Dynamic Viscoelasticity of Low-Density Polyethylene/In-Situ-Grafted Carbon Black Composite

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ABSTRACT: The study on the dynamic viscoelastic properties of grafted carbon black (g-CB) filled low-density polyethylene (LDPE) was carried out. Because of formation of CB networking, the characteristic modulus plateau and loss tangent arc appears. Addition of grafting monomer like butyl acrylate (BA) and acroleic acid (AA) enhances the interaction between particles and matrix due to accelerated formation of micronetworking in the composites induced by forming branch chains of AA and BA with multiunit. The decrease of the temperature corresponding to α_c mechanical relaxation together with AA (BA) addition given by the position of loss tangent (tan δ) peak for LDPE is owed to the formation of long-chain polymer grafted between CB and the matrix, which facilitates the slip of the lamella of LDPE. The influence of maleic anhydride (MA) on enhancing interaction between LDPE and CB is not so pronounced, as compared with AA and BA because of no formation of long chain between CB particle and polymer matrix. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 4127–4132, 2006

Key words: polyethylene; conducting polymers; viscoelastic properties; networks

INTRODUCTION

It is well-known that the incorporation of fillers such as carbon black (CB), graphite (GP), and carbon fiber (CF) into polymers gives them unique conductive properties like positive temperature coefficient (PTC) and piezoresistance behavior. Possessing these properties, polymeric conductive composites have been widely served as polymer conductors, semiconductors, heat transferring media, and stress-sensitive organs in the fields of electric and electronics industry.[1–4] CB aggregates in the polymer matrices tend to agglomerate, and especially at high concentrations, to form continuous filler network that results in the electrical properties of the filled polymers.[5] It is understood that resistivity of CB-filled polymer composites depends on CB surface area and structure. Moreover, structure of the CB plays a dominant role in controlling microstructure of the composites.[6–8] The effect of CB is governed by the degree of its dispersion, its particle size, aggregate shape, structure, and porosity.

Exactly, the interaction is too strong for particles to move and, on the contrary, is too weak to stabilize the microstructure of the composites. Hence, a proper adhesion interaction between the polymer matrix and particles is expected.[9,10]

Viscoelastic behavior of CB-filled polymer has been one of the focuses in the field of particles-filled polymeric materials.[11–15] A phenomenon, so-called "second plateau," that the dynamic viscoelastic functions, e.g., storage modulus (G') and loss modulus (G''), are independent of frequency (ω) at very low frequencies (terminal region), has been thought to be an important information concerning viscoelastic behavior of multicomponent polymer systems. Moreover, the appearance of this phenomena is related to the formation of higher-order structure of the particles, such as agglomerated structure, skeleton, or network structure.[16] The similar second plateau, which has been found in the study of dynamic viscoelastic properties of rubber particles filled polymer system, suggested that phenomenon resulted from high-order structure formed by rubber particles,[17,18] while for polystyrene (PS) melt-filled with grafted glass beads system, from high-order structure formed by grafted glass beads in PS melt, as compared with ungrafted-bead-filled system.[19] Three types of filler-polymer-filler interactions resulting in agglomeration have been proposed,[20] such as direct bridge, primary entanglement, and secondary entanglement. It is assumed that the presence

of direct bridging chain, a single chain adsorbed on two separate aggregate, is responsible for the appearance of the plateau. In our previous study,[21] we obtained *in situ* melt-grafted-CB filled LDPE composites and studied the electrical properties of the composites. In the present article, we pay our attention to the effect of different species of grafting monomers on the viscoelastic behavior of the composites at both melt and solid state.

EXPERIMENTAL

LDPE (density = 0.910 g cm^{-3}, melting flow index (MFI) = 3.5 g/10 min, melting temperature (T_m) = 110°C) and electrically conductive CB (particle diameter = 22 nm, BET special surface area = 150 m^2 g^{-1}, dibutyl phthalate absorption = 1.25 cm^3 g^{-1}) were used as the matrix polymer and the filler in the current work, respectively. Three types of chemically pure monomer used for grafting were acrylic acid (AA), butyl acrylate (BA), and maleic anhydride (MA). The initiator was chemically pure dicumyl peroxide (DCP).

