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# Rheological investigation of creep recovery for UHMWPE or carbon nanotubes in isotactic polypropylene matrix

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**Abstract:** Isotactic polypropylene/ultrahigh-molecular-weight polyethylene blends (iPP/UHMWPE) and iPP/carbon nanotubes composites (iPP/CNTs) were prepared by a coagulation method followed by compression molding. The percolation thresholds for melts of iPP/UHMWPE blends and iPP/CNTs composites determined by rheometer, were beyond 5.0 wt% and close to 4.0 wt%, respectively. The creep and creep-recovery behavior of iPP/UHMWPE and iPP/CNTs melts were systematically investigated by rheological measurements. The results indicated that UHMWPE and CNTs played similar roles in the material's elastic recovery, the addition of 2.0 wt% UHMWPE or 0.2 wt% CNTs increased the elastic recovery about 10 fold in comparison with neat iPP.

**Keywords:** carbon nanotubes; creep recovery; polyethylene; polypropylene.

## 1 Introduction

Isotactic polypropylene (iPP), as one of the most important commodity polymers, has been extensively used in industry. However, the lack of elasticity at low temperature below room temperature has imposed great limitations on the application of iPP. To overcome the deficiency, blending with other polymers or fillers is a feasible method to modify the rheological property of iPP melts, which has recently attracted much attention (1–3). For instance, Xu et al. reported that the efficiency of load transfer between nanotubes and polymer chains

in the melts is a critical factor to influence the resulting viscoelastic performance of iPP/CNTs composites melts (1). Both the loss and storage modulus increased with the addition of CNTs due to the interaction between the iPP molecules and CNTs which lead to longer relaxation times. Lee et al. investigated the rheological behavior of iPP/ultrahigh-molecular-weight polyethylene (UHMWPE) blends melts. The results showed that the addition of iPP decreased the melt viscosity (2). Thus, a promising research area for iPP focuses on the improvement of elasticity of melts taking account of its application prospects (4–6). However, little work has been reported regarding the elastic properties of iPP dispersed fillers, especially the difference from these of the iPP matrix, such as polymer or inorganic fillers fluorinated graphene (GF), montmorillonite (HMT), etc. (7–10). In general, it is difficult to determine the zero shear rate viscosities and steady-state recoverable compliances of polymer melts from dynamic-mechanical experiments because of their long relaxation time, which results in the long oscillation time being necessary to achieve a steady-state of oscillation. While the advantage of creep recovery tests is that the steady-state of deformation is reached much faster than in stressing experiments and oscillatory measurements. Therefore, creep and creep recovery, as a time-dependent mechanism of plastic deformation, has incurred increased interest in recent years for the determination of the two characteristic curves of polymer melts with the long retardation time (11, 12). Herein, we chose UHMWPE as the polymer filler and CNTs as the inorganic filler. iPP/UHMWPE blends and iPP/CNTs composites were prepared by a coagulation method. The creep performance of iPP composite melts reinforced by CNTs and UHMWPE were characterized by a parallel plate rheometer. Characterizing the interplay between iPP and fillers will provide an important guide in the choice of these fillers for application and in processing design. Dynamic changes of storage modulus of iPP with different CNTs and UHMWPE concentrations were measured to determine the network formation in the molten state.

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## 2 Experimental

### 2.1 Materials

The iPP sample employed in this work was a commercial product of the Aldrich Chemical Co. (USA). The iPP sample had a weight average molecular weight,  $\overline{M}_w$ , of 340,000 and number average molecular weight,  $\overline{M}_n$ , of 97,000. The UHMWPE used in this study was kindly supplied by the Beijing Second Subsidiary Additive Factory (China)  $\overline{M}_w = 3,360,000$ . The multiwalled carbon nanotubes (MWNTs, purity >95%, made by a chemical vapor deposition method) were supplied by Shenzhen Nanotech Port Co., Ltd. (China). The other reagents were purchased from the Beijing Chemical Reagents Co. (China) and were used as received.

