폴리프로필렌/clay 나노복합체의 유변학적 특성

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Rheological and orientational behaviors of maleated polypropylene/clay nanocomposites

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Introduction

Polymer/clay nonocomposites are attractive composites in which nanoscaled clays are molecularly dispersed. Such composites exhibit the dramatic improvement in mechanical and thermal properties[1-3] and decrease in gas permeability when compared to the pure polymer matrix. Rheological properties of polymer/clay nanocomposites have been studied[4-8]. The viscoelastic properties showed the significant dependence on the mesoscopic structure and strength of polymer-clay interaction. The significant change of viscoelastic properties, especially at the terminal region was observed at all clay loadings in most intercalated and exfoliated nanocomposites system compared to the pure matrix polymer. Especially for exfoliated nanocomposites the tethered the chains to the clay (based on nylon-6[4,5] and poly(ε-caprolactone)[5]) showed the significant change in the viscoelastic properties. The morphology effect of nanocomposites on viscoelastic properties was not obvious because most polymer nanocomposites have the unique morphology according to the polymer-clay system. In recent years, although Hoffmann et al. reported the linear viscoelastic property in model system of polystyrene/organoclay nanocomposites[6] were highly affected by the morphology, other properties were not investigated.

To understand the rheological properties of the polymer/clay composites, the structure of the clay particles must be considered. Each clay platelet has very high aspect ratio. Unfortunately all clay palatelets always don't exhibit unique aspect ration in the nanocomposites because platelets were stacked. So the clay dispersion state (or "morphology") plays a very crucial factor in the properties of polymer/clay composites. The effective aspect ratio of clay was highly influenced by the clay dispersion state. This must be the key to understand properties of nanocomposites.

On this account, Maleated PP nanocomposites is used as the model system on the study of the morphology effect in the nanocomposites because the intercalated and exfoliated morphologies are observed. The various rheological properties such as oscillatory storage modulus, non-terminal behavior, relative steady shear and shear induced orientation was investigated to compare the rheological responses of nanocomposites with different morphologies.

Experimental

Three types of maleated polypropylene/clay composites with different morphologies have

been prepared using two types of maleated polypropylene (HMPP with M_w of 185,000 and LMPP with M_w of 59,000) and two types of clay, which is pristine montmorillonite (Na-MMt) and montmorillonite (C18M) modified with stearylamine. The composite was prepared by melt intercalation method in the brabender mixer at 200 °C. Characterization of the composites was listed in Table 1.

All rheology measurements were performed on Rheometric Scientific, ARES, a strain controlled rheometer, with cone and plate geometry in oscillatory and steady-shear modes. The plates had a diameter of 50 mm and a cone angle of 0.04 rad. All measurements were carried out under nitrogen at 200 °C. All data of linear viscoelastic measurements presented in this paper have been verified to be in the linear regime. Each frequency sweep in oscillatory modes was done by decreasing from 100 to 0.01 s^{-1}. Linear viscoelastic measurements were performed before and after sufficient steady shear in order to induce the alignment of the clay. The steady shear was applied for 20 min. at the shear rate $1s^{-1}$.

Result and Discussion

Intercalation capability and final morphology of maleated polypropylene/clay composites were summarized in Table 1. Regardless of clay content LMPP/C18M nanocomposites were exfoliated and HMPP/C18M nanocomposites were intercalated. However HMPP/MMT composites were deintercalated because HMPP was immiscible with MMT.

Storage moduli of LMPP/C18M, HMPP/C18M and HMPP/Na-MMT composites measured at 200 °C were shown in Fig. 1. The curves of storage for all samples show monotonic increase with the clay loading at all frequencies, as expected for the filler effect and show the higher storage modulus at the high frequency than at the low frequency. Exfoliated LMPP/C18M nanocomposites exhibit the steepest increase rate of moduli with addition of C18M. HMPP/MMT has the lowest increase rate. Additionally all composites exhibit non-terminal yield behavior at the low frequency. The change of terminal slopes also depends on not only clay loading but also their morphologies. The typical slopes of G' and G" for monodisperse polymer are 2 and 1, respectively. LMPP was 1.61 and 1 and HMPP was 1.51 and 0.98, which might be attributed to their wide molecular weight distribution. Terminal slopes of all composites decrease with increasing clay loading. LMPP/C18M have faster decreasing rate of terminal slope than HMPP/C18M and terminal slopes of HMPP/MMT show the least sensitive with clay loadings. Especially, the terminal slopes of LMPP/C18M converge to zero slope between 5 and 10wt%.

