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Rheological Properties of Polystyrene-Organophilic Layered Silicate Nanocomposites

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Summary: A series of nanocomposites based on polystyrene (PS) and organophilic layered silicates (OLS) were prepared by solution blending method using organophilically modified silicate with ammonium salt of poly(styrene-*ran*-(4-vinylbenzyl chloride)). Two different types of base layered silicate were used for the preparation of the nanocomposites: sodium montmorillonite (Na-MMT) and synthetic smectite (SWN). The morphology and thermal stability of the PS/OLS nanocomposites were characterized by TEM and TGA. The rheological properties of the nanocomposites were investigated using a stress-controlled rotational rheometer under small amplitude oscillation and steady transient shear in their melt state. In addition, the effects of the contents and aspect ratio of OLS on the melt rheological properties were investigated.

Keywords: morphology; nanocomposite; organophilic layered silicate (OLS); rheological property; thermal stability

Introduction

Polymer nanocomposites containing organophilic layered silicates (OLS) have attracted a considerable research interest in resent years. The polymer nanocomposites often have superior physical and mechanical properties, including enhanced modulus, reduced gas permeability and increased heat resistance due to their nano-size dispersion of fillers.[1,2]

Generally, the nanocomposites with organophilic layered silicates are prepared by either solution blending or melt blending using various kinds of thermoplastic polymers. The majority of these researches showed that it was difficult to obtain highly dispersed nanocomposites, primarily because of lack of sufficient compatibility between the polymer matrix and OLS employed.[3]

Therefore, a fundamental issue in the preparation of nanocomposites is how to provide attractive interactions between layered silicates and polymer matrix. Lee *et al.* reported the preparation of nanocomposites composed of polystyrene-*block*-hydroxylated polyisoprene copolymer[4] or polycarbonate[5] and showed an organoclay treated with a surfactant having hydroxyl groups might form a hydrogen bonds during mixing and gave rise to a high degree of exfoliation of organoclay aggregates.

In the case of nanocomposites based on polystyrene, several synthetic routes were examined to produce polystyrene/OLS nanocomposite, aiming at improving the exfoliation of OLS.[6,7] The reported results involve *in-situ* bulk and solution polymerization of styrene using co-reactive organophilic montmorillonite,[8,9] or melt compounding of OLS in polystyrene with poly(styrene-*co*-vinyloxazoline)[10] and

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polystyrene-*block*-poly(ethylene oxide)[11] as compatibilizers. Weimer *et al.*[12] introduced initiator for the nitroxide mediated living radical polymerization on the clay surface, thus improving control of polystyrene grafting onto silicate surfaces and substantially enhancing degree of exfoliation.

From the view point of processing, the rheological study of polymer/clay nanocomposites is very crucial to predict the processibility.[13–16] The rheological investigation of polymer nanocomposites in molten state is concern to the technicians to obtain plastic products with better quality during injection molding, spinning, blowing, and other polymer processing.[17] Understanding the rheological properties of polymer-clay nanocomposites is crucial to gain a fundamental understanding of the processability and structure-property relations for the materials. For example, the linear rheological behavior of two end-tethered exfoliated hybrid systems prepared by in situ polymerization (poly(ε-caprolactone)/clay, nylon-6 or nylon-11/clay) has been reported.[18,19] The rheological behaviors of poly(epichlorohydrin)/organically modified montmorillonite nanocomposites have been investigated in steady shear condition.[20] It has been conjectured that, in the case of polymer-clay nanocomposites, the melt rheological properties would be crucially dependent not only on the strength of polymer/OLS interaction but also on the inherent viscoelastic properties of the matrix in which the layers or collection of layers are dispersed.

In this paper, we designed and prepared highly dispersed PS/OLS systems based on a poly(styrene-*ran*-(4-vinylbenzyl chloride)) with a ion-exchangeable functional group. Their morphologies and thermal stability were investigated TEM and TGA. In addition, the rheological properties of PS/OLS nanocomposites in molten state were examined in both oscillation and steady shear modes with a rotational rheometer. The effects of OLS contents on the melt rheological properties were investigated.

Experimental

Preparation

The polystyrene used in this study was a general purpose grade (GPPS), produced by LG Chem. Co., LTD. The two kinds of source clays, sodium montmorillonite (Na-MMT) and synthetic smectite (SWN) with cationic exchange capacity (CEC) of 157 and 101 meq./100g, were provided by Southern Clay Product Co. and Co-op Japan Co., respectively.

