J Mater Sci (2008) 43:4828–4833
DOI 10.1007/s10853-008-2697-8

Simultaneous measurement of normal force and electrical resistance during isothermal crystallization for carbon black filled high-density polyethylene

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Received: 24 January 2008 / Accepted: 2 May 2008 / Published online: 3 June 2008

Abstract The kinetics of isothermal crystallization for high-density polyethylene (HDPE) containing different volume fraction (Φ) of carbon black (CB) have been evaluated by using differential scanning calorimetry (DSC) at 123, 124, and 125 °C where the rate of crystallization is moderate. Simultaneous measurement of normal force (F_N) and electrical resistance (R) has been performed to probe the process of isothermal crystallization at strain zero. Results reveal that, at the early stage of crystallization, F_N is almost independent of time (t) while relative resistance (R/R_0) changes slightly with increasing time t. However, a significant increment in F_N and a remarkable change in R/R_0 can be observed at the same critical time (t_c), and the value of t_c is dependent on the crystallization temperature and CB content, which is available for describing the isothermal crystallization as a characteristic parameter. It is found that t_c is greater than induction time of crystallization (t_0) due to the less sensitivity of mechanical and electrical responses than enthalpy to the structural changes in the composites. It is suggested that mechanical and electrical simultaneous measurement endows us a novel approach to probing the formation of percolation network involving in crystallization of polymer matrix.

Introduction

It is well known that the process of polymer crystallization is affected by the presence of solid fillers, and as a result, the properties of polymer materials are variable to some extend, especially for composites filled with carbon black (CB), mica, talc, or chalk, etc. [1, 2]. In general, nanofiller acting as nucleating agent can speed up crystallization and increase crystallinity, while the nucleation and growth mechanisms of crystallization highly depend on temperature and filler content [3–6]. Several techniques such as dilatometry, optical microscopy, small angle lighting scattering (SALS), and differential scanning calorimetry (DSC) have been widely used to study the crystallization of polymers, and these methods can monitor changes of density, spherulite size, or enthalpy of fusion during crystallization [7–9]. Recently, it was found that rheological measurement might provide a criterion sensitive to polymer crystallization [10–12]. For filled polymer systems in low frequency (ω) region, the so-called "*second plateau*" appears in plot of viscoelastic parameters such as dynamic storage modulus (G') and loss modulus (G'') versus ω, which is sensitive to formation of high-order structure of filler, for example, agglomerated structure, skeleton, or network structure [13, 14]. To our knowledge, however, few works concerning the influence of isothermal crystallization on the distribution of filler and formation of conductive network for conductive composites have been reported.

In fact, simultaneous measurement of rheological and conductive properties has been made on CB-filled natural rubbers [15] or vulcanizates [16] to examine the CB structure inside these materials. It was found that shear moduli vary in a way similar to electrical conductivity as the amplitude of dynamic oscillation increases. Pan and Mckinley [17] studied viscoelasticity and conduction behaviors of an

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electrorheological fluid suspension using simultaneous measurement technique. In a previous work [18], we examined the simultaneous measurements of the dynamic storage modulus and electrical resistance for ethylene–tetrafluoroethylene copolymer/CB composites melt in a wide strain range and found that increasing CB concentration causes a decrease in critical strain for the linear-to-nonlinear rheological transition, and a corresponding increase in that for the conductor-to-insulator transition.

High-density polyethylene (HDPE) filled with CB is prototypical of composites exhibiting characteristic of resistance switching, whose application has been found in current-limiting devices [19]. To our knowledge, few works concerning isothermal crystallization of HDPE/CB composites have been reported up to date. We have studied the influence of thermal treatment (annealing) on the conduction behavior of HDPE/CB composites and found that the resistance-time characteristic is highly dependent on the crystallization temperature [20]. In the present work, we focus our attention on the isothermal crystallization of HDPE/CB composites by simultaneous measurement of mechanical and conductive behaviors with a modified rheometer at zero strain and attempt to examine the effects of temperature and CB concentration on the process of crystallization. It is noted that as the crystallization proceeds, the volume contraction of the samples induces a tensile force on the plates of rheometry that changes markedly after a critical crystallization degree, and crystallization causes a redistribution of CB particles so that resistance of the sample varies correspondingly.

