

Anomalous electrical behaviour of polymer–carbon composites as a function of temperature

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In the field of electromagnetic interference, there has been great interest in finding a lightweight and conductive shielding material. In this composite study, several carbon blacks and PAN carbon fibres were added to amorphous (polystyrene) and crystalline (polyethylene) polymer matrices. This effort sought to examine the electrical conduction mechanisms and the effects of temperature and processing conditions on the electrical conductivity of polymer–carbon composites. To this end, conductivity experiments were conducted in isothermal, cycled, and annealing temperature conditions.

1. Introduction

In order to improve the electrical conductivity of polymers, one may simply introduce a conductive or semi-conductive material into the polymer matrix (i.e. create a composite). In the case of poly(vinyl chloride) with the addition of carbon particles, one observes a twelve-order-of-magnitude increase in electrical conductivity [1]. The degree to which one enhances conductivity depends upon a great many parameters: the volume fraction of the additive in the polymer; the inherent conductive properties of the filler; the particle size of the conductor; the extent of homogeneity of the composite system; and the intrinsic physical properties of the polymer.

Three distinct physical processes govern electron transport in insulator–conductor composites: percolation, tunnelling, and thermal expansion [2]. In general terms, percolation, like diffusion, is a means of transport within a disordered medium. Although both demonstrate random motion, only diffusion follows a true random-flight model. Whereas in diffusive transport there exists a finite probability for movement in any direction, a percolative walk dictates that certain directions of motion lead to particle entrapment. Conductive particles which become surrounded by an insulator matrix are unable to participate in any percolative path. However, as additional particles are added to the polymer, the conductivity increases dramatically at or about a specific volume of conductor. This abrupt change in conductive properties occurs at the percolation threshold. At this critical volume of filler, one observes a continuous path of conducting particles through the polymer. As one exceeds the percolation threshold, the composite conductivity approaches the intrinsic conductivity of the conductor [3–5].

If the volume fraction of conducting filler is below the percolation threshold, the conductive particles are

no longer in contiguous chains but are separated by the insulating matrix. When the separation distance is small (< 10 nm), electrons can tunnel quantum mechanically between conductors [2, 3, 6, 7]. In addition, conductor particle size, particularly cross-sectional area, greatly impacts on conductivity due to the greater area over which the electrons may tunnel. The enhanced tunnelling capacity overcomes the insulative effects of the polymer and causes an increase in conductivity.

Past research has determined that the property of polymers to expand thermally creates a strong dependence of conductivity on temperature. Therefore, the separation distance between conductive particles varies with temperature [2, 3, 8, 9]. Thermally induced movement of the matrix and, consequently, the specific geometry of the conductive filler greatly affect percolation and tunnelling. As the volume fraction of conductor lessens, the conductivity also diminishes. The energy barrier to tunnelling is directly proportional to separation distance; therefore, as temperature increases, one finds a distinct reduction in tunnelling conductivity [2, 10].

An additional component to the electrical performance of the composite is the intrinsic properties of the conductive filler. In the following work, two different materials were used as conducting phases: carbon black and carbon fibres. Three inherent properties of carbon black control its effect upon the electrical conductivity of a composite: size, agglomeration tendencies, and particle structure. Smaller particle size improves conductivity because one may fit more small particles into the same volume and increase the opportunity for percolation paths [11–13]. Consequently, particle agglomeration attenuates conduction [3, 8, 10, 11–14]. Geometries of the primary particle aggregates directly affect the electrical behaviour [11–14]. This property, known as structure, denotes

the aggregation of particles into "tree-like" or branched primary units [2, 11, 12]. A high-structure carbon black generally has higher conductivity than a lower structure sample with the same particle size and same surface-area.

In a good solvent, the polymer-polymer interactions are not as strong as the polymer-solvent attractions. In order to affect a conformation which maximizes this energetically favoured situation, the polymer coil expands to spread out in solution. In a poor solvent, the polymer-polymer attractions are greater than the solvation forces; therefore, the chains contract onto themselves. If a polymer is initially in the presence of a good solvent and if a significant amount of poor solvent (with respect to the polymer, but both solvents are miscible) is added, the polymer will rapidly contract and precipitate out of solution. This rapid contraction of polymer chains may entrap particles which were suspended in solution among the random polymer coils.