The organic modifier in this study, poly(styrene-*ran*-(4-vinylbenzyl chloride)), was synthesized via conventional radical polymerization of the styrene and 4-vinylbenzyl chloride. In this copolymer system, we controlled the content of chloromethyl group and then the functional group was converted into the ion-exchangeable ammonium salt group by the reaction of amine such as pyridine. The organophilic layered silicates (OLS) were prepared by the ion exchange reaction of the pristine layered silicate with ammonium salt of poly(styrene-*ran*-(4-vinylbenzyl chloride)).

Additional details on organophilic layered silicate, the synthesis of organic modifiers, preparation of OLS, film formation and morphological studies are described in elsewhere.[21]

The PS/OLS nanocomposite powders were prepared as followings. The polystyrene was dissolved clearly in chloroform, followed by the addition of OLS into PS solution and mixed vigorously over 12 hrs at ambient temperature. After the hybrid solution was poured in MeOH with stirring, the precipitates were filtered and dried in vacuum oven at 80 °C. The codes of PS/OLS nanocomposites and their properties are summarized in Table 1. In order to measure the rheological properties, all samples in Table 1 were compression molded in a hot press at 180 °C for 2 min. The pellet was 25 mm in diameter and 1 mm in thickness.

Characterization

For the morphology study, transmission electron microscopy (TEM) images of the

Table 1.
Formulation and morphologies of PS/OLS nanocomposites.

Codes	Weight (%)		Base layered silicate	Dispersion states[a]
	PS	OLS		
PSS01	99	1	SWN	Exfoliated
PSS03	97	3	SWN	Exfoliated
PSS05	95	5	SWN	Exfoliated
PSS07	93	9	SWN	Exfoliated
PSM01	99	1	Na-MMT	Exfoliated-Intercalated
PSM03	97	3	Na-MMT	Exfoliated-Intercalated
PSM05	95	5	Na-MMT	Exfoliated-Intercalated
PSM07	93	9	Na-MMT	Exfoliated-Intercalated

[a] Evaluated by TEM.

nanocomposites were obtained using an EN 912 Omega at an accelerating voltage of 120 kV. Thermal stabilities of nanocomposite were investigated by thermo gravimetric analysis (TGA) which was carried out on TA Instrument 2950 at heating rate of 10 °C/min under a nitrogen environment. The rheological properties of the nanocomposites were investigated using a rotational rheometer (Physica, MCR 300, Germany) with a parallel plate geometry using 25 mm diameter plates at a fixed temperature of 200 °C. The shear viscosities were obtained with the sample in the molten state as a function of the shear rate. The viscoelastic characteristics in an oscillatory shear experiment were measured to examine the durability of the nanocomposites under a periodic externally applied stress, in the parallel plate geometry of the MCR 300.

Results and Discussion

The morphological study by TEM is shown in Figure 1, where the TEM images of pristine SWN, Na-MMT, PSS05, and PSM05 were illustrated. The pristine silicates had layer-stacked structures with a few clay layers and their aspect ratio was less than 100 for SWN (Figure 1a) and above 300 for Na-MMT (Figure 1b). On the other hand, the TEM image of PSS05 (Figure 1c) showed that a large portion of SWN layers were exfoliated and randomly dispersed in polystyrene matrix. In PSM05 (Figure 1d), however, the OLS based on Na-MMT was partly delaminated and some multilayer clay tactoids existed. As a result, the PSS and PSM series are designated as exfoliated and exfoliated-intercalated state, respectively, as shown in Table 1.

The thermal decomposition behaviors of PSS and PSM series are shown in Figure 2. We can see that the maximum thermal degradation temperatures of PS/OLS nanocomposites were in about 450 °C because of main chain decomposition of polystyrenic matrix. According to the TGA experiment, the degradation temperatures of the PS/OLS nanocomposites are higher than the neat PS and shifted toward high temperature as OLS loading increased, implying the addition of OLS in the PS matrix improved the thermal stability. Comparing to each series of PSS and PSM, there is no discernable differences in maximum degradation temperatures at same OLS loading.

