

Dynamic Mechanical and Rheological Behavior of Fluoroelastomer-Organoclay Nanocomposites Obtained from Different Preparation Methods

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ABSTRACT: A comparison among different preparation methods of fluoropolymer/clay nanocomposites based on a fluoroelastomeric matrix (Tecnoflon[®] P959) and organomodified montmorillonite clay (Cloisite[®] 20A) is reported. While melt blending leads to intercalated structures, the X-ray diffraction patterns of solution blended nanocomposite suggest a better delamination of the clay platelets within the fluoropolymeric matrix (no diffraction peaks) if the solvent evaporation step is carried out very slowly (72 h) at ambient pressure and moderate temperature. For the solution blended-slow

evaporation nanocomposite, dynamic mechanical analysis and dynamic rheological measurements show a strong increase in G' , a lower damping peak at T_g , and a pseudosolid like behavior in the terminal flow region, suggesting a likely exfoliation of the organomodified clay in the fluoroelastomeric matrix. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4484–4487, 2006

Key words: fluoroelastomers; nanocomposites; solution blending; rheological properties; exfoliation

INTRODUCTION

Fluoroelastomers¹ are increasingly used as high performance seal materials in many industrial applications due to their excellent heat, oil, and chemical resistance. To further improve these performances, the realization of fluoroelastomer nanocomposite materials seems very attractive. This approach could lead to a new generation of fluorinated rubbers with improved mechanical properties and still good barrier properties even reducing the overall fluorine content in the material (therefore lowering its cost). Actually polymer nanocomposites like those obtained from layered phyllosilicates,^{2,3} or nanoclays, typically exhibit impressive mechanical and barrier property improvements at low filler loading (<10% by wt). However, such results are closely related to the achievement of exfoliation or delamination of the large stacks of silicate nanoplatelets into single layers. Processing issues are therefore at the center of the research activity in this field. So far, the scientific literature concerning fluoropolymer-clay nanocomposites are relatively scarce,^{4–10} and mainly concern intercalated vinylidene fluoride (VDF) containing homopolymers and copolymers.

Exfoliation of organomodified nanoclays in a fluoropolymer matrix is admittedly a difficult result to be

obtained, since interfacial interactions between polymer and polar nanofiller are expected to be energetically not favored because of the very low solubility parameters of fluoropolymers.¹¹ Some interactions are feasible due to the sufficiently high polarity of the VDF unit $-\text{CF}_2\text{CH}_2-$. However, very recently a work appeared concerning exfoliated fluororubbers,¹² where exfoliation was attributed to exothermic interactions between clays and polarized $\text{C}^{\delta+}-\text{F}^{\delta-}$ bonds.

In this work, a comparison between melt and solution blending processing techniques are reported, using a VDF based elastomeric terpolymer (Tecnoflon[®] P959) compounded with an organomodified montmorillonite clay (Cloisite[®] 20A). The resulting nanocomposites were characterized by X-ray diffraction (XRD), dynamic mechanical analysis (DMA), and dynamic rheological measurements, showing very diversified behaviors. The combined indications of structural analysis and the peculiar rheological behavior suggest the possible formation of exfoliated nanostructures in some cases.

EXPERIMENTAL

Materials

Tecnoflon[®] P959 (a polyvinylidene fluoride-*co*-hexafluoropropylene-*co*-tetrafluoroethylene amorphous terpolymer containing 53% of VDF monomer) was kindly supplied by Solvay-Solexis, Bollate (MI), Italy. The dimethylditallow ammonium modified montmorillon-

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ite (Cloisite[®]20A) was purchased from Southern Clays. Anhydrous tetrahydrofuran (THF, from Aldrich) was used as received.

Preparation of rubber nanocomposites

The base compound consists of P959 fluoroelastomer filled with 6 phr (i.e., 6.05 vol % or 5.66 wt %, corresponding to 3.51 wt % of inorganic filler) of organomodified nanoclay. Three different preparation processes were followed as described below.

Melt blending

The compound was prepared by mixing polymer and nanoclay in a Brabender[™] Internal Mixer operating at 60 rpm and room temperature for 20 min.

