

Effects of silver nanoparticle on the physical properties of syndiotactic polypropylene

Chul Ee Kang, Byoung Chul Kim*

Division of Applied Chemical & Bio-engineering, Hanyang University, 17,
Hangdangdong, Seongdong-gu, Seoul 133-791, Korea, Tel.: +82-2-2220-0494;
fax: +82-2-2297-4941

*E-mail address : bckim@hanyang.ac.kr

ABSTRACT

The effects of silver nanoparticle on the physical properties of syndiotactic polypropylene (sPP) were investigated in terms of rheological responses and crystallization behavior under shear. Silver nanoparticle played as the nucleating agent of sPP by increasing crystallization temperature (T_c) and heat of crystallization (ΔH_c). The introduction of silver nanoparticles more than 1 wt% brought about the rise of dynamic viscosity when compared to pure sPP. sPP with 5 wt% silver nanoparticle exhibited the higher $\tan \delta$ and lower relaxation time than the others in the low frequency range. However, the effects of silver nanoparticle on the rheological properties became less noticeable when the loading level was higher than 5 wt%.

Keywords : sPP, silver-nanoparticle, crystallization, shear, nanocomposite, rheology

1. INTRODUCTION

Recently, owing to the advancement in the preparation of nanoscale filler, its application to polymer composites attracts great interest in the substitution of micronscale fillers with nanoscale ones. The nanocomposites exhibit the outstanding advantages derived from nanoscale phenomena such as much enhanced processing properties, lower thermal expansion coefficient, higher swelling resistance and lower gas permeability, even at very low loading level. In addition, the presence of nanoparticles can modify the crystallization and melting behavior of polymeric materials[1-5].

Syndiotactic PP is claimed to have higher levels of transparency, heat resistance, and low temperature toughness compared with isotactic PP[6]. In this study, syndiotactic PP/silver nanocomposites were prepared by melt mixing and the effect of silver nanoparticles on the physical properties were discussed focusing on the rheological responses and crystallization behavior under shear.

2. EXPERIMENTAL

2-1. Material

Syndiotactic polypropylene (sPP: number average molecular weight = 17400), were purchased from Aldrich, Inc. In addition, a round-shaped silver nanoparticle (average size = 46.2 nm, standard deviation = 6.45) was supplied by NP-Tech, Inc. (Korea). The sPP was vacuum dried at 60 °C for 24 hrs before a melt mixing with the silver nanoparticles. The sPP and silver nanoparticle were dry mixed by tumbling them in a bottle. This mixture was then melt-compounded in an internal mixer (Haake Rheomix 600) for 5 min at 190 °C at the rotor speed of 60 rpm. The loading levels (X) of the silver nanoparticles were 0.01, 0.1, 0.5, 1, 5 wt%, and they were coded by sPP-X.

2-2. Measurement of physical property

Microscopic analysis (TEM and SEM)

Transmission electron microscopic (TEM) observation was performed using a JEOL JEM-2000FXII microscope with an accelerating voltage of 200 kV. The samples were ultrathin-sectioned by using a microtome equipped with a diamond knife and then were deposited on copper grid. Field emission scanning electron microscopic (FESEM; JEOL, JSM-6340F) observations were carried out on the surface of the nanocomposites in film state. In addition, the FESEM was also used to study the morphology of fracture surfaces of the tensile specimens. The surfaces of the samples were sputter-coated with a thin gold layer prior to scanning.

Rheological properties

The rheological properties of the nanocomposites were investigated by a rotational rheometer (Advanced Rheometric Expansion System (ARES); Rheometric Scientific, Inc.) in an oscillatory mode. The parallel plate geometry with a diameter of 25 mm was employed. The plate gap and strain level were 1 mm and 5%, respectively. The specimen was melted at 150 °C between the parallel plates. After the excess flushed-out sample during gap-setting was trimmed off, the specimen was kept for 5 min at the temperature in nitrogen atmosphere to remove the residual stress. Dynamic frequency sweep measurement was

conducted over the angular frequency range of 0.05 to 500 rad/s at 150 °C. In addition, for time sweep measurement the given shear rates of 1 and 5 rad/s were applied immediately after quenching from 150 °C to the predetermined crystallization temperature, 90 and 100 °C. The variation of G' was monitored as a function of time.