Experimental

Sample preparation

The composites were prepared by mixing of HDPE (5000s, Yangzi Petrochem. Corp., density 0.954 kg m^{-3}, melting point 130 °C, and melt flow index 0.090 g min^{-1}) and CB (VX_c-605, Shanghai Cabot Chem. Co., Ltd., particle size 25 nm, nitrogen absorption special surface area 63 m^2 g^{-1}, and dibutyl phthalate DBP absorption 1,480 mm^3 g^{-1}) on a two-roll mill at 165 °C and 60 rpm for 10 min and then by compression-molding at 165 °C and 14.7 MPa for 10 min to form sheet specimens. A small content of antioxidant (antioxygen B215) was incorporated in the composites in order to avoid thermal oxidation during isothermal crystallization. After naturally cooled to room temperature, the sheet was cut into disks of 7.9 mm in diameter and 1.2 mm in thickness.

Method and testing

Illustration of simultaneous measurement of normal force (F_N) and resistance (R) is given in Fig. 1. A resistance measurement device with a 7150 Plus Digital Mutimeter (Schlumberger) was attached to an advance rheometric expanded system (ARES, Rheometrics Co., USA). R was measured at a dc voltage of 1 V. The temperature was measured on the lower plate of rheometer. In order to remove the thermal and strain history, sample disks were cooled to the experimental temperatures after being melted in the rheometer at 160 °C for 5 min. The cooling stage lasted about 1 min. During the isothermal crystallization, the temperature was controlled at 123, 124, and 125 °C, respectively, and the temperature fluctuation was controlled in ±0.2 °C. The isothermal crystallization was conducted at strain zero and F_N was measured in the static mode.

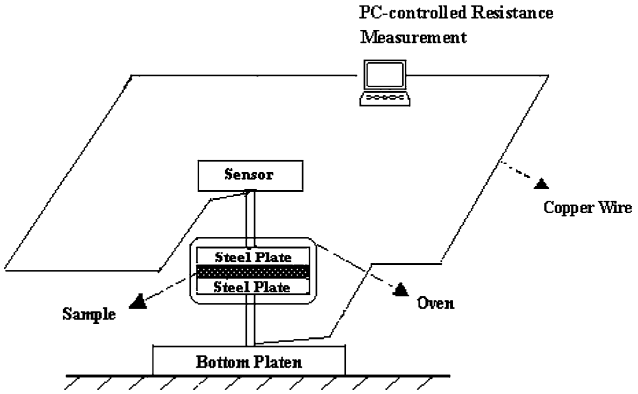

Fig. 1 Scheme of simultaneous measurement of normal force (F_N) and resistance (R)

The isothermal crystallization of the samples was also performed in a Q100 differential scanning calorimeter (DSC, TA instruments-Waters LLC, USA) under the same temperatures as those used for the normal force and resistance measurements.

Results and discussion

Figure 2 presents resistivity (ρ) as a function of volume fraction (Φ) of CB for the HDPE/CB composites. ρ drops dramatically more than 10 orders of magnitude over the percolation region from 0.05 (Φ_1) to 0.11 (Φ_2) corresponding to the insulator-to-conductor transition, which is resulted from the formation of interconnected CB pathways with increasing Φ [21]. According to Nakamura et al. [22], the upper limitation of Φ_2 corresponds the transition from tunneling into ohmic conduction.

