

# Rheology of Poly(Propylene)/Clay Nanocomposites

Shu-Ying Gu, Jie Ren, Qin-Feng Wang

School of Materials Science and Engineering, Tongji University, Shanghai 200092, China

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**ABSTRACT:** The linear and nonlinear shear rheological behaviors of poly(propylene) (PP)/clay (organophilic-montmorillonite) nanocomposites (PP/org-MMT) were investigated by an ARES rheometer. The materials were prepared by melt intercalation with maleic anhydride functionalized PP as a compatibilizer. The storage moduli ( $G'$ ), loss moduli ( $G''$ ), and dynamic viscosities of polymer/clay nanocomposites (PPCNs) increase monotonically with org-MMT content. The presence of org-MMT leads to pseudo-solid-like behaviors and slower relaxation behaviors of PPCN melts. For all samples, the dependence of  $G'$  and  $G''$  on  $\omega$  shows nonter-

minal behaviors. At lower frequency, the steady shear viscosities of PPCNs increase with org-MMT content. However, the PPCN melts show a greater shear thinning tendency than pure PP melt because of the preferential orientation of the MMT layers. Therefore, PPCNs have higher moduli but better processibility compared with pure PP. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 2427–2434, 2004

**Key words:** rheology; nanocomposites; clay; poly(propylene); viscoelastic properties

## INTRODUCTION

Nanostructured hybrid organic/inorganic composites have recently attracted considerable attention as researchers strive to enhance the properties of materials via nanoscale reinforcement. In contrast to the conventional particulate-filled microcomposites, clays such as montmorillonite and others, having a large aspect ratio and size, have been recognized as potential candidates for filled materials because they exhibit superiorly physical and mechanical properties when compared with the pure polymer or conventional composites, of which include improved moduli and optical properties, reduced gas permeability, improved solvent resistance, and increased heat resistance. It is projected that polymer/clay hybrids, so-called nanocomposites, will play an increasingly important role as new materials in automotive, packaging, and aerospace applications.

The preparation,<sup>1–6</sup> structures,<sup>1,3,6–8</sup> and thermal/mechanical properties<sup>2–3,8</sup> of polymer/clay nanocomposites have been extensively studied; however, limited work has been carried out on the rheological behaviors of polymer/clay nanocomposites (PPCNs). The rheological properties are related to the distortion or deformation of the nanocomposites. It is instructive to study the rheology of PPCNs for two reasons. First,

rheological properties are indicative of melt-processing behaviors in unit operations such as injection molding. Second, because the rheological properties of particulate suspensions are sensitive to the structure, particle size, shape, and surface characteristics of the dispersed phase, rheology potentially offers a means to assess the state of dispersion of nanocomposites directly in the melt state. So, from processing and application points of view, the mechanical and rheological properties of these nanocomposites are of vital importance. It would also be important to relate their mechanical and rheological properties to the nature and microstructure of the nanocomposites formed.

Previous rheological studies of nanocomposites primarily focused on oscillatory and steady shear aspects of nylon 6, poly(propylene) (PP), poly(ethylene oxide), and polystyrene/polyisoprene block copolymer clay nanocomposites.<sup>9–13</sup>

The materials in this study were prepared by intercalation by using a twin extruder in the presence of a compatibilizer-maleic anhydride functionalized poly(propylene) (PP-g-MAH) as described in the previous article. The structures and mechanical properties were also studied.<sup>14</sup> PP-g-MAH as a compatibilizer can interact with layers of the org-MMT through strong hydrogen bonding between the polar functional group of PP-g-MAH and the oxygen group of org-MMT, which was mentioned in Kawasumi et al.'s previous work.<sup>4</sup> The intercalated org-MMT hybrid can be easily dispersed in the PP matrix to form nanocomposites. This study explored the linear and nonlinear rheology of the PP/org-MMT. Measurements of linear viscoelastic properties revealed the effect of org-MMT on the rheological behaviors of the

Correspondence to: S.-Y. Gu (gushuying@online.sh.cn).