2. Experimental procedure

2.1 Sample preparation

2.1.1. Polystyrene samples

In an ultrasonic cleaner, polystyrene (2.5×10^6 molecular weight) samples (approximately 1 g) were dissolved in a 150 ml beaker of 50 ml warm methyl ethyl ketone (MEK). After the polymer had dissolved fully, the carbon species was added to the already agitating solution. These sonic vibrations rendered further advantages by breaking up the carbon black agglomerates and preventing particle flocculation and settling. The mixing procedure continued for 30 min in order to maximize dispersion. The sample was then added to a 400 ml beaker containing 150 ml swirling cold absolute ethanol. It was in this step that free-moving polystyrene chains contracted upon nearby carbon species as the system was doused into the non-solvent ethanol. The resulting precipitate and solution was then filtered through a Buchner funnel. The filtrate was washed with additional cold ethanol to remove any remaining MEK. Suction was continued

until the sample began to flake and form powder. The flakes were broken up using a spatula to form a fine powder. After placing in a small vial, the material was placed in a near-vacuum for at least 48 h. Following vacuum treatment, the sample was placed in an oven at 80 °C for 72 h.

Approximately 0.4 g sample was placed in a 13 mm diameter vacuum die press, compressed lightly under vacuum, and left in a 190 °C oven for 30 min. While the die was still hot, the sample was further pressed under vacuum using a uniaxial press. After about 5 min while the die was still very warm, vacuum and pressure were released, and the sample was removed. This step prevented the composite from adhering to the metal components of the die. Following removal from the die, the samples were examined for evidence of polymer degradation. Despite the elevated temperature, the compacts appeared smooth and glossy.

2.1.2. Polyethylene samples

Under a nitrogen atmosphere, 1 g polyethylene (2.5×10^4 mol.wt) was dissolved in a three-necked flask of 200 ml refluxing xylene ($T = 140$ °C). The carbon was added carefully to the boiling solution and allowed to mix for approximately 30 min. The solution was quickly cooled by removing the flask from the heating mantel. Using a Buchner funnel, the precipitate was removed and dried. In a further attempt to remove xylene, the sample remained in a 70 °C oven for 24 h. As with the polystyrene samples, approximately 0.4 g composite were placed in a 13 mm die, heated to 140 °C, and pressed into discs. Table I contains a brief comparison of some of the properties of the two polymer matrices [1].

2.1.3. Carbon black and carbon fibres

Three different types of carbon black were used in polystyrene matrices: Black Pearls 2000, Vulcan XC-72, and Sterling NS. A listing of these carbon blacks and some of their properties may be found in Table II [15]. A PAN carbon fibre (0.8 nm diameter)

TABLE I Summary of polymer properties

Polymer	Glass transition temperature (°C)	Melting temperature (°C)	Electrical conductivity ($\Omega \text{ cm}^{-1}$)
Polystyrene	100	none	10^{-15}
Polyethylene	-170 to -85	125-135	10^{-16}

TABLE II Summary of carbon black and graphite properties

Carbon black	Particle size (nm)	Structure	Surface area ($\text{m}^2 \text{ g}^{-1}$)	Electrical conductivity
BP-2000	15	Very high	1475	Very high
Vulcan XC-72	30	High	254	High
Sterling NS	75	Low	25	Medium
Graphite	Variable	Variable	Variable	3.5×10^3 $\Omega \text{ cm}^{-1}$

was also used as a conductive filler in polystyrene samples. In the polyethylene matrices, only BP-2000 was used.

2.2. Electrical conductivity measurements

All bulk electrical conductivity measurements were performed using a two-point probe technique. Two 13 mm diameter platinum electrodes with thin indium plates were placed in compression on each face of the composite sample. The indium was added to enhance electrode-sample contact. Temperature-dependent experiments were carried out in a reaction tube heated by a tube furnace. Alternating current conductivities were performed utilizing a General Radio 1658 RLC digi-bridge.

Owing to the relatively high thermal expansion coefficient of polymers, much effort has been extended to study the thermal-electric behaviour of polymer-carbon composites. During rapid heating and cooling (around $10^{\circ}\text{C min}^{-1}$), these materials have shown a positive temperature coefficient (PTC); that is, resistivity increases as a function of temperature [3, 9, 16]. The polymer with a higher coefficient of thermal expansion increases its effective volume fraction over the carbon species, thus increasing the average particle-particle separation distance. Consequently, if a polymer composite contains a volume fraction of conductive filler just above the percolation threshold then, when the polymer expands slightly, the system falls below the threshold and a large attenuation of conductivity ensues [9]. Although the PTC effect can cover a large temperature range, most literature considers this behaviour near and above the melting point. In this work, a more general definition has been used including temperatures above the glass transition temperature.