CB was preblended with AA (or BA, MA) and DCP at room temperature for 24 h, using ethanol as solution under stirring to generating chemical bonds between CB and the matrix. The polymer and CB (treated or untreated) in certain proportions were melt-mixed in a laboratory-size Brabender XB20–80 plastic order at 160°C, 20 rpm for 15 min. Disks of about 2 and 1.5 mm thickness were prepared by compression molding at 165°C under 10 MPa.

Viscoelasticity measurements were conducted on an Advanced Rheology Expansion System (ARES, Rheometric Sci. Inc., USA). The isothermal dynamic frequency sweep was performed with disk (thickness = 2.0 mm, diameter = 25 mm) under the condition of the frequency range, strain amplitude, and temperature being 100–0.015 rad s^{-1}, 0.05–5%, and 140°C, respectively. All the experiments were carried out in the linear viscoelastic range, using parallel plate mode, to avoid destroying the structure of samples during testing. The dynamic mechanical responses of specimens with rectangular geometry (thickness = 1.5 mm, length = 14 mm, width = 8 mm) were detected under the condition of the frequency, strain amplitude, temperature range, and heating rate being 10 rad s^{-1}, 0.5%, 40–120°C, 4°C min^{-1}, respectively.

To evaluate the variation in the chemical structure of CB before and after melt-grafting, unbonded matrix was extracted above the melting point of *o*-xylene by Soxhlet apparatus for 72 h from the composites with the addition of 18 wt % CB and grafting monomer of different content.[22] The attenuated total reflectance (ATR) mode of a Nicolet 210 Fourier transform infrared (FTIR) spectrometer was used to collect the infrared spectra of the CB particles, which were isolated
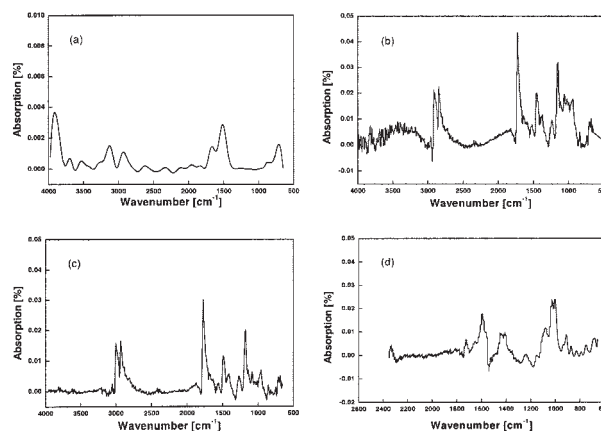
Figure 1 FTIR–ATR spectra for (a) untreated CB and CB grafted with (b) AA, (c) BA, (d) MA.

from the composites and dried in a vacuum oven at 80°C for 48 h.

Thermogravimetric analyses (TGAs) of the CB as received and the CB isolated from the composites for the calculation of grafting percentage were performed with a PerkinElmer TGA-II apparatus under N$_2$ atmosphere at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Fourier-transform infrared spectra analysis

It is well-known that the chemical structure of CB surface is complicated and can be qualitatively characterized through IR spectra. FTIR–ATR spectra were used in this study to investigate the surface character of the grafted and ungrafted CB particles. Generally, the surface of CB contains a lot of multiaromatic rings and some aliphatic carbon atoms together with functional groups such as carboxyl, carbonyl, and epoxy group. FTIR–ATR spectra for untreated CB used here are displayed in Figure 1(a). It is seen that aromatic C—C vibration band appears at 1500 cm^{-1}, while C=O and C—O band are absent. Figure 1(b) shows the FTIR–ATR spectrum of CB grafted with AA. By contrast with Figure 1(a), a carbonyl band at 1730 cm^{-1} as well as a broad hydroxylic carboxyl bond with maximum at 3500 cm^{-1} can be observed. The FTIR–ATR spectrum for CB grafted with BA, as shown in Figure 1(c), is similar to Figure 1(b). FTIR–ATR spectrum of the CB particles grafted with MA is shown in Figure 1(d), indicating that the lower intensity of carbonyl band than those in Figures 1(a) and 1(b). Therefore, it provides one of the proofs that AA, BA, and MA were all grafted onto the surface of CB.

