Rheological Analysis of Vapor-Grown Carbon Nanofiber-Reinforced Polyethylene Composites

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ABSTRACT: The melt rheological analysis of high-density polyethylene reinforced with vapor-grown carbon nanofibers (VGCNFs) was performed on an oscillatory rheometer. The influence of frequency, temperature, and nanofiber concentration (up to 30 wt %) on the rheological properties of composites was investigated. Specifically, the viscosity increase is accompanied by an increase in the elastic melt properties, represented by the storage modulus G', which is much higher than the increase in the loss modulus G''. The composites and pure PE exhibit a typical shear thinning behavior as complex viscosity decreases rapidly with the increase of shearing frequency. The shear thinning behavior is much more pronounced for the composites with high fiber concentration. The rheological threshold value for this system was found to be around 10 wt % of VGCNF. The damping factor was reduced significantly by the inclusion of nanofibers into the matrix. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 155–162, 2004

Key words: vapor-grown carbon nanofibers (VGCNFs); composites; rheology; polyethylene (PE); viscosity

INTRODUCTION

This research focuses on assessing the practical possibility of using vapor-grown carbon nanofibers (VGCNFs) to produce thermoplastic composites. Their processability and reinforcing effect were analyzed through a comprehensive rheological analysis. VGCNFs have extraordinary mechanical, electrical, and thermal properties. Given these interesting properties, their combination with polymers offers a composite material with promising scientific enhancement.[1–10] Nanofiber-reinforced composites can yield smaller and lighter components that can provide greater flexibility in a variety of applications. The thermal conductivity of VGCNF composites makes them attractive for electronic heat sinks and radiator fins, for example. In the electronic industry, nanofiber composites could be used as electrostatic dissipative (ESD) materials as well as electromagnetic interference (EMI) attenuators because of the high electrical conductivity and the high aspect ratio of VGCNFs. Recent studies on nanofiber/nanotube-reinforced polymers have reported resistivity values on the ESD range (surface resistivity between 10^5 and 10^{11} Ω/sq.).[11–13] To further decrease the resistivity values into the EMI range (surface resistivity $< 10^5$ Ω/sq.), manipulation of the nanofibers is needed such as alignment or metallization of the nanofibers.[13–16] Recently, Yang et al.[17] successfully developed a system of VGCNF/liquid crystal polymer composites, which exhibits 41 dB of EMI shielding effectiveness.

When reinforcement is introduced to a plastic matrix, a compromise is usually made between the improved properties and the increased difficulty in processing. Rheological analysis is considered an effective tool to predict the processing behavior as well as to study the microstructure of the composite. The response of complex viscosity, storage modulus, loss modulus, and tan δ obtained in a rheological analysis provides for a better understanding of structural features such as dispersion of the filler in the matrix, filler concentration, filler size distribution, wettability of the filler, and matrix/fiber interactions. Rheological analysis has been conducted for other type of fiber-reinforced polymer composites using primarily capillary and rotational rheometers.[3,5,18–23] The examined filler systems include short pineapple fiber, short glass fiber, conventional carbon fiber, and even multiwalled carbon nanotube (MWNT). Despite two simple reports about the rheological behavior of VGCNF composites, one with polycarbonate[5] and the other with polypropylene,[23] there is no full investigation on the flow behavior of VGCNF-filled polymer composites. The present article reports results of the investigation of the melt rheological analysis of VGCNF/PE composites. The multipronged objective was to assess the practical feasibility of using VGCNFs to manufacture thermoplastics composites, to investigate the process-

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ability of the composites, and to analyze the reinforcing capabilities of the VGCNFs.

In the past several decades, a few rheological models have been proposed to predict the viscoelastic behavior of composites. Various parameters have been applied in different constitutive equations. The two-parameter power-law model[24] has been used to fit the viscosity in the medium to high shear rate range. The four-parameter Carreau model[24] has been used in the low to medium shear rate range and the Herschel–Bulkley model[24] is successful at predicting shear thinning behavior at all shear rates.[24] Most of the modeled composites were filled by micro or larger scale fillers, which differ considerably from nanoscale fillers. Nanofilled composites have a thermorheological complex behavior affected by large relaxation processes. The development of models that can be applied to nanocomposites presents a challenging area of study.