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**TABLE I**  
**Compositions of PPCNs (wt %)**

Sample	PP	Master batch	TJ4 (Calculated)
PP	100	0	0
PPCN1	95	5	1
PPCN5	75	25	5
PPCN7	65	35	7

PP nanocomposites. Steady shear studies probed the nonlinear rheological properties of the PP nanocomposites.

## EXPERIMENTAL

### Materials

PP (P300) was supplied by Jinsan Petrol and Chemical Co. (Shanghai, China) in the form of granule (melt index = 3.74 g/min). Organophilic montmorillonite (org-MMT) TJ4 was exchanged with dioctadecyl ammonium bromide from sodium montmorillonite (cation-exchange capacity = 120 meq/100 g). The interlayer distance of the org-MMT was about 3.8 nm measured by X-ray diffraction (XRD). The XRD measurements were taken by using a Bruker-axs D8-advance diffractometer with  $\text{CuK}\alpha$  radiation. The inorganic content was about 70.12 wt % by measuring the weights before and after burning its organic parts. The average particle size was less than 20  $\mu\text{m}$ . PP-g-MAH was melt-grafted with P300 by twin-screw extrusion at a temperature between 170 and 190°C. Its grafted percentage was about 0.8% and MI was 3.92 g/min.

### The preparation of nanocomposites

Prior to preparation of nanocomposites, PP-g-MAH/org-MMT master batch PPCN20 was prepared by mixing 80 wt % PP-g-MAH and 20 wt % org-MMT by using a Haake Rheomix 100 intermeshing twin-screw extruder after being dried at 90°C for 12 h. Then the materials were prepared by melt-mixing master batch and PP according to Table I as described in the previous article.<sup>14</sup> Samples were prepared by compression molding of the extruded pellets at 190°C for about 5 min into 1-mm-thick plates and then cut into 25-mm-diameter parallel plates and 45  $\times$  12 mm bars.

### Linear and nonlinear rheology

To determine the limits of linear viscoelastic properties of PP and PPCNs, dynamic strain sweeps of PP and PPCNs were performed on a controlled strain rate rheometer (ARES Rheometer, Rheometrics Scientific, USA) with a parallel plate geometry using 25-mm-diameter plates. All measurements were performed at 190°C and a frequency of 10 rad/s. The gap was set at

a range of 0.8 to 1 mm. Linear rheological measurements were performed at a frequency range of 1 to 500 rad/s. To ensure the linear viscoelastic region, we set the strain to be 0.1%, and then elastic moduli ( $G'$ ), loss moduli ( $G''$ ), and complex viscosities ( $\eta^*$ ) were obtained.  $G'$  represents the strain energy reversibly stored in the substance, whereas  $G''$  represents the amount of energy irreversibly given off by the substance to its environment. To calculate the flow activation energy, dynamic frequency sweep test was performed at different temperatures (180, 190, 200, and 210°C). Nonlinear rheological measurements were performed over a shear rate range of 0.01 to 1 rad/s at 190°C.

Because of the potential for solidlike and slowly relaxing fluid structure in the materials, the prior deformation history of the samples was carefully controlled. For all the measurements, samples were equilibrated in the rheometer after loading at the desired temperature for 20 min. All measurements were performed with a 2000 g cm transducer with a lower resolution limit of 2 g cm.

## RESULTS AND DISCUSSION

### Linear viscoelastic properties

Figure 1 plots the elastic modulus dependence of strain for PP and PPCN5 at 190°C at a frequency of 10 rad/s. It is indicated that the regions of linear viscoelastic behavior for PP and PPCN5 are very wide and insensitive to the presence of org-MMT. The linear viscoelastic regions extend to a strain of 20% under the testing conditions. Therefore, the linear viscoelastic properties of PP and PPCNs were conducted at a strain of 0.1%.

