

Dynamic Rheological Properties for HDPE/CB Composite Melts

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ABSTRACT: A study on the dynamic viscoelastic properties of carbon black (CB)-filled high-density polyethylene (HDPE) in the molten state was carried out. When the temperature was above 180°C in an air atmosphere, the storage modulus G' , loss modulus G'' , and loss tangent δ showed particular characteristics. In the low-frequency region, the modulus increased with increase of the testing time while the $\tan \delta$ obviously decreased. Also, the higher the temperature, the more notable was the change. We can detect these changes from the deviation of G' (G'') against ω plots from the linearity and the appearance of a characteristic plateau phenomenon. The width and height of the modulus plateau increased with increase of the temperature. When temperature was below 180°C, the testing time and the temperature

had no effect on the viscoelastic parameters of HDPE. However, if we used 99% nitrogen gas as the atmosphere, substituting for air, the viscoelastic parameters revealed an undiscernible change, different from that in an air atmosphere. No changes were found under the protection of the antioxidant B215. This phenomenon indicated that HDPE can be oxidized at a temperature higher than 180°C. Nitrogen gas and an antioxidant agent can prevent HDPE from crosslinking. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2160–2167, 2003

Key words: crosslinking; composites; viscoelastic properties; annealing

INTRODUCTION

Because of the potential application in preparing conductive functional material such as self-adjusting heat-transfer devices, fuses, and overcurrent protectors, composites of high-density polyethylene (HDPE) filled with carbon black (CB) have attracted wide attention in the fields of scientific research and industrial applications.¹ However, up to now, there has been no full understanding of the conduct mechanism of CB/HDPE composites, as well as the positive temperature coefficient (PTC) effect. It is well known that electrical properties of a filled polymer are involved in the microstructure of carbon black networking.² A volume expansion model by Kohler³ suggested that a PTC jump is caused by the great differences in the thermal expansion coefficients between the particle and the matrix. Kost et al.⁴ and others^{5–8} attributed the change of the electric behavior to deformation–reformation

of the CB networking according to the relationship among the strain, stress, and conductivity of polymer conductive composites. There is not enough experimental proof for a theoretic presumption of conductive networking and its temperature dependence.

Dynamic rheology testing is believed to be a preferential method for dealing with the structure/morphology of materials because the structure of materials exposed to the testing processes is not destroyed under small-strain amplitude.⁹ The so-called second plateau, a phenomenon in dynamic viscoelastic functions, for example, the storage modulus G' and loss modulus G'' , which exhibit a special response corresponding to linear viscoelasticity, is thought to give important information concerning the viscoelastic behavior of multicomponent polymer systems at very low frequencies (terminal region).¹⁰ Moreover, the appearance of a second plateau in the terminal region is considered to be induced by the formation of a higher-order structure of particles, for example, an agglomerated structure, skeleton, or network structure.¹¹ Studies of the dynamic viscoelastic properties for rubber particle-filled polymer systems suggested that the second plateau results from a high-order structure formed by rubber particles,^{12,13} while a PS melt filled with grafted glass beads system is a high-order structure formed by the beads in the melt, as compared with an ungrafted bead-filled system.¹⁴ In present article, we studied the formation and development of CB/HDPE conductive composites on the basis of a

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sensitive response of the dynamic rheological behavior to structure variation under small-strain amplitude to explore the relationship between structure variation and the dynamic viscoelastic properties of CB/HDPE composites.

EXPERIMENTAL

The polymer used was a high-density polyethylene (HDPE) provided by the Yangzi Petrochemical Corp. (Nanjing, China), with a melting index of 0.090 g min^{-1} , density of 0.954 g cm^{-3} , and melt point of 128°C . The CB filler employed had a particle diameter of 77 nm , a BET special surface area of $43 \text{ m}^2 \text{ g}^{-1}$, a dibutyl phthalate absorption of $1.21 \text{ cm}^3 \text{ g}^{-1}$, and an iodine absorption of 43 mg g^{-1} . The antioxidant was obtained from the Ciba-Geigy Corp (Basel, Switzerland). (B215): The relative molecular weight was 647 and the melt point was $180\text{--}185^\circ\text{C}$.

The composites of HDPE/CB were prepared on a two-roll mill at 165°C for 15 min. Disks of about 2- and 1.5-mm thickness were prepared by compression molding at 165°C under 10 MPa.

Rheological measurements were carried out in an Advanced Rheology Expansion System (ARES). The dynamic mechanical responses of specimens with a rectangular geometry of 1.5-mm thickness were detected under the condition of the frequency, strain amplitude, temperature range, and heating rate being 10 rad s^{-1} , 0.05–0.2%, $60\text{--}150^\circ\text{C}$, and 4°C min^{-1} , respectively. An isothermal dynamic frequency sweep was conducted with a disk of 2.0 mm in thickness and 2.5 mm in diameter under the condition of the frequency range, strain amplitude, and temperature range being $10^2\text{--}0.25 \text{ rad s}^{-1}$, 0.05–5%, and $140\text{--}210^\circ\text{C}$, respectively. Samples were held at 135°C and the testing temperature for 10 min before measurement.

The measurement for the gel content of the HDPE sample was conducted above the melting point of xylene by a Soxhlet extractor for 48 h. Before extracting, samples were kept at 200°C in an air atmosphere for 70 min.

