Rheological Behavior of Spinning Dope of Multiwalled Carbon Nanotube/Polyacrylonitrile Composites

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Summary: The spinning dope of Multiwalled carbon nanotube/polyacrylonitrile composites was prepared by *in-situ* polymerization in 50wt% NaSCN solution. The rheological behavior of the dope containing carbon nanotubes from 0.19wt% to 1.9wt% was investigated using rotational rheometry at 60^0C.The nanotubes have diameters between 30–50nm and lengths ranging from 6 to 10 μm. The apparent viscosity decreases with the addition of carbon nanotubes; this can be explained by the inhibition of carbon nanotubes during polymerization progress. The spinning dope containing various contents of carbon nanotubes exhibits a shear thickening effect. However, the dynamic rheological test shows there is a peak of complex viscosity with the increasing in frequency.

Keywords: carbon nanotubes; *in-situ* polymerization; nanocomposites; polyacrylonitrile; rheology

Introduction

Composites of carbon nanotubes(CNTs) in polymeric matrices have attracted considerable attention in the research and industrial communities due to their unique mechanical and electrical properties. CNT/polymer nanocomposites possess high stiffness, high strength, and good electrical conductivity at relatively low concentrations of CNT filler.[1-3] A key issue in producing CNT/polymer nanocomposites is the ability to control dispersion of the CNTs in polymeric matrices. This, however, hinges on an in-depth understanding the rheological behavior of the CNT/polymer composites, a topic that has not received much attention.

Recently, the melt rheological properties of different CNT/polymer composites have been studied. For example, Petra Potschke et al.[4] examined the melt rheological properties of multiwalled carbon nanotube(MWNT) filled polycarbonate nanocomposites formed by melt extrusion. To our

DOI: 10.1002/masy.200451218

knowledge, there are no reports on the solution rheological behavior of spinning dope of MWNT/polyacrylonitrile(PAN) composites. The purpose of this paper is to study the effects of MWNT's addition on the rheological properties of the spinning dope. And the probable structure changings with the increase of shear rate have also been discussed.

Experimental

The MWNT were prepared in our laboratory, and the experimental procedure was described in our previous works[5]. The prepared MWNT were ultrasonically purified in mixture acid of HNO_3/H_2SO_4 (3:1, v/v), then cleaned with deionized water, filtrated and dried. After that, the MWNT dispersed in 50wt%NaSCN solvent was added to mixture solution containing acylonitrile (ACN), methyl methacrylate (MMA), itaconic acid (ITA), 2,2-azobisisobutyronitrile(AIBN) and 50wt% NaSCN. The mixture was stirred and heated at 78^0C for one hour. The spinning dope was obtained after demonomerizing. The process of polymerization was listed in Table 1.

Table 1. Process of polymerization

ACN (wt%)	MMA (wt%)	ITA (wt%)	PH (-)	Temp. (°C)	Time (hr)
89.5	10	0.5	4.5	78	1

The purified MWNT samples were examined by TEM (JEOL 100CX2). The rheological measurements were performed using rotational rheometry RS1 (Haake) at 60^0C(using a cone plate geometry). The molecular weights of the samples were examined with a Waters gel permeation chromatograph (GPC, model 1500) with Ultrastyragel columns (7.8×300mm), using $DMF/NaNO_3$ as the eluate. The experiments were carried out at 50^0C, with a pumping rate of 1ml/min.

Results and Discussion

TEM studies show that the prepared MWNT samples have diameters ranging from 30 to 50nm and length between 6 and 10um. Figure1 shows the TEM image of purified MWNTs. As can be seen from Figure 1, the surface of the nanotube is very clean. Most of the impurity phases such as amorphous carbon and graphitic nanoparticles are removed.

process (Figure 2), the formation of the PU network is complete, and polymerization of styrene can only proceed in the immediate vicinity of the preformed PU network, due to topological hindrances. Therefore, higher miscibility between PU and PS is expected by using this sequential method.

Contrary to previous *in situ seq* full- and graft- IPNs based on the same precursor components and prepared similarly[5] (except for the use of a thermal initiator, which decomposes at 60°C, instead of a photoinitiator) which were opaque, the present *in situ sim* and *in situ seq* PU/PS films are slightly turbid and perfectly transparent, respectively (Figure 3).

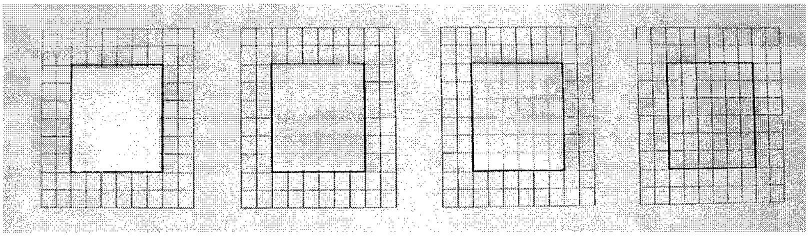

Figure 3. Aspect of 35/65 PU/PS f-IPN films obtained under various experimental conditions: from left to right: *in situ sim* (thermal decomposition of initiator), *in situ seq* (polymerization of styrene at 60°C), *in situ sim* (photopolymerization at room temperature), *in situ seq* (idem).

