

Effects of interface on the physical properties of nanoparticle-filled composites

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ABSTRACT

To investigate the effects of interface affinity on the physical properties the rheological properties of nanoparticle-suspended polyacrylonitrile (PAN) and polystyrene (PS) solutions in dimethyl acetamide (DMAc) were measured. The polymer solutions were prepared at various loading levels of ZnO; 0.1, 1, 2, and 5 wt% to the weight of polymer. The PAN solutions with ZnO nanoparticles showed higher dynamic viscosity (η') than pure PAN even at such an extremely low loading level, 0.1 wt%. They showed a maximum value of η' at 1 wt% ZnO concentration. In addition, PAN solutions with 5 wt% ZnO showed a greater degree of shear thinning than the others. However, η' of PS solutions with ZnO higher than 2 wt% was lower than that of the pure PS. With PAN solutions, the maximum values of storage modulus (G') and loss modulus (G'') were observed at the 1 wt% loading level. PS solutions containing ZnO nanoparticles more than 2 wt% gave lower values of G' or G'' with increasing particle concentration when compared with pure PS solution. In the case of PAN solutions ZnO nanoparticles decreased the value of loss tangent ($\tan\delta$) over the frequency range examined whereas they increased it in PS solutions.

Keywords: polyacrylonitrile, polystyrene, zinc oxide nanoparticle, rheology

1 INTRODUCTION

Recently, modification of polymer matrix by incorporating inorganic nanoparticles is a subject of interest because it endows polymer/inorganic composites with excellent performance such as mechanical properties, thermal properties, and chemical resistance[1-6]. Many experimental methods have been adopted to prepare well-dispersed organic/inorganic nanocomposites. To name a few includes *in-situ* polymerization and direct melt or solution compounding with specially designed equipments[7-11]. Among various fabrication methods to obtain such composite materials, direct mixing of polymer with nanoparticle in a co-solvent is considered as a convenient and easily applicable way to disperse nanoparticles homogeneously in polymer matrix. In this case, interface between polymer matrix and nanoparticle has a profound effect on the physical properties of the suspension system. When nanoparticles are introduced in

the polymer solution the flow properties of polymer solution might be changed differently from that of micron-sized particle filled system. The adsorption phenomena of polymers on solid particles are known to influence strongly the microstructure of polymer/particle systems [12]. This leads to very different rheological behaviors because of attractive or repulsive forces between polymer chains and particles caused by polarity [13]. Thus, comprehension of the rheological properties of the polymer solution where inorganic nanoparticles are introduced gives significant clues to determining optimum condition of fiber spinning or film processing.

In this study, the effects of polymer-particle interaction on rheological properties of zinc oxide (ZnO) nanoparticle-filled suspensions were investigated. The polymers used in this study were polyacrylonitrile (PAN) and polystyrene (PS) which stand for polar and non-polar polymers, respectively. ZnO was dispersed in the solvent prior to the dissolution of the polymers to give homogeneous dispersion in a primary particle size.

2 EXPERIMENTAL

2.1 Sample Preparation

Zinc oxide (ZnO) nanopowder was purchased from Aldrich, whose particle size mostly ranged from 50 to 150 nm. PS (melt index = 7.5) and PAN were also a commercial polymer purchased from Aldrich. *N,N*-Dimethylacetamide (DMAc: Kento Chemical co.) was selected as a solvent of the polymers because it also showed a good dispersion of ZnO nanoparticles. ZnO was first dispersed in DMAc with an ultrasonic vibration for 10 minutes, which played an crucial role in breaking apart the agglomerate of ZnO. PAN and PS were then dissolved in the solution at 70 °C with vigorous stirring. Final concentrations of PS and PAN solutions were 40 and 10 wt%, respectively. ZnO contents (X) were 0.1, 1, 2, and 5 wt% based on polymer in the solution, which were coded by PS-X or PAN-X.

2.2 Measurement of Rheological Properties

Advanced Rheometric Expansion System (ARES) (Rheometric Scientific, Inc.) was employed to measure the rheological properties of the polymer solutions containing ZnO nanoparticles. The parallel plate geometry with a diameter of 50 mm was used. The plate gap and strain level

were 1 mm and 10%, respectively. Dynamic frequency sweep measurement was conducted over the angular frequency range of 0.05 to 500 rad/sec at 70 °C. The solution was kept for 10 min prior to the measurement to ensure the stabilization at the temperature. To prevent the evaporation of the solvent during measurement, heavy mineral oil (Aldrich) was fully applied to the samples between plates.