Grafting percentage calculation

CB in the composites with the addition of grafting monomer during melt-blending was isolated by the

TABLE I
Grafting Percentage on CR Obtained by the Melt-
Grafting of the Monomers in the Presence
of CR and LDPE (18 wt % CR)

Sample	Grafting monomer content (wt %)	G1 (%)	G2 (%)
CB-g-AA	539	7.2	3.8
	8.67	13.4	7.4
CB-g-BA	5.39	5.9	3.1
	8.67	9.8	6.7
CB-g-MA	5.39	3.7	1.6
	8.67	5.4	2.3

extraction of the unbonded matrix from the composites in a Soxhlet apparatus with o-xylene for 72 h. As a certain amount of fine CB particles leaked out of the filter paper during the extraction, the percentage of grafting was roughly estimated in two ways. The first was directly based on the thermal degradation curve of the isolated CB, and the second one depended on the estimated amount of the grafting polymers and the CB dosage:

$$\varphi_{g1} = w_0/w_1 - 1 \qquad (1)$$

$$\varphi_{g2} = \varphi_{g1}\, w_2/w(1 + \varphi_{g1}) \qquad (2)$$

where φ_{g1} and φ_{g2} denote the grafting percentage determined by the two methods. w_0 and w_1 stand for the residual weight percentages of CB as received and of CB isolated at 500°C in N_2, respectively. w_2 is the weight of CB isolated from the composites, and w is the weight of CB added to the compounding system.

Table I lists the percentages of the copolymer grafted on the CB surface through melt-grafting. Although the values are not precise enough, both φ_{g1} and φ_{g2} follow the same tendency. The higher is the grafting monomer dosage, the higher the grafting percentage is, demonstrating the appropriateness of the calculation of φ_{g1} and φ_{g2}. Considering the results of FTIR–ATR, as well as X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (FTIR–TGA) measurements reported in our previous paper,[21] it is believable that the grafting monomer is grafted onto the CB surface. Moreover, it is understood from Table I that even if the dosage of grafting monomer is same, the grafting percentages vary with the types of the monomers, and AA gives the highest grafting percentage. That is to say, AA is easiest to be grafted onto CB among the three kinds of grafting monomer we used here, and MA is the most difficult one.

Dynamic viscoelastic properties

It is well accepted that the dynamic viscoelastic properties of particles-filled polymer composites are very

sensitive to the occurrence of amplitude in the oscillatory shear tests. The reason for this is believed to be the structure formed by the filler particles. Therefore, all the experiments in this study were carried out at low shear strain to ensure no destruction of sample's structure. Figure 2 shows the dynamic viscoelastic behavior for LDPE containing various CB concentrations. It is obvious that G' increase with increasing CB concentration, and the relationship between frequency ω and G' deviated from linearity at the low ωs. On the other hand, with increasing CB concentration' the obvious reduction in the ω dependence of G' at low ωs can be found. The characteristic modulus plateau appears when the CB concentration is beyond 10 wt %. At the same time, tan δ decreases rapidly with the increase of CB concentration. Similarly, Yurekli et al.[5] found the plateau modulus exhibits a somewhat discontinuous change when CB content is at about 9 vol % for the CB-filled elastomer system and assumed that the CB fillers form a continuous percolated network structure beyond this CB content. Furthermore, at the low-filler content, the reinforcement seems a result of
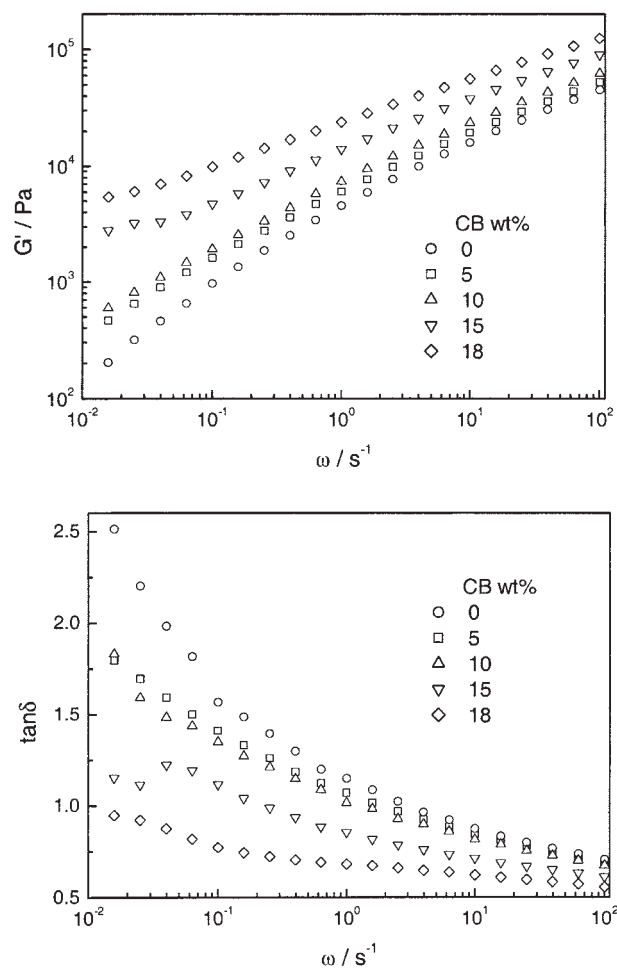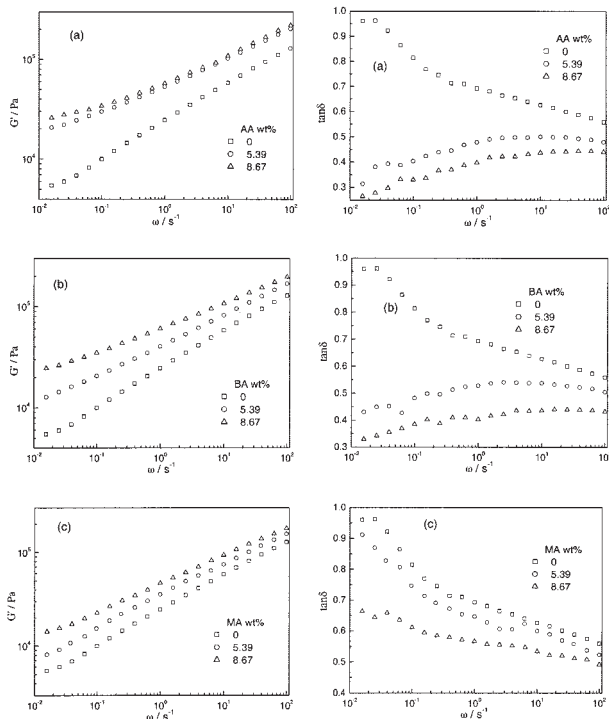
Figure 2 Frequency ω dependence of dynamic storage modulus G' and loss tangent tan δ for CB/LDPE composites.