RESULTS AND DISCUSSION

Temperature dispersion curves of dynamic viscoelastic functions for HDPE, B215/HDPE, and CB/HDPE

Figure 1 gives the temperature dependence of the dynamic storage modulus G' , dynamic loss modulus G'' , and loss tangent $\tan \delta$ for the HDPE, CB/HDPE, and B215/HDPE systems. The relaxation transition of a 3–4 magnitude occurs when the temperature approaches 130°C , which is attributed to HDPE melting. The almost same transition temperature exhibited implies that the addition of the CB particle does not affect

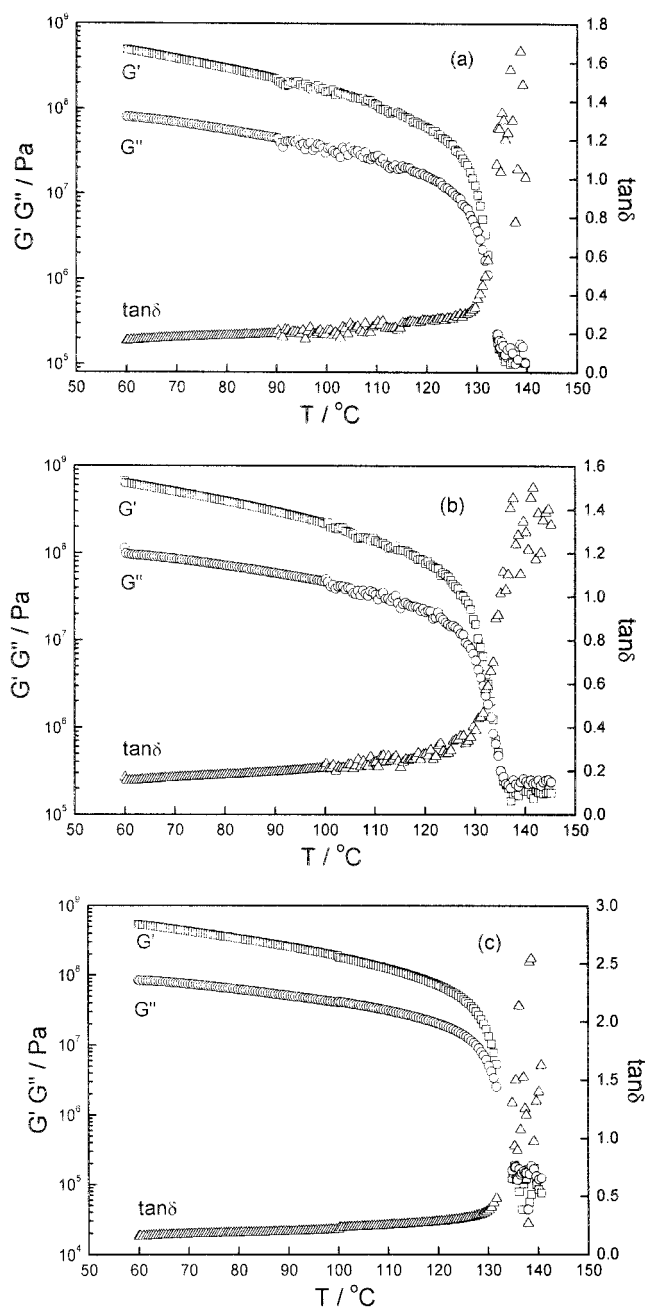


Figure 1 Temperature–dispersion curves of dynamic storage modulus G' , loss modulus G'' , and loss tangent $\tan \delta$ for (a) HDPE, (b) CB/HDPE(14/100), and (c) B215/HDPE (0.5/100).

the melt temperature of HDPE. For HDPE and the corresponding particle-filled composites, full melting occurs under 135°C .

Frequency dependence of dynamic viscoelastic properties for CB/HDPE with stepping-up/down temperature

Figure 2 presents the frequency dependence of dynamic viscoelastic functions for the samples exposed

