

Dynamic Rheological Behavior of High-Density Polyethylene Filled with Carbon Black

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ABSTRACT: The dynamic rheological behavior of high-density polyethylene (HDPE) composites filled with carbon black (CB) was studied by controlling periodic small shear strains at constant temperatures. The results shed light on the relationship between the behavior of dispersed fillers and polymeric matrix systems. At sufficiently high filler concentration a structural skeleton seems to appear, which significantly raises the modulus at the low frequency region. High structure, finer size acetylene black raises the modulus

significantly more than does the low structure and larger size one (e.g., N550). Oxidized CB increases the modulus in the whole frequency region for the enhanced interaction between polymer matrix and CBs. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 3527–3531, 2002

Key words: rheology; viscoelastic properties; HDPE/CB composites; matrix; shear

INTRODUCTION

The incorporation of solid filler particles into polymer dramatically varies the regularity of its flow. Thus, the study of viscoelastic behavior of filled polymers is of important scientific and practical significance. The dependency of viscoelastic behavior, especially dynamic properties, of carbon black (CB)-filled rubbers on temperature has been the subject of numerous investigations.^{1–3} The viscoelastic behavior of the filled systems is strong, depending on such characteristics as CB morphology,² surface activity, and loading level.³ Many studies have centered on high-density polyethylene (HDPE) systems filled with CB with respect to their electrical conductivity uses.^{4–6} However, the conductivity is unstable for the irregular structure of the composite,⁷ although much progress has been made toward stabilizing the conductivity.^{7–10} Obviously, the structure of the composites is the fatal factor to determine its stability; thus a deeper comprehension of the structure of composites is necessary. Viscoelastic behavior is a reflection of the internal structure. Some information should be acquired through

the study of dynamic rheological behavior of the systems. Up to now, few investigations focused attention on the dynamic rheological behavior of HDPE composites filled with CB.¹¹ The purpose of this present work was formulated as an investigation of a CB-filled HDPE system, to establish the specific effect of CB on the viscoelastic behavior of HDPE and to understand the structure of the filled system.

EXPERIMENTAL

High-density polyethylene (HDPE2480, Qilu Petroleum Co., China), with a melt index of 0.14 g/10 min and density of 0.943 g/cm³, was selected as the polymer matrix. The carbon black was acetylene black [a-CB; average size, 42 nm; Brunamer–Emmitt–Teller (BET) value, 63 m²/g; dibutyl-phthalate (DBP) value, 3.3 mL/g; Chun'an Chemical Co., China]. Another carbon black was N550 type (average diameter, 77 nm; BET, 43 m²/g; DBP, 1.21 mL/g; Qingdao Carbon Black Plant, China). Oxidized CB (*o*-CB) was prepared by immersing acetylene black into 65% nitric acid (aq.) for 12 h, after which it was washed with distilled water and dried. The composites were mixed on a two-roll mixer at 170°C for 15 min. CB contents (in wt %) are listed in Table I. Circular shape samples were molded at 170°C, 6 MPa for 20 min, with a size of $\phi 25 \times 1.8$ mm. Dynamic rheological behavior was carried out using the advanced rheometric expansion system (ARES). The frequency range was from 10⁻² to 10² rad/s by a dynamic frequency sweep test in a controlled strain. Samples were mounted between two

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TABLE I
Carbon Black Contents (in wt %) of the Composites

Type of CB	CB contents (%)						
a-CB (%)	0	5	8	10	15	20	30
o-CB (%)	0					20	
N550 (%)	0					20	

parallel plates with a gap of 1.8 mm. Six fixed temperatures, 150 to 200°C at intervals of 10°C, were selected.