In the present study, a small-amplitude dynamic oscillation test was selected as the testing method to avoid perturbing the fiber orientation in the composites.

EXPERIMENTAL

Materials

VGCNFs, Pyrograf-III™ (PR-24-AG), with diameters ranging from 50 to 200 nm, were obtained from Applied Sciences, Inc. (Cedarville, OH) They were purified and functionalized according to procedures from Lozano et al. where the VGCNFs were refluxed in dichloromethane for 5 days, followed by filtration with deionized water and refluxing for 24 h. The nanofibers were rinsed again, vacuum filtered, and vacuum dried at 110°C for 48 h.[25]

A high-density polyethylene (HDPE; HXM 50,100, with density of 0.949 g/cm^3 and MFI of 10 g/min at 190°C), from Chevron Phillips Chemical Co. (The Woodlands, TX), was chosen as the matrix. Polyethylene was chosen because it is a linear polymer that can contribute to the development of highly aligned nanofiber systems.

Preparation of composites

The dispersion of nanofibers in polyethylene was achieved by mixing VGCNFs with HDPE matrix in a Haake Rheomixer 600 (Thermo Haake, Portsmouth, NH) miniaturized internal mixer. The mixing was performed at 190°C, 65 rpm for 15 min. Then the composites were hot pressed at 200°C at a pressure of 4000 psi for 1.5 min. Samples were cut into coupons of 2 cm in diameter and 1 mm in thickness for the rheological tests.

Rheological testing

The rheological analysis was conducted on a Haake RheoStress RS 150 rheometer with the high-temperature measuring system TC501, ceramic rotors, and an electric heating system. The rotational measurements were performed using a parallel-plate sensor PP20 (Ø = 20 mm) with an initial gap of 1 mm. The samples were set between the parallel plates preheated to 190°C. The linear viscoelastic range (where the modulus is independent of strain) was determined by a strain sweep before testing the viscoelasticity of the composites under a frequency sweep. This strain sweep test was conducted under different frequency conditions (0.1, 1, 10, and 100 Hz). The frequency sweep was then conducted to obtain the corresponding curves for storage modulus (G'), loss modulus (G''), damping factor (tan δ), and complex viscosity (η^*). These tests were conducted in dynamic (oscillation) mode, with a frequency range of 628.3 down to 0.062 rad/s, collecting six data points per decade.