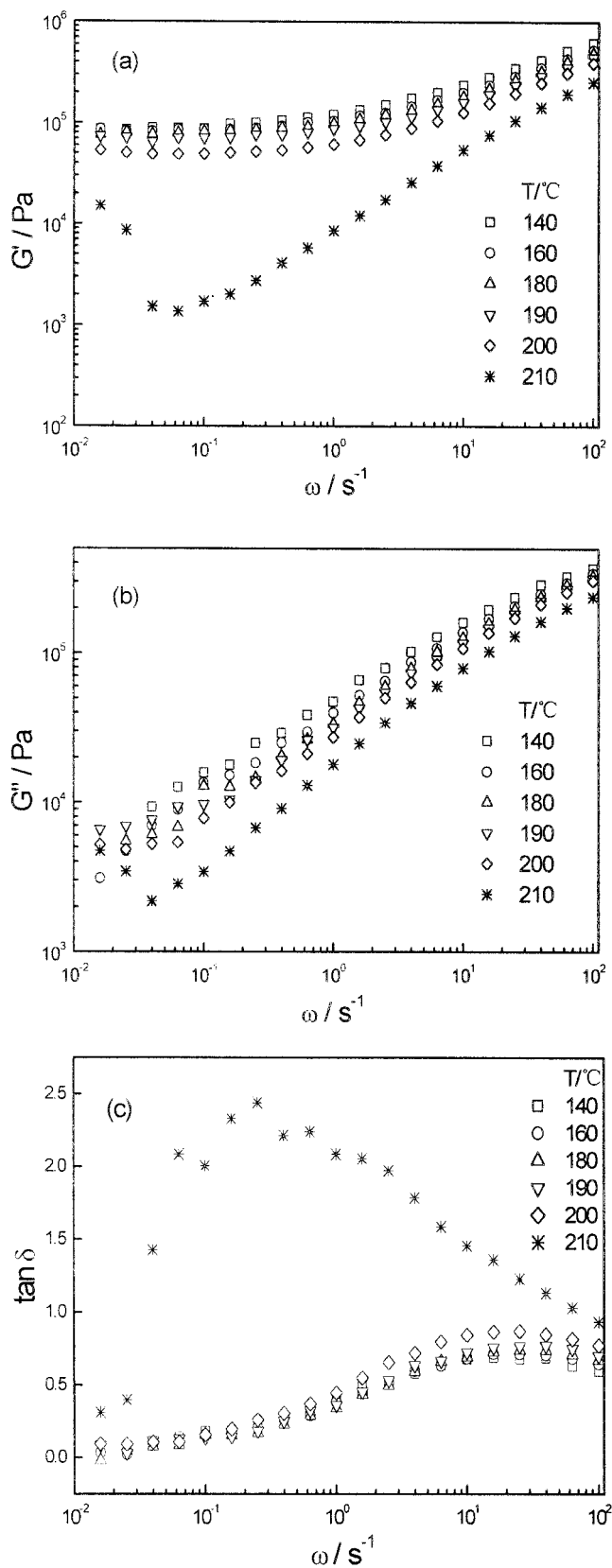


Figure 2 Frequency dependence of dynamic viscoelastic functions for CB/HDPE (14/100) with stepping-down temperature: (a) G' ; (b) G'' ; (c) $\tan \delta$.

to stepwise cooling. It is obvious that under the highest testing temperature, 210°C, relationships between the frequency ω and G' and G'' deviate from linearity. Also, an interesting phenomenon was found: that as the temperature increased to 210°C, a characteristic plateau phenomenon appeared. Furthermore, the plateau modulus increased gradually as the temperature decreased, while the frequency region corresponding to the plateau becomes wider. According to common understanding, the appearance of the plateau results from the formation of a higher-order structure of particles.

Figure 3 shows the dynamic rheological behavior of CB/HDPE composites in a wide frequency region from 10^{-2} to 10^2 s^{-1} . Figure 3(a) indicates that there exists a linear characteristic $G'-\omega$ relationship below 180°C within the whole frequencies. When the temperature increases and approaches 190°C, G' obviously increases at low frequencies and the $G'-\omega$ curve deviates from linearity, which generally is referred to as the so-called second plateau. An analogical deviation also occurred in the relationship of G'' and ω , as shown in Figure 3(b). Hence, it is suggested that the appearance of the plateau mentioned above deals with the formation of a network within the matrix of the CB/HDPE composites.

But contrary to Figure 2 in which the modulus decreases with increasing temperature, the modulus in Figure 3 increases with increasing temperature. The change of $\tan \delta$ as a function of temperature in these two figures is also different. It is believed that the temperature is not the only factor that influences the dynamic rheological parameters of the composites. Even though we found the plateau that appears in Figure 3 at a testing temperature of 210°C, when carefully reviewing the difference of G' between Figures 2 and 3, we could not find it in Figure 2 at the same temperature. This illuminates that the time of keeping the samples in a high-temperature atmosphere before testing maybe an important factor in inducing formation of a modulus plateau. To explore the influence of time and temperature for the second plateau, we tried to understand the relationship among the time, temperature, and rheological parameters as functions of the frequency, as discussed in the following.

Time and temperature dependence of dynamic viscoelastical properties for CB/HDPE

Figure 4 shows the dynamic rheological properties of CB/HDPE composites under different temperatures. All samples were kept in an atmosphere testing temperature for 70 min before the sweep test. As shown in Figure 4(a), the plots of G' against ω have a linear character under 140 and 160°C. When the temperature approaches 180°C, G' did not decrease but increased abnormally and the increasing of G' is more obvious