Solution blending-fast evaporation

The organophilic clay was swollen in THF (1% w/v) at room temperature by vigorous stirring. The fluoropolymer was separately dissolved in dry THF (concentration 10% w/v) and stirred to obtain a clear solution. The two solutions were then poured together. After 20 h stirring, the blend was rapidly dried under reduced pressure (30 mmHg) at 50°C to obtain the final nanocomposite material.

Solution blending-slow evaporation

The solution blend was prepared as before, but it was then cast in a PTFE mold and dried at 50°C for 3 days at ambient pressure. Reduced pressure (30 mmHg) was finally applied to the nanocomposite film (about 500 μm thick) until constant weight was reached.

For each procedure, three separate blending experiments were carried out to evaluate the repeatability of results.

Characterization of nanocomposites

X-ray diffraction (XRD) patterns were obtained using a Philips PW 1710 diffractometer with Cu K_α radiation ($\lambda = 1.5406 \text{ \AA}$). The range of 2θ scans was 2–15°. The basal spacing d of the clay was estimated from the (001) peak in the XRD pattern according to the Bragg's law, $n\lambda = d_{hkl} \sin \theta$

Dynamic mechanical analyses (DMA) were performed with a Mettler Toledo DMA/SDTA 861^e dynamic mechanical analyzer in shear sandwich mode from –100 to 200°C at a frequency of 1 Hz and a strain of 0.25%.

The rheological properties were measured by a stress controlled rheometer (Rheometrics DSR200) in an oscillatory mode with parallel plate geometry using 25 mm diameter plates at 180°C, measuring the storage

and loss moduli (G' and G'') as functions of angular frequency (ω). The strain region in which the material can be regarded as linear viscoelastic (<4%) was determined by separate stress sweep experiments.

RESULTS AND DISCUSSION

Figure 1 compares the XRD patterns of P959/nanoclay nanocomposites prepared by melt and solution blending (in both fast and slow evaporation modes). The organically modified clay Cloisite[®]20A exhibits a typical reflection at $2\theta = 3.52^\circ$ corresponding to a d -spacing d_{001} of 25.1 Å according to Bragg's law. For nanocomposites prepared by melt and solution blending-fast evaporation, the d_{001} peak of the clay shows lower intensity (higher disorder) and shifted to low angles corresponding to an increase in the d -spacing from 25.1 to 31.1 Å and 32.3 Å, respectively. This phenomenon is typical of intercalated nanocomposite structures.

For the nanocomposite prepared by solution blending method-slow evaporation, the d_{001} peak observed at 25.1 Å for pristine clay completely disappears. Interestingly enough, absence of XRD diffraction peaks could be reproducibly obtained only when a very slow solvent evaporation procedure was carried out, as explained in the Experimental section. For that reason, the solution blended nanocomposite obtained with fast evaporation procedure was not considered further.

As known,² the absence of XRD peaks is often related to the full delamination of the clay nanolayers within the polymer matrix, i.e., the formation of an exfoliated nanostructure. However, XRD characterization alone is not sufficient and the assessment of the state of dispersion of clay in the polymer should be confirmed by specific morphological analysis like TEM, or indirectly through rheological measurements.^{13–16}

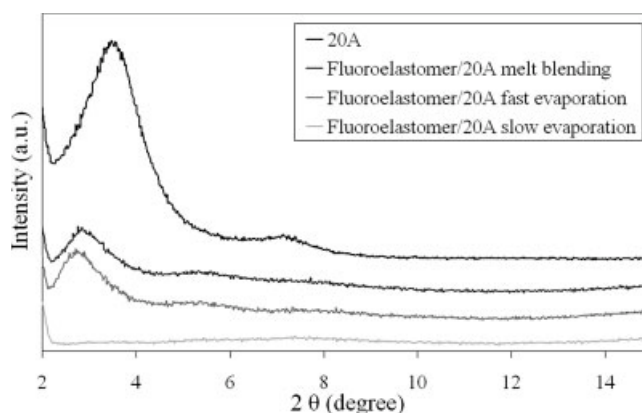


Figure 1 X-ray diffraction patterns for: (a) Cloisite[®]20A, (b) P959/20A nanocomposite by melt blending and P959/20A nanocomposite by solution blending with (c) fast, and (d) slow evaporation of the solvent.