RESULTS AND DISCUSSION

Linear viscoelastic range determination

In this study, a rotational viscometer with a parallel-disc configuration was chosen to examine the rheological behavior of the nanocomposites. The advantage of the parallel-disc configuration is that it can be used for filled polymer systems of extremely high viscosity and elasticity. The basic limitation is that only low shear rates and low frequency oscillations can be applied to yield reliable data for the composites. The oscillation testing method was chosen because it provides more detailed information about the elasticity of a sample. The creep and relaxation tests were made with a given constant load (stress or strain), whereas the oscillation test was conducted under varying loads (frequency and amplitude sweep) with controlled shear stress or controlled strain. The results are the dynamic quantities for the shear moduli (complex dynamic shear modulus G^*, storage modulus G', and loss modulus G''), damping factor (tan δ), and the dynamic complex viscosity η^*. During the oscillation testing, the linear viscoelastic range of the sample must not be exceeded. Once it is exceeded, the sample structure is destroyed and the obtained rheological data do not represent the actual property of the original samples. Thus it is critical to determine the linear viscoelastic range. Figure 1 represents typical strain sweep results with frequency of 0.1, 1, 10, and 100 Hz. It is obvious that for all the frequencies tested, the storage modulus exhibits a stable plateau up to the strain of 0.01. A strain value of 0.001 was selected for the frequency sweep experiment. This strain value falls in the linear viscoelastic range for all samples. It
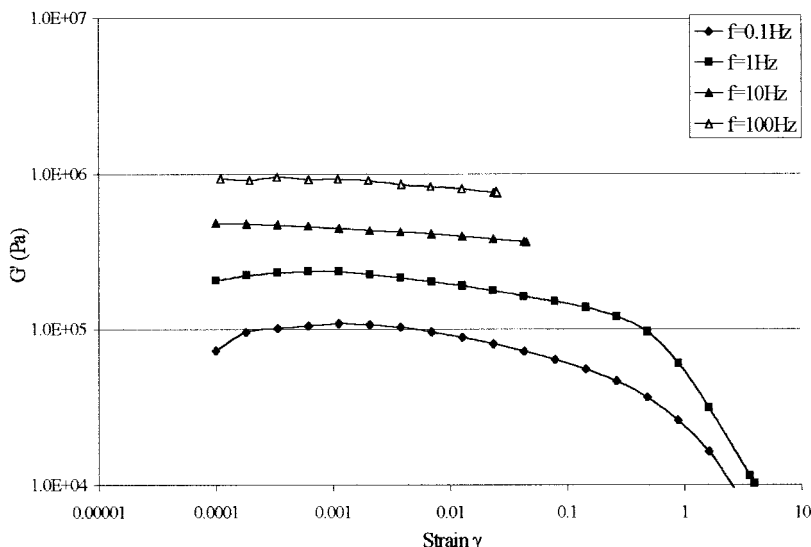
Figure 1 Linear viscoelastic range of the composites.

is observed that the storage modulus increased as frequency increased.

Storage modulus and loss modulus

The storage modulus G', loss modulus G'', complex viscosity η^*, and damping factor tan δ were obtained from the frequency sweep test. Variations of the dynamic storage modulus G' and loss modulus G'' with frequency f, for VGCNF-reinforced polyethylene at 190°C, are shown in Figures 2 and 3, respectively. Both storage modulus and loss modulus increased as frequency and concentration of VGCNF increased. However, the increase in storage modulus is much more dramatic than the corresponding increase in loss modulus. Additionally, Figures 2 and 3 show that the

modulus-enhancement effect of VGCNF in polyethylene composites is significantly higher at low frequencies than at high frequencies (the typical frequency of conventional manufacturing techniques such as extrusion or injection molding). In Figure 2, the storage modulus (low-frequency range) was increased from 0.003 MPa (pure PE) to 0.72 MPa (30 wt % VGCNF) at 0.0628 rad/s, an increase of about 24,000%, whereas the increase of G' at 628 rad/s is about 330%. The same phenomena are also observed in Figure 3 for loss modulus. For both storage modulus and loss modulus, the slope of modulus curves becomes flatter with the increase of nanofiber concentration. With 30 wt % of VGCNFs, the moduli are nearly independent of frequency. Compositions of less than 10 wt % VGC-NFs tend to produce a small increase in modulus and
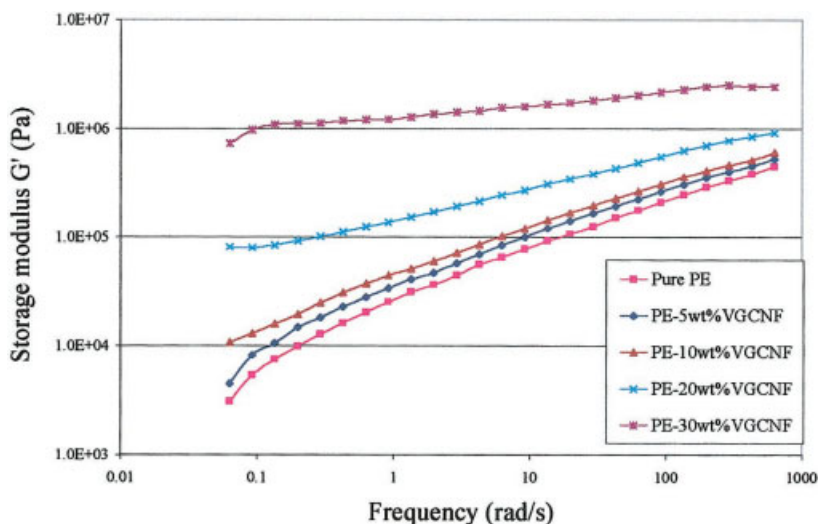