### 2.2 Preparation of iPP/CNTs and iPP/UHMWPE composites

Alkyl-modified CNTs,  $\text{CNT}(\text{COOC}_{18}\text{H}_{37})_n$ , modified with  $\text{C}_{18}\text{H}_{37}\text{Br}$  were prepared as in a previous study (1); the average aspect ratio was about 28–56. For simplicity, the  $\text{CNT}(\text{COOC}_{18}\text{H}_{37})_n$  was abbreviated here as CNTs. A coagulation method was used to prepared iPP/CNTs composites and iPP/UHMWPE blends. At first, iPP was dissolved in xylene at 125°C and the CNTs or UHMWPE were dispersed individually in xylene in an ultrasonic bath for 2 h. Then, the CNTs/xylene or UHMWPE/xylene suspension was added into iPP/xylene solution with vigorous stirring for 1.5 h at 125°C. The suspension was then poured into a large amount of cold methanol. After filtration and drying in vacuum at 60°C for 3 days, the iPP/CNTs composites and iPP/UHMWPE blends were obtained. iPP blends containing 0.5, 1.0, 2.5, 5.0, and 10.0 wt% UHMWPE and composites with 0.5, 1.0, 2.5, 4.0% CNTs were prepared. Neat iPP was subjected to an identical preparation procedure for comparison purposes.

### 2.3 Rheological measurements

Rheological measurements were performed on a stress-controlled rheometer (TA-AR2000, TA Instruments Co., New Castle, DE, USA) with parallel plates (diameter of 25 mm) in nitrogen atmosphere. Before the rheological measurements, the dried samples were pressed in vacuum at 180°C into disks with a thickness of 1 mm and diameter of 25 mm. Oscillatory time sweeps were performed to ensure

that the dried neat iPP, iPP/CNTs and iPP/UHMWPE composites did not show obvious storage modulus and viscosity changes for at least 3 h at the testing temperature. Oscillatory frequency sweeps ranging from 0.1 to 500 rad/s with a fixed strain of 0.5% (falling in the linear viscoelasticity regime) were performed at 180°C for the iPP/CNTs composites with different CNTs concentrations. Creep and creep-recovery experiments according to Figure 1 were performed. In the creep test, a constant shear stress  $\tau_0$  was applied and the resulting time-dependent deformation  $\gamma(t_{cr})$  was measured. The creep compliance  $J(t_{cr})$  in the linear viscoelastic range can be described by

$$J(t_{cr}) = \gamma(t_{cr}) / \tau_0 = J_0 + \psi(t_{cr}) + t_{cr} / \eta_0 \quad [1]$$

with  $J_0$  being the elastic compliance,  $\psi(t_{cr})$  the viscoelastic portion of the compliance, and  $\eta_0$  the zero shear-rate viscosity. In the following creep-recovery experiment the shear stress  $\tau_0$ , was set to zero at  $t_0$ , and the recoverable deformation  $\gamma_r(t_0, t_r)$  was measured. For a given preceding shear stress this quantity generally depends on the creep time  $t_{cr}$  and the recovery time  $t_r$ .

The recoverable compliance  $J_r(t_0, t_r)$  as defined by

$$J_r(t_0, t_r) = \gamma(t_0, t_r) / \tau_0 \quad [2]$$

in the linear range of deformation was a measure of the elasticity of the material. As the values for  $J_r(t_{cr}, t_r)$  were smaller compared to  $J(t_{cr})$  for most polymers, as for our samples, a double-logarithmic plot was used in the following to present the results of the creep-recovery tests. Furthermore, for the creep and creep-recovery measurements the same time axis was used, i.e.  $t_r$  and  $t_{cr}$  both started at the time zero. The amount of elastic recovery, as defined by  $\varepsilon = \gamma(t_{cr}, t_r) / \gamma(t_{cr})$ , the iPP/CNTs composites and iPP/UHMWPE blends were recorded for comparison.

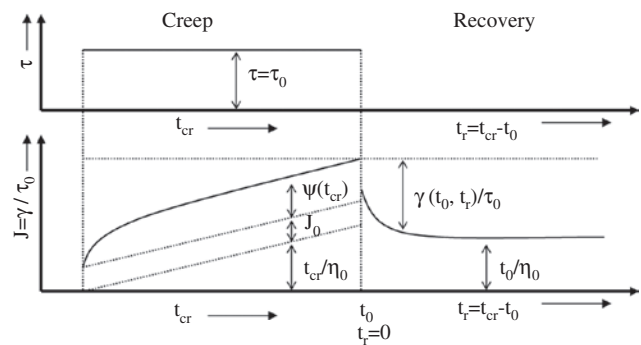
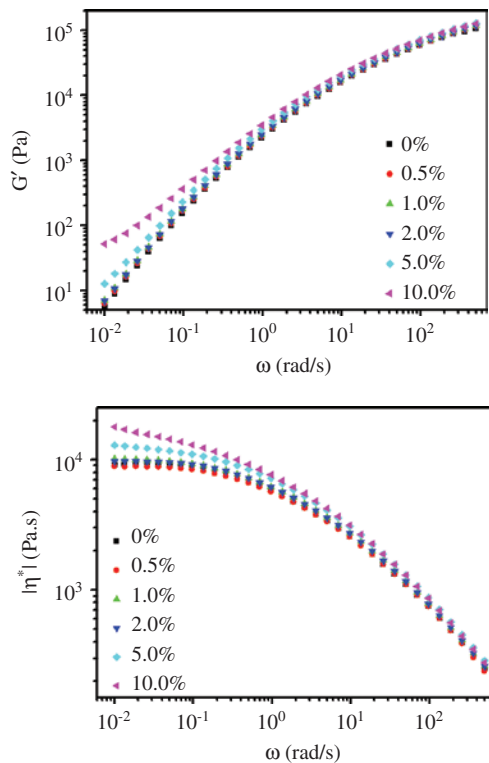


