

Effect of Clay Surfactant Type and Clay Content on the Rheology and Morphology of Uncured Fluoroelastomer/Clay Nanocomposites Prepared by Melt-Mixing

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ABSTRACT: Fluoroelastomer/clay composites were prepared by melt mixing in an internal mixer using Cloisite® Nanoclays: NA, 15A, 20A, 30B, and 93A at three different concentrations viz. 2.5, 5.0, and 10.0 phr. Rheology, X-ray diffraction (XRD), and transmission electron microscopy (TEM) were used to characterize the composites prepared. Dynamic rheological measurements showed significant increase in storage moduli (G') in the terminal frequency region for the uncured composites prepared from Cloisite® 15A and 20A. At higher frequencies, organically modified nanoclays plasticize the polymer matrix leading to lower

modulus values. Using all three characterization techniques, Cloisite® 15A and 20A were shown to have intercalated structure in the fluoroelastomer matrix, whereas other nanoclays were shown to have inferior dispersion. The storage modulus increases proportionally with increase in the clay loading and no clay aggregation was observed at higher loadings. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 3597–3604, 2009

Key words: elastomers; nanocomposites; rheology; morphology; surfactants

INTRODUCTION

Fluorocarbon elastomers (FKM), and more specifically, the copolymers and terpolymers synthesized from vinylidene fluoride (VDF), hexafluoropropylene (HFP), and tetrafluoroethylene (TFE) are widely used in automotive, chemical, petrochemical, aerospace, and food processing industries, primarily as seals, gaskets, O-rings, and hoses.¹ The carbon-fluorine bonds in the backbone provide extremely high temperature resistance, and chemical and oil resistance. FKM compounds have limited low temperature flexibility and are not easy to process. These elastomers have moderate tensile strength at room temperature when compared with hydrocarbon rubbers and retain only a portion of it, when used at high temperatures.

There are continuing efforts to enhance properties of rubber compounds to extend their application to new areas and to improve their current performance. In the past decade, polymer-clay nanocomposites have drawn significant attention because of the unique properties they exhibit.^{2–4} However, it has to be emphasized that most previous studies have been devoted to thermoplastics and thermosets, leaving

elastomers highly unexplored.⁵ Some recent review articles have discussed the recent achievements in rubber/clay nanocomposites focusing on their preparation techniques and property enhancements.^{5,6}

Composites of polymers and layered silicates will have different morphologies greatly based on the interfacial forces between the clay surface and the polymer matrix. Conventional composites (i.e., macrocomposites) are obtained when the polymer molecules do not enter silicate galleries. Intercalated composites result when the polymer molecules penetrate the silicate galleries and increase the inter-layer distance. Exfoliated composites occur when the silicate layers are isotropic and fully dispersed by the polymer chains. Exfoliated silicate layers enable high interfacial interaction between polymer chains and therefore provide higher mechanical reinforcement, impermeability, and thermal stability.⁷ One often quoted claim in rubber/clay nanocomposites is that 10 phr (parts per hundred of rubber) of layered silicates can provide an enhancement in mechanical properties equivalent to that obtained with 40 phr of carbon black in natural rubber, provided the exfoliated state is obtained.⁸ Though exfoliation provides improved properties compared with the intercalated morphology,⁹ the exfoliated state is often difficult to achieve with conventional mixing techniques and it is more easily obtained by techniques like *in situ* polymerization¹⁰ or solution mixing.^{11–14} On the other hand, the intercalated state is relatively easier

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TABLE I
Characteristics of Cloisite[®] Nanoclay Grades¹⁷

Grade	Modifier	Structure of modifier	Conc. (meq/100 g clay)	d_{001} (Å)	Density (g/cm ³)
NA	None	None	None	11.7	2.86
15A	Di(hydrogenated tallow-alkyl) dimethyl ammonium ^a	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{N}^+ - \text{HT} \\ \\ \text{HT} \\ \\ \text{CH}_3 \end{array}$	125	31.5	1.66
20A	Di(hydrogenated tallow-alkyl) dimethyl ammonium ^a	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{N}^+ - \text{HT} \\ \\ \text{HT} \\ \\ \text{CH}_3\text{CH}_2\text{OH} \end{array}$	95	24.2	1.77
30B	Tallow alkyl methyl di(2-hydroxyethyl) ammonium ^a	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{N}^+ - \text{T} \\ \\ \text{CH}_3\text{CH}_2\text{OH} \\ \\ \text{H} \end{array}$	90	18.5	1.98
93A	Di(hydrogenated tallow-alkyl) methyl ammonium ^a	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{N}^+ - \text{HT} \\ \\ \text{HT} \end{array}$	90	23.6	1.88