RESULTS AND DISCUSSION

Although HDPE is a highly crystalline polymer, its dynamic rheological behavior was studied above its melting point to make the study feasible. In Figure 1 the dynamic storage modulus G' is plotted double-logarithmically versus the radian frequency ω of the composites filled with various contents of CB at 170°C. The storage modulus increases with increasing CB loading levels; moreover, the modulus increases markedly at the low frequency region at a higher CB concentration. It seems that, although the viscoelastic behavior of polymer-based disperse systems depend primarily on the properties of the polymer, the carbon black structure causes certain specific features in the elasticity of the system. The results showed that, at a low carbon black content, the processes characteristic of the polymer matrix predominate, whereas with increasing filler concentration the network structure becomes the prevailing process, which raises the modulus, especially at the low frequency zone. The $\log G'$ of each curve in the figure increases with increasing values of $\log \omega$, which almost yields a straight line in HDPE, and low CB content-filled system, which is related to the transition of the material from a fluid to a forced high-elasticity state.

The loss factor ($\tan \delta$) versus ω is also plotted in Figure 1. The $\tan \delta$ value obviously decreased with the

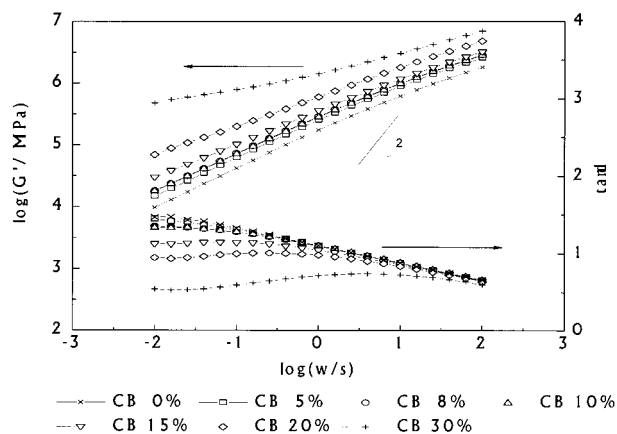
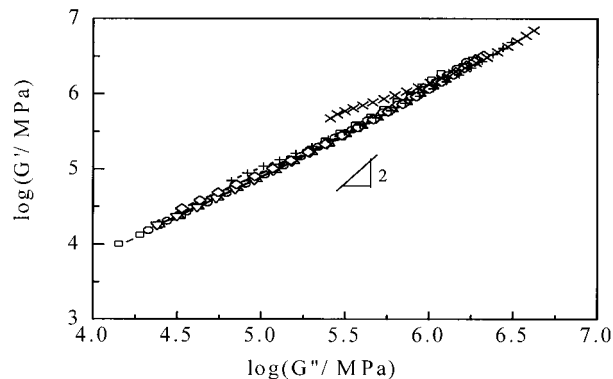


Figure 1 Plots of $\log G'$ and $\tan \delta$ versus $\log \omega$ of HDPE filled with various contents of carbon black at 170°C.



$\log G'$ against $\log G''$ of HDPE filled with various contents of carbon black at 170°C
 —□— CB 0% —○— CB 5% —△— CB 8%
 —▽— CB 10% —◇— CB 15% —+— CB 20%
 —×— CB 30%

Figure 2 Plots of $\log G'$ versus $\log G''$ of HDPE filled with various contents of carbon black at 170°C.

increasing of frequency in low CB content and decreased with the increasing of CB content in the low frequency region as well. A maximum loss factor peak was observed in 30% CB content-filled system at which G' and G'' emerge as a transition. It is well known that $\tan \delta$ is defined by the ratio of G'' to G' . G'' is related to the filler network, which remains during dynamic deformation, and G' to the breakdown and reformation of the network. In other words, $\tan \delta$ reflects the ratio between the network portion that is capable of being broken down and reconstituted and the portion that remains unchanged during dynamic strain. Consequently, $\tan \delta$ is sensitive to CB structure in the composites. The greater the network portion withstanding dynamic deformation and the smaller the portion being broken down and reformed, the lower the value of $\tan \delta$. This suggests that the development and the strength of the secondary filler network have major effects on $\tan \delta$.

The relationships between $\log G'$ and $\log G''$ of composites at various CB contents are shown in Figure 2. The relationship $\log G' \propto (2 - \beta)\log G''$ exists in most polymeric blends, especially for homogeneous polymer blends.¹² A linear relation exists in the pure HDPE melt and the melt of low CB content-filled systems, whereas the slopes are less than 2, which shows notable differences from the results of Yanovsky.¹¹ The linearity was broken at high CB content, which is more obvious in the 30% CB-filled system. The figure shows that G'' increases more significantly than G' at high CB loading levels, indicating an extreme change in the structures of the filled systems.