2.3. Time-temperature experiments

Using the apparatus discussed above, two different types of temperature dependent experiment were conducted. In the first case, temperatures were increased at about 10°C increments and held for at least 24 h at a given temperature. The conductivities were measured as readings stabilized. The temperature was in-

creased to near 120°C for polyethylene and 135°C for polystyrene. In the second variety of experiment, the samples were heated as stated previously and then cooled at approximately 10°C increments. During the cooling process, it became imperative that a 24–36 h period of equilibration occur in order to decrease conductivity fluctuations. After returning to room temperature, the cycle was repeated. For polyethylene, this temperature of 120°C was chosen as a maximum temperature for two reasons: first, polyethylene begins to melt at around 125°C ; and secondly, the indium plates soften, flow, and finally melt at 156°C . In the third experimental procedure, polystyrene samples were heated to 140°C , cooled to room temperature, their conductivity measured by a four-point probe, then reheated repeatedly to 140°C in a 200 h experiment. In Fig. 1, an outline of these experimental procedures is given.

3. Results and discussion

3.1. Two-point probe with changing temperature

In Fig. 2, the effect of temperature on conductivity is shown. Fig. 2 also provides insight into the temperature-conductivity profile for 13, 20 and 23 vol% BP-2000 in a polyethylene matrix. In these experiments, care was taken to avoid exceeding the melting temperature of polyethylene ($\approx 125^{\circ}\text{C}$) in order to prevent a catastrophic loss in conductivity (when the polymer melts it expands) [9]. In all three samples, the electrical conductivity increased as a function of temperature. Additionally, it was found that the lower the volume per cent of carbon black in a sample, the greater was the increase in conductivity. Past work has suggested that polyethylene-based composites show a positive temperature coefficient (PTC) [1, 8, 9]. This terminology refers to resistivity rather than conductivity. By this convention, this work indicates a negative temperature coefficient (NTC), disagreeing with earlier efforts.

To ensure experimental validity, several studies were conducted to examine the possible existence of systematic error. Materials, such as AgCl whose electrical behaviour has been studied as a function of

(a) Polyethylene	→ increase temp. at 10°C increments	→ hold for 24 h	→ measure conductivity	→ repeat until $T \approx 120^{\circ}\text{C}$
(b) Polystyrene	→ increase temp. at 10°C increments	→ hold for 24 h	→ measure conductivity	→ repeat until $T \approx 135^{\circ}\text{C}$
(c) Polyethylene	→ increase temp. at 10°C increments decrease temp. at 10°C increments	→ hold for 24 h	→ measure conductivity	→ repeat until $T \approx 120^{\circ}\text{C}$
(d) Polystyrene	→ heat sample and hold at 140°C	→ cool to room temperature	→ measure conductivity	→ repeat until sample has spent 200 h in total at 140°C

Figure 1 A schematic representation of the procedures followed in time-temperature measurements: (a) polyethylene time-temperature experiments, (b) polystyrene time-temperature experiments, (c) polyethylene cycling experiments, and (d) polystyrene annealing experiments.

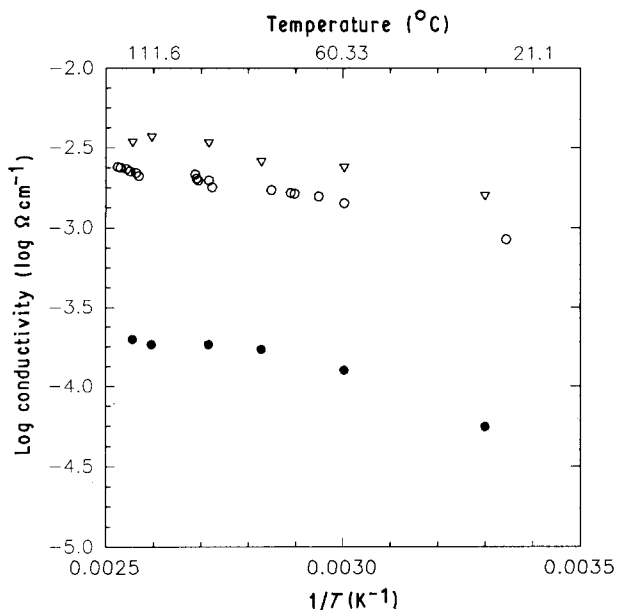


Figure 2 Conductivity versus temperature for polyethylene-carbon black (BP-2000) samples. (∇) PE 23, (\circ) PE 20, (\bullet) PE 13.