Figure 1: Schematic diagram of a creep-recovery test.

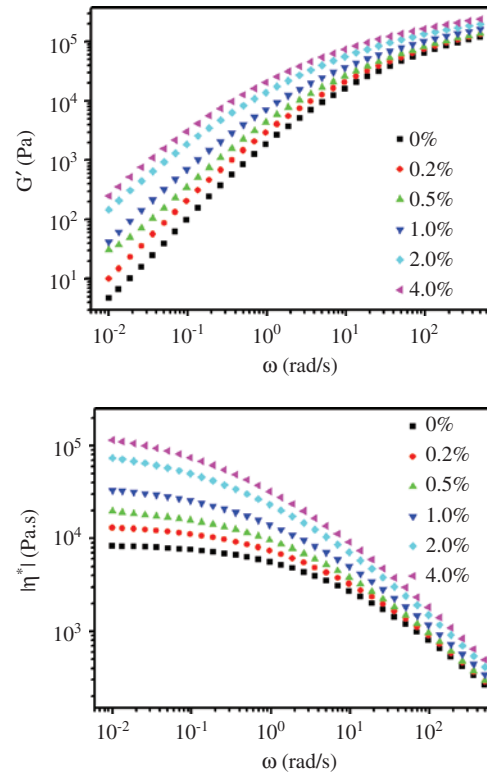
### 3 Results and discussion

#### 3.1 Influence of UHMWPE and CNTs on the melt rheological properties

Figures 2 and 3 reveal the changes of storage modulus ( $G'$ ) and complex viscosity ( $\eta^*$ ) with frequency for the iPP/UHMWPE blends with different UHMWPE and iPP/CNTs composites with different CNTs concentrations at 180°C in the molten state. At low frequencies, blends with UHMWPE concentrations below 5.0% showed a typical  $G'$  response of a viscous material with the scaling property of approximate  $G' \propto \omega^2$  indicating a terminal flow behavior. With increasing UHMWPE concentration, the viscosity curves of blends showed steeper slopes and no plateau regions were observed over the studied frequency range, which were ascribed to the interactions between UHMWPE and iPP chains slowing down the motions of the iPP molecular chains, the retardation time become longer, the viscosity increasing. However, Figure 2 presents changes of the storage modulus ( $G'$ ) and complex viscosity ( $|\eta^*|$ ) for iPP/UHMWPE blends with different UHMWPE concentrations at 180°C below 5%; were negligible. As to the iPP/CNTs composites in Figure 3, with the increasing

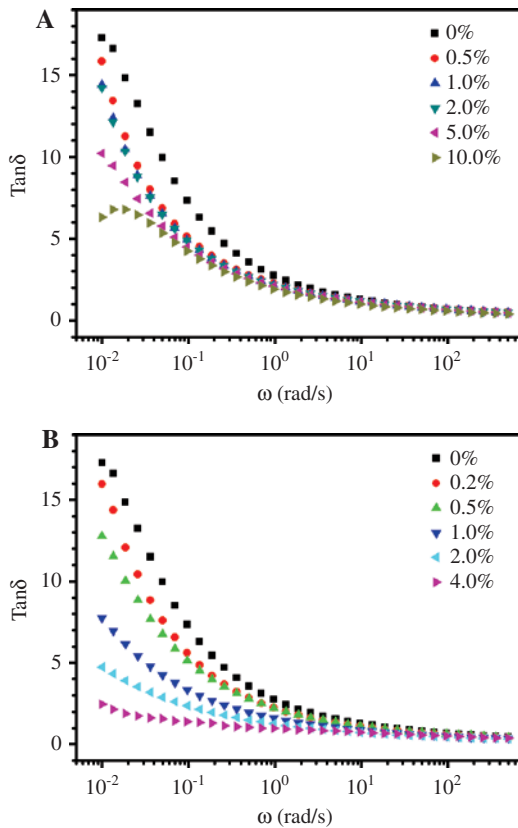


**Figure 2:** Storage modulus ( $G'$ ) and complex viscosity ( $|\eta^*|$ ) for iPP/UHMWPE blends with different UHMWPE concentrations at 180°C.