Crystal structure

Wide angle X-ray diffraction (WAXD) experiments were carried out by Rigaku Denki (D/MAX-2000) with Nickel filtered CuK α radiation of 40 kV and 100 mA. Scanning was carried out on the equator in the 2 θ range from 5 to 80° at the scan speed of 5°/min.

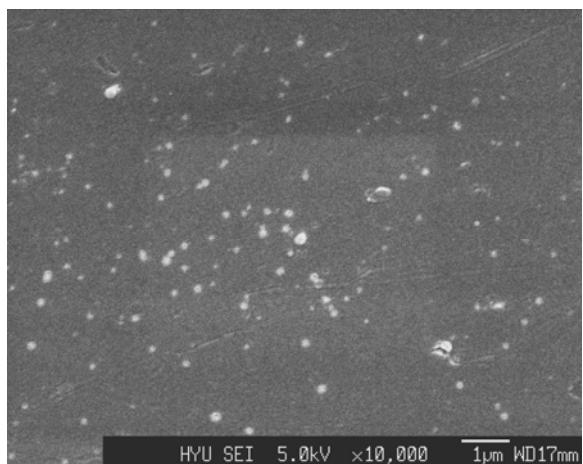
Thermal properties

Differential scanning calorimetry (DSC) measurements were carried out by DSC 2010 (TA Instruments, Dupont). The sPP/Ag nanocomposites were held at 150 °C for 5 min to eliminate the thermal history, and the cooling scan was obtained with cooling the sample at a cooling rate of 10 °C/min. The heating scan was obtained for the specimen isothermally crystallized under shear from 10 to 150 °C at a heating rate of 10 °C/min in nitrogen atmosphere. Thermal gravimetric analysis (TGA) was carried out using SDT2960 (TA Instruments, Dupont). Samples were heated to 800 °C for sPP/Ag nanocomposites at a heating rate of 10 °C in a nitrogen atmosphere.

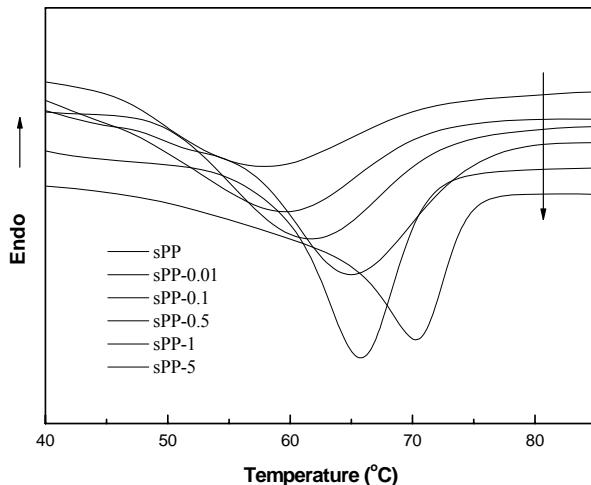
3. RESULTS AND DISCUSSION

Figure 1 presents FESEM image of the surface in film state and fractured surface of sPP-5. Both images present well-dispersed silver nanoparticles in the sPP matrix without large agglomerates.

The cooling scan thermograms of as-prepared samples show that sPP is a slowly crystallizing polymer as shown in



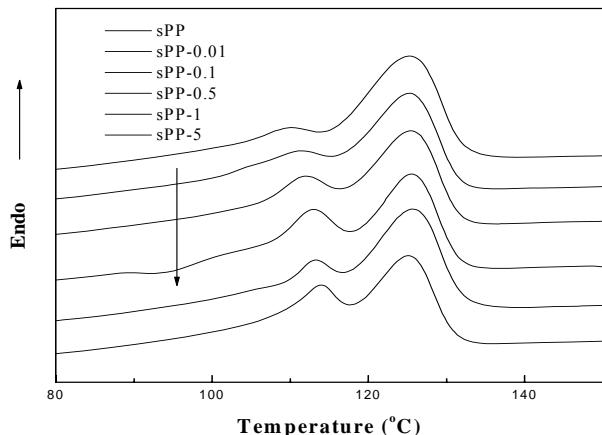
<Figure 1>



<Figure 2>

Figure 2. The introduction of silver nanoparticles produces an increased crystallization peak and heat of crystallization with increasing the loading level. This suggests that silver nanoparticle induce the heterogeneous nucleation and increase the degree of crystallization. In addition, the presence of silver nanoparticle brings about a sharp crystallization peak. This indicates that uniform size of crystal is formed by the presence of silver nanoparticles.

