Available online at www.sciencedirect.com
SCIENCE DIRECT®

Polymer 47 (2006) 2442–2447

polymer

www.elsevier.com/locate/polymer

Correlation between percolation behavior of electricity and viscoelasticity for graphite filled high density polyethylene

Gang Wu [a,b], Jun Lin [c], Qiang Zheng [a,b,*], Mingqiu Zhang [d]

[a] *Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China*
[b] *Key Laboratory of Macromolecule Synthesis and Functionalization, Ministry of Education, Hangzhou 310027, People's Republic of China*
[c] *College of Medical Science, The First Affiliated Hospital, Zhejiang University, Hangzhou 310003, People's Republic of China*
[d] *Materials Science Institute, Zhongshan University, Guangzhou 510275, People's Republic of China*

Received 8 June 2005; received in revised form 8 February 2006; accepted 9 February 2006
Available online 28 February 2006

Abstract

A study on the correlation between electrical percolation and viscoelastic percolation for graphite (GP) filled high-density polyethylene (HDPE) conductive composites was carried out through an examination of the filler concentration φ dependence of the volume resistivity ρ and dynamic viscoelastic functions. The frequency ω dependence of G' at low ωs decreased obviously with increasing GP concentration. The relationship between φ and the proportion of dynamic storage modulus of the composites to that of the polymer matrix, namely the relative dynamic storage modulus (G'_c/G'_p), at low frequency region was studied. It is found that there are two critical threshold, φ_{r1} and φ_{r2}, in plots of $\varphi \sim G'_c/G'_p$, which is close to the electrical percolation threshold φ_1 and φ_2, respectively. Moreover, there exists φ-dependence of the dynamic loss tangent (tan δ) and a peak in plot of tan δ versus ω when φ approaches the loss angle threshold, $\varphi_{\delta 1}$ (8 vol%). When $\varphi > 20\%$, the second loss angle threshold, $\varphi_{\delta 2}$, the tan δ shows almost no dependence on the GP content. $\varphi_{\delta 1}$ and $\varphi_{\delta 2}$ is close to the electrical percolation threshold. A modified Kerner–Nielson equation was also obtained and used to analyze the formation of network structure in the matrix by substituting variable parameter K for constant A. The results indicate that the parameter K increases discontinuously with increasing φ, revealing this parameter is associated with GP concentration, and the critical threshold φ_{K1} and φ_{K2} is close to the electrical percolation threshold φ_1 and φ_2, respectively. Furthermore, the viscoelastic percolation for GP/HDPE composites can be verified on the basis of the modified equation.

Keywords: High density polyethylene; Dynamic rheological properties; Kerner–Nielsen equation

1. Introduction

Compared with metal materials, electrically conductive polymer matrix composites provided unique electrical and mechanical properties, such as light weight, low cost, ease of processing and corrosion resistance and have attracted a great deal of academic and commercial interests over the past two decades [1]. These conductive composites have been widely served as polymer conductors, semi-conductors, heat transferring media and stress sensitive organs in the fields of electric and electronics application [2–7].

It is well known that the properties of filled polymer composites are greatly influenced by the concentration and dispersion of the fillers. Electrical conductivity of these materials discontinuously increases at some concentration of fillers [8,9], which is attributed to the electrical percolation phenomena dealing with network formation of conductive particles in terms of the percolation theory [10]. When the filler concentration increases, the number of conductive paths increase and the average distance between the conducting particles becomes smaller, leading to a decrease in the ρ of the composite [11]. It is believed that ρ depends not only on the types of filler and polymer, but also on the filler dispersion and morphology of the matrix [12–15]. However, up to now, there is still no sufficient understanding of the conducting mechanism for particle filled conductive composites.

