the strain dependence of G' for the nonpolar elastomer, *cis*-1,4-polyisoprene (Natsyn). The storage modulus increased with increasing filler loading, as expected. Overall, the storage modulus of Natsyn and the cited networking effects were much smaller than were those for the polar epoxidized rubber compounds. To an

extent, the organic modification of the clay may play a surface modification role similar to that of silica in the case of nonpolar elastomers. Specifically, surface modification greatly reduces filler–filler interactions, filler-networking effects, and storage moduli at low strains.^{54,55} With the same filler loading, 20 phr, a stronger filler networking effect was observed for C3 compounds having larger interlayer distances. As usual, the filler-

Table III Tensile Properties

Compounds	Modulus at 100% Strain (MPa)	Modulus at 300% (MPa)	Tensile Strength (MPa)	Elongation at Break (%)
ENR50				
10 phr Hi-Sil	1.17	3.08	16.3	683
10 phr Na–Mt	1.34	3.48	15.2	661
20 phr Na–Mt	1.87	5.17	16.1	600
30 phr Na–Mt	3.07	7.83	15.2	483
10 phr C1	2.15	4.40	12.6	907
30 phr C1	5.82	9.20	9.89	392
10 phr C2	2.15	4.50	11.8	778
30 phr C2	9.89	—	14.8	274
ENR25				
No filler	0.10	2.36	13.2	690
20 phr Na–Mt	1.73	4.51	16.1	635
30 phr Na–Mt	2.10	5.50	13.9	538
Natsyn				
10 phr Hi-Sil	0.55	1.05	5.01	772
10 phr C2	1.00	2.32	17.7	955
20 phr C2	1.11	2.74	17.0	889
10 phr C3	1.12	2.05	12.8	944
20 phr C3	1.67	3.40	23.4	917

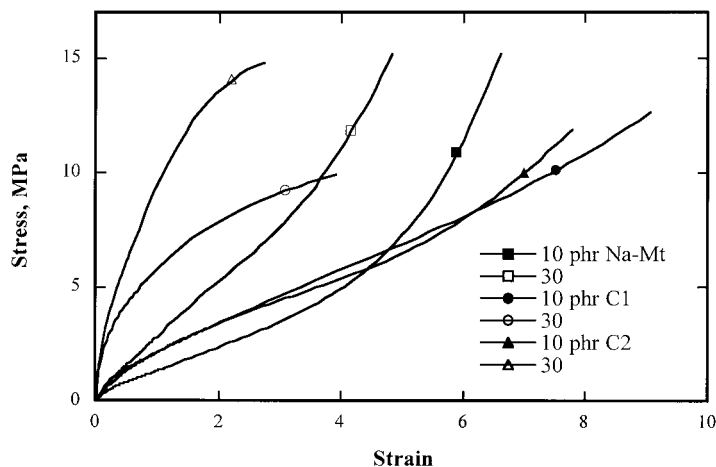


Figure 13 Stress-strain curves in tension for ENR50 compounds with various clay fillers.

networking effect depends on the interlayer distance of the clays, with larger interlayer distances corresponding to larger active volumes and increased filler-network effects.

Values of the Loss Tangent

The quantity $\tan \delta = G''/G'$ represents the ratio of work converted to heat to work recovered, for a given work input. With regard to the filler effect, it is thought that $\tan \delta$ is the ratio of the portion of the filler structure capable of being broken down and reconstituted to the portion remaining unchanged during dynamic strains.^{54,56} The factor governing $\tan \delta$ is thus the state of filler networking, and, in general, the stronger the filler network, the lower the value of $\tan \delta$. For conventional fillers, the hydrodynamic effect on $\tan \delta$ is eliminated by forming the quotient of G'' and G' . Above the glass transition temperature of the elastomer, the $\tan \delta$ obtained using carbon black is higher than that using silica due to its weaker filler-filler interactions and stronger polymer-filler interactions.^{54,57} The difference in the dynamic properties (G' and $\tan \delta$) between carbon black and silica are reduced in polar rubbers since the strong filler-networking effect of silica is lessened due to the increased affinity between the silica surface and the polar elastomer.^{58,59}

For modified clays, $\tan \delta$ may involve more complicated mechanisms. For ENR50, compounds with clay C1 have stronger polymer-filler interactions, but have a lower $\tan \delta$ than that of the C2 compounds, as shown in Figure 11.⁴⁴ This means that the portion of the network structure of intercalated C1 capable of

being broken down and reconstituted is smaller than that of intercalated C2. In other words, C1 behaved more like silica, while C2 behaved more like carbon black. This may result from the difference in filler-filler interactions due to different organic modifications, specifically the fact that C1 was the more polar filler. In addition, since the clay fillers were intercalated by the rubbery polymer, the strength of the clay filler networks should also depend on the amount of the intercalated polymer which determines the interparticular reinforcement via joint shells and polymer links.^{54,60} The strain dependence of $\tan \delta$ for the 10 phr C1 compound shows a different behavior, specifically undergoing a minimum modulus at high strains. This behavior may be due to the exfoliation of modified clay into the rubber matrix.