Figure 2 Storage modulus versus frequency at 190°C for the VGCNF-reinforced PE composites.
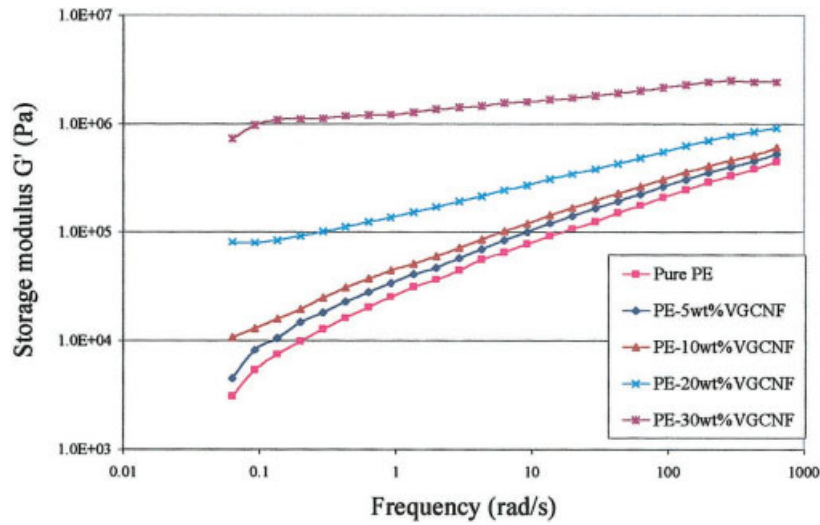
Figure 3 Loss modulus versus frequency at 190°C for the VGCNF-reinforced PE composites.

the curves follow closely with the unfilled PE with increasing frequency. Composites with more than 10 wt % of nanofiber exhibit a dramatic increase in modulus, especially storage modulus, indicating a threshold phenomenon for the modulus against nanofiber concentration. The threshold value is between 10 and 20 wt %. At higher concentrations of nanofibers, connectivity is more pronounced, as evidenced by the enhanced elasticity. In summary, in low-concentration composites, the storage modulus enhancement is attributed to stiffness imparted by the fibers that allow efficient stress transfer, which is controlled mainly by the matrix/fiber–matrix interface rather than by the reinforcing fibers. Beyond threshold concentration, the

modulus enhancement is mainly attributed to the interconnected nanofiber network structure within the matrix. This behavior is generally observed in fiber-filled polymeric melts.[21,26]

As mentioned earlier, at all frequencies, the storage modulus G' increase is much higher than the corresponding increase in loss modulus G''. To study the changes in the viscoelastic parameters, the storage modulus G' and loss modulus G'' are plotted simultaneously in Figure 4. The frequency at which a crossover point between G' and G'' occurs can be observed. The crossover points shifts to the lower-left side with increasing concentration of VGCNFs, indicating that the composite with higher VGCNF concentration be-
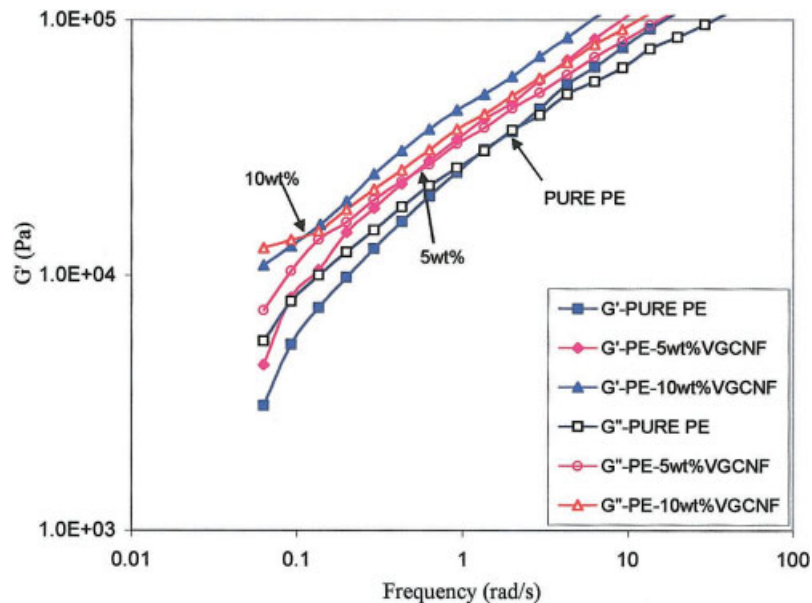