The elastic moduli ( $G'$ ), loss moduli ( $G''$ ), and complex viscosities ( $\eta^*$ ) of PP and PPCNs are compared in Figures 2, 3, and 4, respectively. Comparison of the linear viscoelastic response of the materials shows the significant effect of the clay, particularly at low frequency. At low frequency, PP/org-MMT nanocomposite melts have higher elastic moduli, loss moduli, and complex viscosities compared with pure PP and show a monotonic increase with MMT content. At high frequency, however, the elastic moduli, storage moduli, and complex viscosities of PP and PPCN melts come nearer. The reason for the increasing of  $G'$ ,  $G''$ , and  $\eta^*$  might arise from the confinement of polymer chains within the MMT layers. Indeed, it has been reported that the viscosities of confined polymer melts are greater than those of bulk chains.<sup>15</sup> The  $G'$ ,  $G''$ , and  $\eta^*$  of PPCN5 are several times those of PP, as shown in Figures 2, 3, and 4. To investigate the confinement of polymer chains, we have measured the dynamic rheological behaviors of PP and PPCNs at various temperatures and calculated the flow activation energy ac-

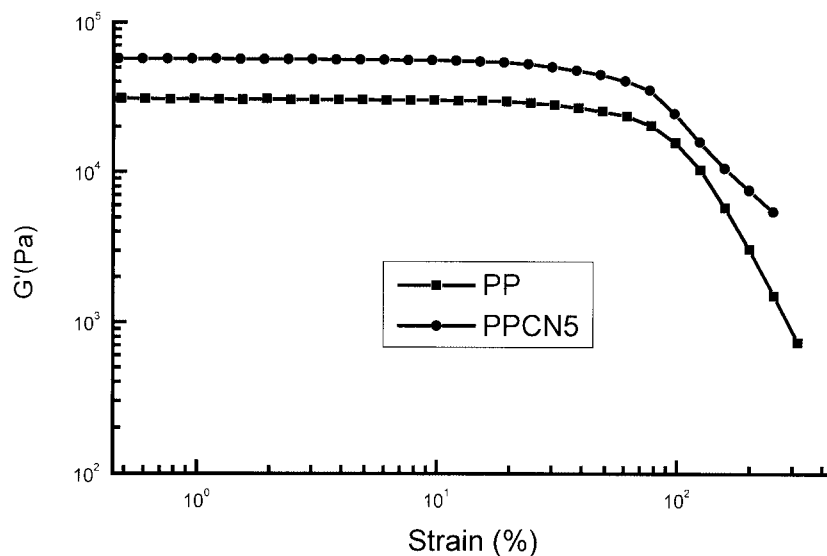


Figure 1 Dynamic strain sweep tests of PP and PPCN5 at 190°C.

according to Arrhenius function (see Fig. 5).<sup>16</sup> The results are listed in Table II.

On the one hand, it is obvious that the flow activation energy of nanocomposites is higher than that of pure PP, which is not consistent with the results of the previous work<sup>11</sup> (What leads to the difference needs to be studied further.) The higher flow activation energy causes a larger energetic barrier for segmented motions in the confined space and thus causes an increase of  $G'$ ,  $G''$ , and  $\eta^*$ . The increasing flow activation energy was strengthened because of the strong hydrogen bonding between the polar functional group of PP-*g*-MAH and the oxygen group of MMT. On the other hand, the slower relaxation behaviors of PPCNs are the underlying physics for the increased  $G'$ ,  $G''$ , and  $\eta^*$  of the confined polymer, which will be discussed later.

At low frequency, the PP and PPCN melts are liquidlike ( $G' < G''$ ), while inheriting solidlike behaviors at high frequency ( $G' > G''$ ). The transition from liquidlike to solidlike behaviors occurs at a crossover frequency ( $\omega_c$ ). The crossover frequencies of PPCNs shift toward lower frequencies with the increase of MMT content, which is called pseudo-solid-like behaviors. The crossover frequencies of PP, PPCN5, and PPCN7 are 16.75, 9.35, and 6.73 rad/s, respectively. The pseudo-solid-like behaviors of PPCNs might also be due to the slower relaxation behaviors.