Figure 3 shows DSC curves of isothermal crystallization of the HDPE/CB composites with different CB volume fractions calculated at room temperature. The CB volume fractions are selected at the insulator-to-conduction ($\Phi = 9$ vol%), slight above Φ_2 ($\Phi = 13$ vol%) and much higher than Φ_2 ($\Phi = 17$ vol%), respectively. Also shown are the isothermal crystallization curves for the HDPE

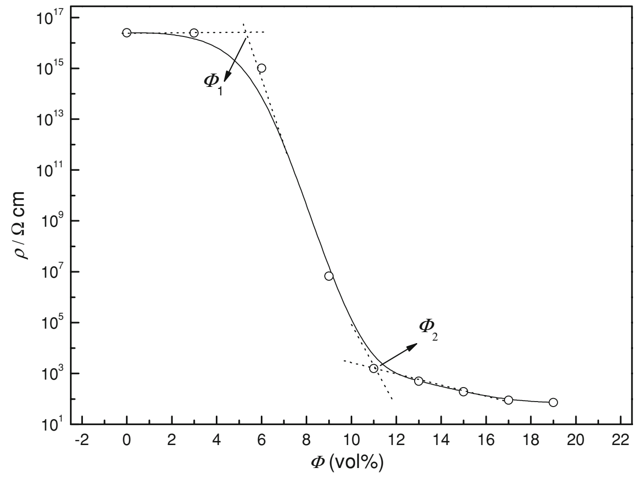

Fig. 2 Volume resistivity (ρ) as a function of on CB volume fraction (Φ) for the HDPE/CB composites

matrix. The induction time of crystallization (t_0) is defined by the time point where heat flow begins to increase. In polymers and polymer composites, t_0 should be proportional to the time needed for critical nucleus formation. As shown in Table 1, t_0 depends both on filler content Φ and crystallization temperature (T_c). Of pure HDPE, t_0 is 416, 483, and 918 s at 123, 124, and 125 °C, respectively. Increasing CB content causes a reduction in t_0 at given temperatures, revealing that CB particles actually act as nucleation species and promote the crystallization process [3–6]. On the other hand, t_0 decreases with decreasing temperature for the composites with given CB contents.

Figure 4 demonstrates relative crystallinity $[X(t - t_0)]$ as a function of time (t) during isothermal crystallization for HDPE and for the composites with three different CB contents. Dependence of half time of crystallization ($t_{1/2}$) on T_c is shown in Fig. 5. During isothermal crystallization,