^a Tallow is a mixture of C₁₄-C₁₈ alkyl chains (~65% C₁₈; ~30% C₁₆; ~5% C₁₄).

to attain and has been reported to improve the properties of composites significantly.²

Using melt mixing to prepare rubber/clay nanocomposites has the advantage of exploiting conventional rubber mixing equipment and methodologies, and therefore, possesses significant benefits from an industrial viewpoint. Previous studies on FKM/clay nanocomposites prepared by melt compounding have reported the effect of clay on the vulcanization characteristics¹⁵ and processing of the composites.¹⁶ It is widely known that the nanoclay dispersion state dictates the final properties of the composites. However, a comprehensive study focusing on the dispersion behavior of melt-mixed and uncured FKM/clay composites has been clearly absent. Considering that the organic content in the nanoclays may affect the curing process modify the curing characteristics as well as final properties such as optimum curing time and cross-link density,^{5,15} it is important to determine the effects of different grades of clays on the properties of a rubber compound before the curing process. Thus, the parameters that dictate the final behavior of composites are limited to the efficiency of clay dispersion in the rubber matrix and the mixing process, but not the cross-link density or other properties, which are susceptible to be altered by nanoclays during the curing process.

In this study, fluorocarbon rubber is melt mixed with unmodified and organically modified nanoclays

in an internal mixer. FKM compounds prepared with five different commercial nanoclays have been studied. Characterization of the uncured composites has been performed by dynamic rheology, X-ray diffraction (XRD), and transmission electron microscopy (TEM). In addition to comparing the reinforcement efficiency of different clays on FKM compounds, the plasticizing effect of organically modified nanoclays is presented.

EXPERIMENTAL

Materials

Dyneon[™] FPO 3741, a terpolymer of VDF, HFP, and TFE with fluorine content of 69.5%, specific gravity 1.89, and Mooney viscosity 38 ML (1 + 10) @ 121°C was obtained from Dyneon, 3M. Different grades of nanoclays viz. Cloisite[®] NA (untreated), 15A, 20A, 30B, and 93A were obtained from Southern Clay Products. Table I shows the clays used and their characteristics.¹⁷

FKM/Clay composite preparation

Clays were used in three different loading levels viz. 2.5, 5.0, and 10.0 phr. Mixing was carried out in a Haake Rheomix Series 600 with Banbury blades. FKM rubber was initially masticated for 2 min at

45 rpm and then clay was added in one part. Mixing was done for another 15 min at 45 rpm. Compound temperature was maintained at around 75°C during mixing. Fill factor was set at 0.70 and the thermal expansion was taken into consideration when calculating the mixing quantities.¹⁸ For convenience, the composites were denoted in the format XX(X)YY, where XX(X) is the grade of clay and YY the phr loading of the clay. Ex. 15A10 would denote a sample with 10 phr of Cloisite® 15A.

X-Ray diffraction and rheology

For XRD and rheological characterization, samples of FKM/clay composites of 25 mm diameter and 2 mm thickness were prepared by compression molding at 90°C and 10 MPa for 2 min. X-ray diffraction was performed by using a Rigaku diffractometer (CoK α , $\lambda = 0.1789$ nm) operated at room temperature in the range of 2–10° (2–12° except for NA clay and its composites). The detector (2θ) was rotated at twice the speed of sample (θ). Dynamic rheological characterization was done in a Rheometrics RMS800 with parallel plate fixture at a temperature of 180°C and angular frequencies from 10⁻² to 10² s⁻¹. Strain sweep experiments were carried out to find the linear viscoelastic region and then frequency sweep studies were performed within this region.

Transmission electron microscopy

To qualitatively analyze the composites, transmission electron microscopy was performed on a JEOL 2010 TEM equipped with a thin-window energy-dispersive X-ray spectrometer (EDS) operating at an accelerating voltage of 200 kV. The samples were cryo-ultra-microtomed in a Leica ultramicrotome at a temperature of -120°C without staining. The thickness of the microtomed sample was about 90 nm.