In the study of the structure/morphology of heterogeneous materials, dynamic rheology testing is believed to be a preferential method for the reason that the structure of materials exposed to the testing processes is not destroyed

---

[*] Corresponding author. Address: Department of Polymer Science and Engineering, Zhejiang University, Zheda Road 38#, Hangzhou 310027, People's Republic of China. Tel./fax: +86 571 87952522.
E-mail address: zhengqiang@zju.edu.cn (Q. Zheng).

0032-3861/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2006.02.017

under small-strain amplitude [16]. Furthermore, the special response of the viscoelastic behavior for the multi-phase/multi-component composites at low frequencies (terminal region) is thought to give valuable information of the morphology and structure of the composites [17–21]. Recently, it has been found that the characteristic viscoelastic response exists in the relationship between filler concentration and the appearance and development of heterogeneous structure. The phenomena that the critical transition of the viscoelastic properties takes place with increasing filler concentration are attributed to the 'viscoelastic percolation' phenomena [22,23]. The concentration where the critical transition of the viscoelastic functions takes place is defined as 'viscoelastic percolation threshold' for convenience.

It is believed that the high density of the network usually results in both a high dynamic storage modulus (G') and high electrical conductivity [23]. The correlation of electrical conductivity with dynamic rheological properties is of great interest since both phenomena involve in the formation and change of conductive particle network which could be formed under a stress field and conducted electrons under an electrical field. Up to now, the correlation between electrical percolation and rheological percolation has been detected in composites filled with CB, VGCF and carbon nanotube [23–25].

In our previous study [24], we correlated the viscoelastic percolation with electrical percolation behavior of CB/HDPE composites through comparing electrical percolation threshold with viscoelastic percolation threshold of the composites and evaluated the formation and development of network structure by means of modified Kerner–Nielson equation. Due to the difference in filler–filler, filler–matrix interaction as well as surface energy of fillers, the correlation mentioned above does not exist in CF/HDPE composites. In order to reveal the main reason resulting in the correlation between viscoelastic and electrical percolation, additional experiment should be done to provide more information. Here, we chose GP as the filled particle for the reason that GP has different structure compared with CB, which leads to weak filler–filler and filler–matrix interaction, and at the same time, GP has higher surface energy than CF. The correlation between viscoelastic percolation and electrical percolation of the GP/HDPE composites was studied and a modified Kerner–Nielson equation was applied in estimating the formation and development of network structure for the composites.

2. Experimental

2.1. Materials

The high density polyethylene (HDPE) used in this study is 5000S (melting index = 0.090 g min^{-1}, density = 0.954 g cm^{-3} and $T_m = 128$ °C) provided by Yangzi Petrochemical Corp., China. The filler was graphite (GP) (particle diameter = 24.11 μm, special surface area = 0.288 m^2 g^{-1} and density = 2.85 g ml^{-1}) employed by HuaDong Graphite Processing Factory, China. The antioxidant (B215) (relative molecular weight = 647 and $T_m = 180$–185 °C) was obtained from Ciba-Geigy Corp., Switzerland.

2.2. Sample preparation

The GP/HDPE composites of different GP volume loading from 2 to 28 vol% were prepared on a two-roll mill at 165 °C for 15 min. Disks about 2 mm in thickness and 25 mm in diameter were prepared by compression molding at 165 °C under 10 MPa for the following rheological measurements. Disks about 1.5 mm in thickness, 100 mm in both width and length were prepared by compression molding at 165 °C under 10 MPa and cut to appropriate pieces for the following resistance measurements.

2.3. Dynamic rheological measurements

Rheological measurements were conducted on ARES rheometer (Rheometric Scientific Inc., USA). The isothermal dynamic frequency sweep was conducted with disk of 2.0 mm in thickness and 25 mm in diameter under condition of the frequency range, strain amplitude, temperature being 10^2–0.01585 rad s^{-1}, 0.05–5%, 140 °C, respectively.