3 RESULTS & DISCUSSION

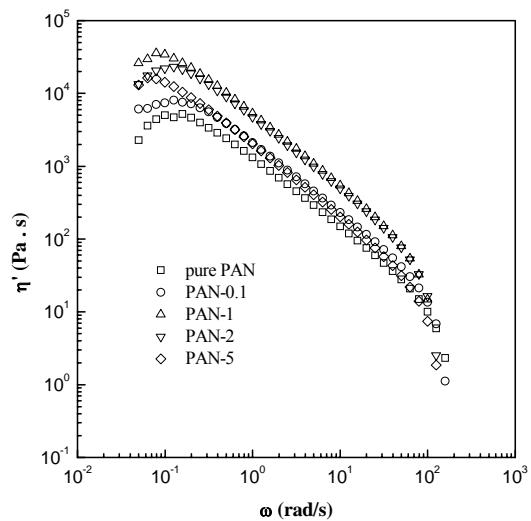


Figure 1. Dynamic viscosity curves for PAN/ZnO solutions in DMAc.

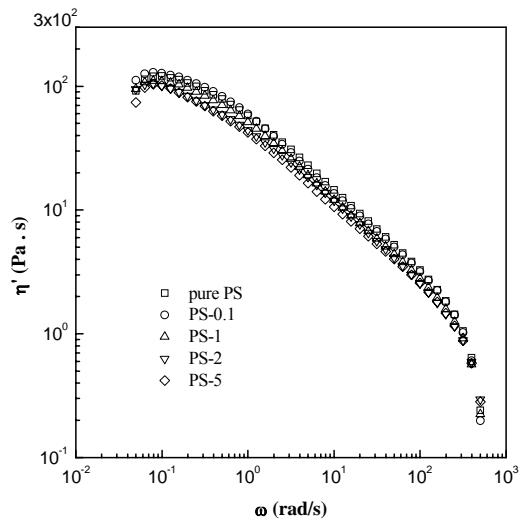


Figure 2. Dynamic viscosity curves for PS/ZnO solutions in DMAc.

Figure 1 and 2 present the dependence of dynamic viscosity (η') on the ZnO nanoparticles at 70 °C for PAN and PS solutions in DMAc, respectively. PAN solution

shows the lower Newtonian region in the low frequency region less than ca 0.1 rad/sec followed by shear thinning. Incorporation of ZnO nanoparticle increases η' of the PAN solutions even at extremely low loading level 0.1wt%, which may come from the extraordinary large surface area of nanoparticles. A strong interaction between ZnO nanoparticles and polymer chains serves to constrain the mobility of PAN chain in the solution leading to high viscosity. The constant viscosity in the Newtonian range doesn't increase monotonously with particle concentration. It shows a maximum at 1 wt%. PAN-1 and PAN-2 show little difference in η' after lower Newtonian region and PAN-5 shows even lower viscosity than those. This indicates that a critical value of loading level exists in increasing the viscosity. Macromolecular entanglement network is certainly reinforced, at high ZnO volume fractions, by possible adhesion at the filler-polymer interface. ZnO nanoparticle in PAN-1 plays a role as a crosslinking agent very effectively. However, substantial crosslinking site is decreased over some loading level because agglomerate is formed resulting from close distance between particles. Thus, when more than some level is incorporated, some part of the adsorbed polymer on the particle is confined completely by excessive nanoparticle, leading to the reduction of the polymer concentration in the liquid phase [14]. This is responsible for the decrease in viscosity of the suspension. In addition, PAN-5 shows a greater viscosity dependence on frequency than the others. This indicates that PAN chain in the solution with 5 wt% ZnO can be easily destructed and deformed by shear. The contact probability between the two species is increased abruptly under shear and thereby promotes the diffusion of PAN chain in the medium, that is, chain disentanglement. When the shear is applied to this system, the disentanglement happens simultaneously with entanglement. Over some shear rate, disentanglement is preferential with increasing frequency leading to decrease in viscosity. Above critical loading level, the interaction between nanoparticle and polymer may play a role in lessening the entanglement ratio under shear leading to increase in the degree of shear thinning. That is, it may produce relatively highly oriented structure with increasing frequency. In addition, the little difference in viscosity between pure PAN and ZnO filled system is observed at high frequency more than ca. 100 rad/s. This may be explained that role of ZnO nanoparticle which restricts the mobility of PAN chain in the solution becomes weak at high shear rate.