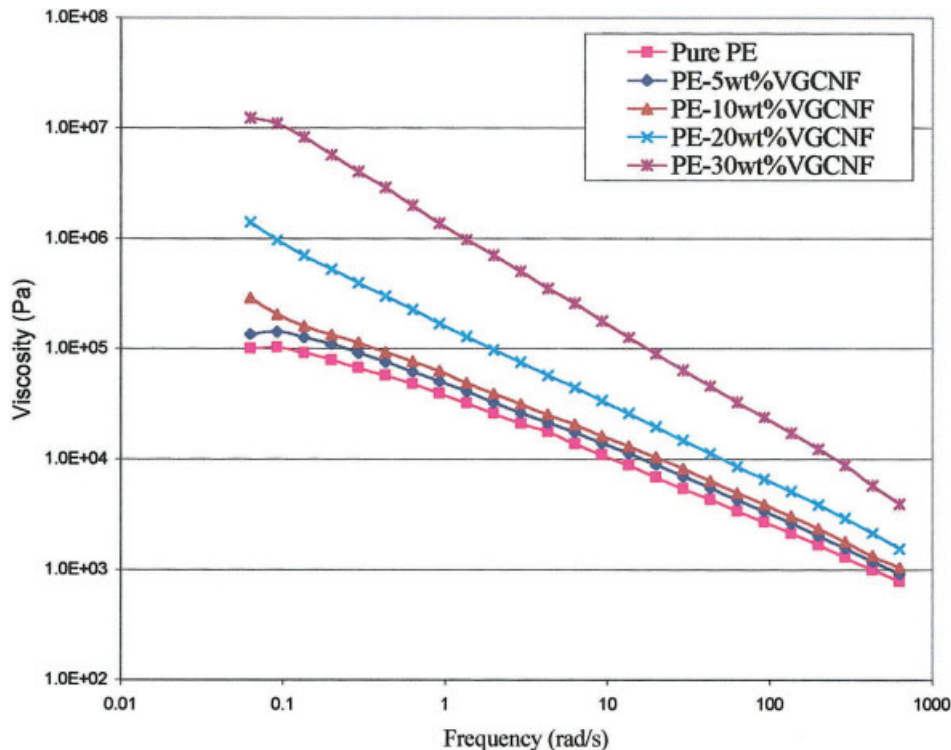**Figure 4** Shift of cross point of G' and G''.

Figure 5 Complex viscosity versus frequency at 190°C for the VGCNF-reinforced PE composites.

gins to exhibit elastic-like behavior at lower frequencies. This behavior was also observed by Lozano et al.[23] on the VGCNF/polypropylene (PP) system.

