

Polymer Communication

Positive and negative temperature coefficient effects of an alternating copolymer of tetrafluoroethylene–ethylene containing carbon black-filled HDPE particles

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Abstract

A conductive polymer composite was prepared by melt-mixing of an immiscible semicrystalline polymer blend of an alternating copolymer of tetrafluoroethylene–ethylene (ETFE), high density polyethylene (HDPE), and carbon black (CB). The optical microscopy and time-of-flight secondary mass spectrometry results indicated that the CB particles were selectively localized in the HDPE phase. In addition, it was found that the CB-filled HDPE particles formed a dispersed phase in the ETFE matrix. A double-positive temperature coefficient (PTC) effect was observed in the composite, caused by the large thermal expansion due to the consecutive melting of HDPE and ETFE crystallites. The negative temperature coefficient (NTC) that was observed in this system could not have been caused by the formation of flocculated structures because the size of the CB-filled HDPE particles is significantly large, so that their mobility is extremely limited even at high temperatures. This conclusion was confirmed by observing the morphology of the composite at temperature ranging from 25 to 250°C. These results suggest that new mechanisms need to be uncovered to explain the NTC effect of conductive polymer composites. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Tetrafluoroethylene–ethylene; High density polyethylene; Positive temperature coefficient and negative temperature coefficient effects

1. Introduction

After the positive temperature coefficient (PTC) effect was first observed in a carbon black (CB)-filled low density polyethylene composite by Frydman [1] in 1945, many researchers have studied the PTC effect due to the potential applications of PTC materials in industry [2–14]. In general, it has been well accepted that the strong PTC effect of CB-filled semicrystalline composites is caused by an increase in the average interparticle or aggregate distance of CB due to the large thermal expansion as a result of the melting of the polymer crystallites [7].

It should be noted, however, that most of the earlier studies were focused on the composites comprising CB and a single semicrystalline polymer [1–13]. Few studies have been conducted on the PTC and negative temperature coefficient (NTC) effects of CB-filled immiscible polymer blends. Our previous results of CB-filled PVDF/HDPE

composites have shown that the morphology can significantly influence the PTC and NTC behaviors of the composites [14]. It was found that when the PVDF and CB-filled high density polyethylene (HDPE) form the dispersed and continuous phases, respectively, the PTC and NTC behaviors are similar to those of a CB-filled neat HDPE composite containing an equivalent amount of CB in the HDPE phase. However, when the PVDF and CB-filled HDPE form a co-continuous phase, the PTC effect is not significantly disturbed but the NTC effect is delayed to a higher temperature.

Uncrosslinked CB-filled semicrystalline polymer composites exhibit a sharp decrease in resistivity when temperature is above the T_m of the polymers. This phenomenon is referred to as the NTC effect. It has been suggested that the NTC effect of a CB-filled single semicrystalline polymer composite is caused by the formation of a flocculated structure when the viscosity of the polymer is sufficiently low at elevated temperatures [11–13]. However, the NTC effect of CB-filled polymer blends has not been elucidated in detail. The objective of this paper is to elucidate the PTC and NTC effects of a CB-filled immiscible semicrystalline polymer

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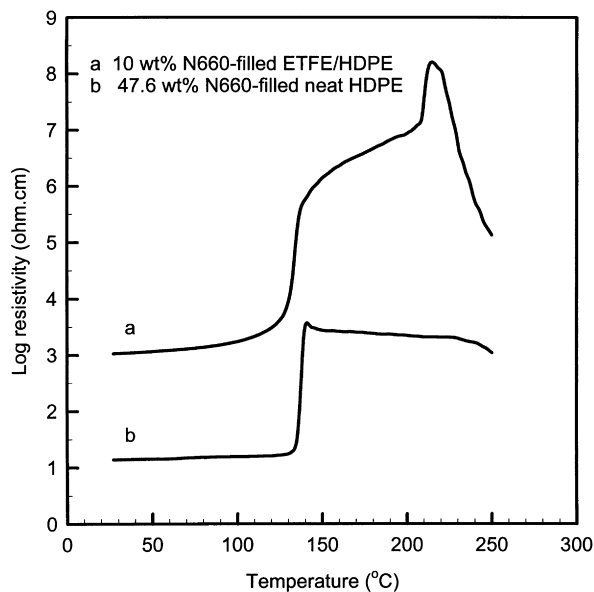


Fig. 1. Log resistivity of 10 wt% N660-filled ETFE/HDPE(4/1) composite and 47.6 wt% N660-filled neat HDPE composite as a function of temperature.

blend when CB is selectively localized in the dispersed phase, which is the semicrystalline polymer that has the lower melting point.

