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Positive temperature coefficient effects of carbon black-filled polytetrafluoroethylene composites

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Abstract: Carbon black (CB)-filled polytetrafluoroethylene (PTFE) composites were prepared by compact molding of a dry-mixture of CB and polymer powders followed by a sintering technology. The composites show a very low percolation threshold about 5 vol. %, which can be attributed to the segregated distribution of CB in the interfacial regions of PTFE particles. The PTFE/CB composites exhibit a high PTC transition temperature (>300 ^{0}C), high PTC intensity (3.5) and no NTC effects. The absence of NTC effect of the composites was attributed to the extremely high viscosity of PTFE at temperatures above its melting point, which restricts the migration of CB particles and prevents the formation of new conductive networks.

Key words: NaOH/thiourea/urea; coagulation; coagulate rate; mass transfer; mechanism

Introduction

Polymer resins are excellent electrical insulators, however, they can become conductive composites when blended with some kinds of conductive fillers (e.g., carbon black, carbon fiber and metal powders), the critical amount of filler necessary to build up a continuous conductive network and accordingly to make the material conductive is referred to as the percolation threshold [1-2].

Some conductive composites show a sharp resistivity increase when the temperature is close to the melting point (T_m) of the semicrystalline polymer matrix, this effect is commonly designated as the positive temperature coefficient (PTC) resistance. Because of the commercial significance of such a temperature-activated switching feature, polymer based PTC materials can be utilized in a number of applications, such as temperature sensors, self-regulating heaters and over-current protection devices [3-4].

The remarkable PTC effect was mainly observed for conductive filler-filled semicrystalline polymers and the PTC effect is often followed by a negative temperature coefficient (NTC) effect with further increase of temperature above T_m [5-6]. Although polymer based PTC materials have been known for more than half a century, a comprehensive understanding of the PTC/NTC effect has not yet been established [7-8]. The most common explanation for the PTC effect is that as the melting temperature of the polymer matrix is approached, conductive paths are broken due to a large thermal expansion caused by the melting of the crystallites [9]. It is also well accepted that the NTC phenomenon is due to the formation of the new conduction networks of carbon black particles when the viscosity of the polymer is sufficiently low at elevated temperatures [10].

The presence of the NTC effect and the poor reproducibility of resistivity over a long period of time have an adverse influence on the application of PTC materials. Many researchers have proposed and developed methods to eliminate the NTC effect and improve the stability of the conductivity, among these methods, either chemical or radiation crosslink could increase the viscosity of the polymer and produce a gel-like structure, thus leading to the stabilization of the CB distribution in the polymer melt [7, 11-12].

The PTC/NTC behavior of CB-filled polyethylene (PE) composites in the past three decades is well established [13-15]. However, when the PE is employed as a polymer host, one of the great disadvantage is the low temperature of use, because the melting temperature of HDPE is about 120 ^{0}C. Several papers have investigated the polymer PTC effect by using polypropylene (PP,T_m =167 ^{0}C) or poly(vinylidene fluoride) (PVDF,T_m =165 ^{0}C) as the polymer matrix [16-18], but the melting point of these polymer is still lower than 200 ^{0}C. There have hardly been any studies on the polymer PTC composites having a melting point higher than 300 ^{0}C because most of the polymer resins have bad thermal stability at high temperature.

In this paper, a semicrystalline polymer, namely, polytetrafluoroethylene (PTFE) was used as polymer matrix because of its very high melting point (327 ^{0}C) and high thermal stability. CB-N55O was used as conductive filler because CB is one of the most commonly used fillers in polymer PTC composites. The PTFE/CB composites were prepared using a very simple blending and sintering method. The obtained composites exhibit a high PTC transition temperature (>300 ^{0}C), high PTC intensity (>3.5). No NTC effect was observed at elevated temperatures in the absence of either chemical or radiation crosslinks.

Results and discussion

Figure 1 shows a semi-log plot of the room resistivity of PTFE/CB composites produced by compression molding of a dry-blended mixture before and after sintering as a function of the CB content. We can see that the electrical resistivity of the composites before and after sintering both decreased sharply with increasing CB content, which indicates that the composites transferred from insulating to conductive. The percolation threshold is about 3 vol. % for un-sintered composites and about 5 vol. % for sintered composites. The percolation thresholds are significantly lower than that of the CB filled polymer composites prepared by conventional melt-mixing method.

