

Influence of annealing on rheological and conductive behaviors of high-density polyethylene/carbon black composites

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Abstract A simultaneous measurement on dynamic viscoelastic and conductive behaviors was carried out to investigate the effect of high temperature annealing on the properties of carbon black (CB) filled high-density polyethylene composites. The results showed that dynamic storage and loss moduli of the composites increased significantly with increasing annealing time, and there existed a liquid- to solid-like transition at a critical time (t_c) which is dependent on temperature and CB content. Accompanying with the variation in dynamic moduli, electrical resistance (R) decreased sharply with time. What's more, the increase of R could be observed in the long time region. The activation energy determined from t_c as a function of reciprocal temperature was found to be irrespective of CB content. The evolutions of moduli and R induced by thermal treatment were discussed on the base of the concept of filler flocculation in the melt.

Introduction

It is known that conductive polymer composites composed of conductive particles and semicrystalline polymers exhibit interesting positive/negative temperature coefficient (PTC/NTC) effect upon heating across the melting

temperature (T_m) of the matrix [1–7]. However, the composites undergoing heating–cooling cycles usually show poor reproductivity of electrical resistance (R) due to the redistribution of conductive particles in the matrix underwent repeated melting and recrystallization [8]. Moreover, carbon black (CB) particles used as common conductive filler are easy to agglomerate in polymer melts [9].

Post heat treatment has been applied to improve the conduction reproductivity [10–16]. Heat treatment could accelerate the structural evolution of CB aggregates [9] and annealing below or above T_m has different influences on the redispersion of particles and also on the PTC/NTC behaviors of the composite [17]. Nevertheless, CB-filled high-density polyethylene (HDPE) may lose PTC/NTC transition after prolonged annealing at temperatures above T_m [18]. Measurement of time-dependent R during heat treatment is helpful for investigating the evolution of conduction property and for optimizing the annealing conditions to improve the PTC performance [18]. The flocculation of CB in polymer melts would finally develop a three-dimensional percolation network accompanying with a drastic change of R . Real-time monitoring the R variation of the composite during isothermal treatment above transition temperatures reveals a dynamic percolation behavior involving in bulk mobility of polymer layer surrounding CB particles [19], and the dynamic percolation process can be accelerated by increasing annealing temperature or filler content [14, 20].

Melt rheology is a preferred approach to gain information on filler dispersion in polymer matrix [21, 22]. The building of a temporary filler network is responsible for the modulus plateau in the low frequency region [21]. Empirical corrections between rheological parameters measured at the melt temperature and electrical resistivity of the composites measured at room temperature have been

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established for CB-filled polymer composites [23–27]. Simultaneous measurement of rheological and conductive behaviors under shear actions has been made for CB-filled natural rubbers [28] or vulcanizates [29] to study the CB network structure in these materials. We have put forward a novel method for simultaneous measurement of dynamic rheological behaviors and R for conductive polymer composites [30]. By using this method, we found that dynamic storage modulus (G') increases while R decreases with increasing strain amplitude for CB-filled ethylene–tetrafluoroethylene copolymer subjected to shear action at 260 °C above T_m and proved that the breakdown of percolation network is closely related to the nonlinear viscoelasticity [31]. We also examined isothermal crystallization of CB-filled HDPE by simultaneous measurement of R and normal force at strain zero [32]. The simultaneous measurement can provide a valid approach to probe viscoelastic and conductive behaviors of conductive polymer composites under various conditions. In the present article, we focus our attention on the simultaneous variations of dynamic moduli and R as a function of time for the HDPE/CB composites to probe the effect of thermal treatment at temperatures much higher than T_m .