Figure 3 Frequency ω dependence of dynamic storage modulus G' and loss tangent tan δ for (a) AA-g-CB, (b) BA-g-CB, (c) MA-g-CB filled LDPE composites (18 wt % CB).

individual, well-dispersed inorganic particle; whereas beyond the critical content, the reinforcement would mainly results from the formation of the filler network.

Figure 3 shows the dynamic viscoelastic properties for g-CB/LDPE (18 wt % CB) composites as a function of grafting monomer concentration. It can be found in Figure 3(a), 3(b) that G' increases with increase of the monomer concentration and the relationship between ω and G' deviates more obviously from linearity, that is to say, the frequency independence of G' becomes more obvious with the addition of AA and BA. By plotting tan δ against ω, we found that this plot changes from linearity to arc with a rise in monomer concentration when CB was pretreated with AA and BA. Within the whole ωs, the higher the AA (BA) concentration, the lower the value of tan δ is. In our previous investigation, the reduction of ω dependence of G' and the change in the value and pattern of tan δ is related to the formation and development of micronetworking structure within the matrix.[23] Hence, the increase of G' should be owed to enhancement of filler–filler, filler–polymer interaction induced by AA, BA grafting, and the multiunit formed by AA or BA grafting CB contact with the matrix and building micronetworking.

Investigating the dynamic viscoelastic properties of g-CB/LDPE composites as a function of grafting monomer species under the same monomer concentration of 5.39 wt % (Fig. 4), the phenomena mentioned earlier are more obvious, especially the noticeable difference of the viscoelastic properties of MA-g-CB/LDPE composites compared with AA(BA)-g-CB/LDPE systems. When MA is used as grafting monomer, no obvious reduction in the frequency dependence of G' at low ωs can be found as compared with AA and BA, despite that the G' increases within the whole ω tested. An obvious difference can be found in the tan δ–ω plots that the value of tan δ merely decreases and no characteristic arc appears. Moreover, it is observed that G' of the composites at melt state over the whole ωs is generally found to be in the rank as AA-g-CB/LDPE > BA-g-CB/LDPE > MA-g-CB/LDPE > CB/LDPE, which is consistent with the order of grafting percentages; and for tan δ: AA-g-CB/LDPE < BA-g-CB/LDPE < MA-g-CB/LDPE < CB/LDPE. The low grafting percentage of MA may be one of the factors leading to these differences.