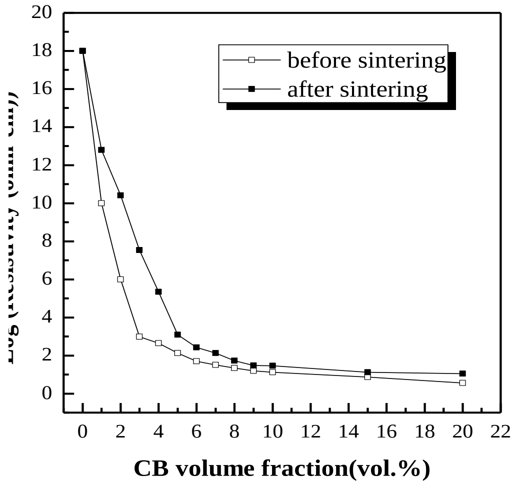

Fig. 1. Variation of the volume electrical resistivity of PTFE/CB composites with the volume fraction of CB.

For polymer based composites prepared by conventional mile-mixing method, CB particles are relatively randomly distributed in the matrix, a sufficient amount of CB particles are needed to establish conductive networks, the experimental values are usually more than 0.10 volume fraction [19-20].

For the composites prepared by dry-mixing method in our research, before sintering, when CB powders were dispersed into PTFE particles in the absence of high shear, CB powders remained essentially located at the interface of PTFE particles and do not penetrate into PTFE particles, thus attaining a segregated distribution of CB phase. This structure allows us to obtain very low values of the percolation threshold [21-22]. After sintering, the segregated distribution of CB phase can be further preserved because the extremely high viscosity of PTFE at its melt state will minimize the migration of carbon particles into the polymer matrix and deformation of the polymer particles during processing. Only a slight degree of intermixing of the carbon black and PTFE particles in the interfacial regions occured when the polymer particles fused together and formed a continues phase in high temperatures above the T_m of PTFE, resulting in a slight increase of the resistivity in comparison with the un-sintered ones [23].

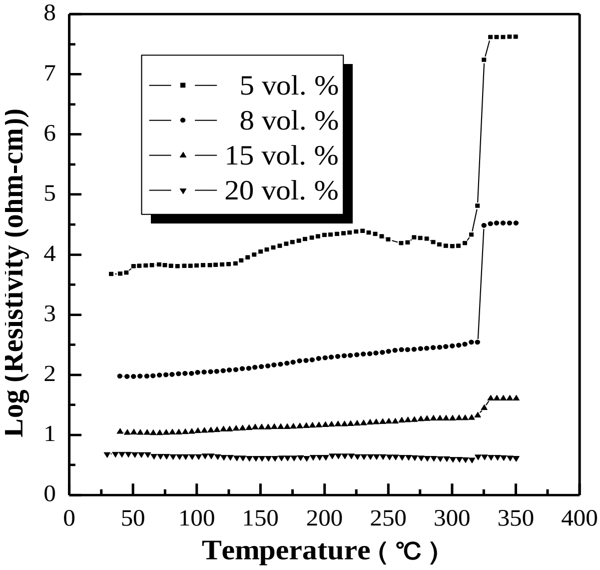

Fig. 2. The resistivity of the PTFE/CB composites as a function of temperature with various CB volume fractions.

As shown in Figure 2, the results indicate that the PTC intensity and room temperature resistivity are highly dependent on the CB concentration. At high loadings of CB, the composites exhibit a very weak PTC effect and a low room temperature resistivity. Typically, at the CB content of 20 vol. %, the room temperature resistivity of PTFE/CB composite is 4.57 ohm-cm, but the composite shows nearly no PTC effect. Both the PTC intensity and room temperature resistivity increased with the decrease of the CB content. These can be attributed to the variation of conduction mechanism in various loading of CB content. At high CB loadings, the CB particles and their aggregates directly contact with one another even at the temperatures above the T_m of PTFE, resulting in a main conduction mechanism of ohmic conduction [24]. The expansion of PTFE particles would only decrease the dimensions of the conductive pathways but not break them up, so the PTC effect of these composites with high CB contents was very weak and got even weaker with the increasing of the CB concentration. Particularly, when the CB concentration is much higher than the percolation threshold value, the decrease of the dimensions of conductive pathways caused by thermal expansion could be neglected, thus, no PTC effect was found in the materials with CB content at 20 vol. %.