#### Nonterminal behavior

For typical bulk polymer fluid in the terminal zone, terminal zone slopes of  $G'$  and  $G''$  are 2 and 1 (i.e.,  $G'$

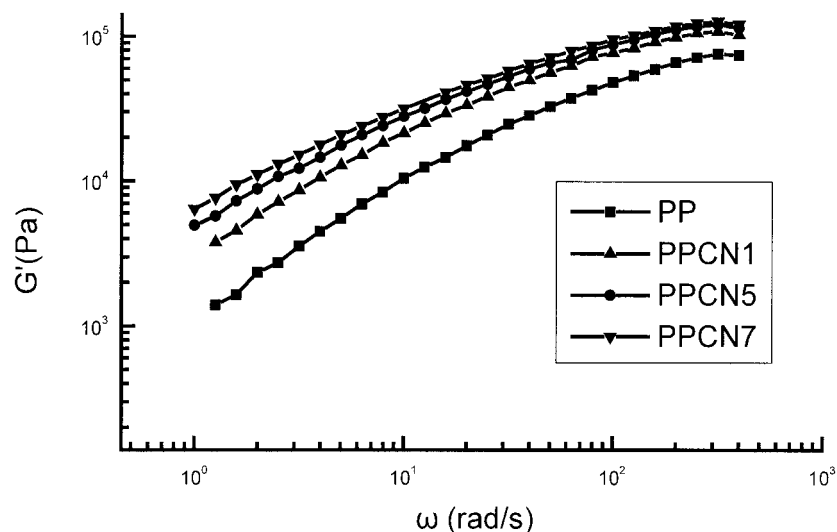


Figure 2 Storage moduli  $G'$  of PP and PPCNs at 190°C.

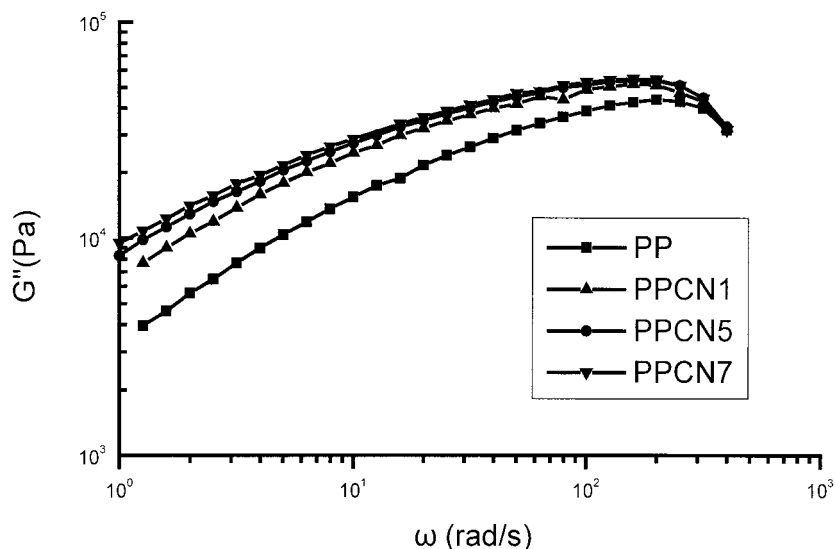


Figure 3 Loss moduli  $G''$  of PP and PPCNs at 190°C.

$\propto \omega^2$  and  $G'' \propto \omega$ ). Terminal zone slopes of all samples were calculated and listed in Table III. The terminal zone dependence of  $G'$  and  $G''$  on  $\omega$  for all samples shows nonterminal behavior with power-law dependence of  $G'$  and  $G''$ , much smaller than the expected 2 and 1, respectively. Furthermore, there appears to be a gradual decrease in the power-law dependence of  $G'$  and  $G''$  with increasing MMT loading. This is consistent with the results of the rheology of PCL-based nanocomposites obtained by Krishnamoorti and Gianelis.<sup>9</sup> Nonterminal flow behavior has been observed in filled-polymer systems exhibiting yield phenomena, but only in cases wherein the filler and polymer are actively interacting and in a dynamic region at lower frequency than those observed in this study.