It is well known that temperature is an important factor in determining the rheological behavior of polymeric composites. The viscoelastic behavior of the 30% CB-filled system at various temperatures is shown in

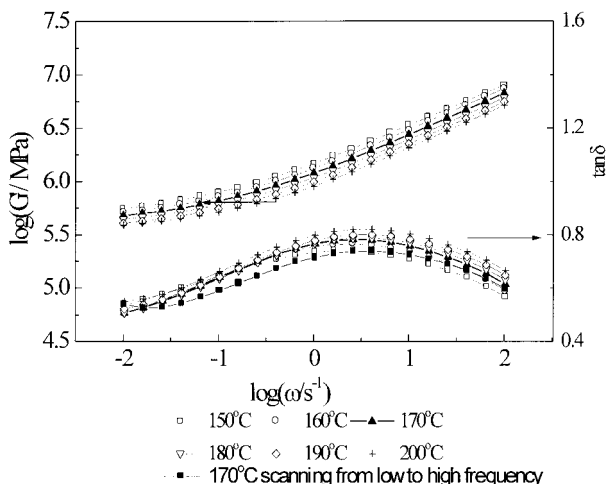


Figure 3 Plots of $\log G'$ and $\tan \delta$ versus $\log \omega$ of HDPE filled with CB (30%) at various temperatures.

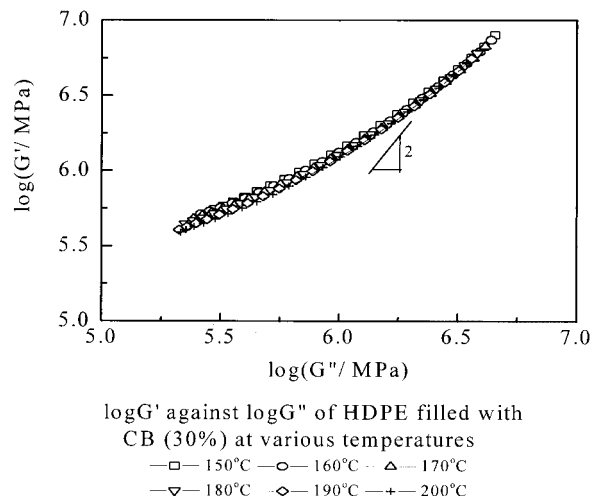


Figure 4 Plots of $\log G'$ versus $\log G''$ of HDPE filled with CB at various temperatures.

Figure 3. All the curves keep the same forms, although the modulus decreases with increases in temperature. The $\tan \delta$ in Figure 3 shows some increase with increases in temperature, obviously at the high-frequency region. It is easy to understand that G'' is more prevalent than G' at high temperature according to the definition of $\tan \delta$, suggesting that the high mobility of polymer chains and the low viscosity at high temperature are helpful in dissipating energy. It is noted that the curves of $\tan \delta$ in Figure 3 for the 30% CB-filled system at 170°C are different at the two frequency scanning modes. The solid square symbol curve in this figure was also present in Figure 1, which was obtained by frequency scanning from low frequency to high frequency; however, the other curves in Figure 3 were obtained from high frequency to low frequency. CB particles are easy to aggregate at high temperature in the low viscous polymeric matrix in a short time,¹³ accompanied by the dissipated energy. Different scanning modes may correspond to various aggregation states of CB particles. The differences in $\tan \delta$ are attributed to the aggregation of CB particles in the composites.

Figure 4 shows the influence of temperature on the $\log G' - \log G''$ relationship during oscillation amplification deformation. They were maintained at almost the same characteristic behavior in spite of varying temperatures. Therefore, $\log G' - \log G''$ depends on the internal structure of the composites.