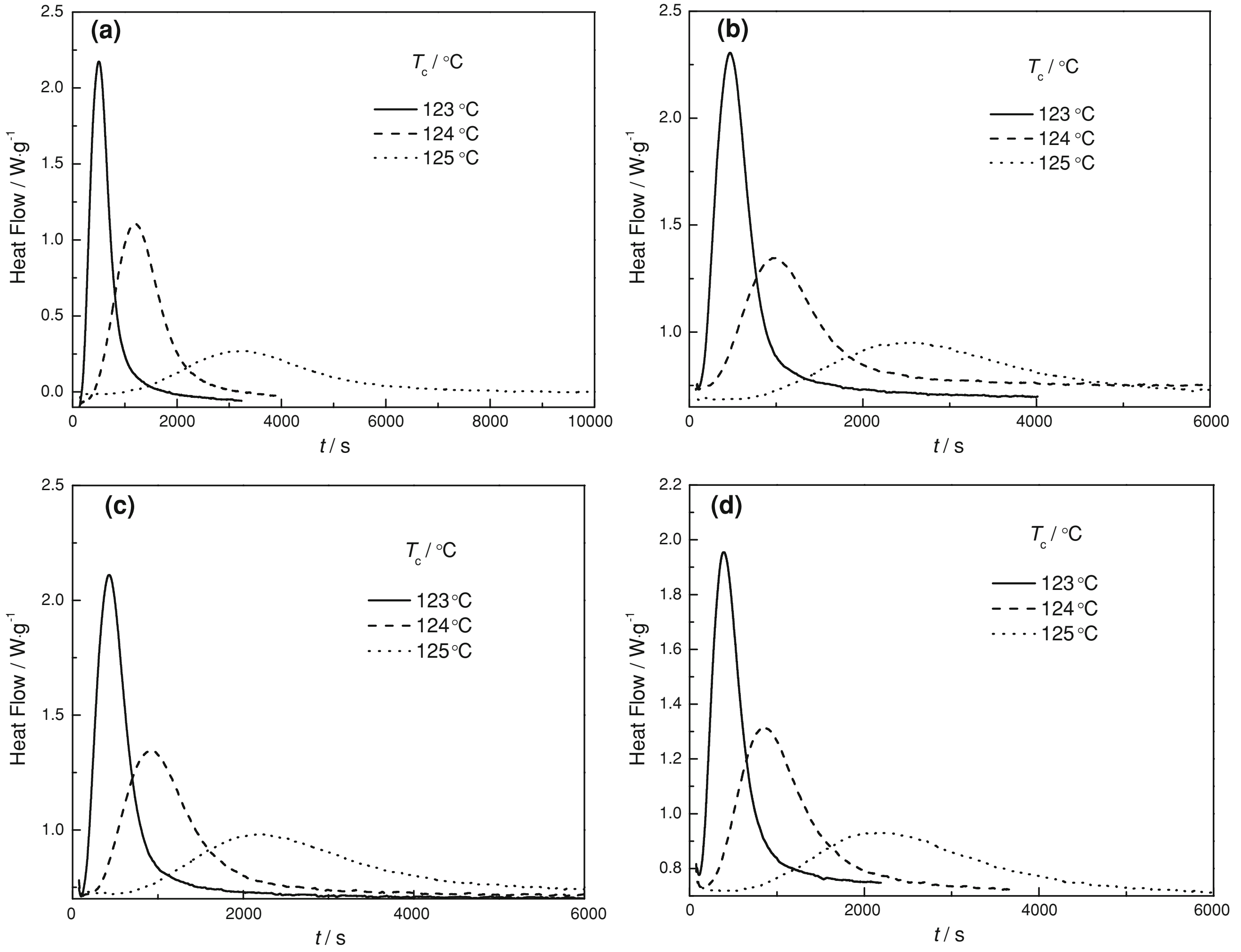

Fig. 3 DSC curves for isothermal crystallization of HDPE/CB composites containing 0 vol% (**a**), 9 vol% (**b**), 13 vol% (**c**), and 17 vol% (**d**) CB, respectively

Table 1 The critical time (t_c), the corresponding variation value of relative resistance ($\Delta R/R_0$), and relative crystallinity (X_c) as a function of CB concentration (Φ) and crystallization temperature (T_c) for HDPE/CB composites

CB volume fraction (%)	Temperature (°C)	t_0 (s)	t_c (s)	$\Delta R/R_0$	X_c
9	123	107	255	7.10	0.04
	124	127	522	4.20	0.04
	125	528	1,617	−0.60	0.09
13	123	105	226	2.2	0.03
	124	113	435	1.49	0.02
	125	453	1,409	2.1	0.08
17	123	100	196	−0.16	0.02
	124	108	322	0.97	0.01
	125	418	1,232	1.18	0.05

the dispersed CB particles, behaving as a nucleation center, can promote crystal growth and thus lower $t_{1/2}$. A difference in $t_{1/2}$ value decreases with lowering the crystallization temperature, and $t_{1/2}$ becomes very close to each other at $T_c = 123$ °C, which is in agreement with the phenomena in filled polypropylene reported by Mucha and Krolikowski [23].

Figure 6 shows typical plots of normal force (F_N) and relative resistance (R/R_0) as a function of t for the composites with $\Phi = 9$, 13, and 17 vol%, respectively. It is seen that F_N and R/R_0 change obviously at almost the same critical time (t_c). The method for determination of t_c from crossover of two linear regions with different slopes is illustratively shown in Fig. 6a. Both electrical and mechanical properties can response to the structural change in the composites undergoing crystallization. For all

