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Carbon black/high density polyethylene conducting composite materials

Part II *The relationship between the positive temperature coefficient and the volume resistivity*

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Carbon black/polymer composites can be used in a variety of industrial applications, where a high conductivity is an important physical parameter. The relationship between the positive temperature coefficient (PTC) effect and the room temperature volume resistivity has been investigated. These are two of the more important operating parameters. Resistivity–temperature measurements were performed on a radiation crosslinked high structure (H) carbon black mixed at different concentrations in HDPE. The results obtained for composites with a range of carbon black properties showed that there was a linear relationship between log (R_2/R_1) and log R_1, where R_2 = maximum resistivity and R_1 = room temperature volume resistivity. The relationship can be taken as a reference line for the assessment of the relative effect that modifying the carbon black structure and changing the mixing variables on the relative magnitude of the PTC effect and the room temperature volume resistivity. The high structure (H) carbon black structural characteristics were modified by both gas phase (carbon dioxide at 900 °C) and liquid phase (nitric acid) treatments. The former treatment procedure resulted in a decrease, while the latter an increase in the volume resistivities of the final composites. These results are discussed in terms of the effect of surface functionality and carbon structural characteristics.

1. Introduction

The relationship between the resistivity of a carbon black/polymer composite and temperature can vary greatly [1]. These materials can exhibit either a positive temperature coefficient (PTC) effect or a negative temperature coefficient (NTC) effect [2]. The resistivity of a composite increases with increasing temperature for a positive temperature coefficient, whilst the reverse is true for a negative temperature coefficient. Radiation crosslinking of carbon black/polymer composites imparts good reproducibility of resistance if the temperature is cycled up to and beyond the melting point of the polymer, and crosslinking can eliminate any NTC effect that would be observed after the melting point of the polymer matrix if the polymer had not been crosslinked [3]. Good tensile strength can be achieved by using the appropriate loading of carbon black and type of polymer.

Resistivity–temperature profiles allow basic conclusions to be drawn with regard to the concentrations of carbon black and type of polymer matrix used in the composite. The effect that modifications of the carbon black structure or mixing conditions on the PTC and volume resistivities can only be studied to a limited extent by this method. Huali *et al.* [4] have presented data for carbon black/polymer composites showing the resistivity–temperature profiles for different composites. They concluded that radiation crosslinking improves the PTC intensity and the electrical reproducibility in thermal cycling. Narkis *et al.* [5] investigated the relationship between the resistivity ratio R_2/R_1 (the ratio of PTC effect to the room temperature volume resistivity) and the concentration (vol%) of carbon black present in the polymer matrix. They found that no conclusion could be drawn with regard to the relationship between the resistivity ratio and the volume resistivity.

Room temperature resistivity measurements on carbon black composite samples, where the carbon black has been oxidized, have indicated that oxygen surface functionality on the surface of the carbon black increases the resistivity of the composite by forming an insulating layer around the carbon black particles [6]. It would therefore be expected that there would also be an increase in the corresponding PTC effect. In this paper an investigation of the systematic modification of the carbon black structure by gasification and liquid phase chemical treatments and the incorporation of these carbon blacks into polymer composites is reported. The relationship between carbon structural

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characteristics and electrical properties have been studied.

2. Experimental procedure

Two carbon blacks were used in this study. A high structure (H) carbon black, was obtained in beaded form from Cabot Corporation, Special Blacks Division. It has a primary particle diameter of 30 nm and a nitrogen Brunamer-Emmitt-Teller (BET) surface area of 254 $m^2 g^{-1}$ at 77K. The low structure (L) carbon black, was supplied by the Columbian Chemical Company. It has a primary particle diameter of 82 nm and a nitrogen BET surface area of 35 $m^2 g^{-1}$ at 77K. The high density polyethylene used, Stamylan 7625, was obtained in a pelletized form from DSM Polymers and Hydrocarbons. The peak melting point was 135 °C.