Experimental

Materials and sample preparation

HDPE/CB composites were prepared by mixing of HDPE (Yangzi Petrochem. Corp., China, density 0.954 g cm⁻³, $T_m = 130$ °C, melt flow index 0.09 g min⁻¹), CB (VXC-605, Shanghai Cabot Chem. Co., Ltd., China, particle size 25 nm, density 1.85 g cm⁻³, nitrogen absorption special surface 63 m² g⁻¹, dibutyl phthalate absorption 1480 mm³ g⁻¹) and antioxidant (B215, Ciba-Geigy Co., Japan, relative molecular mass 647, $T_m = 180$ –185 °C) on a two-roll mill at 160 ± 5 °C and 50 rpm for 10 min. Before being mixed, HDPE pellets and CB particles were dried at 70 °C for 30 h. The composites were compression-molded at 160 ± 5 °C and 14.7 MPa for 10 min to form sheet samples of 7.9 mm in diameter and 1.2 mm in thickness for simultaneous measurement. The CB volume fraction (ϕ) was chosen as 0.15 and 0.17 being above the percolation transition region from 0.05 to 0.11 [32]. In order to avoid possible oxidation crosslinking and degradation of the matrix during the simultaneous measurement, all samples, if not specified, were added with 5 wt% antioxidant B215.

Method and testing

Rheological measurement was performed in an advanced rheometric expansion system (ARES, Rheometrics Co.,

USA) in dynamic mode with a strain of 1.2% and a frequency (ω) of 1 rad s⁻¹. R was simultaneously measured with an automatic measurement system where a 7150 plus Digital Multimeter (Schlumberger) was installed. The applied direct current voltage was 1 V. A cooling–heating–cooling cycle was also performed at a rate of 10 °C/min to an annealed composite for investigating the effect of reproducibility of both moduli and R . The setup of the equipment for simultaneous measurement of R and rheological parameters was described elsewhere [30].

Thermalgravimetric analysis (TGA) test was conducted on a Perkin-Elmer Pyris 6 thermogravimetric analyzer (SDT Q600, TA, USA) at 230 °C under dry air atmosphere for 3 h with a flow of air of 40 mL min⁻¹.

Gel content measurement for high temperature treated composites was conducted using a Soxhlet extractor in boiling xylene [33–35]. Before extraction, HDPE and the HDPE/CB composites with $\phi = 0.17$ were kept at 230 °C in an air atmosphere for 3 h under the condition same as that in the simultaneous measurement on ARES.

Results and discussion

Figure 1 shows weight percentage as a function of time (t) at 230 °C for the HDPE/CB composite ($\phi = 0.17$) and for HDPE. After being annealed for 3 h, the weight losses of both the composite and HDPE are less than 6 wt%, which is mainly assigned to the degradation of the antioxidant. The weight loss of the HDPE/CB composites is slightly larger than HDPE, which might be ascribed to the volatilization of small molecules (such as H₂O, O₂, etc.) absorbed on the surface of CB particles in the composite. The annealed HDPE was extractable completely in boiling xylene, suggesting that B215 used in the samples could

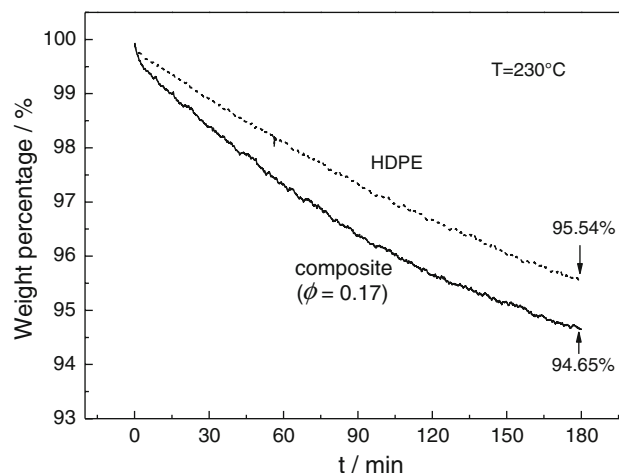


Fig. 1 Weight loss as a function of time (t) at 230 °C for the HDPE/CB composite ($\phi = 0.17$) and HDPE