Temperature dispersion curves of dynamic viscoelastic functions for grafted CB filled LDPE

Figure 5 gives the temperature dispersion curves of G' and tan δ for three kinds of g-CB filled LDPE compos-
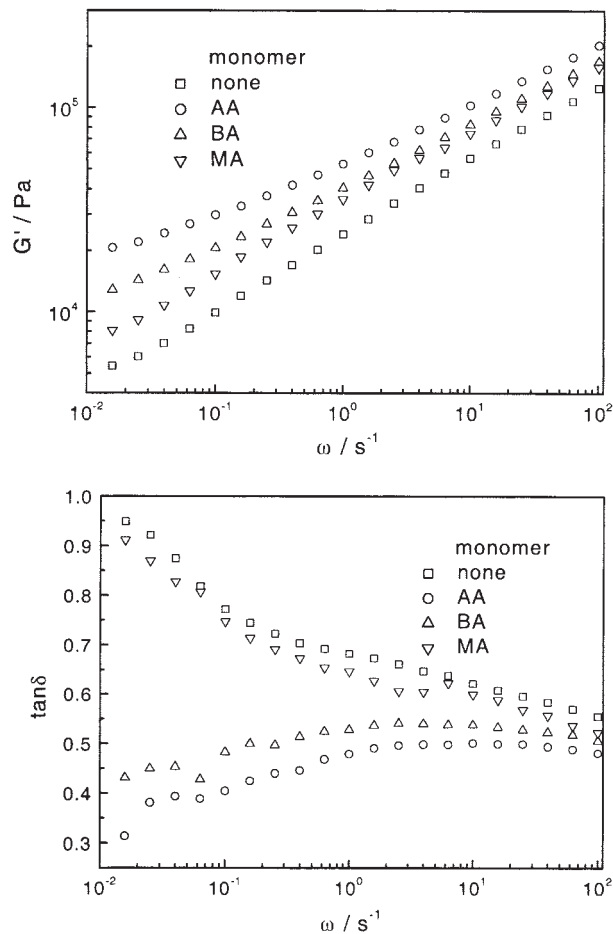
Figure 4 Frequency ω dependence of dynamic viscoelastic functions for g-CB/LDPE(18 wt % CB) as function of grafting monomer type: (a) G' and (b) tan δ.
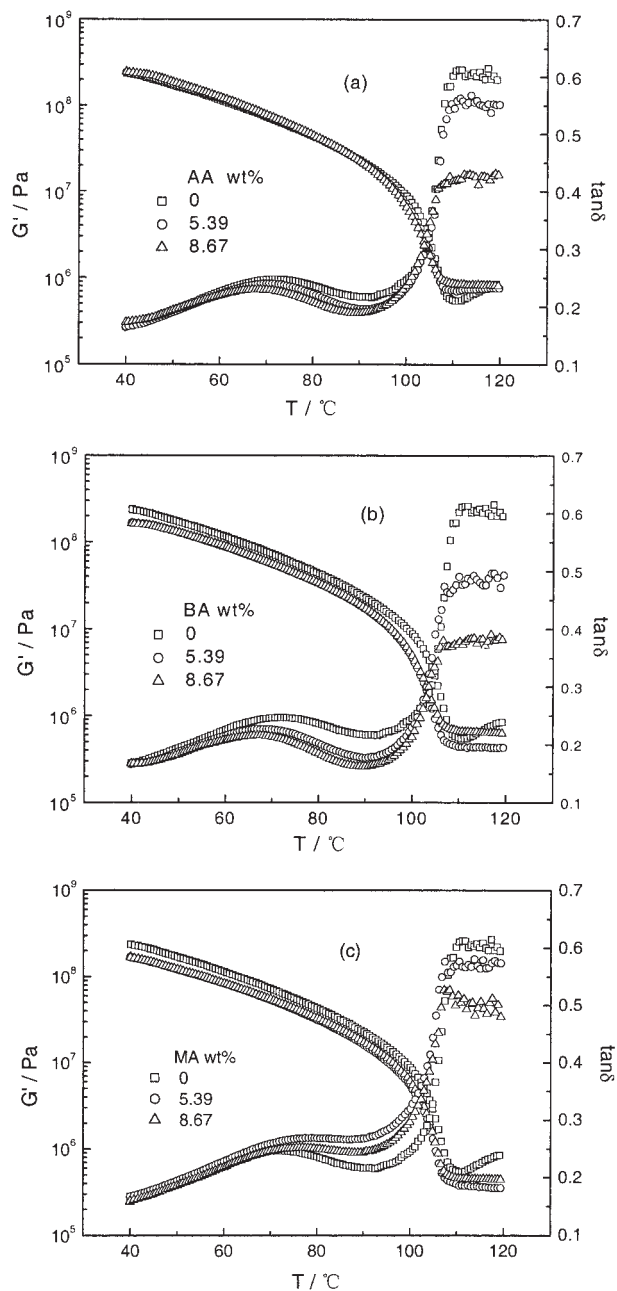
Figure 5 Temperature dispersion curves of dynamic storage modulus G' and loss tangent tan δ for (a) AA-g-CB, (b) BA-g-CB, (c) MA-g-CB filled LDPE composites (18 wt % CB).