Nonterminal low-frequency rheological behavior has also been observed in ordered block copolymers and smectic liquid-crystalline small molecules.<sup>17,18</sup> Several hypotheses have been suggested to explain the rheological behaviors observed in these systems. Koppi et al. have suggested that undulations and defects in the layers might contribute to the low-frequency viscoelastic response in layered block copolymers.<sup>19</sup>

Other ideas mention that the domain structure of the ordered mesophases is responsible because of the dynamic processes on both the microscopic and the mesoscopic length scales. It is also well documented that topological defects also affect rheological properties dramatically, particularly in the low-frequency terminal region. The results of materials with smectic

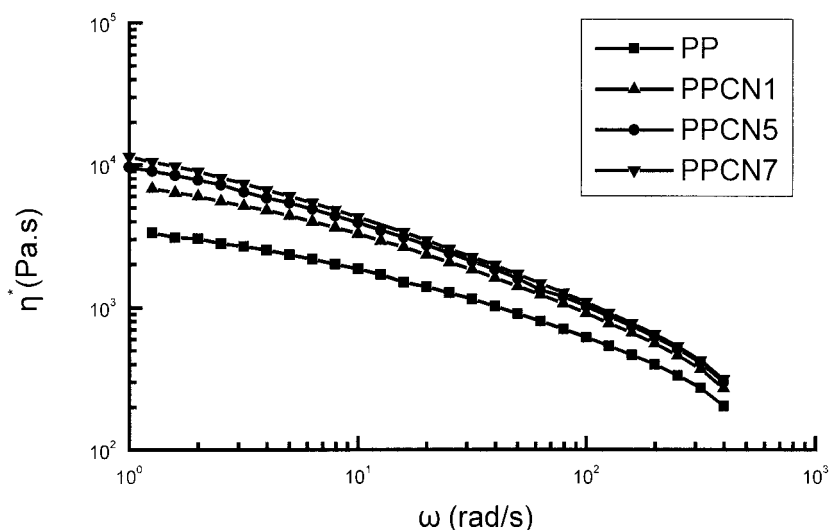


Figure 4 Complex viscosities  $\eta^*$  of PP and PPCNs at 190°C.

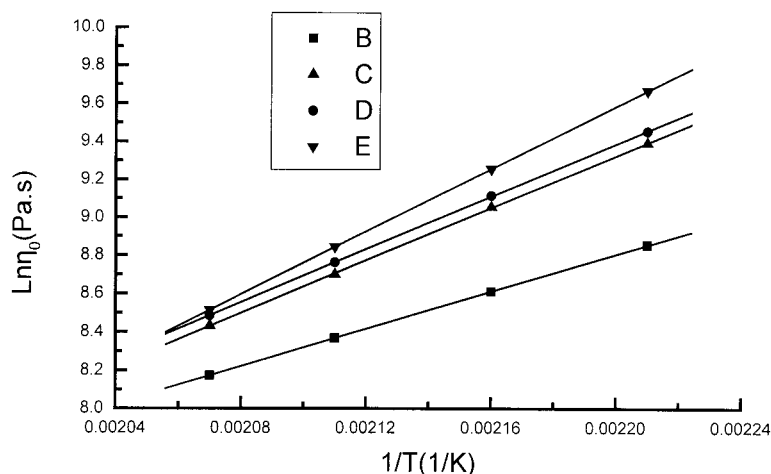


Figure 5 Arrhenius plot of zero shear viscosity as a function of temperature.