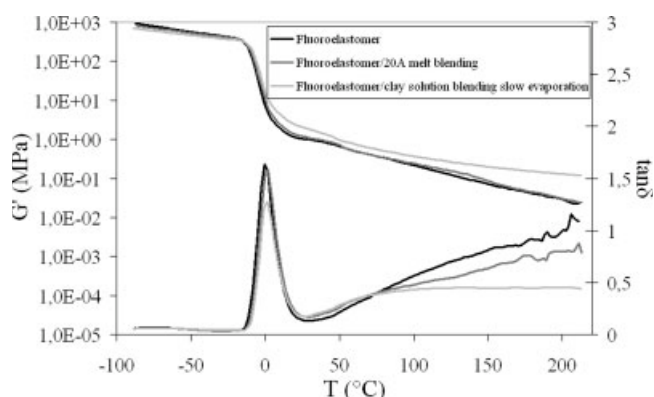


Figure 2 Temperature dependence of G' and $\tan \delta$ for P959 matrix and P959/20A nanocomposites prepared by melt and solution blending (slow evaporation).

As far as DMA of fluoroelastomer nanocomposites are concerned, Figure 2 shows the trend of $\tan \delta$ and storage modulus G' with the temperature for the pure P959 and some of P959-clay nanocomposites. As typical for fluoroelastomers¹ the T_g is quite high (about 0°C), with negligible effect of nanoclay in the present case. Again, only for the nanocomposite prepared by solution blending-slow evaporation a strong increment in G' is observed at high temperature, where the efficiency of entanglements is lower. For example, at 180°C and 1 Hz, G' increases from 4.0×10^{-2} to 1.5×10^{-1} MPa corresponding to a $\Delta G' = +274\%$. The remarkable improvement in G' is higher than that reported by Maiti and Bhowmick on similar systems,¹² and it could be related to stronger interaction between the matrix and the clay. The decrease of $\tan \delta$ peak intensity at T_g , and its small and roughly constant value at high temperature further confirms that.

Figures 3–5 give the $\log G'$ versus $\log \omega$ plots at 180°C for P959 and P959 based nanocomposites, obtained at dynamic rotational rheometer. In such a plot, the reciprocal of the frequency at which G' and G''

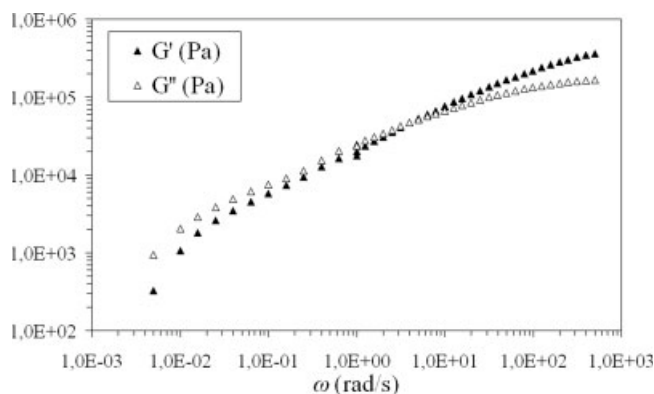


Figure 3 Frequency dependence of storage modulus, $G'(\omega)$, and loss modulus, $G''(\omega)$ for P959 matrix.