2.4. Resistance measurements

A two-probe resistance measurement was carried out for determining the resistivity at room temperature with a 4530 intelligent digital multimeter when the resistance of the samples was lower than 10^7 Ω. Although the four-contact method is more accurate compared with the two electrodes method, the conductivity of the material in our study is relatively poor and the contact resistance would not bring obvious error. A high-resistance meter (ZC36, 10^{-14} A and 10^{17} Ω) was used to determine the resistance higher than 10^7 Ω.

3. Results and discussion

3.1. Percolation behavior of GP/HDPE composites

Fig. 1 shows dependence of volume resistivity (ρ) on the GP concentration (φ). At low φ, the ρ changes slightly with increasing φ, and the relationship between ρ and φ displays two

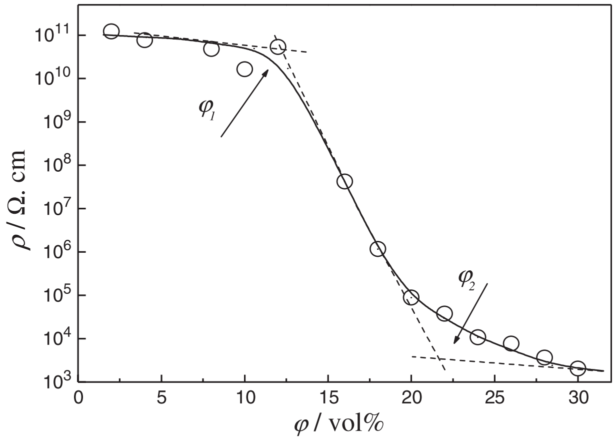

Fig. 1. The dependence of volume resistivity (ρ) on GP concentration (φ) for GP/HDPE composites.

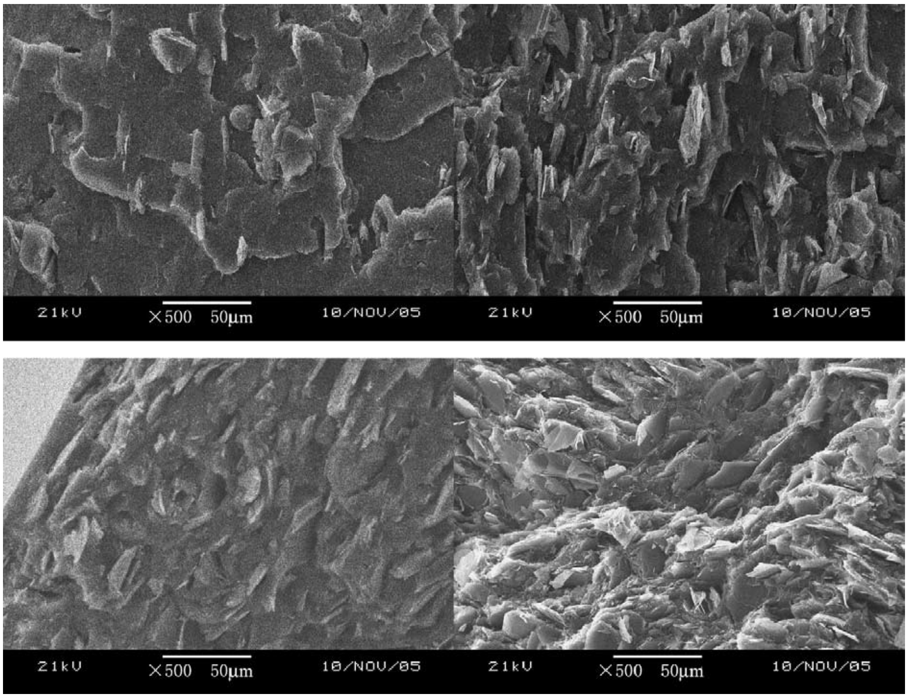

Fig. 2. TEM image for GP/HDPE composites with different GP concentration (a) 4 vol%, (b) 10 vol%, (c) 14 vol%, (d) 26 vol%.