2.1. Gas phase treatment of carbon black

The high structure (H) carbon black was gasified in a vertical reactor at a temperature of 900 °C in carbon dioxide for varying reaction times, between 30 and 2880 min. The sample (80 g) of carbon black was heated and cooled in argon so that a precise reaction time in carbon dioxide could be attained. A temperature of 900 °C was chosen since this was found to be the optimum temperature of gasification of most carbon blacks in carbon dioxide [7]. A sample of carbon black was also heat treated in argon to 1000 °C and held at the heat treatment temperature (HTT) for 16 h, to remove surface functionality from the carbon black surface.

2.2. Nitric acid treatment

200 g of the high structure carbon (H) carbon black was taken and mixed with a solution containing 600 ml of distilled water and 600 ml of concentrated nitric acid. The solution was then refluxed for reaction times of 3, 12 and 24 h. The carbon black slurry was thoroughly washed in a Buchner funnel by washing several times with distilled water after filtration to ensure that all traces of the acid were removed. The carbon black was then allowed to air dry before use.

2.3. Mixing and pressing conditions

The high structure (H) carbon black was mixed with high density polyethylene (HDPE) in a Brabender PLE 651 mixer at a temperature of 152 °C. The standard mixing time was for 15 min and the speed of the mixing blades 30 rpm. These mixing conditions were chosen only after a series of rigorous trials involving the variation of both the mixing time and speed and measuring the resistivity of the pressed composite.

Circular plaques of carbon black/high density polyethylene composite of approximately 0.5 mm thickness were obtained by compression moulding at a temperature of 190 °C between steel plates. The molten composite was then cooled at a rate of 17 °C min^{-1} to room temperature. The composite samples were then crosslinked by subjecting them to a dose from a Dynatron high energy electron beam of 15 MRads at a dose rate of 0.2MRads min^{-1}. These crosslinked composite samples were used for the resistivity–temperature and tensile strength measurements.

2.4. Measurement of resistivity

Room temperature volume resistivity measurements were performed on the carbon black/HDPE composite using the four point probe technique based on BS2044: 1984, method 2 [8]. The cross-sectional area of each test piece was measured, a known current was then passed through the outer two electrodes and the voltage drop across the middle two electrodes was measured.

Strips of the composite were prepared and their ends painted with silver paint leaving a 1.2 cm gap of unpainted composite. Electrodes were then attached to the ends of the dumbbells and the resistivity measured every 2 °C in an oven which was heated to a temperature of 190 °C at a heating rate of 2 °C min^{-1}, followed by cooling at a rate of 2 °C min^{-1}. The resistivity was measured on both the heating and cooling cycles. The temperature programmed measurements of the resistivity were only performed on composite samples after they had been radiation crosslinked.

3. Results

3.1. Resistivity–temperature profiles

Fig. 1 shows a typical resistivity–temperature profile for 35 wt% high structure (H) carbon black in HDPE. R_2 denotes the absolute volume resistivity, corresponding to the positive temperature coefficient, while R_1 denotes the value of the room temperature volume resistivity. Since the composite has been crosslinked there is a PTC effect, which is not followed by an appreciable NTC effect. The hysterisis effect is due to the recrystallization of the polymer matrix on the cooling cycle occurring at a slower rate then the initial melting of the crystalline regions of the composite.

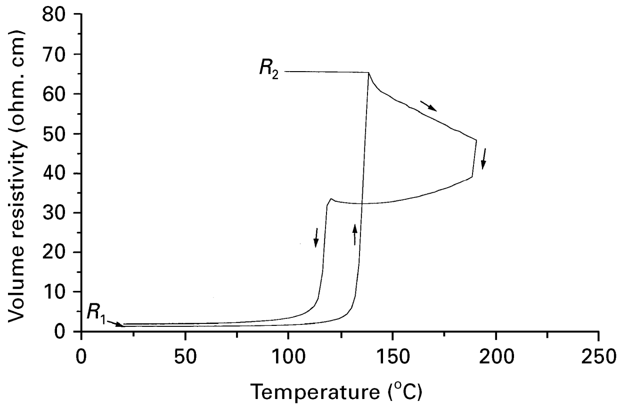

Figure 1 Graph of volume resistivity versus temprature for 35 wt % high structure (H) carbon black mixed in HDPE.