As shown in Figures 2, PS solution also shows very short lower Newtonian region in the frequency less than ca 0.1 rad/sec, followed by shear thinning. It is interesting to note that at the concentration higher than 2 wt%, the dynamic viscosity of the suspensions is lower than that of the pure PS solution. Decrease in the viscosity seems to be attributed to repulsion between nonpolar polymer chain and polar nanoparticle and thereby molecular slip of PS. The ZnO nanoparticles in the PS act more like inert fillers

instead of physical crosslinker in the ZnO filled-PAN solutions. Thus at high ZnO concentration repulsion between polar ZnO and non-polar PS seems to lead to much ordered structure of polymer chain [15]. This suggests ZnO play a role as a molecular slippage agent under shear. This lubricating effect of ZnO exert over some concentration of ZnO nanoparticle. In addition, the most profound difference of η' between the pure PS and ZnO-filled solution is recognizable in the low frequency range and becomes narrow with increasing frequency.

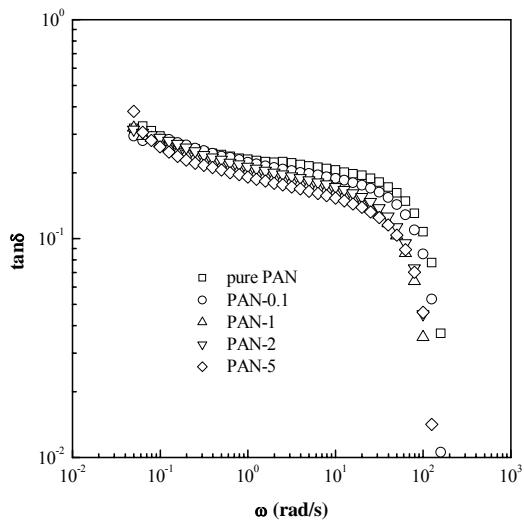


Figure 3. Loss tangent curves for PAN/ZnO solutions in DMAc.

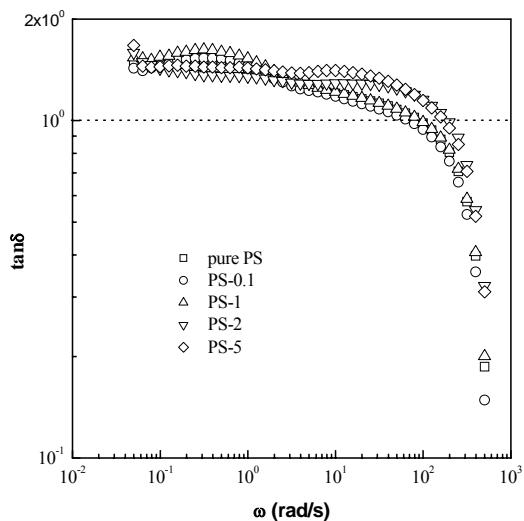


Figure 4. Loss tangent curves for PS/ZnO solutions in DMAc.

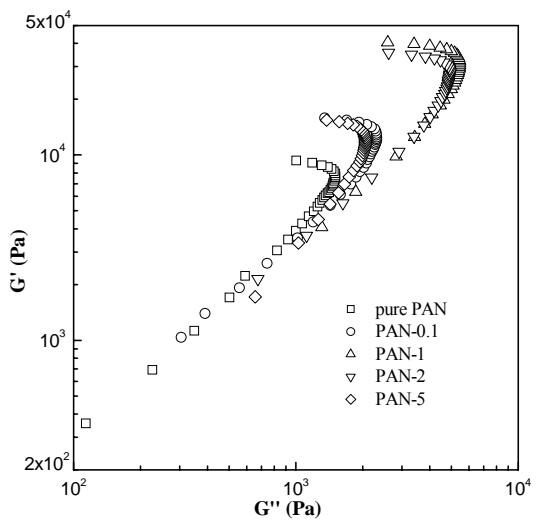


Figure 5. Cole-Cole plots for PAN/ZnO solutions in DMAc.