Figure 5 shows the differences in viscoelastic behavior of the blends filled with various types of CB at a loading level of 20%, investigated at 170°C. The frequency scanning mode is from 10^{-2} to 10^2 rad/s. The system filled with N550 shows a lower G' than that filled with acetylene black at each frequency. The σ -CB-filled system exhibits a slightly increased modulus compared to that of the original a-CB. It seems that the

enhanced interaction between HDPE and CB by oxidation increases the modulus of the composites. Moreover, the $\tan \delta$ values of these three cases pass through a maximum peak almost at the same frequency, respectively, and separate at the low frequency region. The particle size of N550 is larger than that of acetylene black. It is thought that such prominent differences in viscoelastic behaviors of various sizes of CB-filled systems should be attributed to the different secondary structure and the distance between the aggregates.²

Plots of the $\log G'$ versus $\log G''$ of the different types of CB-filled systems at 170°C are shown in Figure 6. The relationship between G' and G'' reveals no differences. By comparing the results shown in Figures 2 and 3, we can draw a conclusion of the relationship between $\log G'$ and $\log G''$ related only to

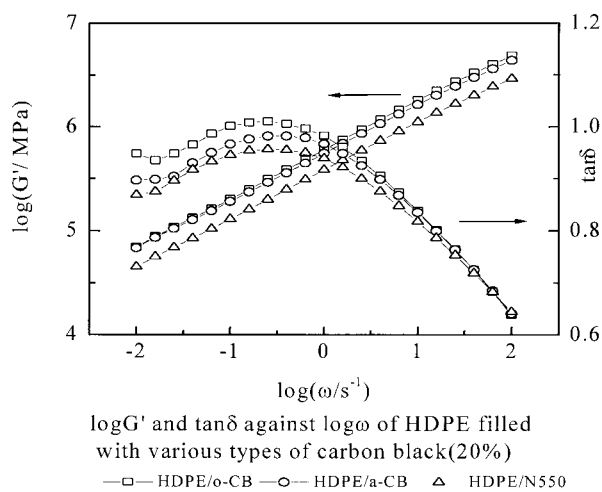


Figure 5 Plots of $\log G'$ and $\tan \delta$ versus $\log \omega$ of HDPE filled with various types of carbon black (20%).

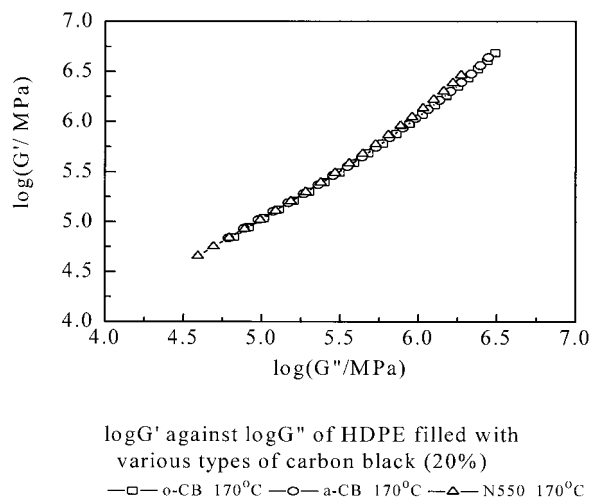


Figure 6 Plots of $\log G'$ versus $\log G''$ of HDPE filled with various types of carbon black (20%).

content of the filler, with no relationship to types of CB and only a slight relationship to temperature.

The incorporation of solid fillers such as CB into the polymer matrix could increase its modulus, as is well known in rubber reinforcement.¹⁴ The earliest attempt to theoretically describe the enhancement of modulus by fillers was made by Smallwood¹⁵ and Guth.¹⁶ Guth and Gold^{17,18} modified Einstein's viscosity equation, which took into account the mutual disturbance caused by spheres at higher concentration, and proposed the follow equation for E :

$$E = E_0(1 + 2.5\phi + 14.1\phi^2) \quad (1)$$

where E_0 is the elastic modulus of the unfilled polymer, E is the elastic modulus of the filled composites, and ϕ is the volume fraction of filler. Figure 7 shows the equilibrium storage and loss modulus at a constant