Figure 4 presents dynamic viscosity (η') curves of sPP and its nanocomposite with silver at 150 °C. All of the samples display pseudoplastic behavior independent of the presence of nanoparticle. The viscosity rise upon the introduction of silver nanoparticles more than 1 wt% occurs and then the difference in the value becomes small with increasing the frequency.



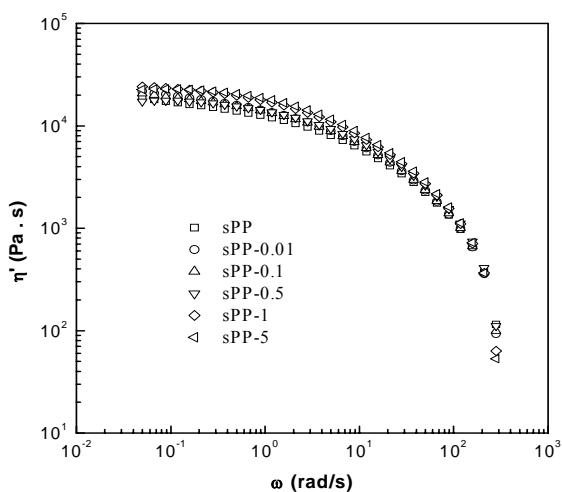
<Figure 3>

This suggests that tethered chains resided in the vicinity of the dispersed nanoparticles increases at a high filler load leading to a high viscosity value. However, at a high frequency the steric constraint of the chains by the silver becomes negligible. That is, the physical interactions between nanoparticle and nonpolar sPP matrix are not so strong that the orientation effects of polymer molecules prevail under high frequency.

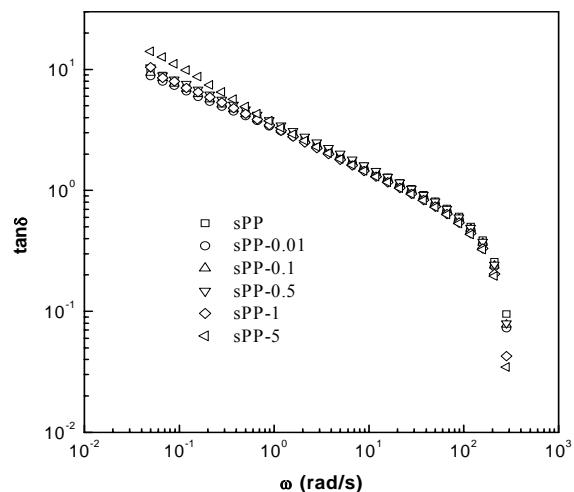
Figure 5 shows logarithmic plot of loss tangent ($\tan \delta$) with frequency. The value of $\tan \delta$ is a quantitative measure of a solid-like, elastic body or a liquid-like, viscous fluid in a system [7]. sPP-5 exhibits the higher value than the others in the frequency less than ca. 1 rad/s. The incorporation of silver nanoparticle at a 5 wt% loading increase more liquid-like properties rather than the solid-like properties. This suggests that in low frequency molecular slippage occurs frequently at the surface of nanoparticle over some loading level. The presence of pseudostructure caused by introducing nanoparticles affects the relaxation behavior as well. Characteristic relaxation times of polymeric materials are calculated using an empirical equation substituted by dynamic rheological parameters,

$$\lambda = G' (|\eta^*| \times \omega^2)$$

where η^* is the complex viscosity. Plot of relaxation time versus frequency is presented in Figure 6. sPP-5 shows the lower λ in the low frequency than the others and almost the same value is followed. The molecular slip seems to take place in the low frequency range as mentioned in Cole-Cole plot. Thus, small time needs for relaxation resulting from the accelerated mobility of the polymer chain.