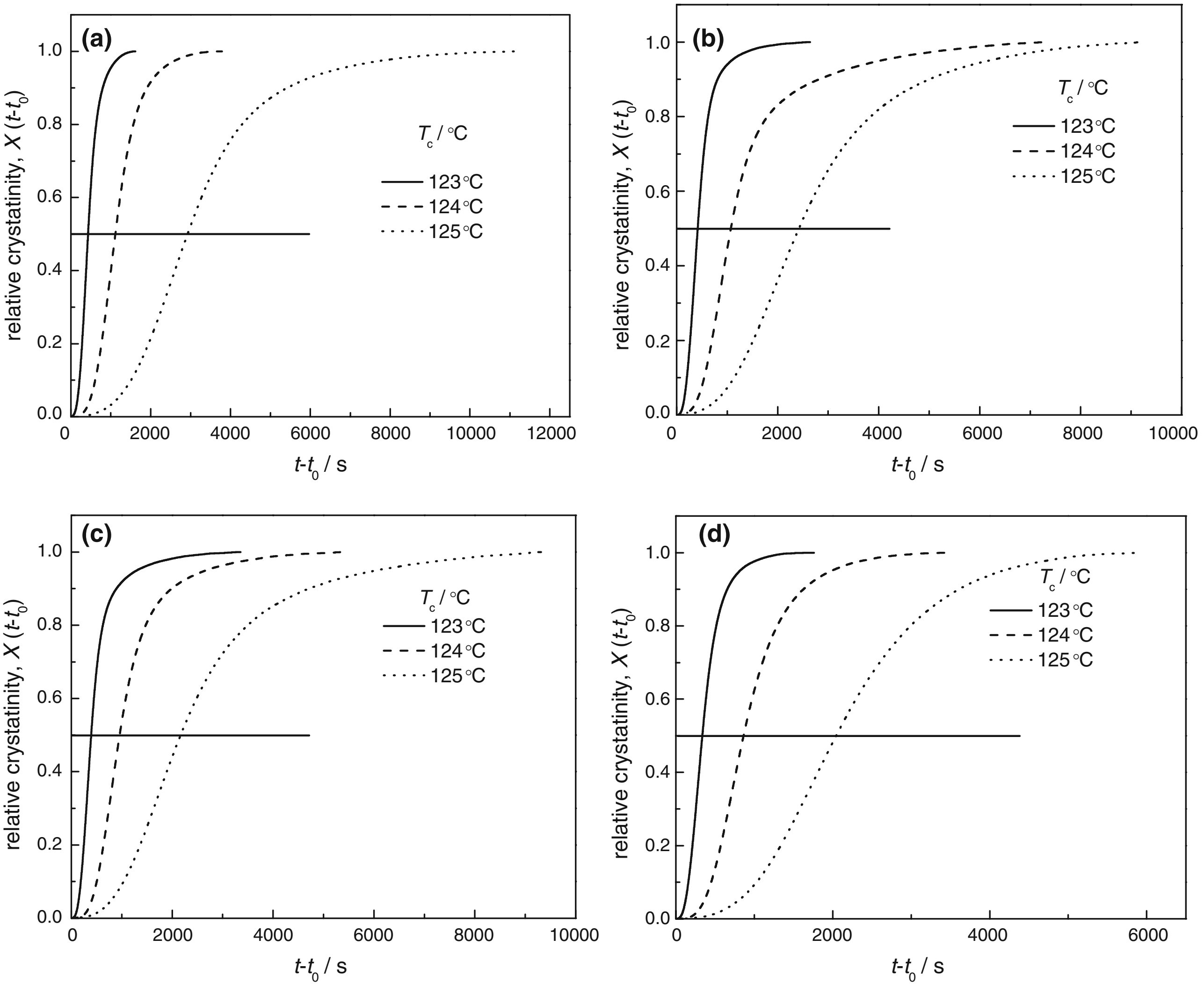

Fig. 4 Relative crystallization [$X(t - t_0)$] as a function of time ($t - t_0$) for the HDPE/CB composites containing 0 vol% (**a**), 9 vol% (**b**), 13 vol% (**c**), and 17 vol% (**d**) CB, respectively