small molecules and short-ordered block copolymers have suggested that the nonterminal low-frequency response is due to the range domain structure and the presence of defects.<sup>18</sup> Effects of domain collective dynamics were studied by Kawasaki and Onuki, who demonstrated that overdamped second-sound modes in an orientationally disordered lamellar phase could result in anomalous low-frequency rheological behavior.<sup>20</sup> Rubinstein and Obukhov also obtained the same result by considering diffusion-controlled annihilation of defects in a disordered lamellar system.<sup>21</sup> In the nanocomposites studied in this article, the organophilic-montmorillonite layers in the hybrids are highly anisotropic with polymer chains intercalated between the layers. Furthermore, there is a strong hydrogen interaction between the PP-g-MAH and MMT layers. Thus, it can be expected that there are domains in these materials even above the melting temperature of the polymers, wherein certain long-range order is preserved and the MMT layers are oriented in some preferred directions. At the same time, there may be defects at the boundaries of MMT layers and polymer. Therefore, the MMT domains and defects in the melts may lead to the nonterminal rheological behavior.

### Relaxation of nanocomposites

To compare the temperature dependence of the relaxation of these nanocomposites, terminal slopes of  $G'$  and  $G''$  at different temperatures were calculated

TABLE II  
Flow Activation Energy of PP and PPCNs

Sample	PP	PPCN1	PPCN5	PPCN7
Flow activation energy (KJ/mol)	40.56	57.40	57.90	68.71

and plotted in Figures 6 and 7. It is obvious that the terminal slopes show an increasing tendency with the increase of temperature for all samples, which is caused by easier motion of molecular chains at higher temperature. However, the increasing tendency of PP/org-MMT nanocomposites is smaller than that of pure PP and the tendency decreases with the increase of MMT content. This may be due to the confinement of motion of molecular chain caused by MMT layers dispersed in PP matrix. At the same time, the interaction between MMT layers and PP-g-MAH creates an energetic barrier to the reptation motion, which leads to a dramatic increase in the relaxation time.

The smaller increasing tendency of terminal slopes of  $G'$  and  $G''$  of nanocomposites indicates that the time relaxation of nanocomposites is slower than that of pure PP that is conformed with the results of stress relaxation data  $G(t)$  (Fig. 8) transformed by dynamic data by using a method developed by Ninomiya and Ferry.<sup>16</sup> The slopes of  $G(t)$  curves decrease with the increase of MMT content, which indicates that the relaxation time increases with the increase of MMT content.

### Nonlinear rheological behavior

In the rheological characteristics of the nanocomposites, the steady shear response of PPCNs will provide

TABLE III  
Terminal Slopes of  $G'$  and  $G''$  versus  $\omega$  of PP and PPCNs at 190°C

Sample	PP	PPCN1	PPCN5	PPCN7
$G'$	0.7141	0.5947	0.5457	0.51
$G''$	0.4825	0.3779	0.3550	0.3510

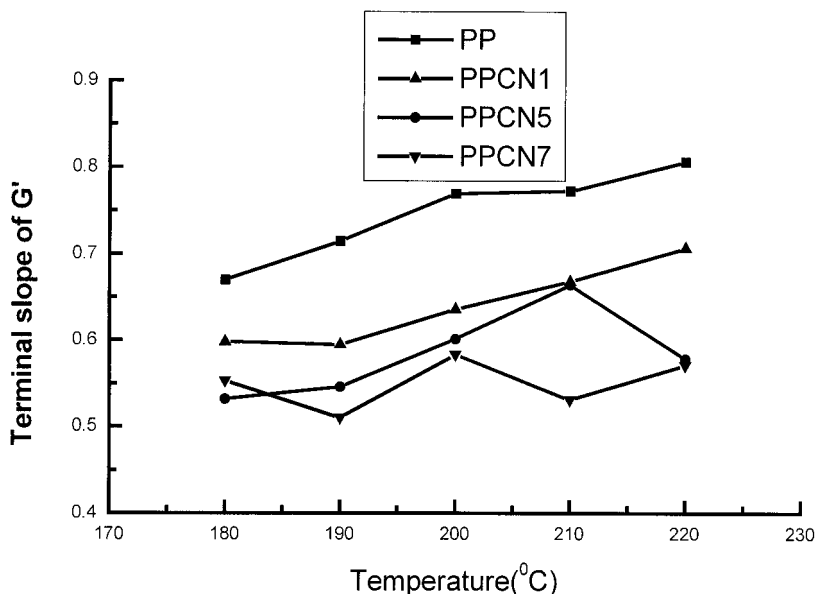


Figure 6 Terminal slopes of  $G'$  versus temperature.