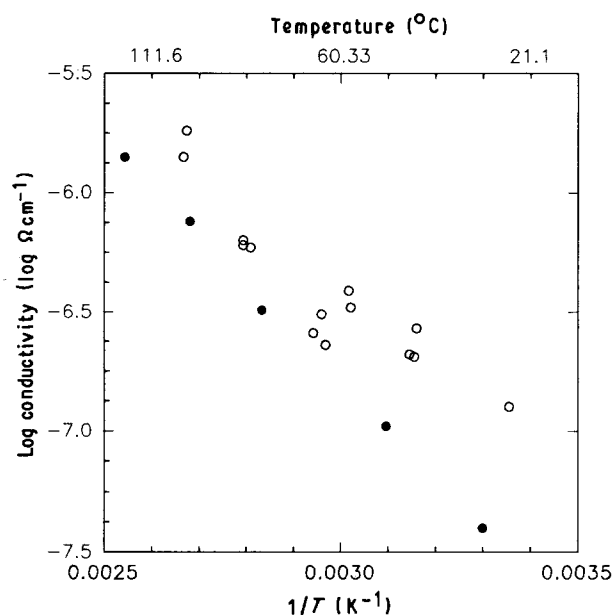


Figure 3 (\circ) Conductivity versus temperature for AgCl compared with literature values (\bullet) [17].

temperature, were monitored (see Fig. 3) in the apparatus [16]. The results showed reasonable agreement with established data. Therefore, it seems logical to conclude that the method of measurement is not responsible for the unusual results.

Another possible cause for these differing data could be the method of sample processing. All composite systems in this study were mixed in solution and precipitated from that same solution. This method differs greatly from the dry shear mixing (often using a Braebender mixer) and the hot pressing used in most past and many current studies [3, 8, 9]. It is conceivable that solution mixing may produce a more random distribution of carbon black particles because the polymer chains rapidly contract around the particles during precipitation. This solution-mixing hypothesis assumes that the particles were homogeneously dis-

tributed in the polymer-solvent solution. This mechanism provides an opportunity for the polymer to surround or coat carbon black aggregates prior to hot pressing, which is not found in shear mixing. This "polymer coating" phenomenon may prevent reagglomeration of carbon black particles and avoid the concomitant loss of carbon black surface area. Above the glass transition temperature, polymer chain motion is initiated which may break up percolation paths. The likelihood for the interruption of these paths increases if some degree of reagglomeration is present or if the particle distribution is not reasonably random. If there has been no significant reagglomeration and the carbon black aggregates are randomly distributed, then any reordering of the composite which destroyed percolation paths would create new ones.

This notion of path repair is supported by the laws of probability which govern percolation theory. In other words, as long as the randomness of the distribution and the surface area of the conductive filler are constant, then the probability of the same number of percolation paths is unchanged. Therefore no loss of conductivity would result. The NTC would be a result of the intrinsic NTC of the carbon black. Conversely, if either parameter were affected, then a PTC would appear.

The question arises: why does the poorly distributed or highly agglomerated composite form percolation paths in the first place? During the sample processing, the material is pressed in a die. The pressing procedure is uniaxial and, thus, improves the probability of particle-particle contact in the pressing direction, because the die walls prevent the particles from spreading out and avoiding each other.

In Figs. 4 and 5, the temperature-conductivity behaviour of polystyrene-based composites is shown. Three types of carbon species are considered in these figures: PAN carbon fibres, NS Sterling carbon black, and BP-2000 carbon black. In Fig. 4, the electrical

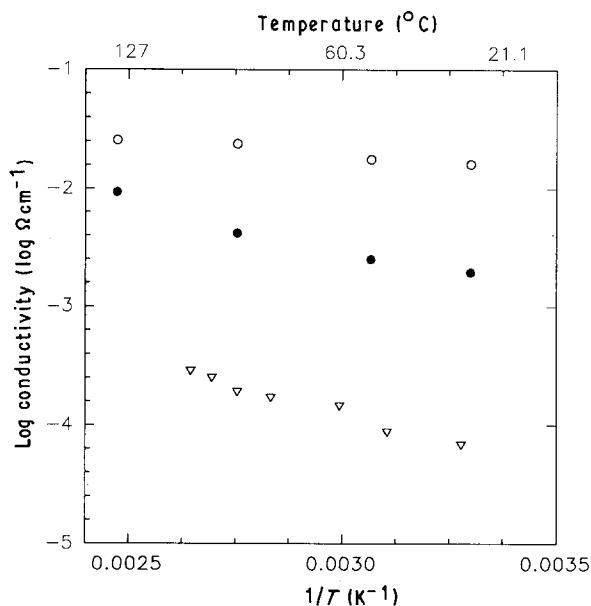


Figure 4 Conductivity versus temperature for polystyrene with (∇) 7, (\bullet) 14, and (\circ) 35 vol % BP-2000.