ites as a function of grafting monomer concentration, in which the same CB concentration (18 wt %) is used. An obvious decrease appears in temperature dispersion curve of G' at 40–100°C. Then, the relaxation transition of LDPE melting occurs when temperature approaches 105°C. The almost same transition temperature exhibited here implies that no change of the melt temperature (T_m) for LDPE occurs with the addition of g-CB. However, the temperature dispersion curves of tan δ show the presence of α_c mechanical relaxation for LDPE within the temperature range from 60 to

90°C. The temperatures corresponding to the tan δ peaks in Figure 5(a) and (b) were found to be dependent on the grafting monomer concentration. The peak appears at lower temperature and the peak value decreases with increasing monomer concentration. It is well-accepted that the α_c transition is related to the slip of the lamella. And to some extent, the decrease of α_c transition temperature is due to the formation of long-chain polymer grafted between CB and the matrix, which makes the slip of lamella easier. However, as shown in Figure 5(c) there is no discernible decrease of α_c transition temperature can be found, which indicates that different grafting structure formed in MA-g-CB/LDPE system compared with AA-g-CB/LDPE and BA-g-CB/LDPE composites.

The results mentioned earlier cannot be explained by the low grafting percentage and may be attributed to the different structure of the grafting monomer. It is worth noting that the enhanced interaction between AA (or BA) grafted CB and LDPE seem to be resulted from the formation of long chain CB-(AA)$_n$ or CB-(BA)$_n$ grafted on LDPE induced by polymerization initiators or by the action of heat and shear.[24,25] On the contrary, no long chains were grafted on CB or LDPE in the case of MA; and therefore, there existed poor interaction between MA-g-CB and polymer matrix compared with AA(BA)-g-CB. AA and BA chains could make the slip of lamella of the LDPE easy, resulting in the decrease of premelting temperature.

At the same time, it is interesting that a remarked difference in tan δ appears around 90°C. It can be found in Figure 5(a) and (b) that the AA or BA-g-CB exhibits lower tan δ below T_m with a increase in AA or BA concentration, while in Figure 5(c) tan δ increases with the addition of MA. It is well-accepted that the decrease of tan δ in front of its peak is dealt with the higher packing density of macromolecular chains.[26] Hence, it is reasonable to believe that the structure of those composites containing AA or BA-g-CB is more stable due to compact packing induced by improved interaction between the grafted CB and LDPE, as compared with the composites containing MA-g-CB.

CONCLUSIONS

The dynamic viscoelastic properties for LDPE filled with grafted CB were studied. The dynamic viscoelastic behavior for composite melts shows that when CB is grafted with AA and BA, the interaction between particles and polymer matrix is enhanced, leading to the formation of micronetworking in the system. The above arguments are supported by existence of characteristic modulus plateau and loss angle arc. According to plots of dynamic viscoelastic functions such as storage modulus (G') and loss tangent (tan δ) versus temperature, we find that the α_c relaxation for LDPE changes with the addition of AA and BA due to the

formation of long-chain polymer grafted between CB and the matrix, which facilitates the slip of the lamella of LDPE. The fact that the influence of MA-*g*-CB is not so pronounced as compared with AA and BA is attributed to no formation of long chain on CB particle.

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