useful information on the material processibility. There exist several studies for the steady shear behavior of polymer/clay nanocomposites.<sup>12,22,23</sup> Here, we have investigated the PP/org-MMT intercalated nanocomposites. The steady shear viscosities,  $\eta$ , as a function of shear rate,  $\dot{\gamma}$ , for PPCNs are shown in Figure 9. It is obvious that the viscosities of nanocomposites are much higher than those of pure PP at lower shear rates. The steady shear viscosity of PPCN5 with 5 wt % MMT is about three times of that of pure PP at the shear rate of 0.01 rad/s.

The shear viscosities of the nanocomposites increase monotonically with MMT loading; the intercalated

nanocomposites display a more serious shear thinning behavior and the shear thinning behavior begins at lower shear rate. In other words, at low shear rate, the addition of very small amounts of MMT results in a significant enhancement in the shear viscosity. At high shear rate, however, the shear viscosities for the nanocomposites are comparable with or even lower than that of the pure PP as a result of the preferential orientation of the MMT layers or even anisotropic tactoids parallel to the flow direction. To investigate the dependence of  $\eta$  on  $\dot{\gamma}$ , Carreau's<sup>24</sup> model was employed to fit the non-Newtonian viscosity curves in Figure 9:

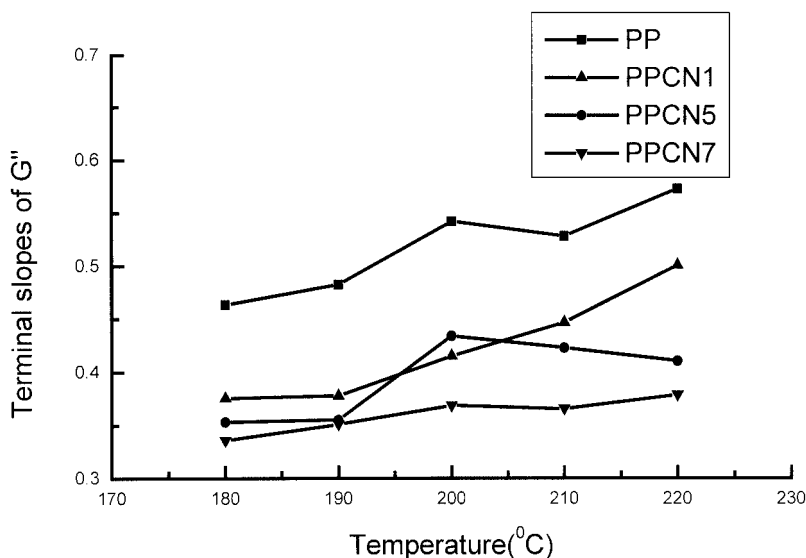


Figure 7 Terminal slopes of  $G''$  versus temperature.