RESULTS AND DISCUSSION

Rheological characterization

The rheological response of polymer composites is sensitive to filler morphology and dispersion, and it has been used to characterize micro- and nano-composites.^{19,20} Figure 1 shows the effect of concentration of Cloisite® 20A, 15A, 93A, and NA on the storage moduli (G') of the composites in the frequency range of 10⁻² to 10² rad/s. It is clear in all cases that as the filler content increases, so does G' . This is expected in rubber/filler compounds, when using reinforcing or semi-reinforcing fillers. However, an insignificant reinforcement effect is observed in compounds prepared with NA and 93A

for the concentrations used. In the case of 20A and 15A, the increase in storage modulus is significant and roughly proportional to increase in filler loading. The data show that at higher filler loadings, the dependence of G' with frequency decreases and leads to a lower slope in the terminal region (low frequency). A zero slope in the terminal frequency region is an indication of solid-like material and a decrease of slope suggests a gradual transition from liquid-like to solid-like behavior, which is a strong indication of improved dispersion and/or enhanced intercalation of layered silicates by polymers.^{21,22}

The plots in Figure 1 show another unobvious, but very interesting, phenomenon in nanoclays. The storage moduli of some compounds prepared using organically-modified nanoclays drops below that of the polymer at higher frequencies, whereas for unmodified clay (NA) filled compounds, the storage modulus is always higher than that of the polymer. So, this is surely an effect arising from the organic content in the nanoclays. This conclusion can be further strengthened by assuring that this behavior does not originate from direct degradation of rubber caused by the mixing conditions (temperature or mechanical stress). A mixing run of the rubber alone under the same conditions was performed and its rheological response was compared with unprocessed sample. The samples showed identical rheological behavior, which reinforces the justification that this behavior results from organic intercalants in nanoclays. However, the exact mechanism by which organic intercalants bring about this decrease in modulus is unclear. Similar observations in a Nylon 6 matrix were reported and it was suggested that this effect could result from thermal degradation of the polymer induced by degradation of surfactants.^{20,23} Another hypothesis is that, some unbound organic surfactant diffuses out from the clay galleries and thereby reduces the modulus of the overall composites at higher frequencies. In the case of 93A compounds, it can be observed that this decrease in storage modulus occurs at all frequencies for low filler content and at high frequency for higher filler content. On the other hand, in 20A compounds, the reinforcing effects of the clay dominate at low frequencies and we do not see this behavior until high frequencies and only for low filler contents.

Figure 2 shows the effect of the type of clay on the storage moduli (G') and loss moduli (G'') of FKM compounds filled with 10 phr as well as the virgin polymer over the frequencies range studied. As previously mentioned, the terminal region has been known to be highly sensitive to morphological changes and filler dispersion.¹⁹ It can be seen that 20A and 15A compounds have a significant increase of G' in the terminal flow region in comparison with

