Temperature dependence of the conductivity in conducting polymer composites

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The temperature dependence of the electrical conductivity of a conducting polymer composite is reported from 77 to 450 K. The relationship between the temperature dependence of the conductivity and the structure of the composite is discussed. The low-temperature electrical resistivity of low-density polyethylene/polypyrrole composite was also investigated and a linear relationship between the resistivity and $T^{-1/4}$ was found in the liquid-nitrogen temperature range.

(Keywords: electrical conductivity; polypyrrole; filled composite)

INTRODUCTION

The electrical properties of conducting composites have been extensively reported, and most works are concerned with carbon–polymer composites. The insulator–conductor transition in these composite systems is often sharp and characterized by a critical carbon loading, the percolation threshold. The complex geometry and structure of carbon-black aggregates and the agglomeration phenomenon reduce the percolation threshold and enhance the conductivity of the composites[1-3].

The strong temperature dependence of the conductivity of polymer composites containing carbon black, which is particularly pronounced at the percolation threshold, is used in the design and fabrication of electrical switching devices. The phenomenon of resistivity of a filled polymer composite increasing with temperature is referred to as a positive temperature coefficient (PTC). PTC often occurs below a transition temperature. Above this temperature, however, a more conductive network may be formed and a lower resistivity is observed. This phenomenon is referred to as a negative temperature coefficient (NTC). PTC behaviour has been reported for filled semicrystalline and amorphous polymers[4-6].

In semicrystalline matrices, Kohler[7] suggests that the PTC mechanism is a function of the difference in the thermal expansion of the material as the melting temperature is approached. The theory of Ohe[8] assumes a more uniform distribution of inter-particle gaps at low temperature. In the vicinity of the melting point, the distribution becomes more random and, although the average gap width is not considerably changed, the presence of a significant number of inter-particle gaps that are too large to allow electron tunnelling results in the elimination of many current paths through the material, with a resultant rise in resistance. This theory does not explain why the distribution should become more random at higher temperature or the influence of matrix nature on the PTC phenomenon. The theory of Meyer[7] supposes that thin crystalline films of polymer are significantly better conductors than amorphous films of polymer and that there is a thin film between the conductive particles. The state of the film causes the change of resistivity on heating.

We recently reported on the conductive behaviour and stability of insulating polymer/conductive polymer composites, the properties of which are comparable to those of the polymer/carbon-black composite[9]. We present here the temperature dependence of the conductivity in the temperature range 77 K < T < 450 K. The difference in the temperature dependence between the different insulating polymer/conductive polymer composites is discussed.

EXPERIMENTAL

The conductive polymer used in our experiments is a polypyrrole powder (PPY) synthesized at room temperature from a 30% $FeCl_3$ aqueous solution and a

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10% pyrrole solution in acetonitrile with a molar $FeCl_3$/pyrrole ratio of 1:2. Two insulating polymers are used: low-density polyethylene (LDPE; DXM 430N) and polystyrene (PS; Perle T8). The composites are prepared as follows: LDPE and PPY are added to toluene (GC, >99%, Merck) and then heated to about 100°C. When LDPE is totally dissolved, the mixture is cooled slowly to room temperature while being continuously stirred. Then the solvent is filtered off and the mixture of LDPE/PPY is dried at room temperature. For the PS, CH_2Cl_2 is used as solvent, and mixing and drying are carried out at room temperature. The mixture of LDPE/PPY or PS/PPY is then pressed into a plate by compression moulding at 120°C for LDPE/PPY and 150°C for PS/PPY under 20 MPa for 5 min, and then for 10 min under the same pressure at room temperature.

The typical dimensions of the sample used for high-temperature measurements were $0.2 \times 0.5 \times 3\,cm^3$. The electrical conductivity of the composite at high temperature was measured by means of a programmable electrometer (Keithley 617). The sample contact surfaces with the probes were polished and silver paint was used in order to decrease the contact resistance. The heating rate was about $2°C\,min^{-1}$ and a thermocouple, which is thermally anchored to the sample surface, is used for measuring the sample temperature. The measurement of the low-temperature electrical resistivity of the composite is limited to the liquid-nitrogen temperature range. The samples, having dimensions $0.2 \times 0.5 \times 1.5\,cm^3$, were usually prepared for a four-contact measurement technique. A gold layer was first evaporated onto the sample surface, then the electrical leads were glued to the sample by means of silver paint. The measurement details are found elsewhere in ref. 10.

RESULTS AND DISCUSSION

The temperature variation of the electrical conductivity of the composite at high temperature is shown in *Figure 1*.

