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RHEOLOGY OF POLYCARBONATE REINFORCED WITH FUNCTIONALIZED AND UNFUNCTIONALIZED SINGLE-WALLED CARBON NANOTUBES

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Nanocomposites of polycarbonate (PC) containing low concentrations of pristine and COOH and OH functionalized single-walled carbon nanotubes (SWNTs, COOH-SWNTs and OH-SWNTs) were prepared by melt-mixing and analyzed using rheology and scanning electron microscopy (SEM). The steady state and linear viscoelastic behavior of each nanocomposite material is presented and compared to that of the neat PC. SEM analysis revealed that samples containing functionalized SWNTs were more dispersible than samples containing the pristine SWNTs.

Keywords: *functionalized carbon nanotubes, polycarbonate nanocomposites, rheology*

Introduction

Since the discovery of carbon nanotubes by Iijima [1], nanotechnology has been steadily gaining popularity in the scientific and industrial communities and is now recognized as one of the most promising avenues of technological development for the 21st century in the scientific discovery. Carbon nanotubes (CNTs) have outstanding mechanical, thermal and electrical properties. As a result, particular interest has been recently given in exploiting these properties by incorporating carbon nanotubes into some form of polymer matrix. In the materials industry, the development of ceramic and polymer nanocomposites is a rapidly expanding multidisciplinary research activity. Hence, polymeric nanocomposite materials are now playing a large role in the development of this area of research. Many types of nano-sized particles have been investigated for use in composite materials. It has been reported that the addition of CNTs [2, 3], nanoclays [4, 5], γ-Al_2O_3 nanoparticles [6] and exfoliated graphite [7] into polymers increases the thermal stability.

The strong interest in nanocomposites, especially in carbon nanotubes, stems from their ability to influence properties such as: mechanical, electrical, thermal, flame resistance, for relatively small concentrations of this type of additive. These additives have already found potential applications in nano-sensors, memory chips made from thin films, electrostatic painting, and biocompatible sensors. Utilization of CNTs for more multifaceted applications however, requires an understanding of perception of how processing conditions (mixing, molding, extrusion) influence nanocomposite properties. Various investigations have been reported regarding the use of CNTs as small fractions of filler, particularly in the development of structural applications due to increased elasticity and durability [8–11].

Improvements in tensile strength, modulus and heat distortion temperature have also been noted. Most of the advanced properties which nanocomposite materials exhibit, stem directly from the CNTs. The electrical conductivity of the CNTs has also drawn much attention in the scientific community. Proper control of the structure and alignment of the CNTs within a polymer matrix may have a broad range of applications. The enhanced properties that come along with incorporating CNTs into a polymer matrix are already drawing much attention from the plastics and automotive industries, as well as many others. These facts lead many to speculate that polymer nanocomposites will eventually replace conventionally filled polymers. Currently, much effort is being concentrated on controlling the nanoscale structure of these materials in order to improve electrical conductivity, physical and mechanical properties, and to make production more cost and energy efficient.

The first step to taking advantage of the superior properties of polymeric nanocomposites is to gain a better understanding of the complicated network of conditions and variables which may complicate man-

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ufacturing processes. While thermoplastic polymer processing operations such as extrusion and injection molding are typically high shear rate processes, the quality of finished parts is often determined by low shear rate behavior, such as die swell caused by extrusion molding. Some of the parameters which affect the processability of such materials include: temperature, particle size, shape and composition, filler concentration, aspect ratio (length:diameter), and particle surface properties. Minute proportions of filler in a polymer matrix may have an effect on viscosity as well as the dynamic properties. Understanding the influence of these variables is a crucial step in the manufacturing process.

Current problems with dispersion of the CNTs within the polymer matrix have created problems with fully utilizing the capabilities of nanocomposite material. The production of durable, well-built nanocomposites depends on the material's ability to bond with the CNTs. The CNTs have a tendency to form aggregates within the polymer matrix, causing undesirable effects. Surface modification or functionalization of CNTs involves physically or chemically attaching certain molecules to the smooth sidewalls and ends of the CNTs. Functionalization can create more bonding sites on the surface of the CNTs and may improve dispersion. Many methods, aimed at improving the dispersion and alignment of CNTs in polymer matrices, including solution mixing [12], in situ polymerization [13] and mechanical melt mixing [14], have been attempted.

Rheology

Rheology is now recognized as an important field of scientific study and plays a crucial role in processes of material development. It finds applications in such industries as polymers, foods, paints, inks, cosmetics and pharmaceuticals.