2. Experimental

The high melting point semicrystalline polymer used was an alternating copolymer of tetrafluoroethylene–ethylene (ETFE) from Du Pont. The low melting point polymer was a HDPE from Philips Petroleum International with an

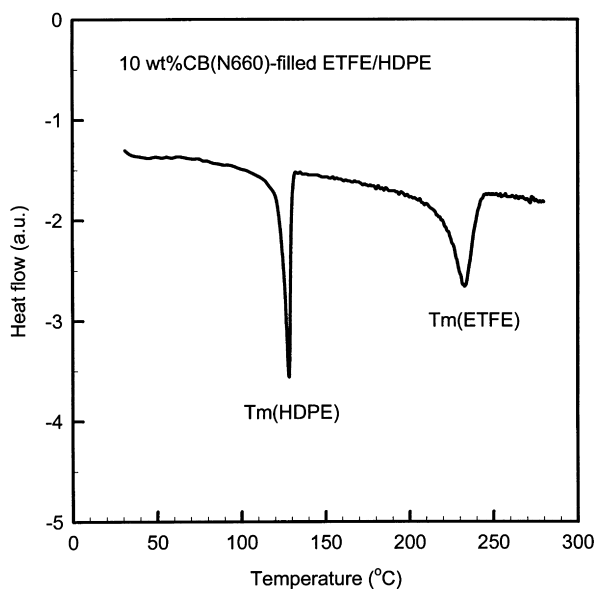


Fig. 2. DSC thermogram of 10 wt% N660-filled ETFE/HDPE(4/1) composite obtained at a heating rate of 2°C/min.

MFI of 0.35 g/10 min. The CB used was N660 from Columbian Chemicals.

The CB-filled ETFE/HDPE composite was prepared by melt-mixing the materials in a Haake mixer at 280°C and 30 rpm for 15 min. The compound obtained was further compressed into a 2-mm sheet by a hot press at 280°C and 16 MPa. The ETFE/HDPE volume ratio was 4/1 and the CB content was 10 wt% with respect to the total weight.

The resistivity of the composite along the thickness direction as a function of temperature was measured at a heating rate of 2°C/min using a computerized system comprising a computer, a multimeter, and a programmable oven. Electrodeposited Ni foil was used as electrodes to eliminate contact resistance. The melting behavior of the composite was studied using a differential scanning calorimeter (DSC) (TA 2910) which was operated at a heating rate of 2°C/min in a nitrogen atmosphere. Before the DSC measurement, the instrument was calibrated with indium as a standard. The morphology of the composite was elucidated by using an optical microscope operating at the transmission mode. The sample for the optical microscopy study was a thin section of 1 μm in thickness prepared by using a cryomicrotome (Leica) at –100°C. Time-of-flight secondary ion mass spectrometry ToF–SIMS measurements were conducted on a Physical Electronics PHI 7200 spectrometer equipped with a ⁶⁹Ga⁺ ion gun. To get a flat surface for the ToF–SIMS measurements, the sample was cut using a cryomicrotome (Leica) at –100°C. An F[–] image of the composite surface was acquired using a ⁶⁹Ga⁺ ion beam operated at 25 KeV and the imaged area was 200 μm × 200 μm. To study the morphology of the composite at different temperatures, a thin section of the composite of 4 μm in thickness was prepared by a cryomicrotome at –100°C. An optical microscope equipped with a hot stage and a recording system was used. The optical microscope was operated at the transmission mode. The sample was heated from 25 to 250°C at the heating rate of 2°C/min.