obvious changes with increasing φ, i.e. when φ reaches φ_1 (12.29 vol%), the first change takes place, implying an insulator–semiconductor transition; and the second, is detected at φ_2 (21.79 vol%), representing a transition from semiconductor to conductor. Between φ_1 and φ_2, a sizeable reduction in ρ is observed. This stepwise change of ρ is thought to be a result of the formation of an interconnected structure and can be regarded as electrical percolation, which means that a very high percentage of electrons are permitted to flow through the sample due to the creation of an interconnecting conductivity pathway at concentrations between φ_1 and φ_2. From the TEM image shown in Fig. 2, the formation of conducting pathway can be detected illustratively. With the increasing of GP loading, more GP particles are observed on the fracture surface of the composites and the distance between GP particles is diminished leading to the formation of the conducting networks.

Fig. 3 shows the ω dependence of G' for GP/HDPE composites as a function of φ. To avoid the formation of additional networks at high temperature, the rheology measurements were carried out at 140 °C, at which the self-agglomeration of the particles is not so prominent that there exists no dominant effect from additional networks. For the reason that there are little functional groups on the surface of GP compared with CB and the interaction between the polymer matrix and GP is much weaker than that between CB and the matrix, the three-dimensional network is hard to be detected and the characteristic modulus plateau is not so obvious as that of the CB/HDPE composites [24]. However, it is still obvious that G' increases with the increase of φ, and the plot of G' versus ω deviates from linearity at the low ωs. The higher the filler concentration, the more obvious the reduction in the ω dependence of G' at low ωs is. From the phenomena mentioned above, the formation of some order structure within the composites can be deduced.

It is found that different testing frequency shows different sensitivity to the three-dimensional network in the composites. Fig. 4 shows plots of the G' versus φ at different ωs. Within the high ω region, especially $\omega \geq 1$ rad/s, the network structure in the matrix is hardly detected due to short time of relaxation. Hence, the linear relationship between G' and φ can be observed. Within the low ω region, especially <1 rad/s, the relationship between G' and φ appears non-linear and the difference in viscoelastic properties induced by variation of φ could be distinguished.

The appearance of the obvious reduction in the ω dependence of G' at low ωs indicates that the viscoelastic properties of the composites are dominated by the fillers.

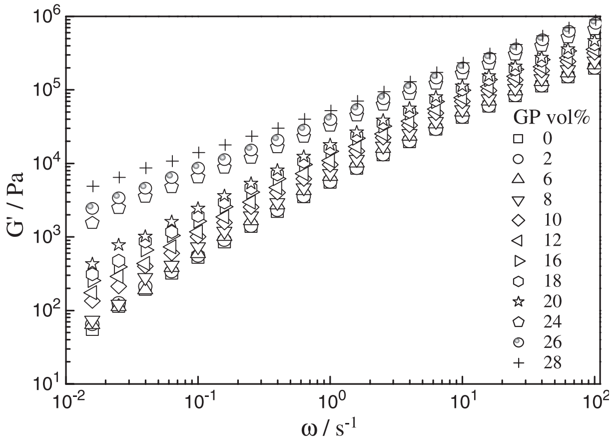

Fig. 3. Frequency (ω) dependence of dynamic storage modulus (G') for GP/HDPE composites with different GP concentration.

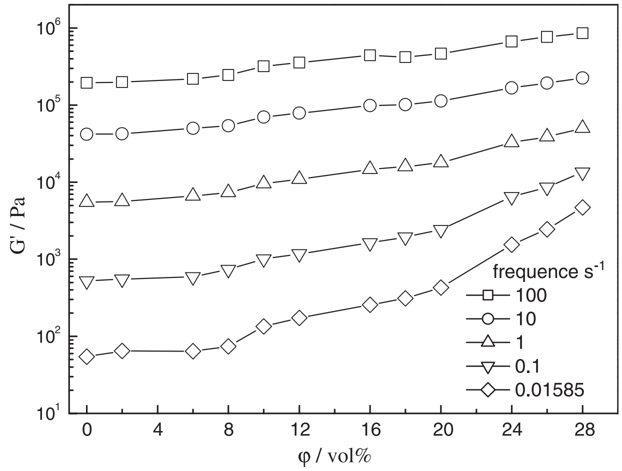

Fig. 4. Storage modulus G' versus GP concentration at different frequencies.