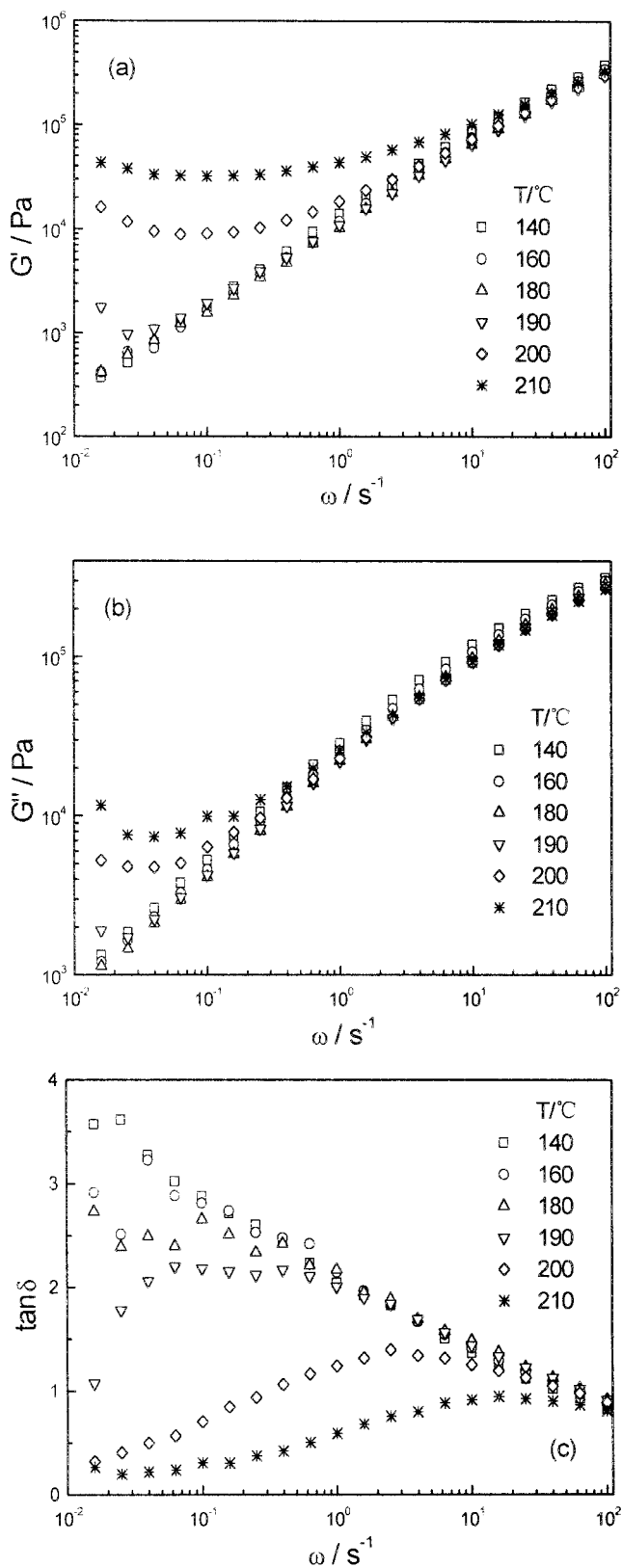


Figure 3 Frequency dependence of dynamic viscoelastic functions for CB/HDPE (14/100) with stepping-up temperature: (a) G' ; (b) G'' ; (c) $\tan \delta$.

in the low-frequency region than in any other region. Figure 4(b) shows that plots of G' against ω and G'' against ω appear as a characteristic plateau under