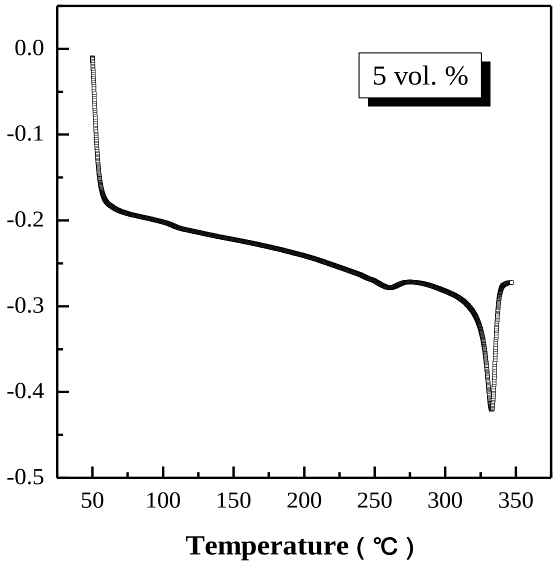

Fig. 3. DSC scans for 5 vol. % CB-filled PTFE composites.

As the CB concentration gradually decreased, the dimensions of conductive pathways get narrower and even not continuous. The main conductive mechanism transformed from ohmic conduction to quantum tunneling conduction where conductivity is mainly the result of electron tunneling through small gap distances separating the CB particles and their aggregates [1]. When the width of the gaps increases by thermal expansion of PTFE matrix, the electron tunneling probability will diminish, which results in a strong PTC effect.

Commonly, without chemical or radiation crosslink, the polymer PTC composites exhibit a NTC effect when the temperature further increases above the melting point of the polymer. The cross-linking treatment not only increases the processing cost, but also results in an increase in the room resistivity. However, the PTFE/CB composites in our research exhibit no NTC effect even at temperatures significantly higher than the melting point of PTFE without any cross-linking treatment. The absence of NTC effect in PTFE/CB composites is attributed to the extremely high viscosity of PTFE matrix which restricts the migration of CB particles and prevents the formation of new conductive networks [25].

Figure 2 also show that the resistivity peaks are observed at about 330 ^{0}C for PTFE/CB composites regardless the CB concentration, a temperature at approximately its T_m of PTFE (T_m =332 ^{0}C) as determined by differential scanning calorimetry (DSC) and shown in Figure 3. This result reveals that the PTC effect of the composites is caused by thermal expansion due to the melting of the PTFE crystallites in the composites.

Conclusions

The PTFE/CB composites prepared by compact molding of a dry-mixture of CB and polymer powders followed by a sintering technology exhibit a low percolation threshold of about 5 vol. %. The low percolation threshold of the composites was due to the segregation of CB in the interfacial regions of PTFE particles. The composites exhibit distinct PTC effects when the CB volume fraction is equal to or slightly higher than the percolation threshold. The composites show a very high PTC transition temperature at about 332 ^{0}C and no NTC effect was observed at elevated temperatures. The extremely high melting viscosity of PTFE restricts the migration of CB particles and prevents the formation of new conductive networks, thus eliminating the NTC effect of the composites.

Experimental part

Materials

The PTFE powder was obtained from SiChuan ChenGuang chemical academe of china and used as received. Electrically conductive CB-N550 was purchased from Cabot Corporation (ShangHai, China). The CB powders were dried in an over at 120 ^{0}C for 2 h prior to mixing. Since PTFE has very high melt viscosity (380 ^{0}C, $>10^{11}$ Pa·s), common processing techniques used for the fabrication of thermoplastics such as injection molding, melt extrusion, etc. could not be employed for the fabrication of PTFE products. Thus, our composites were prepared by a dry mixing method. All of the starting materials were weighed according to the desired compositions and were prepared by dry mixing in a pestle mortar by means of hand. The mixture was cold pressed at 30 MPa, yielding a black disks 16-mm diameter and 2-mm thick. The compacted disks were sintered at a temperature of 380 ^{0}C for 2 h. For electrical properties measurements, the surfaces of the disc were painted with silver paste. The room resistivity along the sample thickness was measured by the “two-terminal method” on a Fluke 45 Dual Display Multimeter when the resistivity is lower than 10^8 ohm-cm, and on a ZC36 High Resistance Electrometer when the resistivity is higher than 10^8 ohm-cm. The resistivity as a function of temperature was measured using a Resistivity-Temperature Tester which comprises of a computer, a multimeter, and a programmable oven. The melting behavior of the composites was determined using a differential scanning calorimeter (DSC) (Q10, TA Instruments) under a nitrogen gas atmosphere.

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