For the PS/PPY composite (*Figure 1a*), the electrical conductivity is almost temperature-insensitive from room temperature up to slightly above T_g. Then above 125°C the conductivity is slightly decreasing in the first heating cycle, but this slight decrease in conductivity disappears in the second heating cycle. The electrical conductivity then begins to increase with increasing temperature, which corresponds to NTC behaviour.

For the LDPE/PPY composite (*Figure 1b*), the PTC and NTC phenomena are both observed. The electrical conductivity decreases first with increasing temperature and reaches its minimum (on heating) at about the melting point of the polyethylene. On cooling, the electrical conductivity increases and the NTC phenomenon is observed. The intensity of the PTC and NTC effects of LDPE/PPY composite is different for different polypyrrole contents.

The PTC is associated with the interruption of the percolation path. When a composite is heated, owing to the difference in thermal expansion between the charge and the polymer matrix, the composite structure is modified, and this results in an interruption of the percolation path. As a matter of fact, the interruption of the percolation path is a dynamic process: simultaneously with the interruption of the percolation path, other new percolation paths can be formed[11].

On heating the LDPE/PPY composite, the thermal expansion induces the interruption of percolation paths, and the PTC phenomenon is observed. It is worth noting that the intensity of PTC for the 40% PPY/LDPE sample is much lower than for the 15% PPY/LDPE sample. It may be considered that, at high polypyrrole concentrations, as the conductive particles are very close to each other, it is easy to form new percolation paths when the interruption of any percolation path occurs due to particle motion. But at low polypyrrole concentrations, the distance between the conductive particles is relatively large (compared to the particle mobility) and the possibility of forming new percolation paths is relatively low. This explains why different intensities of PTC can be observed for different LDPE/PPY composites.

Around the melting point, an increase of the electrical conductivity is observed. New conducting networks due to polypyrrole particle reaggregation are likely to occur[12]. On cooling, the conductivity increases and a maximum is observed, which may be related to the crystallization of polyethylene. When the LDPE crystallizes, it rejects the polypyrrole particles from the crystalline phase and enhances, in this way, the conductive network in the composite. The net result is an increase of the electrical conductivity.

For the PS/PPY composite, the temperature dependence of the conductivity is different from that for LDPE/PPY. No obvious PTC phenomenon can be observed below T_g, while above T_g a significant increase in conductivity is observed.

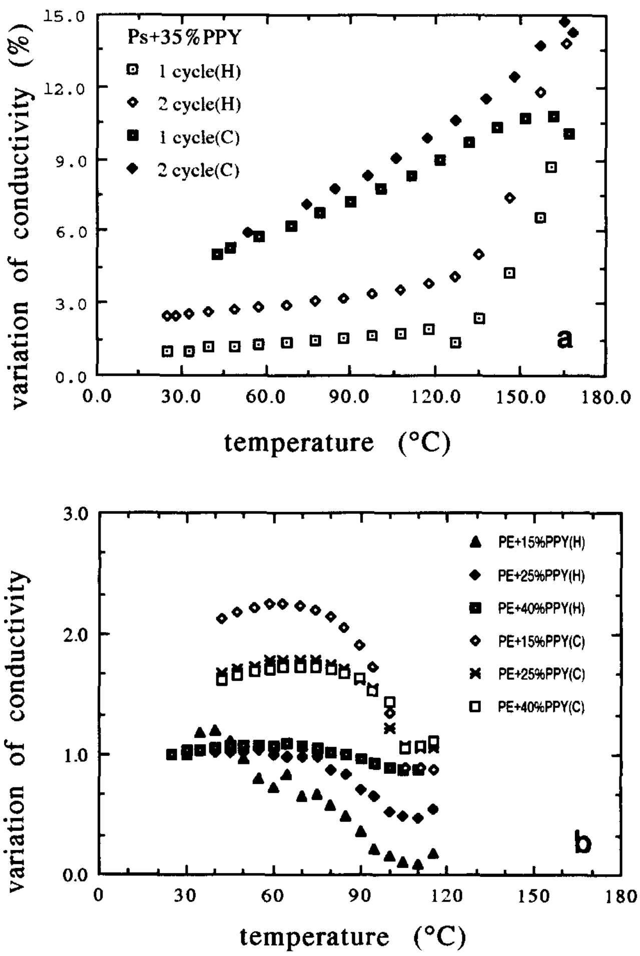

Figure 1 The temperature variation of the composite conductivity during heating (H) and cooling (C): (a) PS + 35 wt% PPY; (b) PE + PPY composites (first cycle)