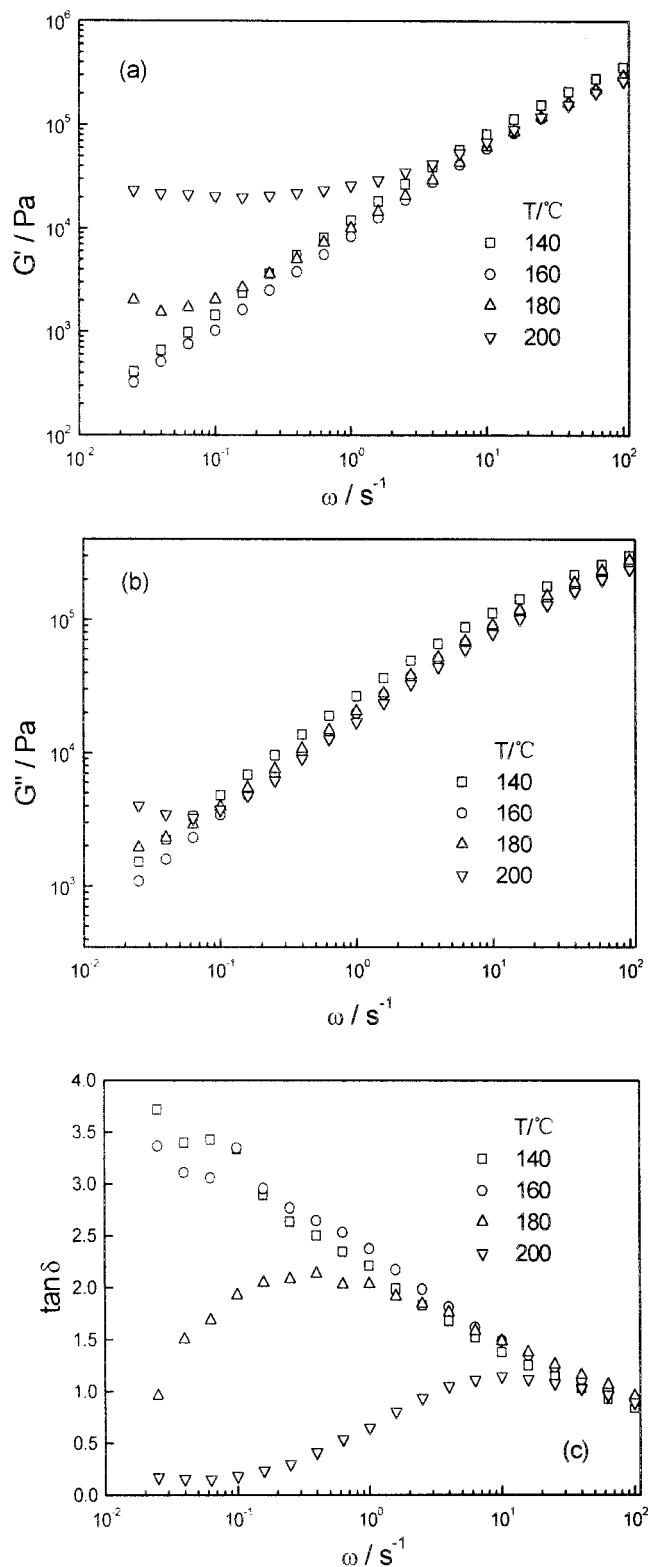


Figure 4 Frequency dependence of dynamic viscoelastic functions for CB/HDPE (14/100) held at a 140, 160, 180, and 200°C atmosphere for 70 min: (a) G' ; (b) G'' ; (c) $\tan \delta$.

200°C. With increase of the temperature, the plot of $\tan \delta - \omega$ changes from linearity to an arc. As shown in Figure 4(c), the higher the temperature, the smaller is the value of $\tan \delta$ in the low-frequency region. These characteristics of rheological behavior imply that the microstructure of CB/HDPE composites changes in the temperature-holding period. On the other hand, if the holding time is constant, the higher the temperature, the more remarked is the change.

Figures 5 and 6 show the dynamic rheological properties of CB/HDPE composites under 200°C. It should be noted that samples were kept under a certain temperature for different times before the test. Figure 5 shows that the rheological properties of the CB/HDPE composites under 200°C depend strongly on the holding time of the temperature before the test. The longer this period of time, the higher is the modulus. In the case when this period of time is 10 min, G' as well as G'' in the low-frequency region obviously increases. When this period of time is 40 min, the characteristic plateau appears in the low-frequency region. Obviously, the plateau modulus increases with increasing time. The rheological character of HDPE as shown in Figure 6 is more or less similar to that of the CB/HDPE composites. The only difference is that the modulus of the CB-filled system is a little higher than that of HDPE in the same condition. The plots of G' against ω for these two systems can be superposed together through a vertical shift. In taking into account the ability of the reinforcement of CB to the polymer matrix, we considered that the shift value is related to the effect of the CB reinforcement. It is suggested that the appearance of the modulus plateau is independent of CB, and it is relevant to the change of the HDPE structure.

Relationship between HDPE oxidant and modulus plateau

Figure 7 presents the dynamic rheological properties of HDPE under 200°C. In practice, nitrogen gas with a concentration of 99% was used as the environmental atmosphere. The holding times before the test were 10 and 40 min. Figure 8 shows the dynamic rheological properties of B215/HDPE under 200°C in an air atmosphere corresponding to the same two holding times before the test. There is no characteristic plateau in Figure 7 or 8 compared to Figure 6. Especially, the temperature is independent of the dynamic rheological behavior for HDPE filled with the antioxidant B215. Figure 7 suggests that nitrogen gas can partially restrain the HDPE structure from changing. On the other hand, it can be observed in Figure 8 that the antioxidant prevents HDPE from changing the structure efficiently. Therefore, it is considered that the oxidation of the HDPE melt is the major cause of the appearance of the low-frequency plateau for HDPE and the CB/HDPE composites.