The dynamic linear viscoelastic behaviors of the nanocomposites in a melt state were examined in a constant strain rheometer in parallel plate geometry. The linear viscoelastic responses such as storage and loss modulus for PS and PS/OLS nanocomposites are shown in Figure 3. It is known that G' and G'' represent the elastic and viscous response of the controlled system, respectively. For both PSS

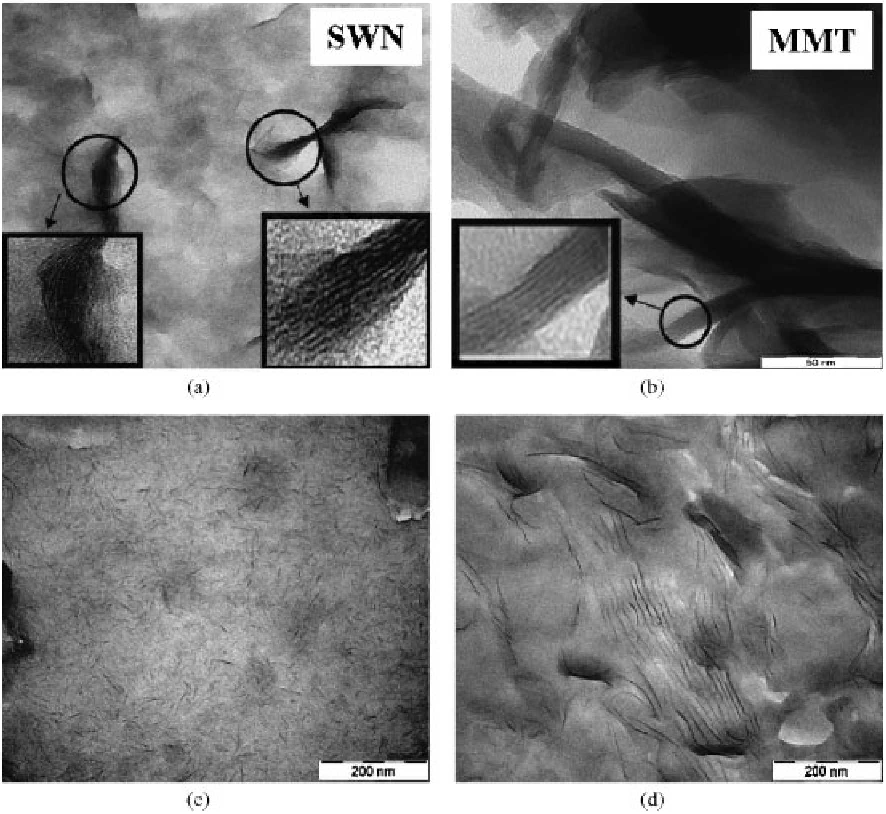

Figure 1.
TEM images of (a) pristine SWN (aspect ratio < 100); (b) pristine Na-MMT (aspect ratio > 300); (c) PSS05; (d) PSM05.

and PSM series, the oscillation data shows that both storage and loss moduli increase at all frequencies region as the OLS contents increase. Also, the crossover point of storage modulus and loss modulus are shifted to left with an increase of OLS loading. It indicates that the nanocomposite materials changes to be more solid-like as OLS loading. However, when the 1 wt% of clay was loaded to matrix, the moduli are not much different from those of pure PS, due to the softening effects of matrix by the organic modifier. Comparing to each series PSS and PSM, the modulus increase for PSS is larger than for PSM. It shows that the clay dispersion in polymer matrix for PSS is better than that for PSM. In addition, the slopes of storage modulus for nanocomposite materials are slightly smaller than that of pure PS. The decrease of the slope of nanocomposites is found to be proportional to the amount of OLS. In other words, the storage modulus became to be independent on frequency with an increase of clay loading. This observation was known to the transition from liquid-like state ($G' < G''$) at low frequency response to solid-like state ($G' > G''$) in the high frequency response.[22]

This change of proportionality can be represented in Figure 4. The Figure 4 shows modified Cole-Cole plot which shows the storage modulus change as a function of loss modulus. For pure PS, the slope is about 1.73 in log scale. It is lower value than that for common polymer melt. This is due to the stiffness of PS because of benzene group. Also, the decrease of slope with clay