The ratios of G'_c/G'_p at 0.01585 rad/s are plotted in Fig. 5 as a function of φ. G'_c is the dynamic storage modulus of the composites and G'_p is the dynamic storage modulus of the matrix. Hence, the variance of G' along with the GP addition can be detected clearly. At low φ, G'_c/G'_p changes slightly with the increase of φ, and with the further increase of φ the relationship between G'_c/G'_p and φ displays two obvious changes, which is called as 'viscoelastic percolation'. When φ is below 10 vol%, G'_c/G'_p increases tardily and when φ reaches 10 vol%, a sudden change of the ratio takes place and G'_c/G'_p increases rapidly compared with that in low φ. Furthermore, when φ reaches 24 vol%, the second sudden change appears and G'_c/G'_p increases with a much higher level. Here, we define the two critical concentration at which two sudden changes take place as the relative modulus percolation threshold, φ_{r1} and φ_{r2}. Compared the threshold data obtained from dynamic rheological measurements with that from electrical testing as shown in Fig. 1, we found that φ_{r1} is very close to φ_1 relevant to the insulator–semiconductor change and φ_{r2} is very close to φ_2 representing the change of semiconductor to conductor.

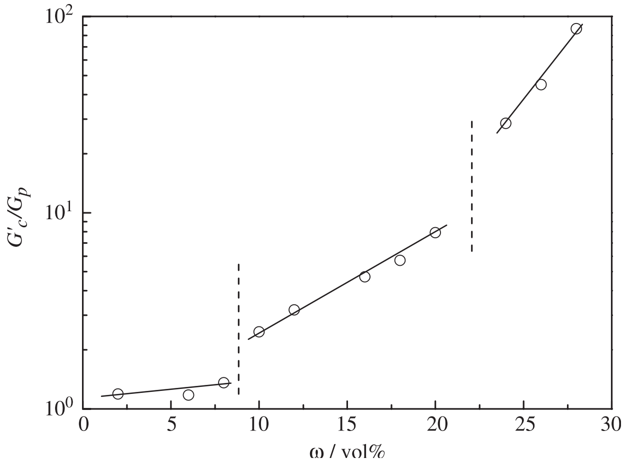

Fig. 5. Concentration dependence of the relative dynamic storage modulus (G'_c/G'_p) at a frequency of 0.01585 rad/s for GP/HDPE composites.

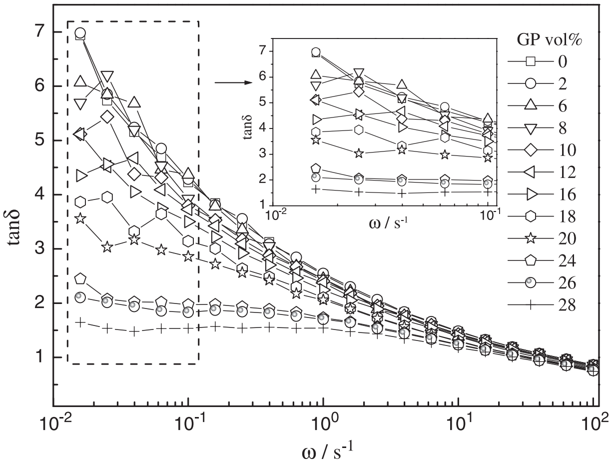

Fig. 6. Frequency dependence of loss tangent for different GP concentration.