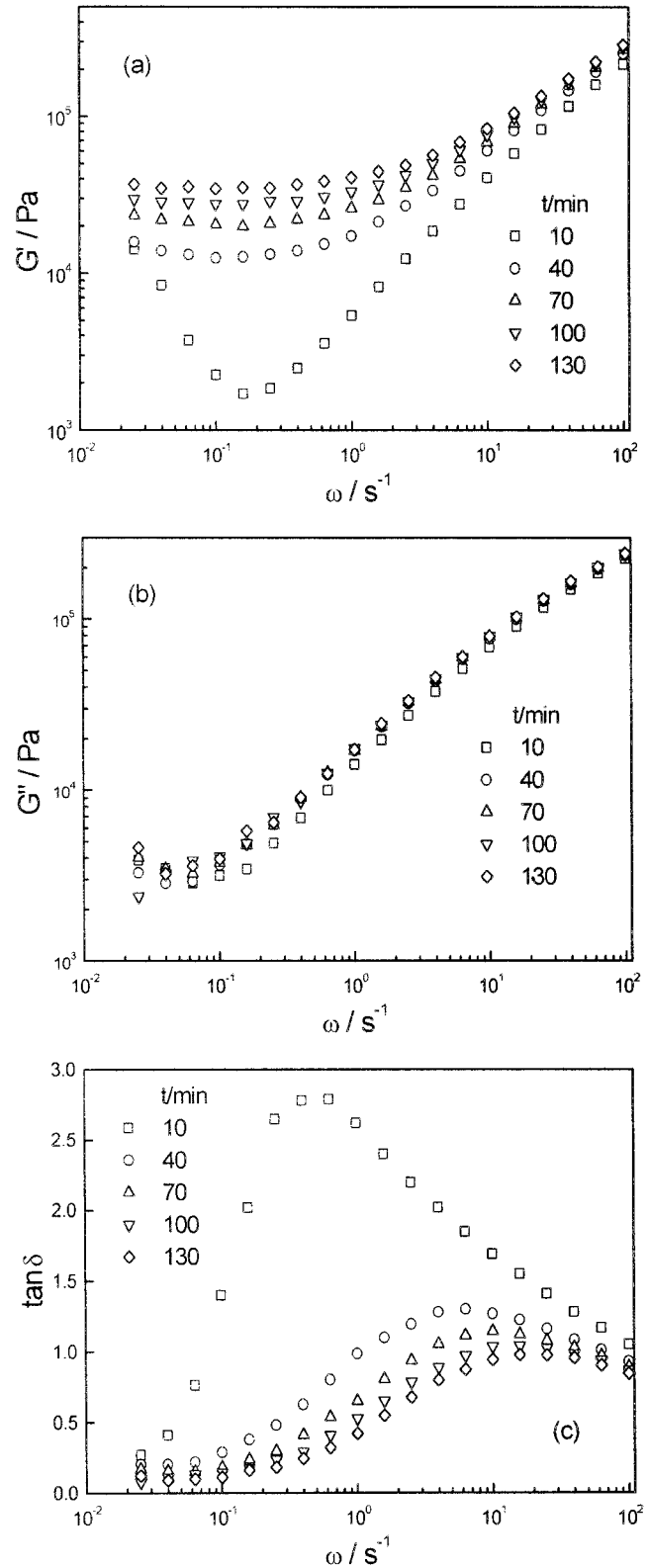


Figure 5 Frequency dependence of dynamic viscoelastical functions for CB/HDPE(14/100) held at a 200°C atmosphere for 10, 40, 70, 100, and 130 min, respectively: (a) G' ; (b) G'' ; (c) $\tan \delta$.

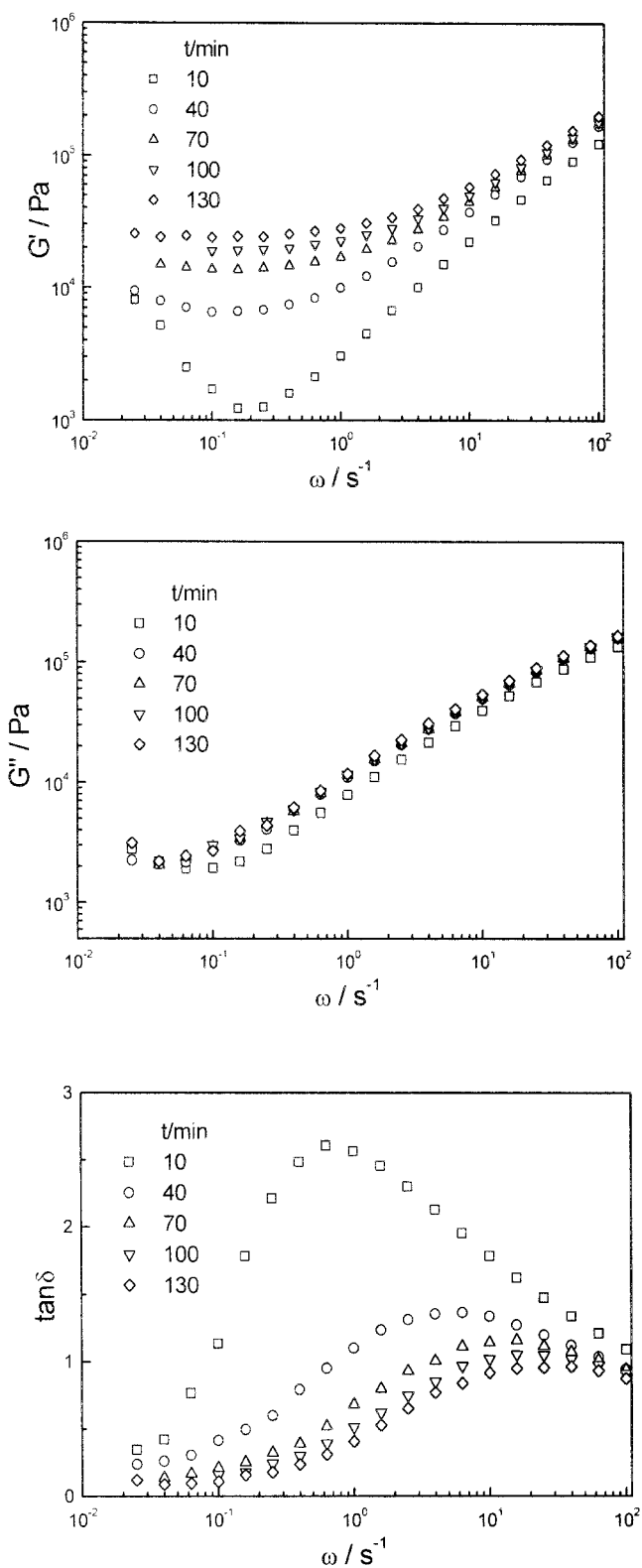


Figure 6 Frequency dependence of dynamic viscoelastical functions for HDPE held at 200°C atmosphere for 10, 40, 70, 100, and 130 min, respectively: (a) G' ; (b) G'' ; (c) $\tan \delta$.