The addition of nano-sized material to a polymer matrix may cause the material to exhibit unusual behavior as the result of the formation of a complex structure. Rheology can be an effective tool for detecting micro-structural changes in a polymer system due to the addition of CNTs. These materials have a behavior that is in between that of a purely viscous fluid and an elastic solid and can be characterized as viscoelastic. With polymer melts, the viscosity also depends on the temperature (i.e. the viscosity decreases with temperature). The behavior of the dynamic moduli G' and G'' in oscillatory shear experiments offers valuable insight into the micro-structural changes happening inside the polymer matrix. Sung *et al.* [11] reported that the functionalization of the CNTs lead to an increase in rheological properties (i.e. the storage and loss modulus G' and G'' and viscosity). Pötschke *et al.* reported that the addition of MWNTs increased the storage and loss modulus at low frequencies [15, 16]. Frequency sweep experiments could be a critical monitor for viscous-to-elastic transition in the nanocomposites. Temperature sweep experiments are useful for measuring the temperature dependence of the viscosity or the thermal transitions in the polymers. Low shear rate measurements in the polymer melt's linear viscoelastic region are a key in material problem solving. Proper dispersal of a relatively small concentration of single-walled carbon nanotubes into polymeric materials is known to cause changes in rheological properties. To date, little has been reported on the rheological behavior of composites formed with functionalized SWNTs.

Experimental

Materials

The food-safe grade polycarbonate (200-10) was obtained from Dow Chemical Company, Midland, MI, USA.

Table 1 Polycarbonate properties

Material property	
Density/g cm^{-3}	1.20
Tensile modulus/GPa	2.41
Tensile strength/MPa	55–75
Elongation at break/%	150
Melting point/°C	267

The carbon nanotubes used were single-walled carbon nanotubes, hydroxyl functionalized single-walled carbon nanotubes and carboxyl functionalized single-walled carbon nanotubes. The properties of these fillers, which were supplied by Cheap Tubes, Inc., Brattleboro, VT, USA, can be seen in Table 2.

Table 2 Carbon nanotube properties

Material property	SWNT	SWNT-OH	SWNT-COOH
Outer diameter/nm	1–2	1–2	1–2
Inside diameter/nm	0.8–1.6	0.8–1.6	0.8–1.6
Ash/mass%	<1.5	<1.5	<1.5
Purity/mass%	>90	>90	>90
Length/μm	5–30	5–30	5–30
Specific surface area/m^2 g^{-1}	407	407	407
Electrical conductivity/S cm^{-1}	>10^{-2}	>10^{-2}	>10^{-2}

Sample preparation

An AR2000 rheometer from TA Instruments with environmental testing chamber (ETC) was used for all rheological experimentation. A 25 mm flat plate geometry with detachable melt ring was used for melt rheology. Samples were melt-mixed directly in the rheometer, and a pre-shear of 10 s^{-1} was applied for 2 min to each.

Subsequent to rheological experimentation, samples were compression molded into discs for SEM and optical microscopy analysis. Samples analyzed using SEM were cryo-fractured in liquid nitrogen, mounted to tacks with silver paint (allowing 24 h to cure), then sputter-coated in gold for 2 min.

Rheological experiments

Temperature ramps were performed from 250 to 300°C at 5°C min^{-1} with a constant shear rate of 20 L s^{-1}. Shear rate ramps were carried out over a range of 0.01 to 100 s^{-1} at a constant temperature (270°C). The measurements for all shear rate ramps were taken in log mode in order to collect more data points in the low shear rate region. As for oscillatory measurements, strain sweeps were performed to determine the linear viscoelastic region of the materials. For the strain sweeps, frequency and temperature were held constant, while the strain percentage was varied. Beyond the critical strain, the material begins to break down and the elastic modulus drops. All other oscillatory measurements were taken within the linear viscoelastic region of the materials. Frequency sweeps, from 1 to 100 Hz were carried out, with 15% strain at 270°C. Oscillatory temperature sweeps were performed from 250 to 300°C at 15% strain and a constant frequency of 25 Hz.

Results and discussion

All fillers increased the viscosity of PC over the range of processing temperatures and shear rates. The SWNTs had the highest infinite rate viscosity, followed OH and COOH, respectively. This can be seen in Fig. 1 below. Viscosity also increased with mass% of CNTs. The shear rate dependency of PC and its nanocomposites is shown in Fig. 1. From Fig. 2 we can observe a significant change in the temperature dependence of PC with the addition of SWNTs, COOH-SWNTs and OH-SWNTs. PC-SWNT samples behaved nearly linearly with respect to temperature.

As we can see from Fig. 3, the addition of CNTs generally decreased the dynamic moduli. Nanocomposites with functionalized SWNTs showed higher modulus values than the pristine SWNTs and were somewhat close to the value of matrix alone at high frequencies. From these results it is conjectured that for this suspension, shear thinning is connected with the breaking of the interconnected networks between nanotubes and/or aggregates of nanotubes, and may not be by nanotube alignment.

From temperatures 250 to 300°C, both concentrations of CNTs decreased the storage modulus *G′* and loss modulus *G*", with the exception of the un-functionalized CNTs, which had slightly higher values for the dynamic moduli at low temperatures. Polycarbonate has secondary transition temperature, represented by the broad peak in *G*' and *G*" around 285°C. SWNTs underwent this transition at lower temperatures than the pure polymer while the functionalized CNTs caused the behavior at higher temperatures. The dynamic behavior of the 2.5 and 5 mass% was very similar with respect to temperature. Minor increases in *G*' and *G*" were noticed with the 5 mass%.