Complex viscosity (η^*)

Experimental results

The complex viscosity is also an important parameter to characterize the rheological properties of a material. The real part of the complex viscosity is an energy-dissipation term similar to the imaginary part of the complex modulus. The dependency of melt complex viscosity η^* of VGCNF-reinforced PE on VGCNF concentration and frequency f at 190°C is shown in Figure 5. A typical pseudoplastic shear thinning behavior for the pure PE and its VGCNF-reinforced composites were observed, similar to the behavior of VGCNF/PP composites studied by Lozano et al.[23] The viscosity decreases with the increase of frequency but increases with the increase of nanofiber content. In a filled polymer system, the presence of fibers perturbs the normal flow of polymer and hinders the mobility of chain segments in flow; therefore the viscosity of the filled polymer system increases.[3] Compositions of less than 10 wt % tend to produce a small increase in viscosity and follow closely with the unfilled PE with increasing frequency. Higher VGCNF loadings show significant viscosity increases where the observed increase in viscosity can be attributed to fiber wetting (polymer/

VGCNF interaction) as well as fiber–fiber friction. This increase in viscosity at low frequencies with increasing nanofiber content is similar to that seen when processing with MWNTs.[21] Therefore the significant decrease in viscosity at higher frequencies shows that the difficulty of processing with nanofibers and nanotubes is not an issue at higher shear rates. An important aspect to observe from Figure 5 is that the composites become more shear dependent in the low-frequency range as the VGCNF concentration is increased. This shear thinning behavior can be attributed to a greater degree of polymer–fiber and fiber–fiber interaction, which require higher shear stresses and longer relaxation times for the composites to flow. It is interesting to note that, at low shear rates, the viscosity seems to exhibit a viscosity threshold at around 10 wt % of VGCNFs, as observed in the VGCNF/PP composites.[23] This viscosity threshold value coincides with the threshold value observed in the modulus analysis.

One more observation here is that at high frequency the viscosity difference for the composites with different VGCNF concentrations is very small, and the curves seem to converge at high frequencies, which explains the successful exploitation of VGCNFs as reinforcements for plastics in conventional processing technology such as extrusion and injection molding.

Substantial temperature changes occur at various stages during processing; thus it is important to study
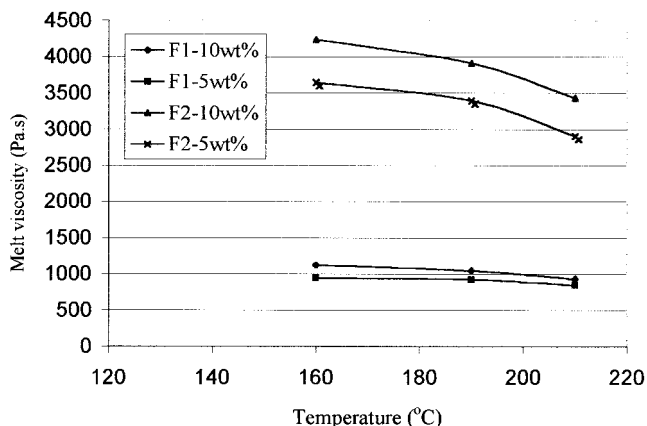
Figure 6 Melt viscosity versus temperature at different shear rates and at different fiber loading (F1 = 628.3 rad/s, F2 = 92.22 rad/s).

the effect of temperature on melt viscosity. The flow curves at 160, 190, and 210°C are presented in Figure 6 for two different fiber loadings (5 and 10 wt %) at two shear rates (92.2 and 628.3 rad/s). It was found that the effect of temperature on decreasing viscosity is more obvious in the case of lower shear rates (92.2 rad/s). Generally, at higher temperature, the melt viscosity is lower because the molecular motion is accelerated as a result of not only the availability of greater free volume but also the decrease in entanglement density and weaker intermolecular interactions. The sensitivity of viscosity on shear rates and temperature is a function of matrix polymer itself and also of the characteristic of reinforcement fillers.