For NR, $\tan \delta$ also increased with increasing filler loadings, as expected. $\tan \delta$ of the compounds with C3 is larger than that of compounds with C2 and with Hi-Sil, as shown in Figure 12. The fact that the behavior of C3 was more like that of carbon black is due to the structure of C3. C3 has more organic content, and its organic modifier has two long alkyl chains, giving it a higher affinity for nonpolar elastomers.

Stress-Strain Results in Tension

Some of the tensile properties of the vulcanizates are shown in Table III.⁴⁴ Compounds of ENR prepared by mixing pristine clay Na-Mt into the rubber melt could attain tensile properties⁶¹ close to or even higher than those of compounds with precipitated silica (Hi-Sil). However, organically

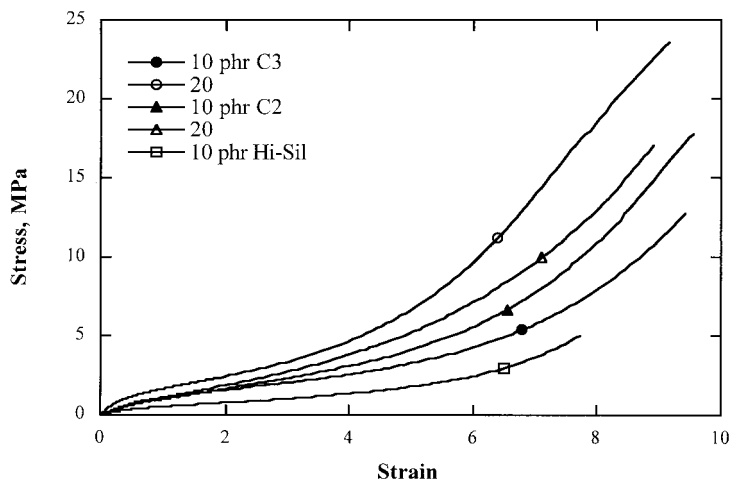


Figure 14 Stress–strain curves for various formulations for the synthetic NR (Natsyn).

modified clay showed different effects. At small strains, vulcanizates with these clays generally had a much greater modulus, as shown in Figure 13. This may result from a very high effective volume fraction and large hydrodynamic reinforcement. The increased effective volume with increasing filler loading led to a drastic decrease in the elongation at break. For both intercalation and exfoliation types of dispersion, the moduli of the C1 and C2 compounds at high strains were smaller than were those for the Na–Mt compounds. One reason for this effect may be the weaker polymer networks. The mixture of the polymer with organo-modified clays obtained by solvent mixing was hardened due to the high active volumes, resulting in a poorer sulfur dispersion.

For the synthetic NR (Natsyn), vulcanizates with organically modified clay fillers had much better tensile properties in comparison to the silica Hi-Sil, as shown in Figure 14. This result was due to better polymer–filler interactions and weaker filler–filler interactions of the modified clays. For 10 phr loading, the C2 compound had better tensile properties than those of C1. Thus, exfoliation had a greater reinforcing effect on the properties of these rubber vulcanizates.

CONCLUSIONS

Reinforcing effects obtained by the introduction of layered silicate fillers are characterized for two important types of elastomers. For the nonpolar elastomer, *cis*-1,4-polyisoprene, organic modification of the clay filler facilitated the intercalation of the elastomer into the clay galleries. Most im-

portantly, the modification was found to be similar to the well-known surface modifications of silica in that it reduced filler–filler interactions, improved filler dispersion, and, thus, efficiently increased the tensile properties of the vulcanizates.

In the case of the polar elastomer (ENR), the mixing of pristine clay into the elastomer led to intercalation, which increased the active surface area of the clay. This reinforcing effect of the pristine clay was found to be comparable to that of high surface area silica. More intercalation was achieved with the organically modified clays. The amount of the intercalated polymer increases the hydrodynamic reinforcement effects. The increased effective volume depended on the interlayer distance, which is determined by the organic modification and the intercalation of the elastomer. Increasing the effective filler volume thus formed more filler network, leading to a high storage modulus at small strains.

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