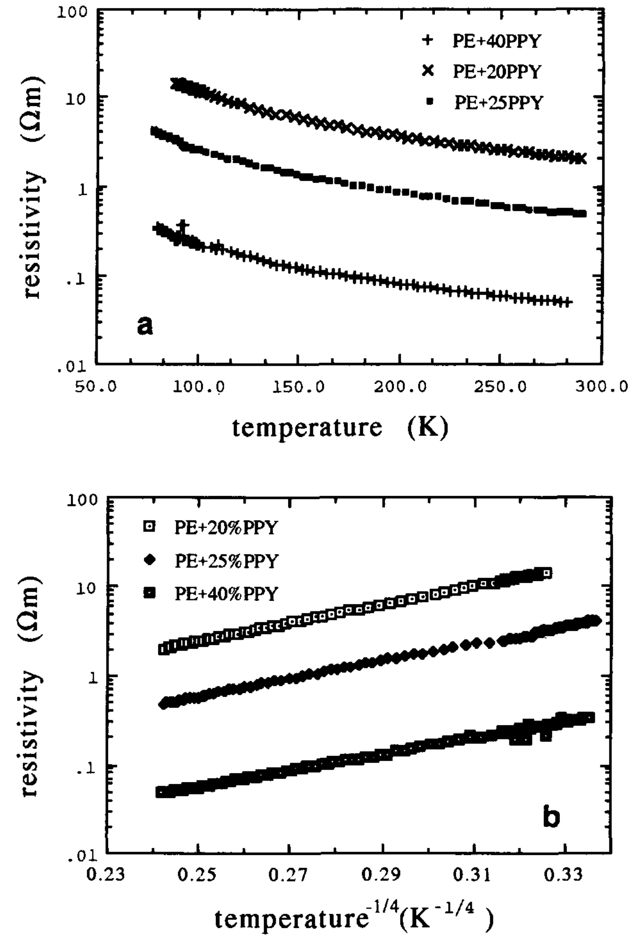

Figure 2 The variation of electrical resistivity of LDPE/PPY composite as a function of: (a) temperature (K) and (b) $T^{-1/4}$ ($K^{-1/4}$)

The polypyrrole particles in PS/PPY composites are well dispersed[9] and a good dispersion is favourable for particle reaggregation leading to new conducting networks, which result in a significant increase in conductivity. On cooling, no maximum in conductivity is observed for the PS/PPY composite. A decrease of conductivity witnesses a partial disappearance of conducting networks that were formed at high temperature.

We recently presented the stability of the electrical conductivity upon composite annealing at 55 or 80°C. The LDPE/PPY composite is unstable but the PS/PPY composite is stable for long annealing periods of time[9]. The annealing mechanism seems to be associated with the relaxation of the polymer chains. The decrease of conductivity during annealing probably arises first from the increase of the distance between the polypyrrole particles due to dilatation, and secondly from a relaxation phenomenon, which changes the contact situation between the polypyrrole particles. The result is either the interruption of direct contact between polypyrrole particles or an increase of the distance between the polypyrrole particles leading to the interruption of the percolation path.

Since the relaxation time of a polystyrene chain at the annealing temperature is longer than the annealing time, the conductivity of the corresponding composite is very stable. Considering the temperature dependence of PS/PPY composite, another possible explanation lies in the proximity of the dilatation coefficient of PPY and PS.

Figure 2 shows the temperature variation of electrical resistivity of the LDPE/PPY composite in the liquid-nitrogen temperature range. It may be seen that the electrical resistivity of the composite increases with the decrease of temperature. The variation of the resistivity of the composite is comparable for the different polypyrrole contents in the liquid-nitrogen temperature range. A linear relationship between the electrical resistivity and $T^{-1/4}$ is observed (*Figure 2*). Considering that this relationship is also found for pure polypyrrole synthesized in the same conditions[13], it may be deduced that the conducting networks in the composite are probably formed principally by direct inter-particle contacts.

CONCLUSION

The temperature dependence of the conductivity of insulating polymer/conductive polymer composites is studied to the range 77–450 K. It shows that the temperature dependence of the conductivity depends on both the insulating polymer and conductive polymer used. A PTC phenomenon is tentatively explained by the interruption of the percolation path and an NTC phenomenon relates to the polypyrrole particle reaggregation to form new conducting networks in the composite. The resistivity–temperature characteristic of LDPE/PPY composite is very similar to that of the polypyrrole in the liquid-nitrogen temperature range, and this suggests that the conducting networks in the composite are principally formed by direct inter-particle contacts.

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