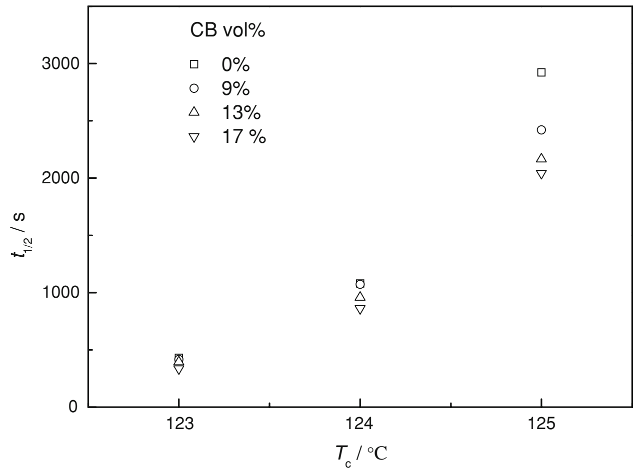

Fig. 5 Half time of crystallization ($t_{1/2}$) as a function of crystallization temperature (T_c) for the HDPE/CB composites

composites, F_N remains constant until t_c; hereafter, F_N decreases remarkably due to the volume contraction accompanying with proceeding of crystallization. On the other hand, the evolution of R/R_0 with t is highly dependent on Φ. For the composite with $\Phi = 9$ vol% (Fig. 6a), R/R_0 decreases slightly with increasing t at $t < t_c$, while it increases significantly at $t > t_c$. The variation of conduction reflects the structural evolution of the percolation network. The decrease of resistance at $t < t_c$ indicates an intrinsic resistance relaxation involving in the rearrangement and agglomeration of CB particles in the matrix, which is accelerated by increasing T_c. The noticeable resistance increment at $t > t_c$ is resulted from the partial destruction of the as-formed conducting pathways due to the large volume contraction induced by crystallization of HDPE.

For the composite with $\Phi = 13$ vol% slightly above Φ_2 (Fig. 6b), R/R_0 increases firstly and then undergoes a remarkable increment at $t < t_c$. The value of t_c approximately corresponds to the resistance maximum. In the induction period of crystallization, thermal motion of HDPE chain could cause a partial destruction of the as-formed CB pathway in this composite with a relatively high CB content. On the other hand, onset of crystallization enhances the destruction of the CB pathways, and as the crystallization proceeds, the volume fraction of CB aggregates in the amorphous phase increases, and the gap between CB aggregates becomes narrower. It is worth noting that the crystallization process promotes the formation of continuous conductive pathways that further build up the percolation network in the amorphous phase, and formation of the percolation network results in the almost linear resistance decay. The transition time where resistance changes from increment to drop increases with increasing T_c, being in agreement with the result of our previous work [20].