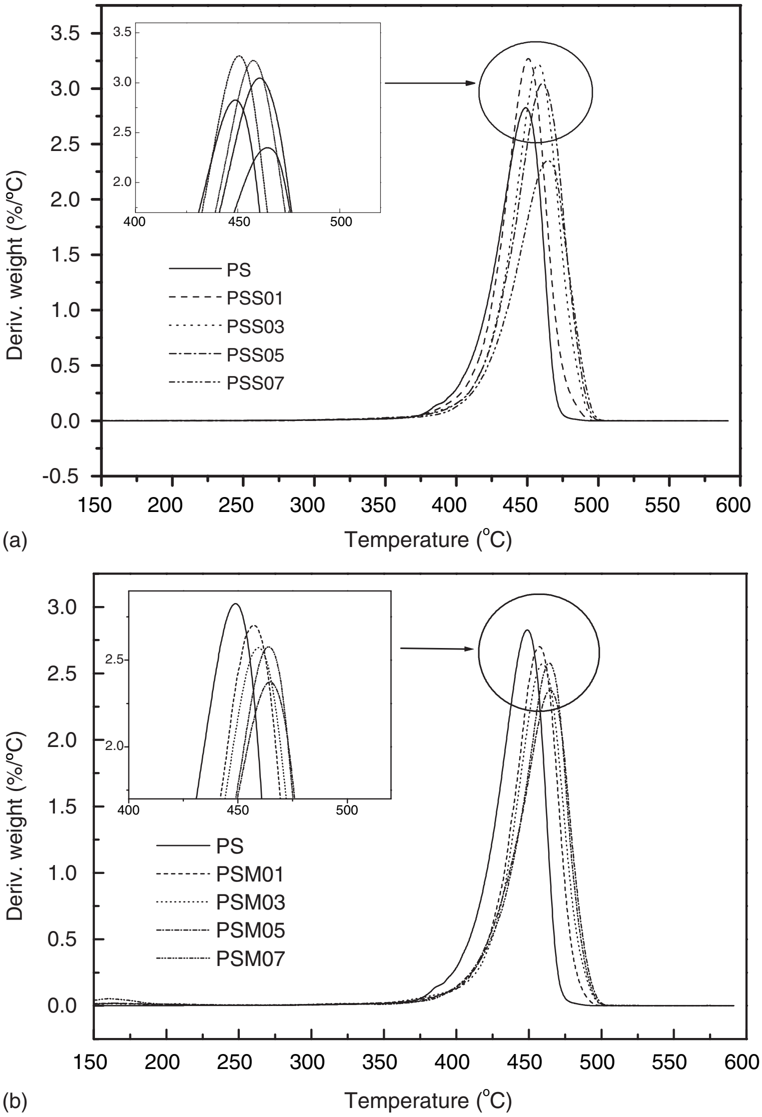

Figure 2.
The TGA derivative curves for the PSS (a) and PSM (b) series under N_2.

contents represents that the nanocomposite materials become more the solid like.

The steady shear response of polymer/clay nanocomposites has important consequences for the processability of the materials. The flow properties of the PS/OLS nanocomposites *via* steady shear measurement in their melt state were investigated. Figure 5 shows the steady shear viscosity as a function of the shear rate for the PS and PS/OLS nanocomposites with different clay loadings at 200 °C. At low shear rates, the viscosity increased with clay contents resulting from the networking structure of clay. Also, at high shear regions, the flow curves for nanocomposite materials shows higher shear thinning behavior as the increase of clay loading, due to the preferential orientation of the layers of the silicates or even