Empirical equations

Earlier investigations on the rheological properties of polymer melts have shown that the data under dynamic conditions can be related to those obtained under steady shearing condition within certain ranges of shear rates and frequencies.[24] Among all the methods, the Cox–Mertz rule[24] is the most attractive one:

$$\eta(\dot{\gamma}) = |\eta^*(\omega)| \quad at \quad \omega = \dot{\gamma}$$

where η is shear viscosity, η^* is complex viscosity, $\dot{\gamma}$ is shear rate, and ω is frequency (rad/s). The relationship simply indicates that for prediction purposes, the magnitude of complex viscosity is comparable with that of shear viscosity at equal values of frequency and shear rate.[24] The relationship has been found to hold well for flexible chain thermoplastic melts, particularly in the lower and intermediate ranges of frequency and shear rate.[24] With respect to the filled polymer system, care has to be taken in applying this rule because of the change of melt flow introduced by the fillers. Based on the Cox–Merz rule, there have

been several rheological models developed to predict the viscoelasticity of filled polymer system, of which the Carreau model[24] is widely used:

$$\eta - \eta_\infty = (\eta_0 - \eta_\infty)/(1 + \lambda^2\varpi^2)^N$$

where η_0 is the zero shear rate viscosity, ϖ is frequency, λ is characteristic time, η_∞ is infinity shear rate viscosity, and N is a power-law parameter. Figure 7 shows how the Carreau model fits the obtained experimental data when the fiber loading is 5 wt %. It can be seen that the fit between empirical equation and experimental data is excellent. However, for composites with higher nanofiber concentration, the Carreau model does not fit the experimental data (data not presented). Therefore the need for development of other models remains a challenging area of study.

Damping factor tan δ

Damping factor tan δ is the ratio of the loss modulus to the storage modulus G''/G'. The variation of tan δ of the polymer and the composites, as a function of frequency, is shown in Figure 8. Just as in other composite systems, damping is improved through the incorporation of VGCNFs. This is attributed mainly to shear stress concentrations at the nanofiber ends in association with the additional viscoelastic energy dissipation in the PE matrix.[20] Relaxation of the PE matrix is concentrated mainly in the low-frequency region. With an increase in the concentration of VGCNFs, the tan δ curve becomes flat as the fiber restricts the relaxation of the polymer. Incorporation of the reinforcing VGCNF mechanically restricted the mobility and deformability of the polymer molecules, raised the storage modulus values, and reduced the viscoelastic lag between the stress and the strain and thus the tan δ values were decreased in the composites.

CONCLUSIONS

In this research, detailed melt rheological analyses of VGCNF/HDPE composites were performed on a rotational rheometer. The effects of nanofiber loading, frequency, and temperature on rheological properties were studied. Specifically, the storage modulus and loss modulus were both increased along with the increase of frequency and nanofiber concentration. The enhancement of storage modulus by inclusion of nanofiber is higher than that of loss modulus. Additionally, the modulus enhancement is much higher in the low-frequency range than that in the high-frequency range. The crossover point of G' and G'' against frequency shifts to the lower-left side for composites with higher VGCNF concentrations, indicating that the composite with higher VGCNF concentration begins to exhibit elastic-like behavior at lower fre-
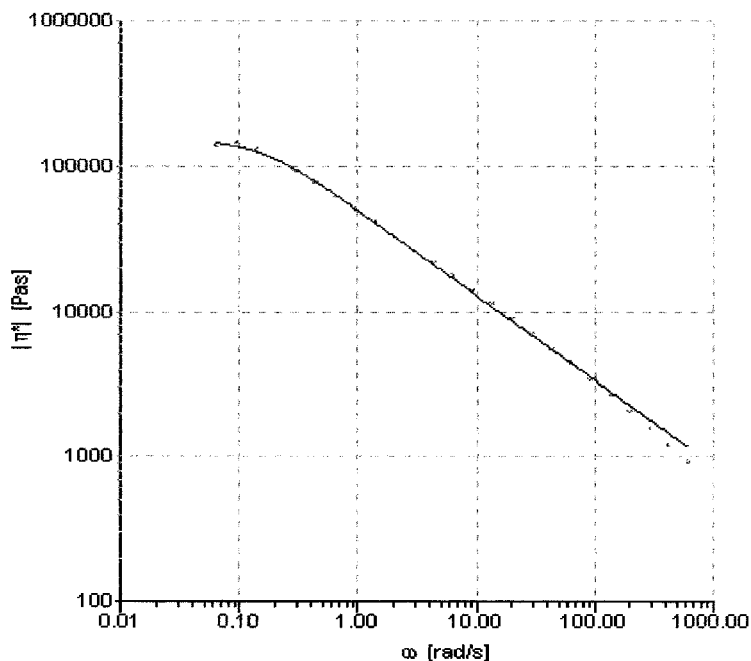
Figure 7 Comparison between steady shear and complex viscosity data for 5 wt % VGCNF/PE composites.