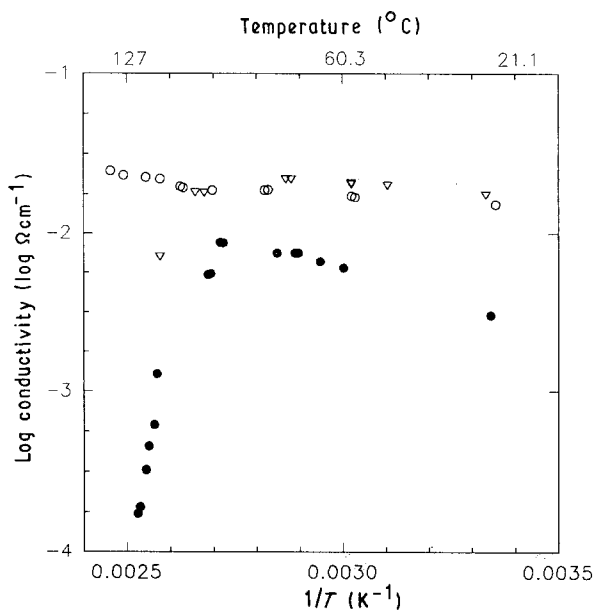


Figure 5 Conductivity versus temperature for polystyrene with (●) 28 and (○) 40 vol % carbon black (NS Sterling) and (▽) 15 vol % carbon fibre.

behaviour as a function of temperature for 7, 14, and 35 vol % BP-2000 is shown. Recall that BP-2000 is a highly structured and ultra-high surface area carbon black which was also used in the polyethylene matrix experiments discussed previously. Like its polyethylene counterpart, polystyrene samples show NTC behaviour above their glass transition ($\approx 105^\circ\text{C}$ from DSC measurements); however, these samples show an increase in conductivity as a function of temperature below the T_g as well.

In Fig. 5, carbon fibres and NS Sterling are the conductive fillers in polystyrene. In the cases of 15 vol % fibre and 28 vol % NS, a dramatic decrease in conductivity occurs above the glass transition temperature. The 40 vol % NS sample shows no change in its NTC behaviour even 30°C above T_g . Major differences in this experiment and the BP-polystyrene work are the size and structure of the conducting phase. Whereas BP-2000 particles are about 15 nm diameter and have a very high surface area, carbon fibres are 8–10 μm diameter and between 0.1 and 0.75 mm long, NS particles are about 75 nm diameter and have a reasonably low surface area. This tremendous disparity in surface area could well account for the differing behaviour. As described for polyethylene, low surface area and a less-than-optimum particle distribution could drastically alter conductivity when chain motion exists. The poor distribution results because of the considerable size difference between BP-2000 and the larger fibres and NS particles. Therefore, fewer particles (or fibres) are required to make up the same volume per cent conductive filler. The fewer number of particles decreases the opportunity to create a percolation path after polymer chain motion has destroyed a previous one. However, if enough particles exist in the matrix, then percolative paths will “die” and “be born” in approximate equilibrium. This may explain why NS-40 behaves as the BP samples. It is also apparent from Fig. 5 that many more NS-28 and

PSF-15 percolation paths are being destroyed by polymer chain motion than are being created due to the large size of the particles and their smaller number.

3.2. Temperature cycling experiments

The second variety of temperature–conductivity experiments are the temperature cycling efforts. The method of measurement is much the same as those described above, with the addition of cooling steps, an additional heating procedure, and a final cooling cycle. In Fig. 6, 13 and 23 vol % BP-2000 in polyethylene were cycled through two heating and cooling cycles spending at least 24–48 h at each temperature. The salient point of both of these figures was that only the initial heating procedure was significantly different from all of the other temperature changes. It appears that following the first thermally induced matrix rearrangement the composite achieves an equilibrium (at least in terms of the temperature–conductivity behaviour).