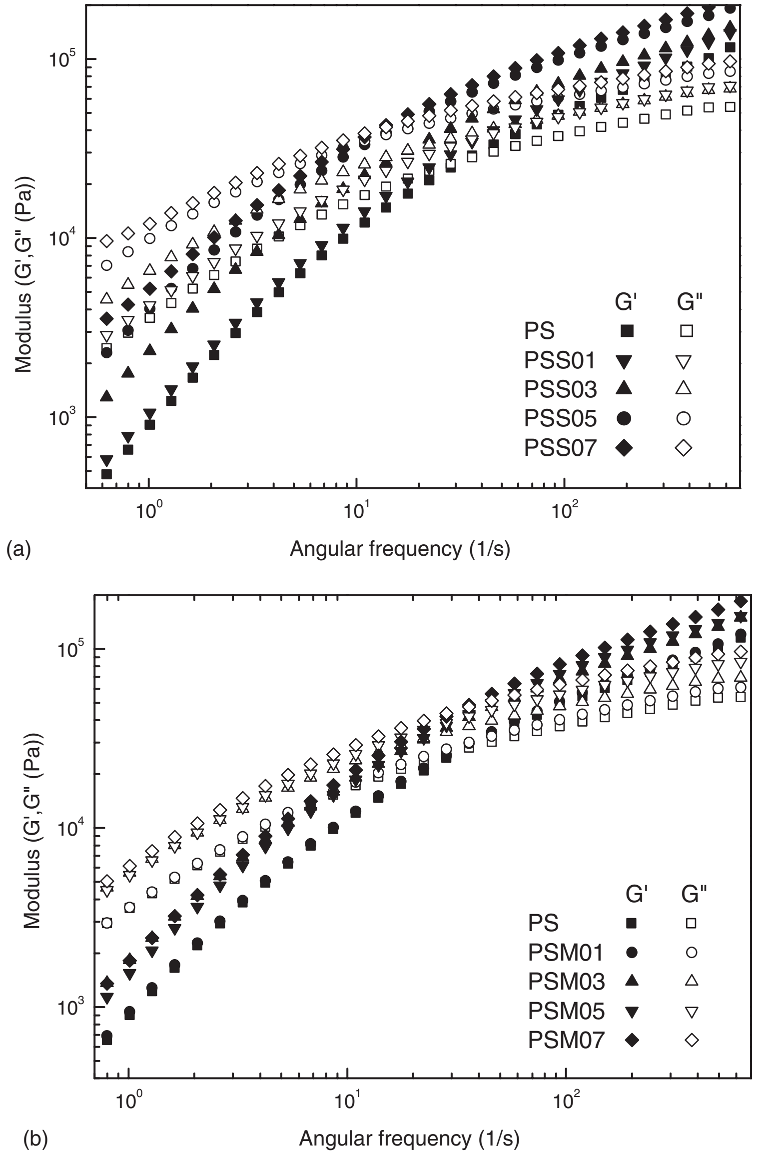

Figure 3.
Storage modulus G′ and loss modulus G″ of PSS (a) and PSM (b) series with various clay loadings at 200 °C.

anisotropic tactoids parallel to the flow direction. Also, the shear thinning for nanocomposite materials in both systems at low shear rate indicates that the clay have intercalated structure in polymer matrix. This represents that the clay orientation influences the polymer conformation in flow direction at low shear rates. Comparing to each series PSS and PSM, the increase of zero shear viscosity for PSS is larger than for PSM. It implies the smectite have better dispersion properties in the PS matrix which might result from the short aspect ratio. The results are matched well with TEM images. PSM containing OLS with large aspect ratio revealed high shear

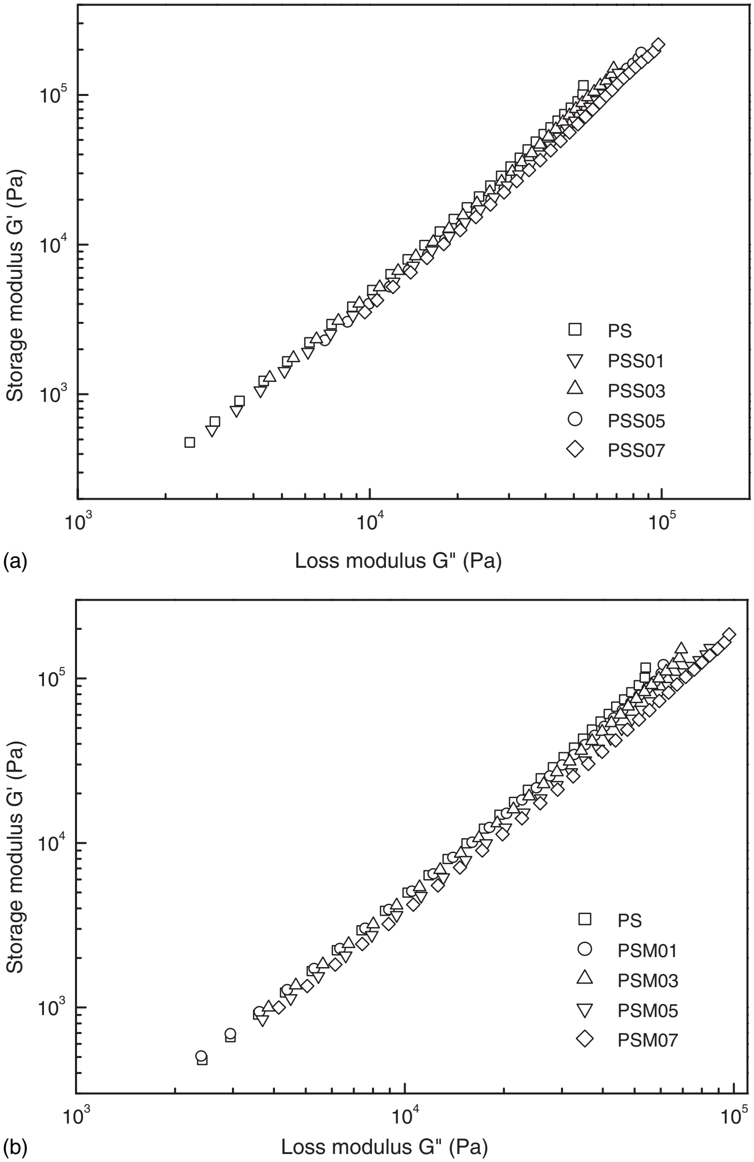

Figure 4.
Storage modulus G′ as a function of loss modulus G″ of PSS (a) and PSM (b) series at 200 °C.

thinning behavior. It also indicates that the shear influence on PSM is larger that that on PSS.