Fig. 6 gives φ dependences of the loss tangent (tan δ) for GP/HDPE with different φ. The higher the φ, the smaller is the value of tan δ in low ω region. It is obvious that when the φ is below 8 vol%, the value of tan δ increases with the decreasing ω. With the increasing φ, the plot of tan δ versus ω changes from linear to arc form and the reduction in the ω dependence of G' at low frequency region can be found. When φ is beyond 8 vol%, which is defined as a tan δ percolation threshold $\varphi_{\delta 1}$, the plot of tan δ versus ω begins to change from linear to arc form and a peak of tan δ appears. The magnitude of the peak decreases with an increase in the φ, whereas the ω corresponding to the peak increases with the φ. The existence of tan δ peak is considered to be a critical relaxation behavior involving in high order structure within polymer matrix [26,27]; and, therefore, it is related to the existence of interparticle networks. When the φ reaches 24 vol%, defined as a tan δ percolation threshold, $\varphi_{\delta 2}$, there is almost no dependence of tan δ on the ω, indicating formation of the perfect network structure. Compared the threshold data obtained here with that from electrical testing as shown in Fig. 1, we found that $\varphi_{\delta 1}$ is very close to φ_1 dealing with the insulator–semiconductor change and $\varphi_{\delta 2}$ is very close to φ_2 representing the change of semiconductor to conductor.

3.2. Kerner–Nielsen equation modification and agglomeration structure estimation for GP/HDPE composites

It is understood that the majority of the theories describing the φ-dependence of rheological properties of diluted filled systems are based on the hydrodynamic approach proposed by Einstein [28]. One quite useful equation presented by Kerner and generalized by Nielsen [29] is given as

$$\frac{G'_c}{G'_p} = \frac{(1 + AB\varphi)}{(1 - B\varphi\psi)} \tag{1}$$

$$B = \frac{(G'_f/G'_p - 1)}{(G'_f/G'_p + 1)} \tag{2}$$

$$\psi = 1 + (1/\varphi_m^2 - 1/\varphi_m)\varphi \tag{3}$$

in which, G'_c, G'_p, G'_f are the dynamic storage modulus of the composite, the polymer matrix, and the filler, respectively. φ is the volume fraction of the filler, φ_m is the maximum packing fraction of the filler, $\varphi_m = 0.637$ for random compact packing of rigid circle particles. For rigid particles, $B \approx 1$ for the reason that G'_f is much higher than G'_p. $\psi\varphi$ is the relative volume fraction. When φ approaches φ_m, $\psi\varphi \approx 1$. The parameter A was reported to be sensitive to the aggregate number and the geometry of the filler.

In general, Eq. (1) is only suitable to describe the relative modulus when φ is lower than the critical value. This is because above the critical concentration, the particles agglomerate to form networks and the rheological properties of suspension change from liquid-like to solid-like behavior. As for Eq. (1), the aggregate number and the geometry of the filler remains invariable and coefficient A can be considered to be a constant when φ is low. However, comparatively, when φ is high, variation of particle agglomeration results in variation of A. In our previous study [24], we modified Kerner equation by replacing variable K for constant A and qualitatively described the agglomeration structure of the CB filled HDPE composites. The modified representation of Kerner equation is given as

$$\frac{G'_c}{G'_p} = \frac{(1 + KB\varphi)}{(1 - B\varphi\psi)} \tag{4}$$

The φ-dependence of K is given in Fig. 7, in which K was calculated from Eq. (4) assuming $B = 1$ and $\varphi_m = 0.637$. It can be seen that when φ is below 8 vol%, K almost remains constant. However, K increases abruptly when $\varphi = 10$ vol%, which is close to the lower threshold of electrical percolation curve. When $\varphi = 24$ vol%, close to φ_2, the other abrupt increase of K takes place. Furthermore, the value of K is relevant to the particle aggregate number, as mentioned above. Hence, it is suggested that correlation between electrical percolation and rheological percolation can be established by Eq. (4) and the increase of K is related to the agglomeration of the fillers.