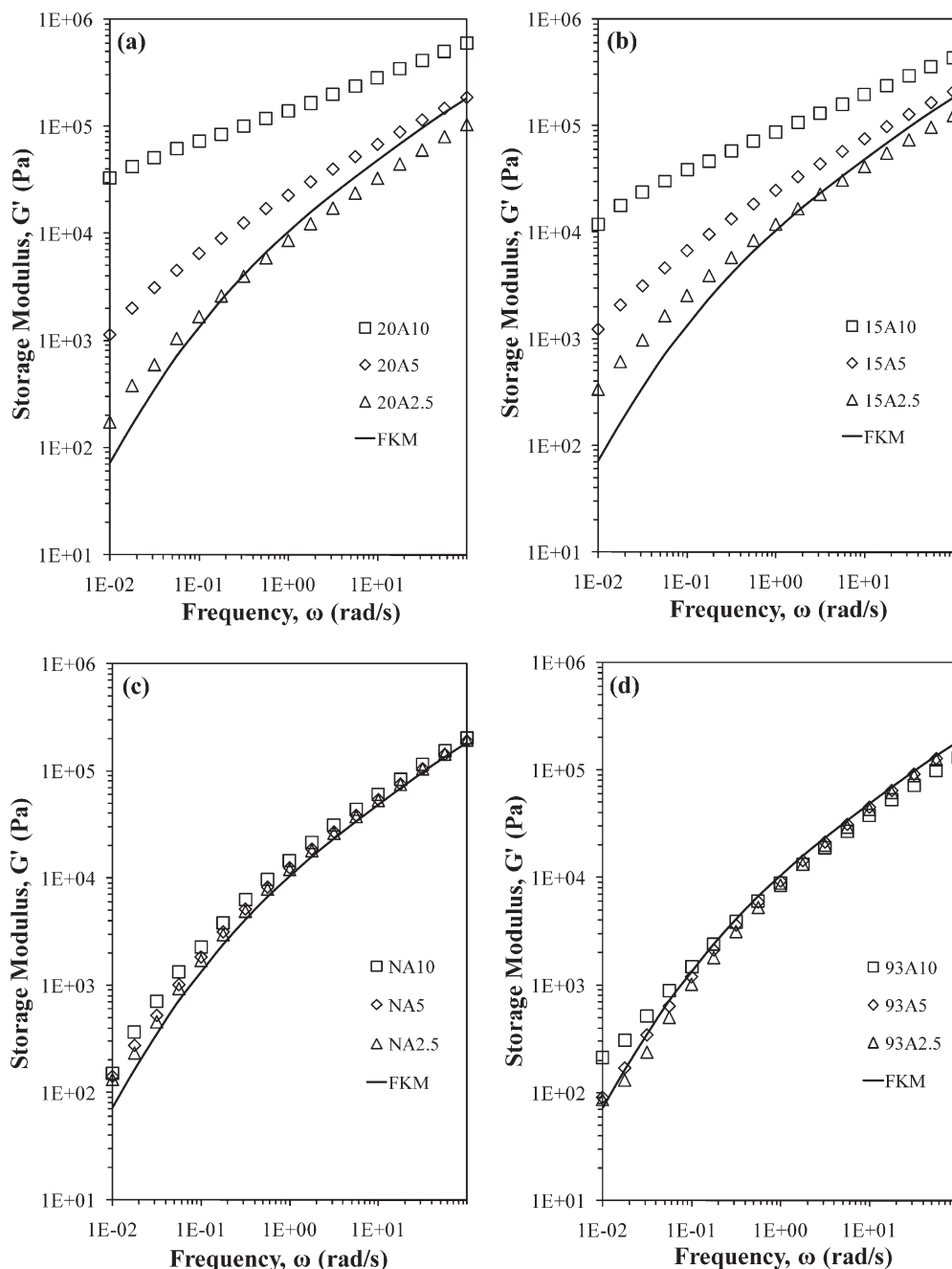


Figure 1 Storage moduli as a function of frequency at 180°C for filled and unfilled FKM composites containing different concentrations of Cloisite nanoclays (a) 20A, (b) 15A, (c) NA, and (d) 93A.

that of polymer (FKM) and other clay compounds. For instance, at the frequency of 10^{-2} rad/s, the G' of FKM, NA10, 30B10, and 93A10 were in the range of 200–700 Pa, whereas G' for 15A10 and 20A10 were 1.2×10^4 Pa and 3.3×10^4 Pa, respectively, which corresponds to an increase of 2 orders of magnitude over other compounds. Figure 3 shows the $\text{Tan } \delta$ (G''/G') values against frequency, which can be used to compare the liquid-like versus solid-like behavior of composites. It is clear that only for the

20A and 15A compounds the $\text{Tan } \delta$ values were always less than unity in the entire frequency range studied, which indicates that G' dominates over G'' in these compounds, in contrast to the behavior of those prepared with other nanoclays. At high frequencies, the rheological properties tend to be dominated by the elastomer matrix¹⁶ rather than the filler morphology, leading to small deviations in this region from the pure polymer. Our results indicate that Cloisite[®] 20A and 15A enabled more dispersed