Figures 9 and 10 show the dynamic rheological behavior of HDPE under 200°C in three different environments. The holding time before testing was ei-

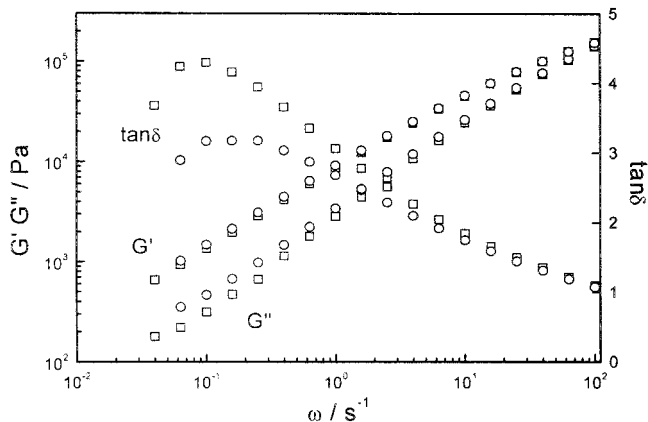


Figure 7 Frequency dependence of dynamic viscoelastical functions for HDPE held at 200°C under N_2 for (\square) 10 and (\circ) 40 min.

ther 10 and 40 min. Under the atmosphere of nitrogen gas, the increase of the modulus becomes less than that under air and the relationships between the dynamic rheological functions and the frequency do not show linearity. However, the relationships between the dynamic rheological properties of HDPE and the frequency obey the linearity law in the case of antioxidant addition.

On the assumption that HDPE cannot be oxidated under the protection of an antioxidant, the frequency dependence of $\tan \delta$ is related to the dynamic rheological behavior of HDPE. Correspondingly, the deviation of $\tan \delta$ may qualitatively reflect the oxidation of HDPE without containing an antioxidant. Figure 9(b) shows that after holding for 10 min before the test the frequencies at which HDPE began to be oxidated in the nitrogen gas and air atmospheres are 1 and 2.5 s^{-1} , respectively. When the dynamic frequency sweep moves from high to low frequency, the corresponding testing time is 83 and 63 s. Figure 10(b) shows that

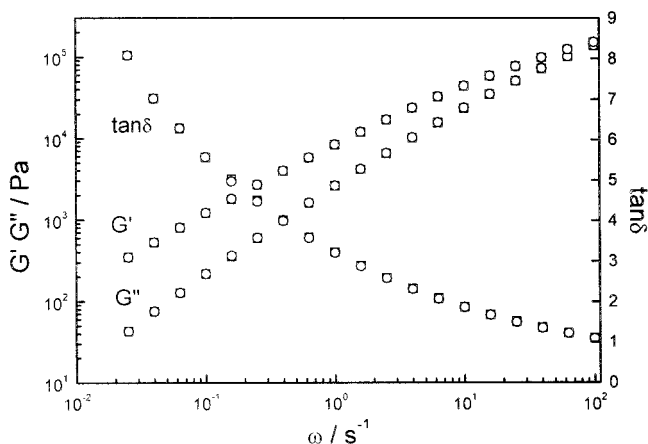


Figure 8 Frequency dependence of dynamic viscoelastical functions for B215/HDPE held at 200°C for (\square) 10 and (\circ) 40 min.

when the holding time is 40 min the frequency is 6.3 and 63 s⁻¹ (47 and 11 s). On the basis of these results, it is considered that the oxidation of HDPE is the cause of the appearance of a plateau of dynamic rheological functions. The trace quantity of oxygen gas can make HDPE oxidize under high temperature. We find that when an irreversible change takes place in the system structure the $\tan \delta$ against the ω plots can more sensitively reflect this change than can the modulus against the ω plots.

Relationship between dynamic viscoelastic properties and crosslinking

Figures 4 and 5 show that G' in the low-frequency region for CB/HDPE composites increases obviously with increase of the temperature or increase of the holding time before the test. In the plots of G' against ω , a second plateau appears under relatively higher temperature and an adequate holding time. Correspondingly, the degree of HDPE oxidation increases