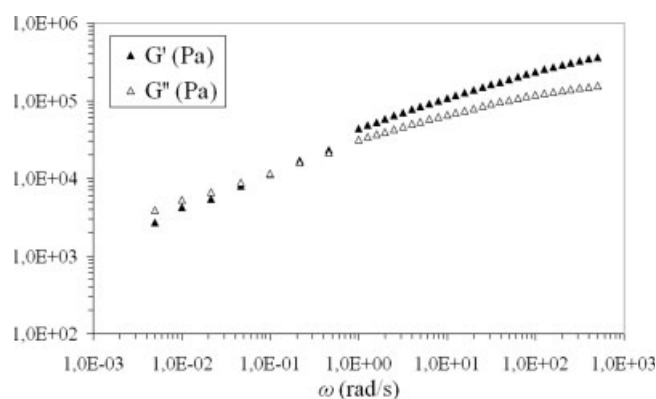


Figure 4 Frequency dependence of storage modulus, $G'(\omega)$, and loss modulus, $G''(\omega)$ for P959/20A nanocomposite prepared by melt blending.

crossover is an estimate of the longest relaxation time¹⁷ of the system at the measurement temperature, $\tau = \frac{1}{\omega_c}$. Some numerical results concerning rheological measurements are shown in Table I. It appears that G' values at 180°C and frequency 1 Hz from DMA and rheometry are in good agreement, even if obtained with different instruments and different deformation geometries (simple shear versus rotational flow). As far as isothermal rheometric measurements are concerned, the unfilled P959 (Fig. 3) exhibits a relaxation time of 1.6 s whereas P959/20A melt blended (intercalated) nanocomposite exhibits a relaxation time of 39.3 s, corresponding to a crossover occurring at lower frequency. The behavior of solution blended nanocomposite-slow evaporation (Fig. 5) is particularly interesting. In the low-frequency region it shows an apparent absence of terminal flow behavior, which is a typical feature of linear polymers. Actually, $G'(\omega)$ becomes weakly dependent on frequency and always exceeds $G''(\omega)$ up to very slow ω , as shown from materials exhibiting a pseudo solid-like behavior. The difference in the rheological response in the terminal flow region

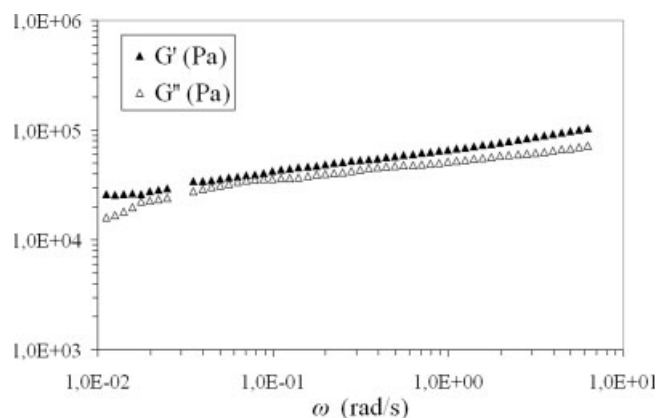


Figure 5 Frequency dependence of storage modulus, $G'(\omega)$, and loss modulus, $G''(\omega)$ for P959/20A nanocomposite solution blending (slow evaporation).

TABLE I
 G' and Relaxation Times τ Calculated from Dynamic Rheological Experiments ($T = +180^\circ\text{C}$)

Compound	G' (MPa) ^a	G' (MPa) ^b	τ (s)
P959 pure	4.0×10^{-2}	5.9×10^{-2}	1.6
Nanocomposite (melt blending)	4.5×10^{-2}	9.1×10^{-2}	39.3
Nanocomposite (solution blending-slow evaporation)	1.5×10^{-1}	1.0×10^{-1}	$\rightarrow + \infty$

^a $\omega = 1$ Hz from dynamic mechanical analysis.

^b $\omega = 1$ Hz from dynamic rheological experiments.

of $\log G'$ versus $\log \omega$ may be related to some different types of nanostructure formed from the clay particles in the fluoroelastomeric matrix. In particular, a pseudo solid-like behavior is often exhibited^{13-16,18} by efficiently exfoliated polymer/nanoclay systems.

The effect of preparation method on the resulting nanocomposite morphology and behavior is therefore dramatic, although not completely clear. It can be qualitatively justified on a thermodynamic basis as follows.