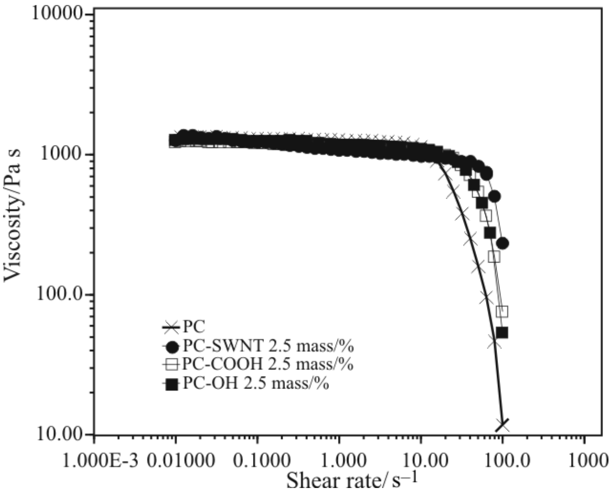

Fig. 1 Shear rate ramp experiment

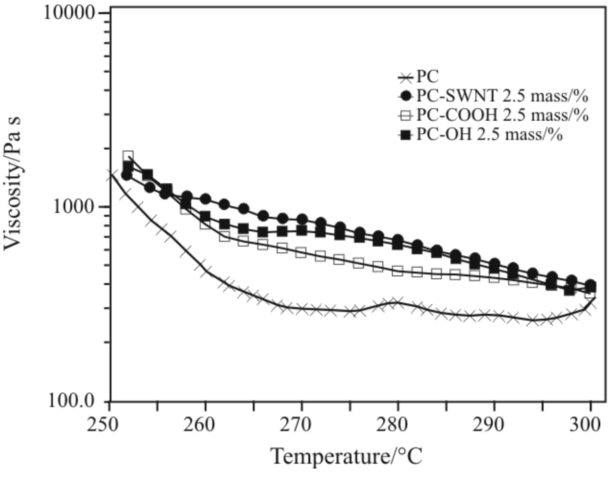

Fig. 2 Temperature ramp experiment

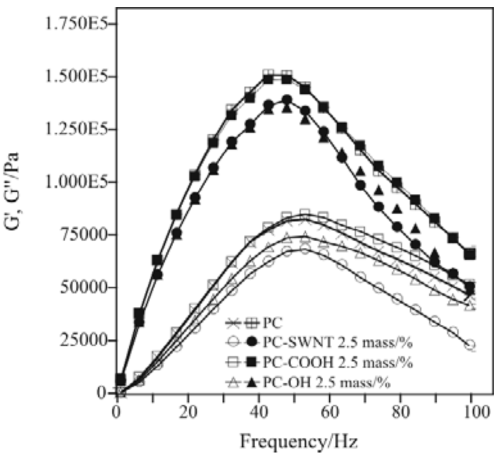

Fig. 3 Frequency sweep experiment
△, □, ×, ○ – G', ●, ⊞ , ■, ▲ – G''

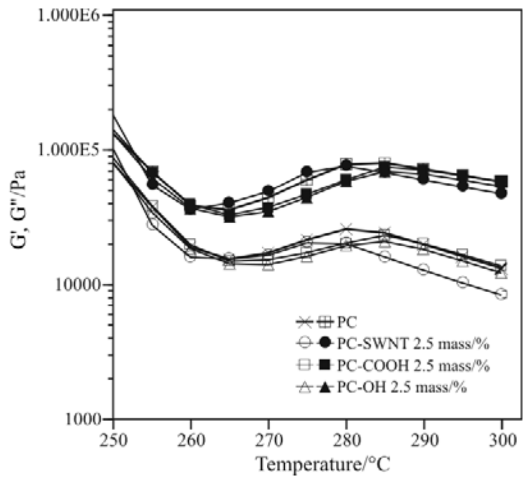

Fig. 4 Temperature sweep experiment: 250 to 300°C
△, □, ×, ○ – G', ●, ⊞ , ■, ▲ – G''

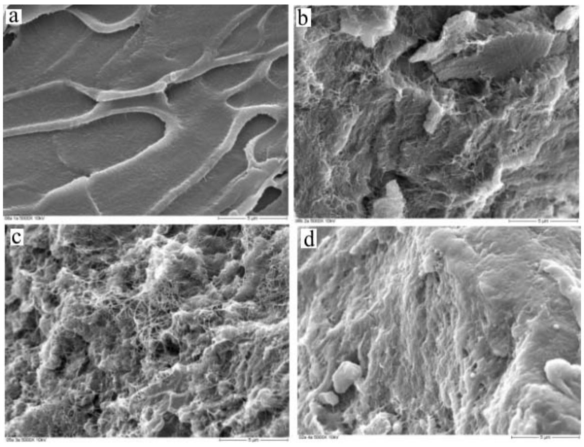

Fig. 5 SEM micrographs of a – PC, b – PC containing 5.0 mass% SWNTs, c – COOH-SWNTs and d – OH-SWNTs

Morphology

Overall we can see that SWNT and its functionalization change some important rheological properties. Preliminary data from SEM micrographs suggest that the dispersion of the OH- and COOH-SWNTs was improved when compared to the unfunctionalized SWNTs. In order to investigate the advantages of functionalization of SWNTs further studies are underway.

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