The layered silicate based nanocomposites could be aligned by the application of large-amplitude oscillatory shear or steady shear[5,7,8]. Fig. 2 shows storage modulus of LMPP/C18M, HMPP/C18M and HMPP/MMT composites with clay of 10 wt% before and after sufficient steady shear. Steady shear applied at shear rate $1s^{-1}$ for 20min to align layered silicate. Sufficient time, 20min at shear rate $1s^{-1}$ for alignment was checked by startup test. The disordering time of the aligned clay was very long time (above $10,000s^{-1}$) rather than experiment time of the oscillatory measurement. Storage modulus of the aligned composites abruptly decreases relative to that of the unaligned at all frequencies. Exfoliated LMPP/C18M has the highest storage modulus drop. Deintercalated HMPP/Na-MMT has the lowest drop.

The linear viscoelastic behaviors of G', G" and η^* and steady shear viscosity were highly influenced by the morphology. It is concluded that the different morphology of clay produces the different aspect ratio of clay and the different aspect ratio of clay influences on rheological properties.

Table 1. Characterization of Na-MMT, C18M and maleated PP/clay nanocomposites

Wt% clay	Sample	Morphology (d-spacing)	Sample	Morphology (d-spacing)	Sample	Morphology (d-spacing)
100	C18M	(1.8nm)	C18M	(1.8nm)	MMT	(1.26nm)
1	LMPP/C18M1	E	HMPP/C18M1	I (3.2nm)		
3	LMPP/C18M3	E	HMPP/C18M3	I (3.5nm)	HMPP/MMT3	D (1.15nm)
5	LMPP/C18M5	E	HMPP/C18M5	I (3.3nm)		
10	LMPP/C18M10	E	HMPP/C18M10	I (3.6nm)	HMPP/MMT10	D (1.15nm)

E : exfoliated, I : intercalated, D: deintercalated
LMPP and HMPP = maleated polypropylene with low molecular weight (Mw=59,000) and high molecular weight (Mw=185,000), respectively; MMT=pristine montmorillonite; C18M=orgnanically modified montmorillonite.
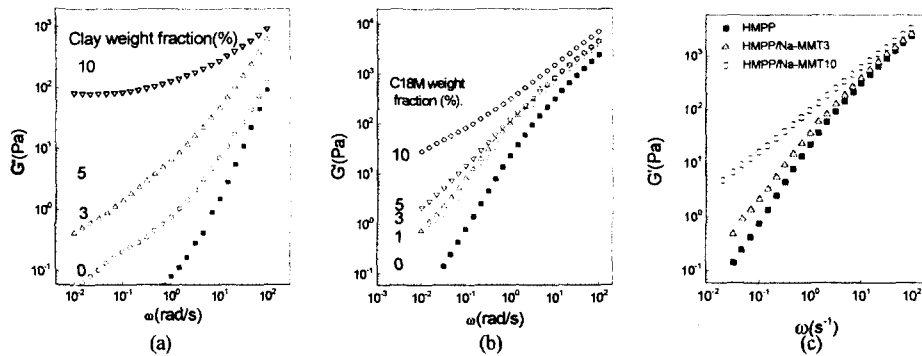

Fig 1. Storage modulus (G') for LMPP/C18M(a), HMPP/C18M(b) and HMPP/MMT(c) composites at 200°C
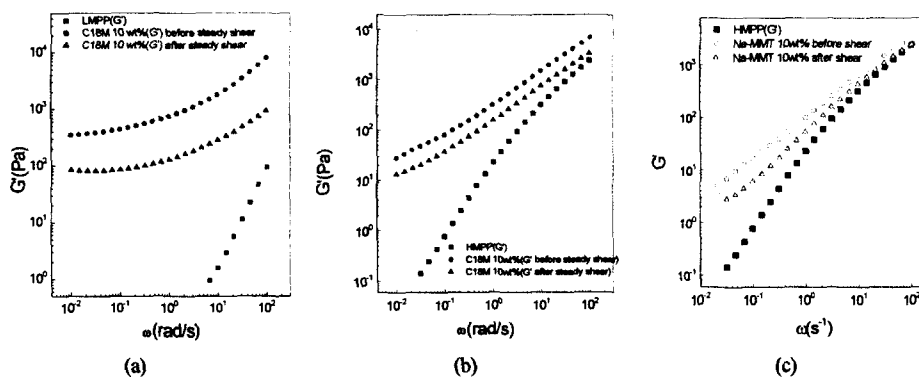

Fig 2. Storage modulus (G') for (a) LMPP/C18M, (b) HMPP/C18M and (c) HMPP/Na - MMT composites with 10 wt% C18M before and after sufficient steady shear

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