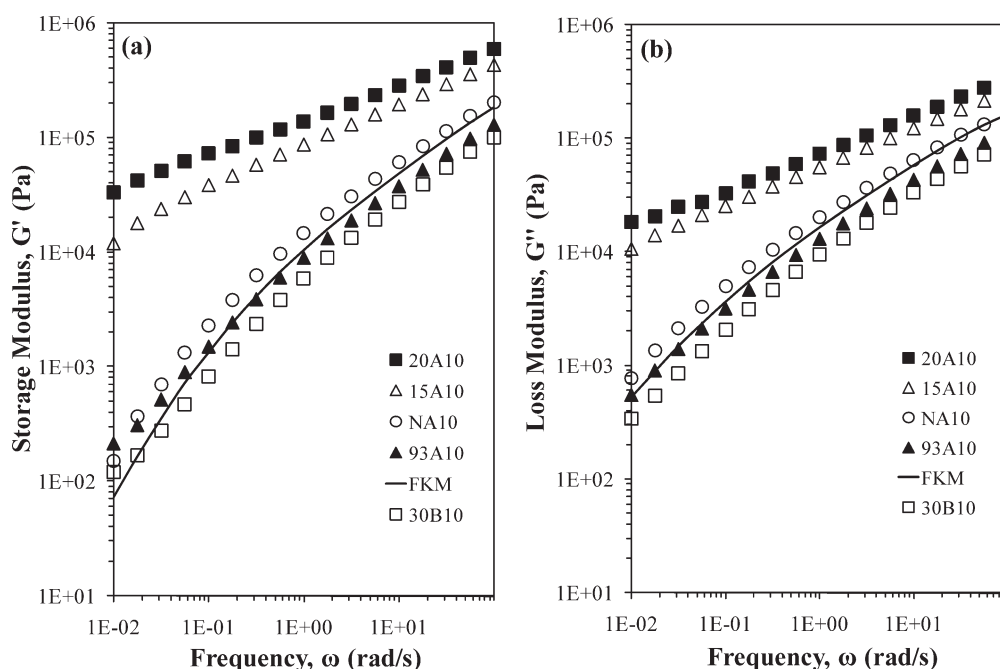


Figure 2 (a) Storage moduli and (b) Loss moduli at 180°C, for all the 10 phr clay filled FKM composites and unfilled FKM, as a function of frequency.

composites with solid-like behavior and higher reinforcing effect. This is in contrast to previous studies of composites prepared by solution processing that indicate better interaction and dispersion of natural nanoclay in FKM. ¹¹

Morphology of FKM/clay nanocomposites

Figure 4 shows the XRD patterns of FKM compounds prepared with different concentrations of clay loading along with the diffractograms of nanoclays. The peak positions were used to find the corresponding d-spacings using Bragg's law of diffraction. For the nanoclays used (NA, 15A, 20A, 30B, 93A) the d-spacings were found to be 1.10, 3.27, 2.55, 1.72, 2.62 nm, respectively, which closely matches the values reported in Table I obtained from the supplier. It can be interpreted from Figure 4 that the composites prepared from NA, 15A, 30B, and 93A [Fig.4(a,b,d,e)] are not intercalated because the calculated d-spacings (see secondary x-axes in Fig. 4) of the composites were not considerably higher than that of the corresponding clays. This could be attributed to the inability of the polymer molecules to intercalate the silicate galleries of these nanoclays. Interestingly, in some of the compounds prepared from 30B and NA, the d_{001} peaks have slightly shifted to higher angles suggesting decreased d-spacing. This behavior has been reported to loss of surfactant in the clay galleries because of degradation at high mixing temperatures ²⁴ or participation of surfactant in Zn-containing complex

formation during vulcanization. ²⁵ In this case, because neither high temperature mixing nor vulcanization was carried out, the loss of surfactant may be related to some other reason. Further study is needed to understand this behavior. Nevertheless, the presence of this behavior in composites made from NA clay, which is not intercalated with organic surfactants, is very peculiar and incomprehensible.

In contrast, in 20A compounds [Fig. 4(c)], there is a sizable shift of the peak position to lower 2θ angles. The compounds were shifted to $2\theta = 2.84^\circ$, which corresponds to a d-spacing of 3.61 nm—an increase of about 1.06 nm from the organically modified nanoclay. From these observations, it can be

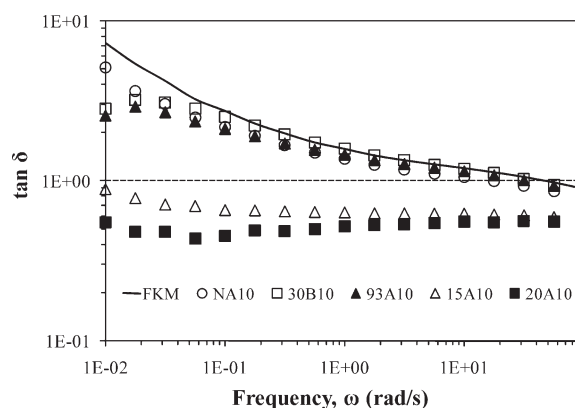


Figure 3 Tan δ at 180°C, for all the 10 phr clay filled FKM composites and unfilled FKM, as a function of frequency.

