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The Dynamic Viscoelasticity of Polyethylene Based Montmorillonite Intercalated Nanocomposites

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Abstract: The viscoelastic behavior of melts for two systems composed of intercalated nanocomposites based on low density polyethylene and 3 wt% loading of cetyltrimethylammonium bromide modified montmorillonite was studied. The results obtained through examining the dynamic storage module G' and dynamic loss module G" values of the composite revealed that the dynamic viscoelastic properties of composite strongly depended on intercalation of polymer, and exhibited dramatically change with altering intercalation conditions. Only when modified montmorillonite content was about 3 wt%, the composite showed a trend of pseudo-solidlike at lower frequencies.

Keywords: Viscoelasticity, polyethylene, montmorillonite, nanocomposites.

Due to possessing special structure/morphology, polymer based montmorillonite nanocomposites exhibit some particular characteristics as compared with the pristine polymers[1~3]. Recently, nanocomposites with intercalated or exfoliated structures have been considered as a novel model for the study of viscoelastic properties [4,5]. Two kinds of polymer/montmorillonite (MMT) intercalated nanocomposites were prepared by melt intercalation under a twin screw extruder (PRISM TES 16 TC, UK). Low density polyethylene (LDPE, MI =7.1 g/10 min, at 190°C, 2.16 kg) can intercalate into the layers spaces of org-MMT (a kind of montmorillonite which was organically modified by cetyltrimethylammonium bromide through ion exchange reaction), especially when adding a kind of compatiblizer, *i.e.* ethylene vinyl acetate copolymer (EVA, MI = 1.6 g/10 min, at 190°C, 2.16 kg). It is well accepted that LDPE is a non-polar polymer and can not intercalate into MMT layers easily because of the poor compatibility between them. In this case even though under the strong stress given by twin screw, the polymer intercalation is not so efficient. Incorporation of EVA, a polar polymer, into these system will acts as a compatibilizer and will improve the interaction between polymer and modifiers. As a result the polymers intercalate into MMT layers more easily. The degree of the polymer intercalating was characterized with the parameters of X-ray diffraction (XRD). The layers space of MMT, d_{001}, was calculated on the basis of the position of 001 plane obtained by XRD patterns.

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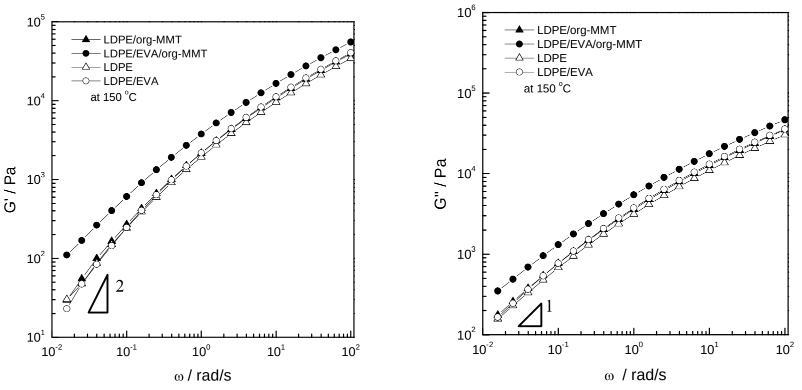
Table 1 gives the calculation results of layer distance parameter d_{001} for MMT and corresponding composites. It can be found that d_{001} of MMT is 1.27 nm, but up to 2.164 nm after MMT being modified by cetyltrimethylammonium, indicating that the modifiers have been intercalated into the layers, and also, polymer chains intercalated into MMT layers under chemical action and strong stress. As a result, d_{001} became higher, being 2.943 nm and 3.343 nm, corresponding to LDPE/org-MMT (97/3) and LDPE/EVA/org-MMT (85/12/3) respectively, indicating the formation of intercalated nanocomposites.

Table 1 The d_{001} of MMT and the intercalated nanocomposites

Samples	Proportion	2θ (°)	d_{001} (nm)
MMT		6.92	1.276
Org-MMT		4.08	2.164
LDPE/org-MMT	97:3	3.00	2.943
LDPE/EVA/org-MMT	85:12:3	2.66	3.343

Figure 1 presents the frequency ω dependence of (a) storage module G′ and (b) loss module G" at 150°C for LDPE, LDPE/EVA(85/12) blends, LDPE/org-MMT(97/3) and LDPE/EVA/org-MMT (85/12/3) composites. It shows that the data obtained for LDPE/EVA/org-MMT (85/12/3) with d_{001} 3.343 nm are quite different from those for LDPE, LDPE/EVA(85/12) blends and LDPE/org-MMT(97/3). The value of G′ and G″ for LDPE, LDPE/EVA and LDPE/org-MMT are almost the same, but lower than that for LDPE/EVA/org-MMT in all frequency range. In high frequency($\omega \geq 10$ rad/s) range, the dependence of module on frequency for the four systems are similar to each other, exhibiting the liquid-like viscoelastic behavior of usual unfilled polymer or low loading filled polymer. But as compared with other three systems, LDPE/EVA/org-MMT revealed extraordinary viscoelastic response in low frequency (ω <10 rad/s) range, namely these viscoelastic functions, especially G′, displayed no discernible dependence on frequency and pseudo-solid-like behavior in terminal range. It is

Figure 1 Frequency ω dependence of dynamic viscoelastic functions



(a) storage module G′

(b) loss module G″

believed that such a difference in frequency dependence of module for the virgin polymer and polymer based intercalated nanocomposites resulted from the difference in their structures, exactly from different d_{001} indexes. For the LDPE/org-MMT composite, the increase value of d_{001} netted only 0.779 nm as compared with that of org-MMT (shown as in **Table 1**), meaning that no much more polymer chains intercalated into the MMT layers. The dispersing condition of MMT in the polymer matrix is similar to those of ordinary inorganic particles. However, for the LDPE/EVA/org-MMT, the polymer chains have been intercalated into MMT layers more easily due to existence of EVA and increase value of $\boldsymbol{d}_{001}$ netted 1.17 nm. Hence the dispersing condition of MMT in the polymer matrix is a favourable to an intercalated nanocomposite form. It is suggested that for such a composite, molecule chain movement of polymer melt will be confined because of the existence of silicate layers; can appear unusual viscoelastic behavior even under MMT content ≤3 wt%.

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References

1. J. W. Cho, D. R. Paul, *Polymer*, **2001**, *42*, 1083.
2. M. Kawasumi, N. Hasegawa, M. Kato, A. Usuki, A. Okada, *Macromolecules,* **1997**, *30*, 63333.
3. M. Zanetti, G. Camino, R. Thomann, R. Mulhaupt, *Polymer*, **2001**, *42*, 4501.
4. R. Krishnamoorti, E. P. Giannelis, *Macromolecules,* **1997**, *30*, 4097.
5. J. Ren, A. S. Silva, R. Krishnamoorti, *Macromolecules,* **2000**, *33*, 3739.

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