3.3. Four-point probe at constant temperature

The final experimental procedure in this study required the measurement of conductivity as a function of time at 140°C (above the glass transition of polystyrene). Fig. 7 shows the increase in conductivity as a function of time. This obvious improvement in electrical conduction is thought to be caused by a realignment of the polymer matrix chains which may create preferred percolation paths of carbon particles. Because the polymer chains are unable to translate at temperatures below their glass transition, a reorganization of the matrix is possible at temperatures above this transition. The glass transition temperature of polystyrene is about 100°C ; therefore, some polymer chain motion should exist at 140°C . An additional interpretation of these results may be that during

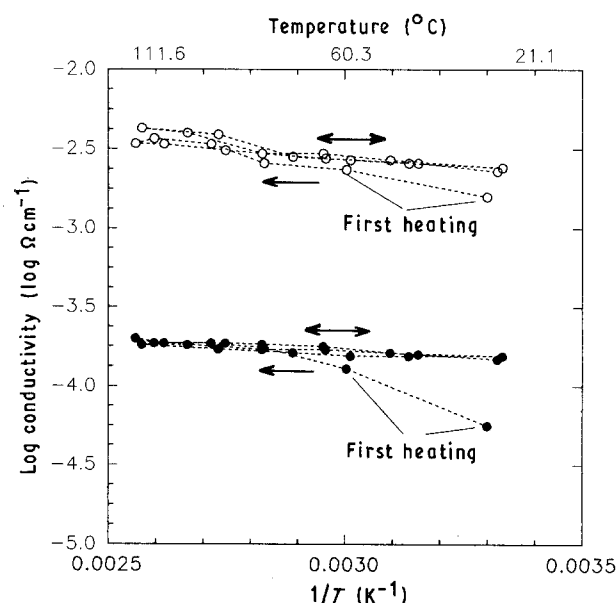


Figure 6 Conductivity versus temperature for heating and cooling cycles for polyethylene with (●) 13 and (○) 23 vol % carbon black (BP2000).

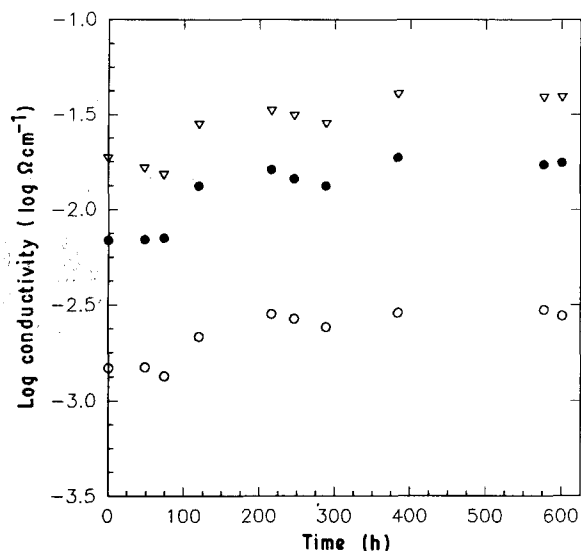


Figure 7 Four-point probe conductivity versus time held at 140 °C of polystyrene-carbon black samples: (○) 14 and (●) 28 vol % Black Pearls 2000 and (▽) 36 vol % Vulcan XC.

sample preparation, the polymer-carbon precipitates do not become totally intermingled during the heating and pressing stage. Furthermore, increased temperature annealing provides enough time to allow a more homogenized composite. Additionally, this intermingling of precipitates creates the opportunity for greater carbon particle-to-particle contact. This phenomenon is accomplished by freeing the outer layer of polymer chains from the precipitate, thus exposing the underlying carbon particle. If more conductive particles are in contact, then conductivity should increase.

4. Conclusion

Past conductivity-temperature work on polyethylene composites has indicated PTC behaviour below the melting temperature. In this work the polyethylene samples showed a reproducible increase in conductivity as a function of temperature.

In polystyrene composites, the high surface area carbon blacks (BP-2000) show uninterrupted NTC behaviour. Carbon fibres and low surface area carbon blacks (NS Sterling) show an NTC until the glass transition region, where a dramatic decrease in conductivity occurs (except for very high volume fractions

of filler). In temperature cycling experiments, polyethylene-carbon black samples show similar stabilization behaviour. After an annealing time of 200 h at a temperature significantly above the glass transition, polystyrene composites undergo an increase and stabilization of conductivity.

These experimental results strongly suggest that a solution-mixed polymer composite undergoes some form of percolation path repair during heating. Consequently, at temperatures below the polymer melting point, the matrix thermal expansion does not overcome the inherent NTC of the conductive carbon, and the composite conductivity increases as a function of temperature.

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