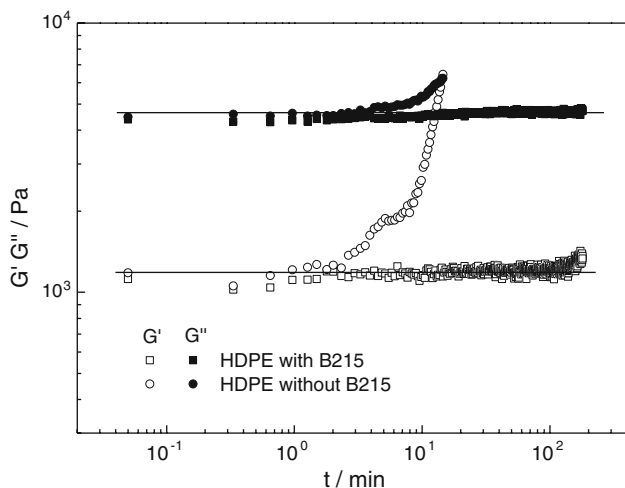


Fig. 2 Storage and loss moduli (G' and G'') as a function of t for HDPE with and without B215 at 230 °C

effectively restrain the thermal crosslinking of the matrix. Though virgin HDPE can be oxidized at high temperatures in air, B215 is effective to prevent HDPE from crosslinking in the vicinity of 200 °C [36]. Figure 2 gives the dynamic time sweep of HDPE with and without B215 at 230 °C. G' and loss modulus (G'') of HDPE without B215 increases sharply from $t = 2$ min, which is ascribed to thermal-induced oxidation crosslinking. On the other hand, G' and G'' of HDPE containing B215 hardly change within 150 min. At the end of measurement, G' of HDPE with B215 begins to increase revealing a beginning of oxidation crosslinking due to the running out of B215.

Figure 3 shows G' , G'' , and R simultaneously measured as a function of t for the HDPE/CB composite ($\phi = 0.17$) exposed to thermal treatment at temperatures from 210 to 230 °C. Both G' and G'' increase with t , and the variations

become faster at higher temperatures. Accompanying with the modulus increments, R decreases significantly, implying the formation of a three-dimensional conductive network in the melt [14, 15, 19, 23]. The R decay in Fig. 3 might be reminiscent the NTC effect above T_m , which is usually assigned to the aggregation of CB particles [18]. At the late stage of thermal treatment, G' increases continuously while G'' tends to level off to constant values. On the other hand, as shown in the inset in Fig. 3, R increases considerably at $t > 23$ min at 230 °C while the increase in R is very slightly at $t > 100$ min at 220 °C. R increase in the long time region could hardly be observed at 210 °C within the experiment time scale.

The viscoelastic behaviors of the molten composites could be related to the three-dimensional structure formed by filler particles through bridging polymer chains [37, 38]. CB particles in polymer melts tend to flocculate depending on attractive potential and distance between the aggregates, which can be accelerated by heat treatment [9]. The size of clusters increases and gap between adjacent CB clusters decreases during the flocculation, leading to the formation of continuous percolating network that immobilizes the matrix chains [39]. The filler networking does not only influence on conductivity but also on stiffness of filled polymers [40]. Uncrosslinked rubber compounds containing CB exhibit an obvious increase in G' during annealing at elevated temperatures, which is accompanied with increments in both AC conductivity and dielectric permittivity [41]. In the case of high temperature annealing here, CB particles flocculate to form more perfect conductive network, resulting in a sharp decrease in R at early stage of measurement. At the same time, the mobility of polymer chains absorbed on the clusters is reduced considerably, resulting in an obvious increase in both G' and G'' .

The filler flocculation has been evidenced recently either by morphological observation of the annealed composites or by modeling the dynamic conduction percolation during annealing [42–46]. Indeed, the conductive polymer composites are in thermodynamic non-equilibrium state and the flocculation of CB particles in the composites depends on both temperature and time that they are exposed to [47–50]. Rather than short-rang van der Waals interactions, the driving force for flocculation is attributed to long-range depletion interactions [51]. The process of flocculation can be accelerated by increasing annealing temperature or filler content [14, 20] and extending annealing time will obtain a higher degree of agglomeration of CB particles. The flocculation of CB particles does not involve in the formation of permanent bonds linking the CB aggregates due to the presence of a thin polymer layer attached to the surface of CB particles. The movement of CB particles during flocculation can cause both the breakdown and the reformation of the conducting clusters. The microstructure change of