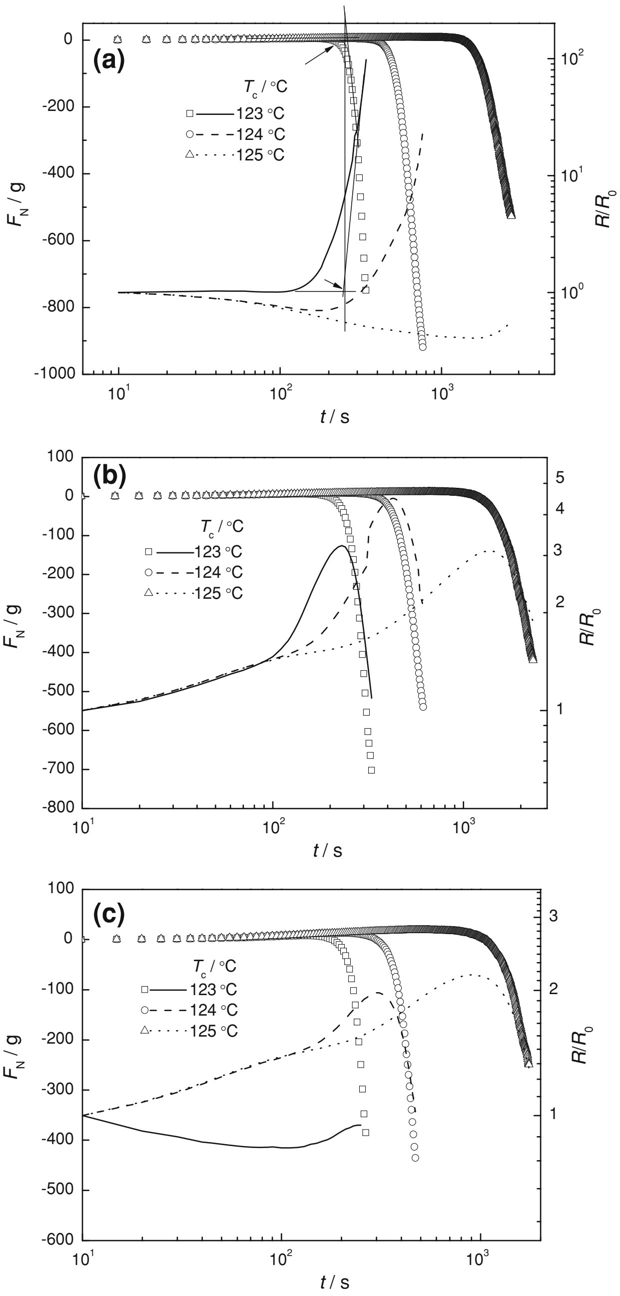

Fig. 6 Normal force (F_N, symbols) and relative resistance (R/R_0, curves) as a function of time (t) for the HDPE/CB composites containing 9 vol% (**a**), 13 vol% (**b**), and 17 vol% (**c**) CB, respectively. The critical time t_c is determined at the cross point of two tangent lines as shown in (**a**)

For the composite with $\Phi = 17$ vol% much above Φ_2 (Fig. 6c), R/R_0 at 125 and 124 °C are quite similar to those given in Fig. 6b, while the maximum amplitude of resistance increment becomes lower. On the other hand, R/R_0 at 123 °C almost hardly changes with t.

It is emphasized that R/R_0 is more sensitive to supermolecular crystalline structure at $\Phi_1 < \Phi < \Phi_2$ than at $\Phi \geq \Phi_2$ during isothermal crystallization, and the R/R_0

variation with respect to t is highly dependent on T_c and CB content. The percolation network may show structural relaxation in HDPE melt before onset of crystallization, which can be realized in the composite with $\Phi = 9$ vol% in the percolation transition region. The crystallization process first causes breakdown of the as-formed pathways, while the large volume contraction during solidification rebuilds the percolation network in the amorphous. Hence, a drop in resistance follows the resistance increment, as demonstrated in the composites with $\Phi = 13$ vol% and $\Phi = 17$ vol%. At higher CB contents, the crystallization-induced resistance variation may screen that from structural relaxation of the as-formed network.

Values of t_c obtained from Fig. 6 are listed in Table 1, together with the corresponding values of relative resistance variation ($\Delta R/R_0$). It is clear that t_c decreases with increasing Φ and T_c, and when the CB concentration is lower than Φ_2, the as-formed continuous conductive pathways are liable to break down during the crystallization of HDPE. The composite with $\Phi = 9$ vol% shows a remarkable variation of resistance at t_c at $T_c = 123$ and 124 °C. Moreover, t_c is longer than t_0 due to the less sensitivity of mechanical and electrical response than that of enthalpy to the crystallization. The values of relative crystallinity X_c at t_c obtained from Fig. 4 are also listed in Table 1. It is seen that X_c is located in 1–10%, which is critical for establishing a normal stress being detectable by the rheometer and for inducing the resistance variation. Although the mechanical and electrical simultaneous measurement is less sensitive to crystallization in comparison with DSC test, it provides a novel method to probe the formation of percolation network resulted form crystallization or solidification of polymer matrix.

Conclusion

The isothermal crystallization behavior of HDPE/CB has been studied through simultaneous measurement of normal force and electrical resistance. It was found that during isothermal crystallization, the supramolecular crystalline structure causes essential changes of mechanical and electrical properties. A significant increment in normal force (F_N) and a marked change in relative resistance (R/R_0) can be observed at the same critical time (t_c). The value of t_c appears sensitive to isothermal crystallization temperature and decreases with increasing CB concentration. The values of relative crystallinity (X_c) at t_c are located in 1–10% estimated from the DSC data. The simultaneous measurement of mechanical properties and electrical resistance is a novel approach to examine the formation of percolation network during the isothermal crystallization of polymer composite in the percolation region.

Acknowledgement This study was supported by the National Nature Science Foundation of China (No. 20774085).

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