Combined with our previous study [24], it is found the correlation between electrical and viscoelastic percolation could be established in CB/HDPE, CF/HDPE composites, while this correlation does not exist in CF/HDPE composites. Considering the difference in the surface structure and surface area among the three fillers, it is suggested that the correlation between the viscoelastic and electrical percolation can be established in the filled crystalline polymers in condition that the fillers have enough large surface area and the filler-matrix networks present in both solid and melting state.

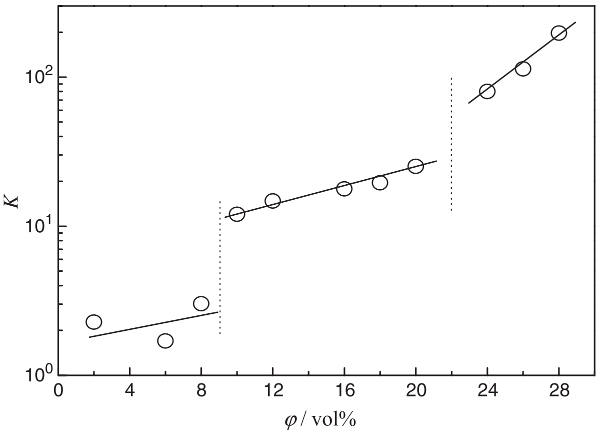

Fig. 7. Concentration dependence of the parameter K for GP/HDPE composites with different GP concentration.

Moreover, various filler structure brings difference in the established correlation. As mentioned above, there are two obvious critical thresholds in the both plots of $G'_c/G'_p \sim \varphi$ and $K \sim \varphi$ for GP/HDPE composites. However, for CB/HDPE composites there is only one critical threshold in the above curves [24], namely, for GP/HDPE composites, more effective correlation can be established between the electrical percolation and viscoelastic percolation as compared with CB/HDPE composites.

Considering the surface of CB which contains a lot of multiaromatic rings and some aliphatic carbon atoms together with functional groups such as carboxyl, carbonyl, and epoxy group, it is believed that the above difference is caused by the difference in surface structure of CB and GP and the resulting different interaction between the particles and the matrix. In the Kerner–Nielson equation, the parameters do not involve in the interaction between the fillers and the matrix, but relate to the packing mode of the fillers. For CB/HDPE composites, the fact that affects the viscoelasitc properties is not only the packing mode of filler but also the interaction between filler and HDPE matrix. The filler–matrix interaction plays a leading role to some extent, especially in the case of high CB loading. When the CB loading is high enough, the relationship between the filler concentration and viscoelastic properties, such as G' and tan δ, is not induced by the variation of agglomeration structure only. It is noted that the high filler–matrix interaction also contributes to the increase of the modulus. That is why we could only find one clear critical threshold in the concentration dependence of the viscoelastic properties. But for GP/HDPE composites, owing to the different surface structure of GP compared with CB, the filler–matrix interaction is much weaker than that of CB/HDPE composites. So the relationship between φ and viscoelastic properties is almost due to the agglomeration structure of the composites. Therefore, we find two obvious critical threshold in the plots of $\varphi \sim G'_c/G'_p$ and $\varphi \sim \tan\delta$, and the relationship between electrical percolation and viscoelastic percolation for GP/HDPE composites is more obvious than that of CB/HDPE composites.

4. Conclusions

Correlation between electrical percolation and viscoelastic percolation for GP filled HDPE conductive composites was investigated. The viscoelastic percolation thresholds (φ_{r1}, $\varphi_{\delta 1}$), involving in beginning of network formation, are found to be close to the lower electrical percolation (φ_1), representing a semiconductor–conductor change. Another viscoelastic percolation thresholds (φ_{r2}, $\varphi_{\delta 2}$) are found to be close to the upper electrical percolation threshold (φ_2), representing an insulator–