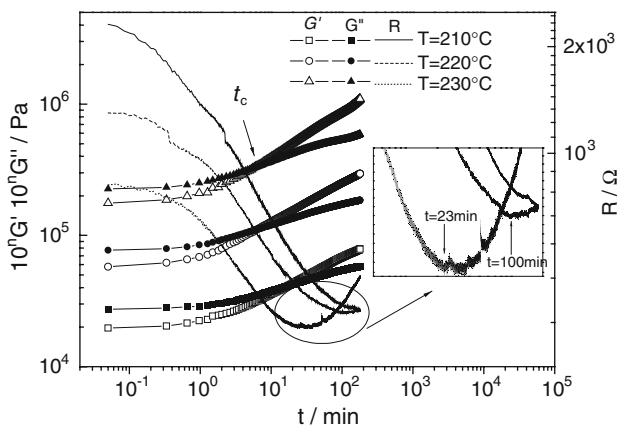


Fig. 3 G' , G'' , and resistance (R) as a function of t for the HDPE/CB composite ($\phi = 0.17$). Moduli at 220 and 230 °C are shifted upward with $n = 0.5$ and $n = 1$, respectively

the conducting network depends on the competition of the two processes [23]. The formation of continuous conductive pathway is dominant for the composites containing high CB contents at high temperatures, which is responsible for the R decay at the earlier stage of annealing in Fig. 3. However, annealing the composites with extended time finally leads to the formation of segregated massy cluster domains, causing partial breakdown of the perfect CB network, appearing as the R increment in Fig. 3 in the long time region.

Rheological percolation is often assumed to account for the liquid- to solid-like transition in filled polymers with increasing filler content [52]. Such transition has been attributed to the formation of the filler network embedded in the viscoelastic liquid [53]. Figure 3 presents a fluid- to solid-like viscoelastic transition occurred at the critical time (t_c) defined as the time when G' and G'' intersect with each other during annealing, which could be ascribed to the CB clustering and networking considering that HDPE oxidation crosslinking is negligible. Similar fluid- to solid-like transition has been observed in CB suspensions containing polyisobutylene succinimide dispersant in hydrocarbon liquid in which the well-dispersed primary CB aggregates agglomerate to form a more tenuous network at high temperatures [54].

Figure 4 shows t_c as a function of reciprocal temperature ($1/T$) for the HDPE/CB composites with $\phi = 0.15$ and $\phi = 0.17$, respectively. t_c decreases with increasing ϕ and is linearly dependent on $1/T$. The activation energy (ΔE) can be estimated according to the Arrhenius equation

$$t_c = A \exp(\Delta E/RT)$$

in which A is a pre-factor and R is gas constant. ΔE was estimated as 99.8 ± 6.8 and 94.2 ± 9.8 kJ mol $^{-1}$ for

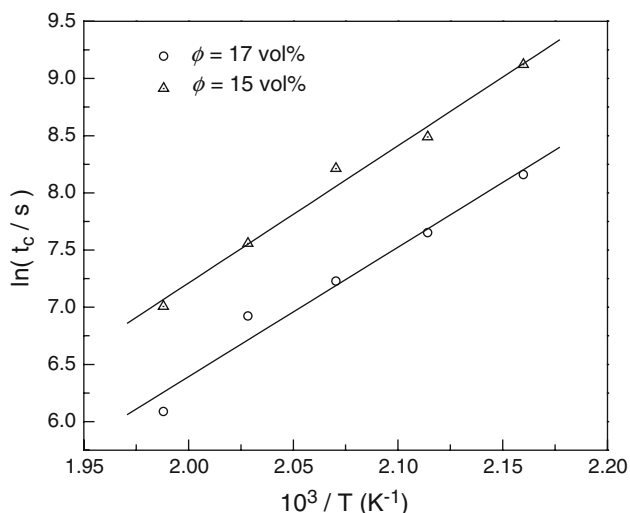


Fig. 4 Relationship between critical time (t_c) and temperature (T) for the HDPE/CB composites with $\phi = 0.15$ and $\phi = 0.17$