During melt blending, polymer has to diffuse through the galleries of the organomodified nanoclays widening the gap between silicate layers, as confirmed by the increased d -spacing at the XRD analysis. The loss of conformational degrees of freedom by confined polymer chains is counterbalanced from the more volume available for organic macrocations, due to gap opening. It is recognized^{2,3} that the overall entropy change is in that case very small ($\Delta S \approx 0$), and the process is thermodynamically ruled by enthalpic contributions. Therefore, exfoliation occurs only when sufficient exothermic interactions between polymer chains and organic macrocation take place ($\Delta H < 0$).

On the other hand, the driving force for nanoclay exfoliation with solution blending method is mainly given by the desorption of the solvent molecules trapped within the silicate galleries, with consequent large entropic gain. In the case under study, it is very likely that enthalpic contributions could not be very favored, being at most limited to the VDF-rich portions of the copolymer: ΔS change becomes therefore predominant. The effect of the solvent evaporation kinetics is less clear. In case of slow drying process at ambient pressure, a cooperative mechanism among diffusing macromolecules and evaporating solvent molecules may occur in the interlayer gap, which effectively favors the delamination of the silicate.

Our results are only partially in agreement with those recently reported by Maiti and Bhowmick.¹² These authors achieved good exfoliation of fluoroelastomers through a smooth evaporation procedure (ambient pressure and temperature), although kinetic effects were not specifically studied. However, they claimed a better interaction between fluoroelastomer and pristine clay on the basis of predominantly enthalpic reasons.

CONCLUSION

Fluoroelastomer/clay nanocomposites have been prepared by both melt and solution blending methods. Interestingly, in the latter case the kinetics of solvent evaporation is a key factor affecting the morphology and behavior of the nanocomposite obtained. The case of very slow solvent evaporation is of particular interest: actually XRD analysis shows the absence of any reflection suggesting a feasible formation of exfoliated nanocomposites. Rheological measurements show a solid-like behavior as indication of very efficient delamination of nanoclays for solution blended compounds, and only when the solvent is evaporated quite slowly. Although the used procedure is still impractical on an industrial scale, it could give useful indications for the preparation of well exfoliated fluoropolymer nanocomposites.

References

- Ameduri, B.; Boutevin, B.; Kostov, G. *Prog Polym Sci* 2001, 26, 105.
- Alexandre, M.; Dubois, P. *Mater Sci Eng* 2000, 28, 1.
- Ray, S. S.; Okamoto, M. *Prog Polym Sci* 2003, 28, 1539.
- Priya, L.; Jog, J. P. *J Polym Sci Part B: Polym Phys* 2003, 41, 31.
- Priya, L.; Jog, J. P. *J Polym Sci Part B: Polym Phys* 2002, 40, 1628.
- Priya, L.; Jog, J. P. *J Appl Polym Sci* 2003, 89, 2036.
- Kim, Y.; White, J. L. *J Appl Polym Sci* 2004, 92, 1061.
- Shah, D.; Maiti, P.; Gunn, E.; Schmidt, D. F.; Jiang, D. D.; Batt, C. A.; Giannelis, E. P. *Adv Mater* 2004, 16, 1173.
- Kader, M. A.; Nah, C. *Polymer* 2004, 45, 2237.
- Pramoda, K. P.; Mohamed, A.; Phang, I. Y.; Liu, T. *Polym Int* 2005, 54, 226.
- Barton, A. F. M. *Handbook of Solubility Parameters and Other Cohesion Parameters*; CRC Press: Boca Raton, 1983; p 280.
- Maiti, M.; Bhowmick, A. K. *J Polym Sci Part B: Polym Phys* 2006, 44, 162.
- Krishnamoorti, R.; Giannelis, E. P. *Macromolecules* 1997, 30, 4097.
- Lim, Y. T.; Park, O. O. *Rheol Acta* 2001, 40, 220.
- Moussaif, N.; Groeninckx, G. *Polymer* 2003, 44, 7899.
- Lee, K. M.; Han, C. D. *Macromolecules* 2003, 36, 7165.
- Macosko, C. W. *Rheology: Principles, Measurements and Applications*; Wiley-VCH: New York, 1994.
- Zhao, J.; Morgan, A. B.; Harris, J. D. *Polymer* 2005, 46, 8641.