Conclusions

We designed and prepared highly dispersed PS/OLS systems using of poly(styrene-*ran*-(4-vinylbenzyl chloride)) as organic modifiers for layered silicates. The rheological behaviors of compression molded PS/OLS nanocomposites were investigated at 200 °C. The rheological properties for both oscillation and steady shear experiment indicated that the fabricated nanocomposite materials changed to solid-like as the OLS contents increased. The critical

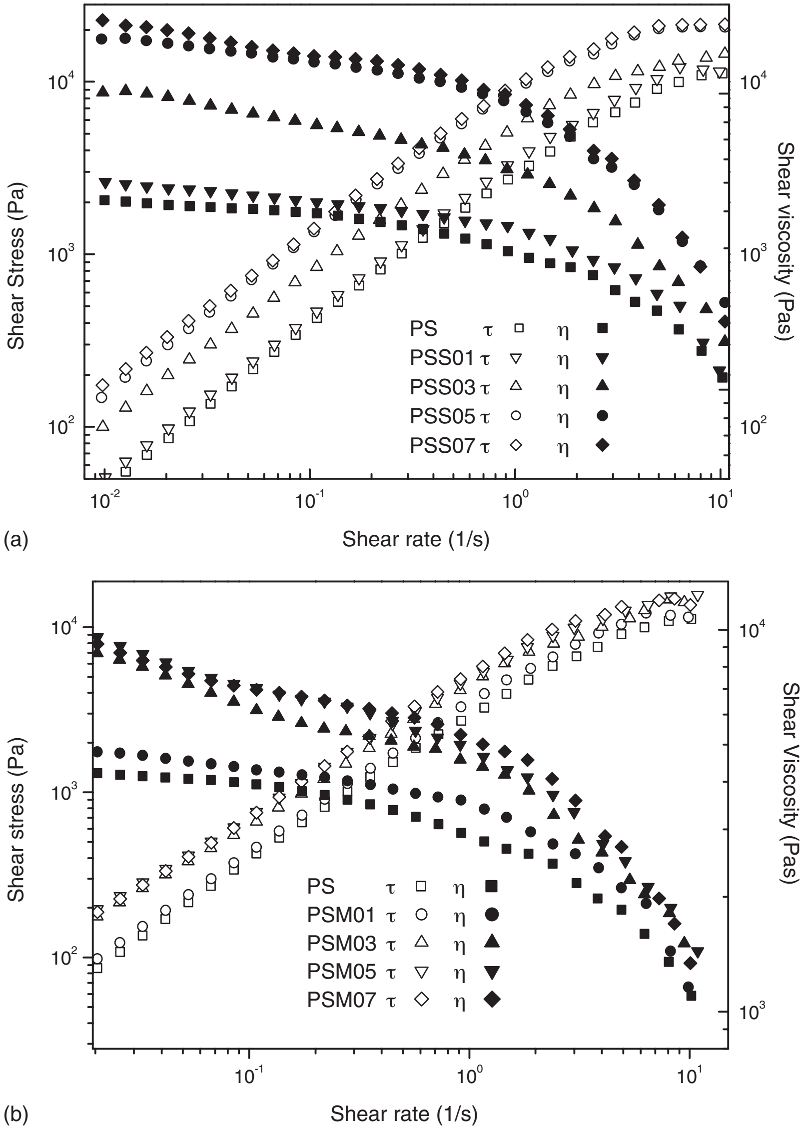

Figure 5.
Steady shear viscosities of PSS (a) and PSM (b) series as a function of the shear rate.

contents of clay for well dispersion in polymeric matrix were observed at 7 wt%. TEM images and rheological properties represented that the PSS series showed better clay dispersion than PSM series at the same OLS content. The measurement of rheological properties indicated that the OLS having short aspect ratio has good dispersion properties in polymer matrix. And also, the steady shear experiment reveled the clay orientation influenced the flow properties. The OLS with large aspect ratio was found to more sensitive to the shear rate at high shear rate region.

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