composites with $\phi = 0.15$ and $\phi = 0.17$, respectively, according to least square fitting. A considerably low value of $\Delta E = 36$ kJ mol $^{-1}$ irrespective of CB content determined from the dynamic resistance percolation time in HDPE/CB composites reflects the mobility of polymer chains absorbed on CB particles at dynamic resistance percolation time [19]. The ΔE values here determined from t_c are insensitive to CB content, suggesting that the fluid- to solid-like transition might be related to the immobilization of absorbed polymer chains at t_c besides the CB flocculation [40]. Indeed, the contact process between two CB particles can be equivalent to the excluding process of polymer molecules between two particles; thus, the flocculation of CB particles in the matrix could reflect the mobility of the polymer layer between CB particles [19], which is also the case of fluid- to solid-like transition.

Figure 5 shows G' , G'' , and R as a function of t during a cooling–heating–cooling cycle for the HDPE/CB composite ($\phi = 0.17$) annealed at 230 °C for 3 h. During cooling the annealed composite from 230 to 115 °C, both G' and G'' increase with decreasing temperature, which is accompanied with an obvious R increment assigned to the breakdown of the as-formed CB network due to the volume contraction of the matrix. The sample exhibits a solid-like character as viewed from $G' > G''$, being reminiscent the effect of thermal treatment. The matrix crystallizes in the close vicinity of 115 °C [22], resulting in a rapid modulus increment and a sharp R decay. Crystallization of HDPE leads to the migration of CB aggregates into amorphous phase of the matrix and the formation of CB network therein [55–57]. During the following heating process, G' and G'' decrease while R increases sharply from 120 to 130 °C, which is readily assigned to the melting of the HDPE crystals and the resultant PTC effect. With increasing temperature above T_m , R decreases markedly

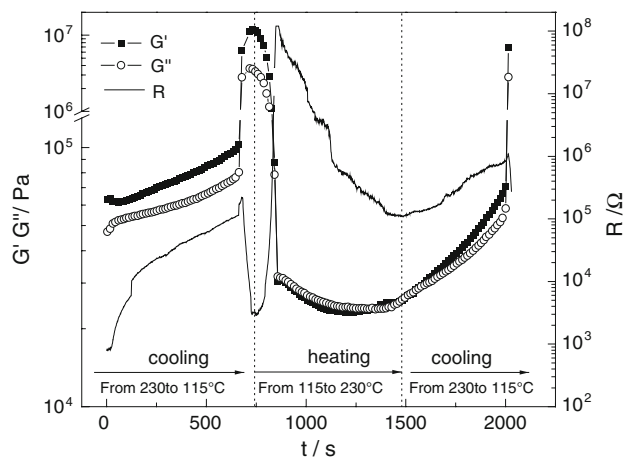


Fig. 5 G' , G'' , and R as a function of t during a cooling–heating–cooling cycle for the HDPE/CB composite ($\phi = 0.17$) annealed at 230 °C for 3 h

appearing as the NCT effect. The R value at 230 °C is more than two orders of magnitude higher than that immediately after annealing. At the same time, G' and G'' become very close to each other and both change only slightly with increasing temperature. Both G' and G'' are considerably smaller than their corresponding values during the first cooling, suggesting that the annealing resulted structure is partially destroyed due to melting and recrystallization. During the second cooling process, moduli and R vary similar to those observed in the first cooling. However, moduli become lower and R becomes higher than their corresponding values during the first cooling, revealing that the structure related to the viscoelasticity and the conduction vary irreversibly upon the thermal cycle. Furthermore, G' becomes higher than G'' at temperatures below 185 °C. The thermal cycle results in a lower degree of CB agglomeration in comparison with the annealed composites, which is responsible for the lower moduli and the higher R in the second cooling in comparison with the first one.

Conclusions

Thermal treatment of HDPE/CB composites containing high CB contents at temperatures much higher than T_m with extended annealing time causes increment of dynamic moduli with time, which is accompanied with R decrease in the short time region followed by R increase in the long time region. A fluid- to solid-like transition occurs at a critical time depending on temperature and CB content, which could be assigned to filler networking upon heat treatment.

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