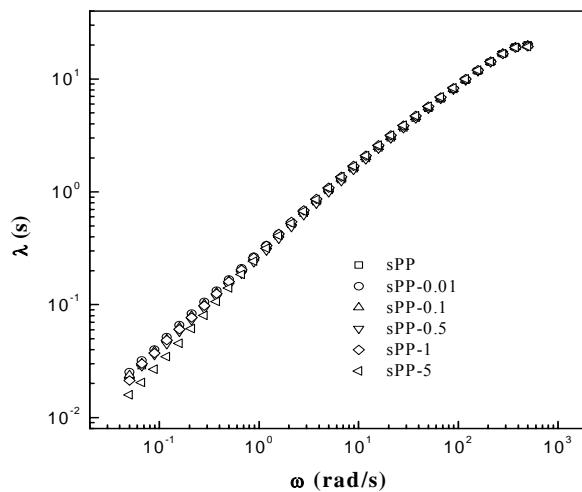


<Figure 4>

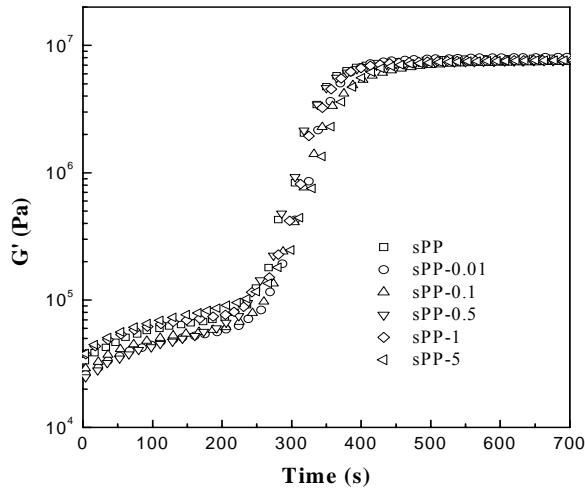


<Figure 5>

Figure 7 shows the variation of G' with time for sPP and its composites with silver nanoparticle at 1 rad/sec at 90°C. In rheological principle, the isothermal crystallization behavior under shear can be evaluated by tracking G' with time at a given temperature. G' increases monotonously with time at the early stage of experiment, which is referred to as an induction time for crystallization. Then an abrupt increase of G' is followed in a minute due to the formation of crystallites [8-9]. With crystallites growth the homogeneous melt system changes to the heterogeneous system and G' increases with time [10].



<Figure 6>



<Figure 7>

4. CONCLUSION

The sPP/silver nanocomposites led to higher crystallization temperature, shorter time to complete the crystallization, and shorter processing time than pure sPP because of promoted crystallization. Thus, the introduction of the silver nanoparticle may of great help to overcome the weak point of sPP in the processing, producing many nucleation sites. In addition, the silver nanoparticles bring about the improved thermal stability of sPP. The incorporation of the silver nanoparticles served to limit the chain mobility leading to a high melt viscosity. However, its interference becomes small with increasing the frequency due to the absence of the interaction between the silver nanoparticle and sPP. The presence of the nanoparticle at a concentration of 5 wt% shows the deviation from the master curve on the logarithmic plot of G' versus G'' , which is indicative of conformational change of the polymer chain. Further, at the loading level, the repulsion between sPP and silver seems to happen because it does not contain any polar groups in its backbone and thereby the molecular slip of polymer chain. This may give rise to low value of $\tan \delta$ and relaxation time in the low frequency. However, at a high frequency the local chain conformation was expected to be randomized as the steric effects by the silver nanoparticle were reduced, resulting in little change in those parameters.

At an isothermal crystallization temperature of 90 °C, the silver nanoparticles retarded the crystallization under shear on the whole. However, at 100 °C it promotes the crystallization up to the loading level 0.5 wt%, after which it increases the crystallization time with increasing the loading level. Polymer crystallization is determined from a concurrent nucleation and growth process. That is, both conditions should be in good harmony for favorable

condition of the crystallization. The silver nanoparticles in the matrix not only act as a nucleating agent but also limit the chain mobility. Thus, the competition between these two conflicting roles of the nanoparticles determines overall crystallization behavior of the nanocomposites.

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