quencies. The composites and pure PE exhibit typical shear thinning behavior as complex viscosity decreases rapidly with the increase of shearing frequency. The viscosity of the composites increases with the increase of nanofiber concentration. The shear thinning behavior becomes more noticeable for the composites with high fiber concentration. From both modulus and viscosity analysis, there exists a perco-
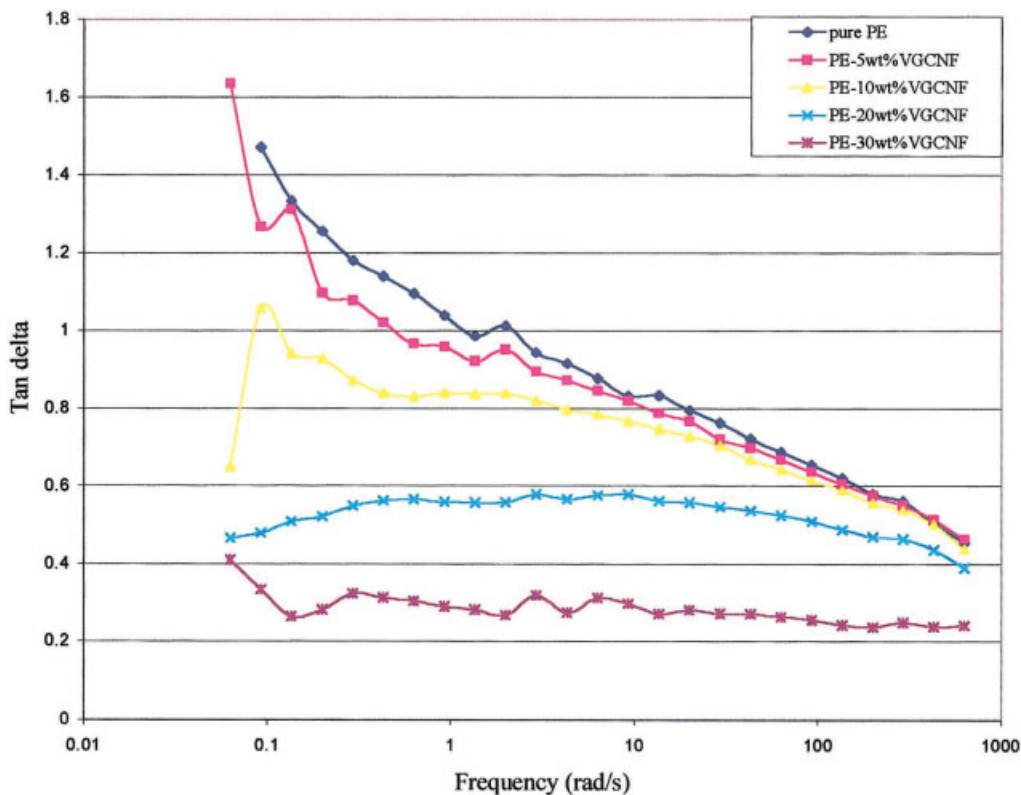

Figure 8 Plot of tan δ versus frequency at 190°C for the VGCNF-reinforced PE composites.

lation phenomenon and the rheological threshold value for this system was found to be 10 wt % of VGCNF. The Carreau model was found to fit the experimental viscosity data well for the 5 wt % VGCNF composites. The damping factor was reduced significantly by the inclusion of nanofibers into the matrix.

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