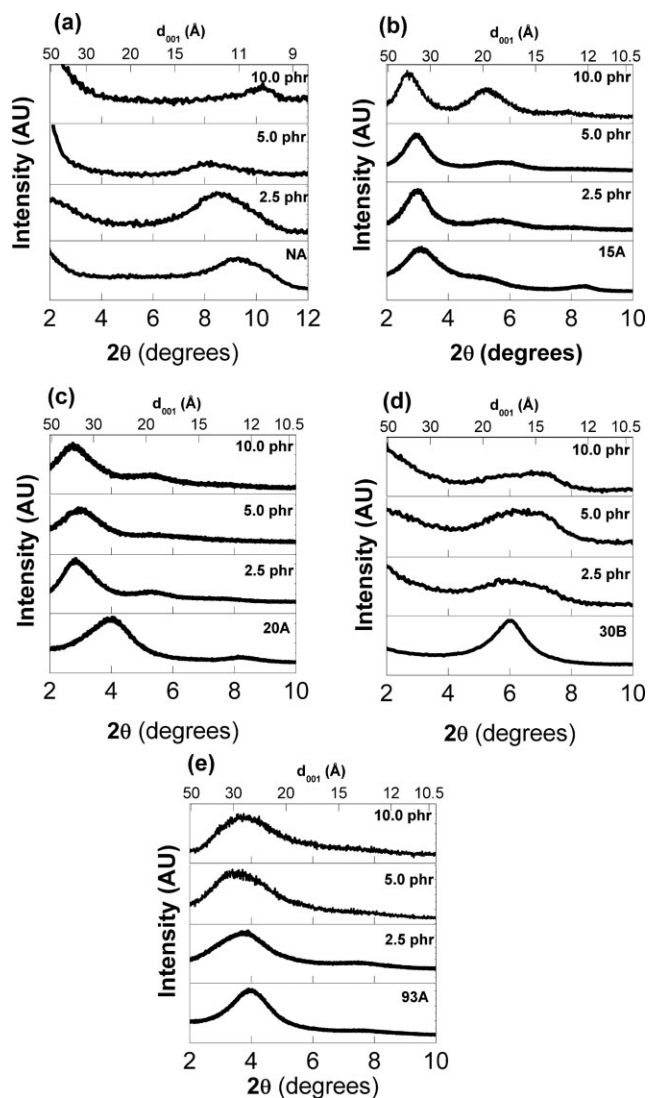


Figure 4 Wide angle X-ray diffractograms for (a) NA, (b) 15A, (c) 20A, (d) 30B, and (e) 93A clays and their respective composites at different concentrations.

inferred that the 20A nanoclay has better affinity for this fluoropolymer, allowing the polymer molecules to enter and expand the silicate galleries. This can be attributed to the surfactants present in the modified clay and their ability to reduce the surface energy of the inorganic matrix, thereby improving the wetting characteristics of the polymer molecules on the surface. Because it is shown that surfactants were vital in improving polymer intercalation in 20A compounds, it becomes imperative to explain the absence of the shift of primary peak in the X-ray spectra of 15A compounds, which was modified by the same surfactant as 20A compounds, i.e., di(hydrogenated tallow-alkyl) dimethyl ammonium. According to the manufacturer, the only difference between 15A and 20A is the surfactant concentration, which are 125 and 95 meq/100 g clay, respectively (Table I). In both cases, the amount of surfactant is

higher than the cation exchange capacity (CEC) of Cloisite® NA, which is 93 meq/100 g clay.^{26,27}

A similar XRD behavior was reported for nanocomposites of polyethylene terephthalate glycol (PETG), using the 15A and 20A nanoclays.²⁸ It was shown that PETG/15A compounds had substantially better reinforcement than PETG/20A compounds.²⁸ The XRD peaks of 20A compounds shifted to lower angles and 15A showed no change, which was similar to our observations in Figure 4. The justification provided was that the 15A compounds were highly oriented compared with 20A, resulting in more platelet-platelet interaction thereby strengthening the composite. However, in the current study, the reinforcement behaviors of 15A and 20A compounds were very similar as seen in the rheological study. Also, since 20A compounds were clearly shown to be intercalated, it is improbable that the reinforcement arises from clay orientation. This drives us to a conclusion that 15A compounds can also be intercalated, but was not directly reflected in the X-ray diffractograms. As pointed out earlier, 15A clay contains a higher concentration of intercalants than 20A. This excess amount of surfactant could remain unbound in the silicate layers, which in their initial state increases the gallery spacing of clays.²⁷ During shear-mixing this excess unbound surfactant could diffuse outwards from the galleries thereby decreasing the d-spacing.²⁹ This combined with simultaneous intercalation of the polymer molecules could have led to the behavior of no or insignificant shift in the peak for the 15A composites reported here.³⁰ A schematic illustration of the mechanism of polymer intercalation in 15A and 20A composites is presented in Figure 5. It is also worthwhile to note that the final d_{001} values of all the composites prepared from 15A and 20A lied within the small range of 3.3–3.6 nm. This is clearly indicative that the interlayer spacing of the silicate galleries in the nanocomposites is unaffected by the difference in initial additional surfactant concentration. It can also be inferred that for this combination of polymer, clay modifier (surfactant) and mixing conditions, the reported interlayer spacing suggests a steady-state structure has been achieved. This behavior has been well documented in previous studies of polymer nanocomposites prepared using the clays Cloisite® 15A and 20A.^{29–32} Another unique trend in 15A and 20A compounds is that the modulus increases roughly proportionally with increasing clay loading, suggesting the presence of intercalation even at higher clay loadings. This contradicts other reports on fluoroelastomers, where above certain clay loading, aggregation results giving inferior dispersion and properties.¹⁶