Since there is a significant difference in the refractive index of PU (n = 1.46) and PS (n = 1.59), the change in optical properties is related to the domain size, and transmission over 90% means that particle sizes under the wavelength of light are obtained when the process develops at room temperature due to higher viscosity which restrains complete phase separation. The refractive index of the films was measured (Table 1): except for the *sim* s-IPN, the refractive index of all samples is higher than the calculated value ($n \sim$ 1.548) obtained by rule of mixture from the refractive index of the individual constituants. Systematically, the *in situ seq* film has a higher refractive index than the *in situ sim* film. Also, deviation from the calculated value increases when going from semi- to full-IPNs, and from loosely graft to tightly graft materials. Taking into account the Lorentz-Lorenz equation[6] which relates density and refractive index, the interpenetrated materials are more dense than the corresponding blends. This makes evident the presence of entanglements leading to forced miscibility which increases according to the previously mentioned order.

contents. The inhibition of carbon nanotubes leads to lower the molecular weights of the dope, which makes the apparent viscosity decrease. When the contents of MWNT are more than 0.53wt%, the spinning dope exhibits a shear thickening effect. The measurements were also carried out in an oscillatory shear mode using a cone plate geometry(35mm diameter) at 60^0C. Figure 3 shows the complex viscosity of nanotube filled PAN spinning dope. For PAN sample, the complex viscosity decreases rapidly with the increasing of the frequency. However, for MWNT/PAN sample, the complex viscosity increases slightly with the frequency's increasing in lower frequency stage, and decreases in higher frequency stage. There is a peak of complex viscosity with the increasing in frequency. It is likely that the PAN segments near to the nanotube surface were less mobile and retarded orientation of PAN macromolecule, leading to the increasing in viscosity at lower shear rate. Similar effects have been observed in other polymer systems filled with finely divided materials[2]. Carbon nanotube, a linear molecular, have also oriented when the shear rate turn much higher. The orientation of MWNT and the PAN macromolecule make the viscosity decreased at higher shear rate.

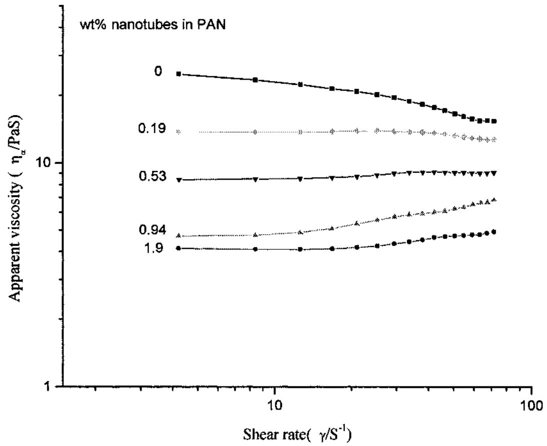

Figure 2. Flow curves of spinning dope of the MWNT filled polyacrylonitrile.

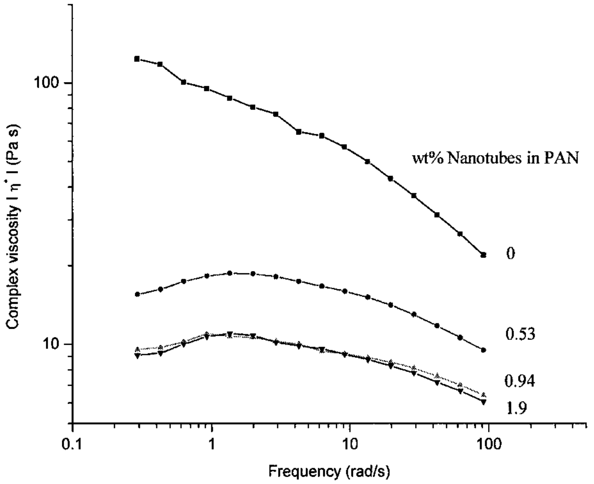

Figure 3. Complex viscosity of MWNT/PAN spinning dope.

Conclusion

The spinning dope of Multiwalled carbon nanotube/polyacrylonitrile composites were prepared with *in-situ* polymerization. The apparent viscosity decreases with the addition of carbon nanotubes. The spinning dope exhibits a shear thickening effect when the contents of carbon nanotubes are more than 0.53wt%. The dynamic rheological test shows that the complex viscosity increases slightly with the frequency's increasing in lower frequency stage, and decreases in higher frequency stage. The rheological behavior indicates that carbon nanotubes may retard the orientation of PAN molecules at lower shear stress and can oriented themselves in the dope at higher shear stress.

Acknowledgement

This project was supported by Science & Techology Committee of Shanghai and the Chinese Academy of Science.

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