**Figure 3:** Storage modulus ( $G'$ ) and complex viscosity ( $|\eta^*|$ ) for iPP/CNTs composites with different CNTs concentrations at 180°C.

CNTs concentration, the storage modulus and complex viscosity were significantly enhanced at the low frequencies. Usually,  $\tan\delta$  can be used as a sensitive parameter to characterize the viscoelasticity and especially the liquid-to-solid transition or 3D physical networks formed for polymer composites. For the materials near the liquid-to-solid transition,  $\tan\delta$  decreases with increasing frequency before the network structure forming for a typical viscoelastic liquid. After the network structure forming, a moderate increase in  $\tan\delta$  appears in the low frequency regime indicating an elastic character. At the point of critical network structure,  $\tan\delta$  becomes independent of frequency because of the intrinsic power law relaxation. The frequency dependences of  $\tan\delta$  for iPP/UHMWPE blends and iPP/CNTs composites are shown in Figure 4. For iPP/UHMWPE blends,  $\tan\delta$  showed a decrease with increasing frequency when the UHMWPE concentration was below 5.0 wt%, indicating a viscous liquid behavior. When the UHMWPE concentration was 10.0 wt%, a moderate increase of  $\tan\delta$  appeared with increasing frequency up to 0.02 rad/s due to a dominant elastic response of the sample. This meant that at UHMWPE concentrations between 5.0 and 10.0 wt%,  $\tan\delta$  was independent of frequency, so the UHMWPE concentration for percolation



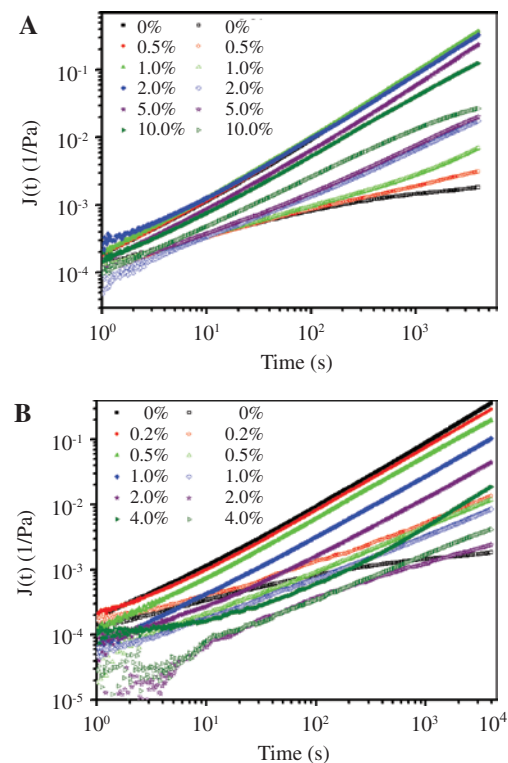
**Figure 4:**  $\text{Tan}\delta$  as functions of frequency for (A) iPP/UHMWPE blends and (B) iPP/CNTs composites with different UHMWPE and CNTs concentrations at  $180^\circ\text{C}$ .

which was attributed to forming 3D physical networks between UHMWPE and iPP molecules was in between 5.0 and 10.0 wt% (13). But for iPP/CNTs composites,  $\text{tan}\delta$  dropped dramatically at the low frequencies with increasing CNTs concentration until 4.0 wt%, the concentration of 4.0 wt% CNTs was thus considered close to the percolation concentration which indicate the 3D physical networks between CNTs and iPP molecules.