Transmission electron microscopy has been effectively used to qualitatively study the clay orientation in many polymer matrices.² However, fluorine atoms are highly sensitive to electron beam

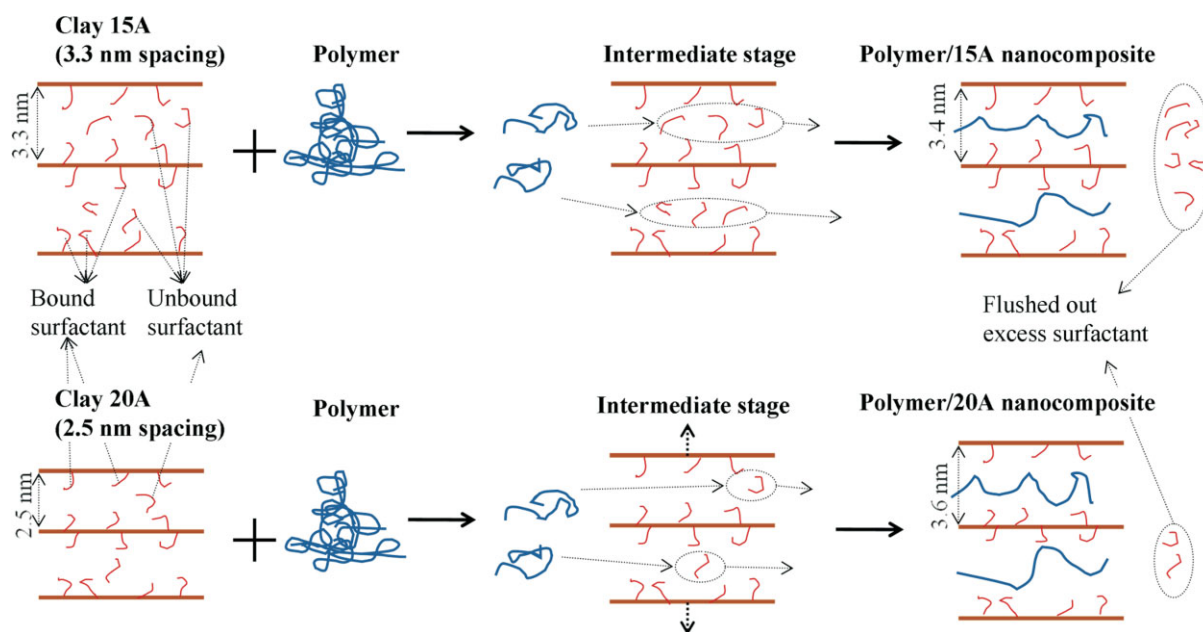


Figure 5 Schematic illustration of the proposed mechanism of polymer intercalation in nanocomposites made with Cloisite® 15A and 20A. Cloisite® 15A has higher concentration of unbound surfactants than 20A, which provides a higher increase in the initial inter layer-spacing. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

irradiation attributed to their higher cross-sectional area compared with that of carbon atoms,³³ which can lead to intense changes in the exposed area of the specimen. Experimentally, it was found that TEM characterization of FKM/clay composites was challenging. TEM images of the composites with and without using a cryo-stage were severely affected, especially at high magnifications. Figure 6 shows the low and high magnification TEM images of the composite with 10 phr of 15A clay. The low

magnification image shows that preferred platelet orientation is not present, whereas high magnification shows the clay layers dispersed and intercalated by polymer molecules. TEM and rheological characterization certainly strengthens the hypothesis that 15A compounds were intercalated. In previous studies on FKM/clay nanocomposites,^{11,12,15,16} cross-linked specimens were used for TEM characterization, which suggests that cross-linking improves stability to high-energy electron beam irradiation.