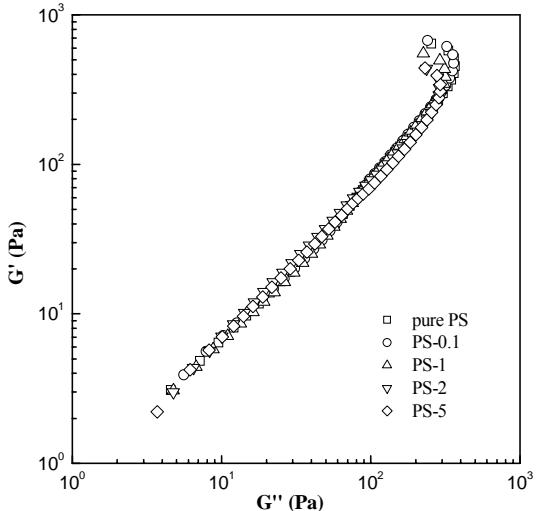


Figure 6. Cole-Cole plots for PS/ZnO solutions in DMAc.

Figure 3 and 4 show the variation of loss tangent ($\tan\delta$) with frequency for PAN and PS solutions with ZnO nanoparticles at 70 °C. $\tan\delta$ is a quantitative measure of solid-like elastic or liquid-like viscose properties of a system. PAN solutions give a value of $\tan\delta$ much less than 1 indicating ever-presence of gel structure over the entire frequency range examined as mentioned in G' and G'' data. PAN solutions with ZnO nanoparticles present lower $\tan\delta$ than pure PAN solution at the corresponding frequency. This may be explained by promotion of intermolecular interaction through polar crosslinking. PS solutions give the value of $\tan\delta$ more than 1 over most of the frequency range examined. PS-2 and PS-5 solutions show high $\tan\delta$ at the frequency more than ca 2 rad/s. This indicates that the repulsion and molecular slippage at the surface of

nano particle occur due to little interaction between PS matrix and particle leading to the relative increase of liquid-like properties to solid-like properties. In addition, the onset frequency for shear induced gelation is shifted from ca. 80 to 200 rad/s at high loading level because of lubrication effect from little interaction between them.

The logarithmic plot of G' against G'' , so called Cole-Cole plot, is exhibited in Figure 5 and 6. It is well recognized that homogeneous polymer melts and solutions produce a single master curve independent of concentration and temperature whose slope is 2. Pure PAN and ZnO filled solution gives slope less than 2 indicating heterogeneity of the systems. This seems to result from gel-structure of the systems. In addition, PAN solutions don't give a master curve depending on the loading level. This suggests that ZnO gives rise to a conformational change of PAN matrix in the solution resulting from strong interaction between polar polymer and nanoparticle. However, PS solutions show a single master curve of which the slope is ca. 1 irrespective of incorporation of ZnO nanoparticles. This indicates the effect of ZnO is not as large as changing the conformation of PS chain in the solution due to little interaction between PS molecules and ZnO.

4 CONCLUSION

Attractive or repulsive force between polymer chain and nanoparticle, which might be caused by their polarity difference, gave rise to very different rheological behaviors of nanoparticle-filled suspensions. Incorporation of ZnO nanoparticles increased η' of PAN solutions even at extremely low loading level, 0.1 wt%, resulting from unusually large specific surface area of ZnO nanoparticle while it decreased those of PS solutions over 2 wt% with increasing loading level. A strong interaction between PAN chain and ZnO served to constrain polymer chain mobility leading to an increase in chain rigidity. However, repulsion between PS chain and ZnO seemed to allow disordered chain segments to be straightened out leading to the behavior of extensional flow. In the Cole-Cole plot PAN solutions didn't give a master curve depending on the loading level, while PS solutions showed a single master curve irrespective of incorporation of ZnO nanoparticles. This proved ZnO nanoparticle could change the molecular conformation of polymer in the solution depending on polarity difference between polymer and nanoparticle. ZnO nanoparticle also produced an increase in the relaxation time for PAN solution and a decrease for PS solution. In conclusion, understanding these rheological properties of polymer/ZnO solutions is of great help to determine optimum condition of fiber spinning or film casting in the preparation of the nanocomposite.

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