3. Results and discussion

Fig. 1 depicts the log resistivity of the 10 wt% N660-filled ETFE/HDPE composite and a 47.6 wt% N660-filled HDPE composite as a function of temperature. Two sharp resistivity jumps are observed for the ETFE/HDPE composite. This phenomenon is markedly different from that of any CB-filled neat semicrystalline polymer composite which exhibits only one resistivity jump when it is heated. As temperature increases, the first resistivity jump of the ETFE/HDPE composite is observed at about 140°C, which is slightly higher than the melting point of HDPE. When the temperature further increases, the composite does not show any NTC effect but rather a strong PTC effect until the temperature exceeds the second peak temperature of about 215°C. We refer to this phenomenon as the “double-PTC

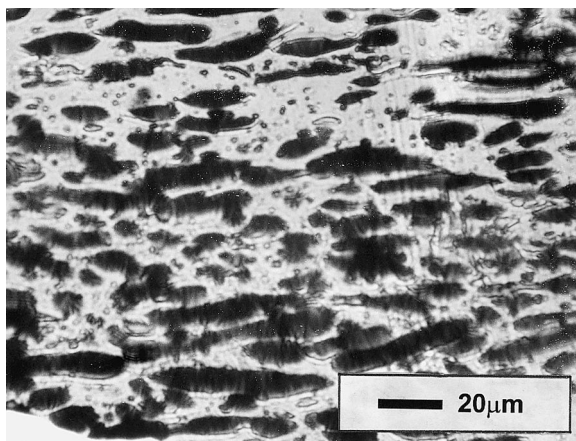


Fig. 3. Optical micrograph of the cryomicrotomed section of 10 wt% N660-filled ETFE/HDPE composite.

effect” and define the first and second resistivity jumps as the first and second PTC effects, respectively.

Fig. 2 displays a DSC thermogram of the composite. A comparison of Figs. 1 and 2 indicates that the melting of HDPE and ETFE crystallites and the two sharp resistivity jumps occur at similar temperatures. Therefore, the large volume expansion owing to the melting of HDPE and ETFE crystallites must be responsible for the first and second PTC effects, respectively.

As indicated earlier, the morphology of CB-filled immiscible polymer blend composites can significantly influence the PTC and NTC effects of the composites [14]. To get a deeper understanding of the physics behind the PTC and NTC effects of the composite in this study, its morphology was studied by optical microscopy. Fig. 3 shows an optical micrograph of the composite in which a two-phase structure is observed. Due to the high volume ratio of ETFE/HDPE, the light and dark areas are identified as the ETFE and the N660-filled HDPE, respectively, with the ETFE forming the continuous phase and the CB-filled HDPE forming the dispersed phase. To confirm this conclusion, an F^- image of a sample surface was obtained and is

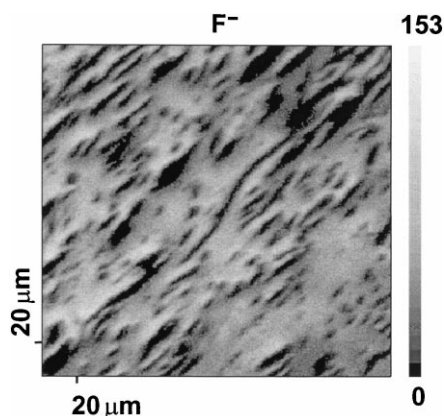


Fig. 4. F^- image of the composite surface.

shown in Fig. 4. As shown in Fig. 4, the light areas that have a high F^- intensity represent the ETFE phase, while dark areas that show the absence of F^- represent the carbon-black filled HDPE. The results of optical microscopy and ToF-SIMS are consistent. This morphology is very similar to that of the CB/HDPE composites prepared by the so-called composite filler method [10]. A composite filler is prepared by two steps. First, a conventional conductive polymer composite is prepared by mixing of CB and a polymer. Second, the obtained composite is crosslinked by either an electron beam or a chemical crosslinking agent, and then ground into a fine powder (composite filler) with the particle size less than 250 μm . This powder is dispersed in another semicrystalline polymer as a conductive filler.

The CB-filled HDPE phase in the ETFE/HDPE conductive composite that contains approximately 47.6 wt% of CB can be taken as a composite filler. In order to understand the electrical properties of the CB-filled HDPE phase, a 47.6 wt% N660-filled neat HDPE composite was prepared employing the same processing conditions used for the processing of the CB-filled ETFE/HDPE composite. The resistivity of 47.6 wt% N660-filled neat HDPE composite as a function of temperature is shown in Fig. 1. The room temperature resistivity of the CB-filled HDPE is much lower than that of the CB-filled ETFE/HDPE composite due to the absence of the ETFE separating the conductive dispersed phase. When temperature is over the melting point of HDPE, the resistivity of the CB-filled HDPE composite does not change significantly. However, the resistivity of the CB-filled ETFE/HDPE composite continues to increase owing to the thermal expansion of the ETFE, which further separates the conductive dispersed CB-filled HDPE particles.