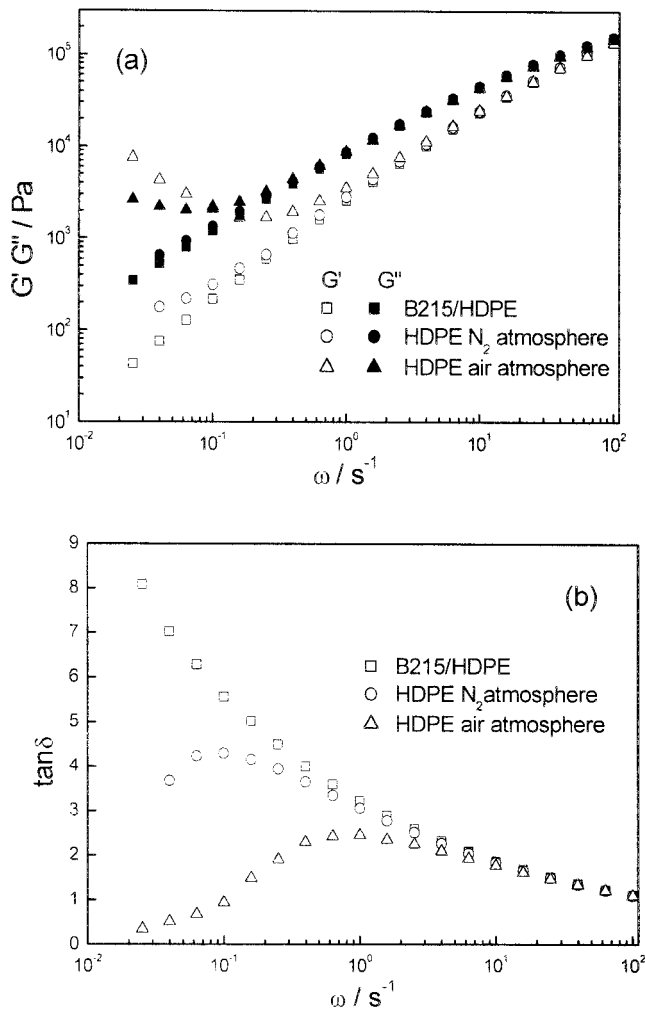


Figure 9 Frequency dependence of dynamic viscoelastic functions for HDPE held at 200°C for 10 min.

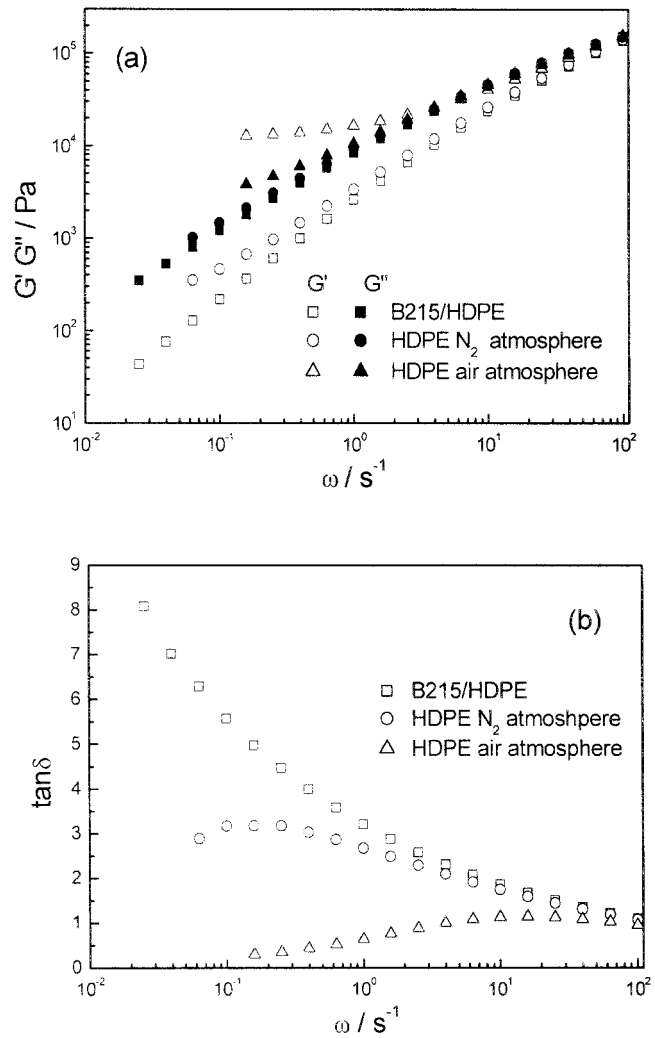


Figure 10 Frequency dependence of dynamic viscoelastic functions for HDPE held at 200°C for 40 min.

with increase of both the temperature and holding time before the test. The results of the test for HDPE under the protection of nitrogen gas and the antioxidant indicate that the decrease of $\tan \delta$ and the increase of the modulus is related to the oxidation of HDPE.

It also can be found in Figures 9(b) and 10(b) that the change of $\tan \delta$ is much more significant in the low-frequency region than in the high-frequency region. The relaxation time in the high-frequency region is so short that the relaxation changes of a crosslinking and noncrosslinking structure appear undiscernible. Hence, we cannot distinguish the difference of their viscoelastic behavior. In the low-frequency region, the crosslinking structure shows a characteristic viscoelastic response compared with HDPE. Through extracting the HDPE sample, we found that 14.7 mg of an undissolved yellow substance remained from 112.0 mg of the heat-treated HDPE, that is, the gel content is 13.13%, which gives a confirmation for the above-

mentioned view that crosslinking takes place within HDPE under the effect of oxygen and high temperature.

CONCLUSIONS

The dynamic viscoelastic properties for HDPE and its carbon black-filled composites were studied. According to plots of the dynamic viscoelastic functions, the storage modulus G' , loss modulus G'' , and loss tangent δ versus frequency, a characteristic plateau phenomenon was observed in the terminal region. Above 180°C, the width and height of the modulus plateau increased with increase of the time and temperature. This phenomenon can be related to the oxidation of HDPE. The existence of CB particles has no effect on the crosslinking of HDPE. Nitrogen gas and the antioxidant B215 can prevent HDPE from undergoing oxidation. It is believed that the $\tan \delta$ against ω plots can more sensitively reflect the irre-

versible change of HDPE than can the modulus against ω plots.

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