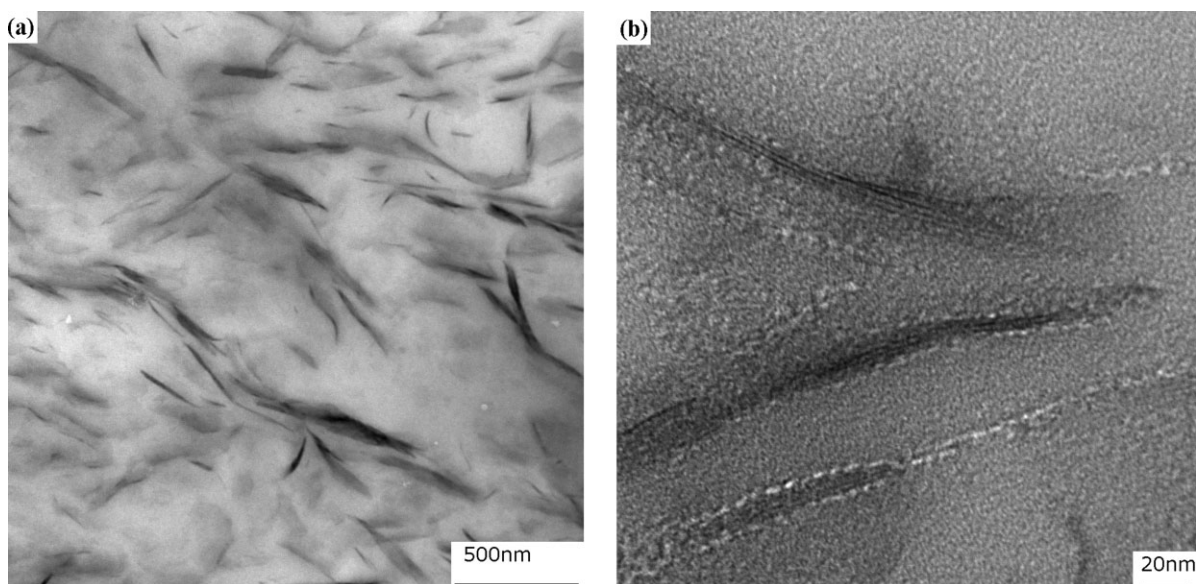


Figure 6 Low (a) and High (b) magnification TEM images of 15A10. Low magnification image shows the presence of a mixture of finely dispersed and bundles (stacks) of clay layers.

As previously mentioned, it is beneficial to perform a comparative analysis of the efficiencies of different nanoclays on uncured compounds, as the surfactants in the nanoclays were shown to influence the vulcanization process and vulcanizate properties.^{25,34,35} However, it is also important to cross-link these compounds to examine the impact of nanoclays on the final compound properties and these results will be reported in a future publication. It is expected that the observed reinforcement effects of nanoclays 15A and 20A will be preserved in their corresponding vulcanizates and provide enhancement in mechanical, barrier, and dynamic mechanical properties.

CONCLUSIONS

Fluoroelastomer layered silicate composites were prepared by melt mixing using an internal batch mixer. The morphology and rheological properties of the composites prepared using unmodified and organically-modified nanoclays at different concentrations were studied. A transition from liquid-like to pseudo solid-like behavior was observed with the increase in clay concentration for composites prepared with Cloisite[®] 15A and 20A. The increase in storage modulus of composites prepared with different concentrations of Cloisite[®] 15A and 20A indicated significant clay dispersion and higher reinforcement than those prepared with Cloisite[®] NA, 30B, and 93A. This was attributed to the reduction of the surface energy imparted to the clays by the presence of di(hydrogenated tallow-alkyl) dimethyl ammonium surfactant in Cloisite[®] 15A and 20A. XRD characterization of compounds prepared with different concentrations of Cloisite[®] 15A does not indicate a significant increase in the intergallery distance of the nanoclay in comparison to the 1.06 nm increase in d_{001} obtained for 20A compounds. This difference has been attributed to the presence of unbound surfactant in the silicate galleries that affects the mechanism of intercalation in 15A and 20A compounds. The silicate gallery spacing in these nanocomposites (15A and 20A) was shown to be independent of the excess surfactant quantity present above the CEC of the natural montmorillonite.

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