The resistivity of the CB-filled ETFE/HDPE composite decreases as the temperature rises above the melting point of ETFE. The observation of this NTC effect in a CB-filled semi-crystalline polymer at temperatures above the melting point of the semi-crystalline polymer is very common [4–8, 12–14]. The elimination of the NTC effect, which can be achieved by crosslinking of the polymer, is usually attributed to an increase in the viscosity of the polymer. Increased viscosity is believed to be essential for the stabilization of the CB distribution in the polymer matrix. Otherwise, flocculated structures that increase the conductivity of the composite will be formed owing to the van der Waal's force of attraction that exists among the CB particles. A careful examination of Fig. 3 reveals that the smallest size of the CB-filled HDPE particles is above one micron. Therefore, it is highly unlikely that the NTC effect of this composite is caused by the formation of flocculated structures because the CB-filled HDPE particles are of a significantly large size. To further support this conclusion, the morphology of a composite sample was observed by an optical microscope at temperature ranging from 25 to 250°C, as shown in Fig. 5. The volume ratio of the CB-filled HDPE phase looks much higher than 25% because it is a

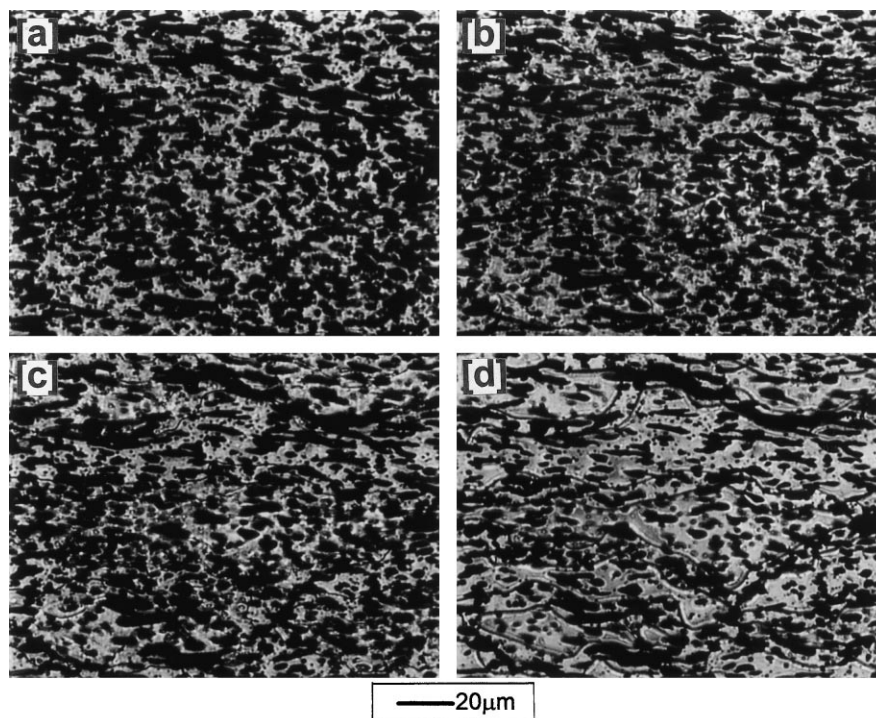


Fig. 5. Optical micrographs of the sample at various temperatures: (a) 25°C; (b) 140°C; (c) 215°C; and (d) 250°C.

relatively thick sample. A careful examination of Fig. 5 shows that the distance between the CB-filled HDPE particles increases as the temperature increases. At 250°C, no flocculated structures are observed. Thus, the results of this paper suggest that the flocculated structures formed by CB particles may not be the correct explanation for the NTC effect observed in CB-filled semicrystalline polymers. More studies are needed to identify and explore the real mechanism(s) underlying this effect.

4. Conclusions

Our results indicated that for the 10 wt% N660-filled ETFE/HDPE composite, CB particles are only selectively localized in the HDPE phase, and that the CB-filled HDPE forms a dispersed phase in the ETFE matrix. A double-PTC effect was observed and the cause was identified as the large thermal expansion owing to the consecutive melting of HDPE and then ETFE crystallites. The NTC effect that we observed in this system could not have been caused by the formation of flocculated structures because the size of the CB-filled HDPE particles is significantly large so that their mobility is extremely limited even at high temperatures. These results cast doubt on the common belief that the NTC effect observed in CB-filled semi-crystalline polymer composites is a result of the formation of flocculated structures.

Acknowledgements

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