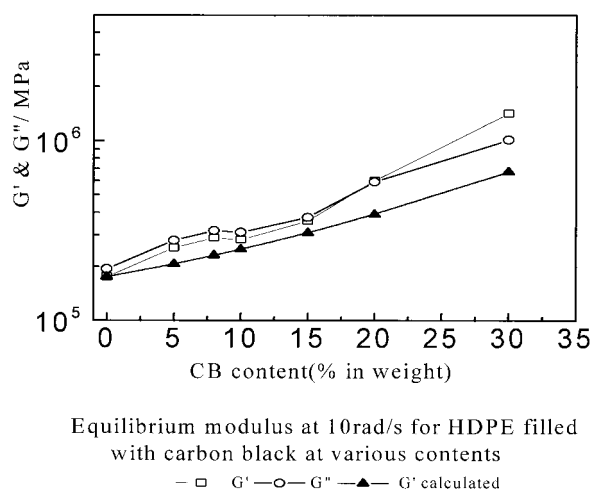


Figure 7 Equilibrium modulus at 10 rad/s for HDPE filled with carbon black at various contents.

TABLE II
Effective Volume Fraction Coefficient f Against Volume Fraction ϕ

ϕ	0.026	0.0427	0.0539	0.0829	0.1136	0.1801
f	1.2206	1.1707	1.1455	1.1015	1.0762	1.0720

frequency of 10 rad/s versus volume fraction of CB in the composites both for the experimental data and calculated from eq. (1) (G' , G'_0 , and G'' , G''_0 instead of E and E_0 , respectively, when calculated). The actual experimental results show higher values than the theoretical results, thus implying that this equation is inadequate for reinforcing fillers. This is attributed to the fact that the equation is based on the following assumptions: spherical particles, particles wetted by the polymer, low strain, perfect dispersion, negligible particle-particle interaction, and the characteristics of the polymer not being affected. It is difficult to satisfy such conditions, given that (i) most carbon black aggregates depart considerably from the spherical shape, and (ii) the mobility of the polymer matrix is not uniform because of filler-polymer interaction. Moreover, particle-particle (or aggregate-aggregate) interaction enables the particles to agglomerate. Again, this affects the uniformity and continuity of the polymer matrix.² Based on the occlusion of polymer within the interstices of carbon black aggregates and the assumption that occluded polymer is shielded from deformation and acts as part of the filler, Medalia substituted ϕ in the above equation by an effective volume fraction ϕ_{eff} ^{19,20}:

$$E = E_0(1 + 2.5\phi_{\text{eff}} + 14.1\phi_{\text{eff}}^2) \quad (2)$$

The effective volume fraction ϕ_{eff} can be converted from the filler volume fraction by introducing a factor f , that is,

$$\phi_{\text{eff}} = f\phi \quad (3)$$

which involved all the effects of filler properties on modulus through effective loading.

If we let the modulus calculated from eq. (2) be equal to the actual experimental results shown in Figure 7, factor f could be determined by volume fraction ϕ , as listed in Table II. The value of f decreases with the increase of ϕ , which means the ratio of effective volume fraction decreases. It could be assumed that, as one of the consequences of formation of CB networking at high CB loading levels, the polymer trapped in the CB agglomerates or secondary structure is immobilized, in the sense that it is shielded from deformation under stress. However, the formation of CB aggregates decreased the immobilizing of polymer on the surface of each CB particle. As a result, the effective volume fraction of CB would be lower as

long as the secondary structure exists, which is different from the results of Wang.²

The complex structures of the filled systems lead to the variance of viscoelastic behavior of the composites, which is effectively reflected by dynamic rheology.

CONCLUSIONS

The dynamic rheological behavior of the composites can be changed by incorporating CB into the HDPE matrix. The modulus of the composites increases with the increase of CB loading level. There is a secondary plateau (rubber plateau) in the high CB loading level corresponding to the formation of a continuous network of CB particles. The $\log G'$ keeps a linearity with $\log G''$ in low CB loading levels; the slope is less than 2, although the linearity is broken at high CB content. Incorporation of finer size CB particles effectively increases the modulus for easier dispersal in the matrix. Oxidized CB also increases the dynamic modulus of the composites for the enhanced interfacial function.

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