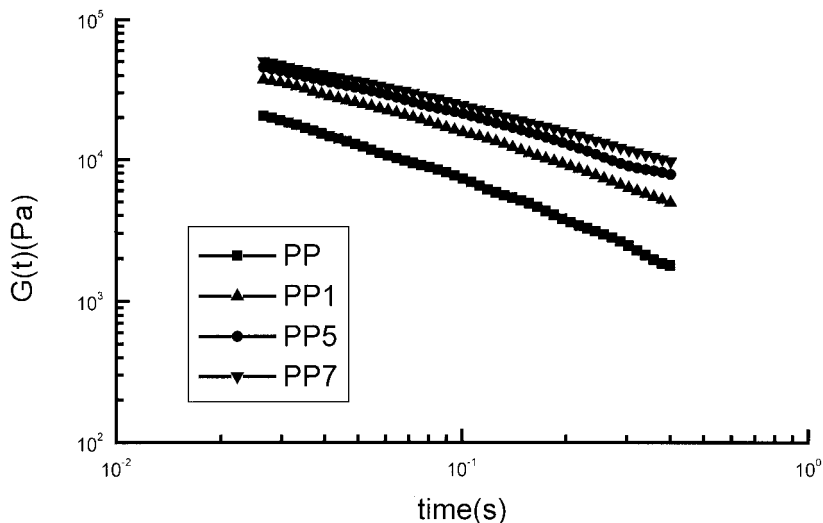


Figure 8 Relaxation moduli of PP and PPCNs at 190°C.

$$\eta = \eta_0/[1 + (\gamma t_1)^2]^{(1-n)/2} \quad (1)$$

Here,  $\eta_0$  is the zero shear rate viscosity,  $t_1$  is the characteristic time, and  $n$ , which is called the non-Newtonian Index, is a dimensionless parameter. The slope of  $\eta$  versus  $\dot{\gamma}$  on a log-log plot in the power-law region is  $(n - 1)$ . The calculated values of  $n$  for PP, PPCN5, and PPCN7 are 0.7679, 0.5388, and 0.5294, respectively. That is to say, the addition of MMT leads a dramatic decrease of  $n$ , which is in conformity with the serious shear thinning behavior of PP/org-MMT nanocomposites.

CONCLUSION

The linear and nonlinear shear rheological behaviors of PP/org-MMT nanocomposites were investigated

by an ARES rheometer. The storage moduli, loss moduli, and dynamic viscosities of PPCNs show a monotonic increase with MMT content due to the confinement of polymer chains and the strong hydrogen bonding between the polar functional group of PP-g-MAH and the oxygen group of org-MMT.

The addition of MMT causes pseudo-solid-like behaviors and slower relaxation behaviors of PPCN melts. For all samples, the dependence of  $G'$  and  $G''$  on  $\omega$  shows nonterminal behavior with power-law dependence of  $G'$  and  $G''$ , much smaller than the expected 2 and 1, respectively. The steady shear viscosities of PPCNs are much higher than those of pure PP at lower shear rate. At high shear rate, however, the shear viscosities of the nanocomposites are comparable with or even lower than that of pure PP as a result of the preferential orientation of MMT layers. There-

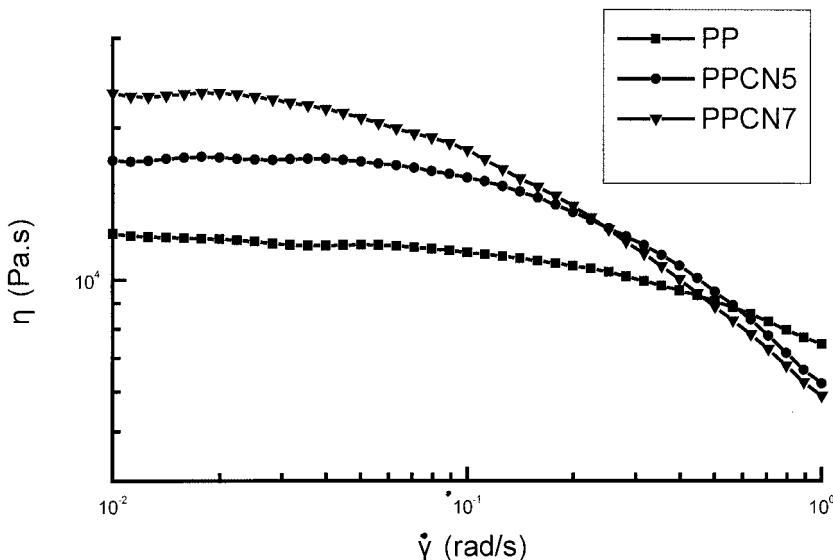


Figure 9 Steady viscosities of PP and PPCNs at 190°C.

fore, PPCNs have higher moduli but better processibility compared with pure PP.

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