semiconductor change corresponding to the perfect network structure formation. It is found that the viscoelastic percolation threshold detected from dynamic rheological measurements could be correlated to the electrical percolation threshold. Substituting K for A, a modified Kerner–Nielson equation was represented and used to analyze the formation of network structure. It is suggested that the parameter K is associated with GP concentration. The increase of parameter K reflects the formation and development of network structure within the matrix. Combined with our previous study on CB/HDPE, CF/HDPE composites, it is suggested that the correlation between the viscoelastic and electrical percolation exists in the filled crystalline polymers in condition that the fillers have enough large surface area and the filler–matrix networks present in both solid and melting state. The difference in the correlation between the two percolation behaviors for CB, GP filled HDPE is owing to the different filler–filler, filler–matrix interaction caused by various surface structure of the two different filler particles.

Acknowledgements

This work was supported by the National Nature Science Funds of China (grant 50373037), National Science Funds for Distinguished Young Scholars (grant 50125312), and Key Program of National Nature Science Foundation of China (grant 50133020).

References

[1] Taya M, Kim WJ, Ono K. Mech Mater 1998;28:53–9.
[2] Hsu WY, Holtle WG, Barkley JR. J Mater Sci Lett 1988;7:459–62.
[3] Petrovic ZS, Martinovic B, Divjakovic V, Jaroslava BS. J Appl Polym Sci 1993;49:1659–69.
[4] Li F, Qi L, Yang J, Xu M, et al. J Appl Polym Sci 2000;75:68–77.
[5] Norman RM. Conductive rubbers and plastics. New York: Elseriver; 1970.
[6] Thongruang W, Spontak RJ, Maurice Balik C. Polymer 2002;43: 2279–86.
[7] Thongruang W, Spontak RJ, Maurice Balik C. Polymer 2002;43: 3717–25.
[8] Medalia AI. Rubber Chem Technol 1986;59:432.
[9] Malliaris A, Turner DJ. J Appl Phys 1971;42:614.
[10] Miyasaka K, Watanabe K, Jojima E, Aida H, Sumita M, Ishikawa K. J Mater Sci 1982;17:1610–6.
[11] Jarmila V, Petr S, Vojtech K, Otakar Q. Synth Met 2000;113:86–7.
[12] Sumita M, Asai S, Miyadera N, Jojima E, Miyasaka K. Colloid Polym Sci 1986;264:212.
[13] Shimizu Y, Tanemura M, Sumita M, Miyadera N, Miyasaka K. Soc Fiber Sci Technol 1986;42:543.
[14] Karasek L, Sumita M. J Mater Sci 1996;31:281.
[15] Zhang C, Yi XS, Yui H, Asai S, Sumita M. Mater Lett 1998;36:186–90.
[16] Utracki LA. Polymer alloys and blends. New York: Carl Hanser; 1989 p. 131–74.
[17] Takahashi M, Li L, Masuda T. J Rheol 1989;33(5):709.
[18] Graebling D, Muller R. Colloids Surf 1991;55:89.
[19] Bousmina M, Muller R. J Rheol 1993;37:663.
[20] Graebling D, Muller R, Palierne JF. Macromolecules 1993;26:320.
[21] Graebling D, Benkira A, Gallot Y, Muller R. Eur Polym J 1994;30:301.
[22] Zheng Q, Song YH, Wu G, Song XB. J Polym Sci, Part B: Polym Phys 2003;41:983–92.
[23] Wu G, Asai S, Hattori T, Higuchi R, Washiyama J. Colloid Polym Sci 2000;278:220–8.
[24] Gang W, Zheng Q. J Polym Sci, Part B: Polym Phys 2004;42:1199–205.
[25] Pötschke P, Fornes TD, Paul DR. Polymer 2002;43:3247–55.
[26] Romani F, Corrieri R, Braga V. Polymer 2002;43:1115–31.
[27] Gang W, Song YH, Zheng Q, Du M, Zhang PJ. J Appl Polym Sci 2003;88: 2160–7.
[28] Einstein A. Ann Physik 1914;34:591–605.
[29] Nielson LE. Polymer rheology. New York: Dekker; 1977.