### 3.2 The creep-recovery behavior of iPP/UHMWPE and iPP/CNTs composites

The creep-recovery experiment has been proven to possess a high reliability for characterizing the elastic properties of polymer melts (14). Before the creep and creep-recovery experiments, the shear stress and creep time are chosen which makes sure the experiments reach steady state conditions of the deformation. A shear stress of 20 Pa and creep time 4000 s were enough for iPP to reach a steady state. In comparison to the neat iPP, the addition of fillers caused striking differences in the retardation time. The iPP/

UHMWPE blends and iPP/CNTs composites did not reach the linear steady-state recovery compliance where the terminal curve was still steep. The creep compliances for two measurements of iPP/UHMWPE blends and iPP/CNTs composites in the same concentration at 20 Pa were excellently reproducible. Moreover, small differences were found for the recoverable compliances which may be due to inhomogeneities of the filled materials distribution (15). Longer time of creep and recovery could not be applied owing to the limitations in the melt stability of the samples. Although the steady state had not been reached, the steady-state recovery compliance was larger than the measured value  $J_r$  ( $t_r=4000$  s). Figure 5 exhibits the results of the creep and creep-recovery experiments at a shear stress of 20 Pa for iPP/UHMWPE blends and iPP/CNTs composites with different UHMWPE and CNTs concentrations at  $180^\circ\text{C}$ ; the creep time and recovery time were both 4000 s. Small amounts of UHMWPE significantly increased the elastic compliance of iPP measured in the linear range of deformation. In particular, an enhancement of elasticity by a factor of up to 10 was measured for a concentration of 2.0 wt%. Whereas the recoverable creep compliance became smaller with increasing UHMWPE concentration over 2.0 wt%. Additionally, the



**Figure 5:** Creep and creep-recovery experiments at a shear stress of 20 Pa for (A) iPP/UHMWPE blends and (B) iPP/CNTs composites with different UHMWPE and CNTs concentrations at  $180^\circ\text{C}$ ; both the creep time and recovery time were 4000 s.

storage modulus and complex viscosity (Figure 2) indicated a marginal influence of the UHMWPE. However, the recovery compliances significantly increased with the addition of the UHMWPE. For the iPP/CNTs composites, 0.2 wt% CNTs did not change the creep compliance, but had an important influence on the recoverable compliance.

### 3.3 The comparison of elastic recovery for the iPP /UHMWPE blends and iPP/CNTs composites

The elastic recovery amounts of the iPP/UHMWPE blends and iPP/CNTs composites are compared in Table 1. The time of both creep and recovery was 4000 s; the elastic recovery data were summarized. It was very surprising that the elasticity of 2.0 wt% UHMWPE for iPP/UHMWPE blends and 0.2 wt% CNTs for iPP/CNTs composites had the same change trend, which showed an enhancement by a factor of around 10 in contrast to that of the neat iPP. As can be seen from the Table 1, the amount of elastic recovery for iPP/CNTs composites increased much more than those of iPP/UHMWPE at the same concentration. The finding of an increase in elasticity for the iPP/UHMWPE blends and iPP/CNTs composites can be explained by the enhancing interactions between the iPP molecules and the UHMWPE or CNTs surfaces. Furthermore, according to compare of the elastic recovery amounts, the results implied that the elastic recovery amounts were larger in the case of the iPP/CNTs composites than that in the case of iPP/UHMWPE blends for the same concentration, such as 1.0%, 2.0% iPP/UHMWPE blends and iPP/CNTs composites. In addition, the elastic recovery of 10.0 wt% iPP/UHMWPE blends and 4.0 wt% iPP/CNTs composites almost were identical. Therefore, UHMWPE and CNTs, as polymer and inorganic filler, played the similar roles in the material's recovery of iPP melts, although composites with CNTs enhanced elastic recovery than blends with UHMWPE.

**Table 1:** The elastic recovery amount for the iPP/UHMWPE blends and iPP/CNTs composites, both the creep time and recovery time were 4000 s.

iPP/UHMWPE (%)	Elastic recovery (%)	iPP/CNTs (%)	Elastic recovery (%)
0	0.50	0	0.50
0.5	0.84	0.2	4.67
1.0	1.86	0.5	5.94
2.0	5.33	1.0	8.20
5.0	8.40	2.0	9.10
10.0	21.24	4.0	22.07

## 4 Conclusions

iPP/UHMWPE blends and iPP/CNTs composites were prepared by a coagulation method followed by compression molding. The creep-recovery behavior was investigated by rheological measurements of polymer melts. Small amounts of UHMWPE and CNTs significantly influenced the shear compliance. In the rheological measurements, the UHMWPE and CNTs played the similar roles in material's elastic recovery; that is, the addition of 2.0 wt% UHMWPE or 0.2 wt% CNTs increased the elastic recovery about 10 fold in comparison with neat iPP.

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