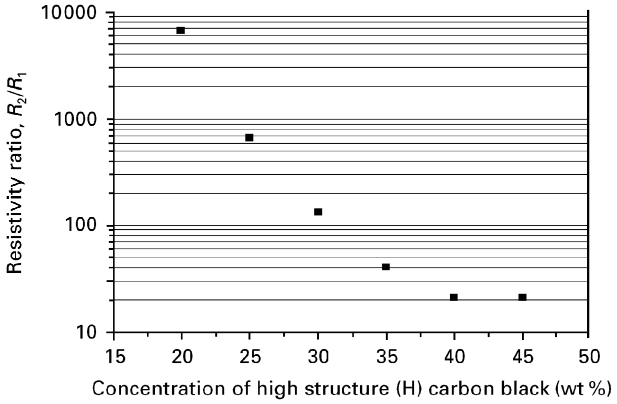

Figure 2 Graph of R_2/R_1 versus concentration of high structure (H) carbon black in HDPE.

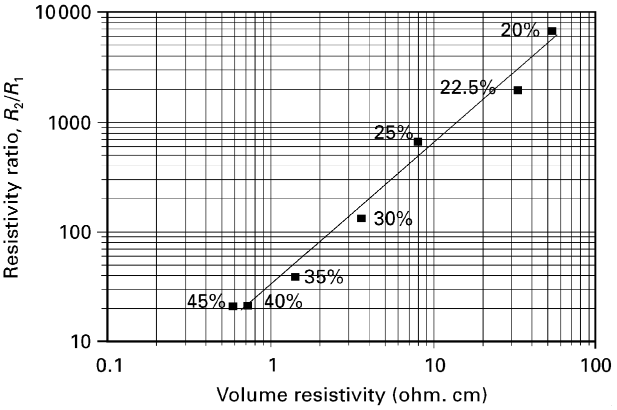

Figure 3 Graph of R_2/R_1 versus volume resistivity for high structure (H) carbon black samples in HDPE mixed at different concentrations (wt%).

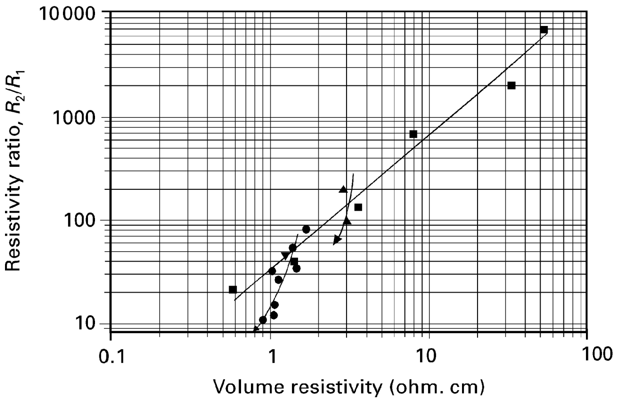

Figure 4 Graph of R_2/R_1 for high structure (H) carbon black samples, showing carbon dioxide treated samples in HDPE. Key: (■) untreated carbon black (H), (●) 35 wt% (CO_2 treatment, (▲) 30 wt% CO_2 treatment and (▼) 35 wt% HTT. The arrows show increasing gasification time.

3.2. Determination of reference line

If R_2/R_1 is plotted against concentration (wt%) of high structure (H) carbon black in HDPE, Fig. 2 is obtained. This shows resistivity values for composite samples of high structure (H) carbon black/HDPE, only with the carbon black loading above the percolation loading threshold, φ'_c. The form of this graph is similar to that reported by Narkis *et al.* [5]. A similar conclusion can be drawn that at lower concentrations of carbon black the ratio R_2/R_1 will be greater. If the carbon black concentration is reduced, the room temperature volume resistivity will increase correspondingly. This representation of the data is satisfactory for comparing different concentrations of carbon black in a given polymer matrix, but is of limited value if investigating the effects of mixing variables and carbon black modification on the PTC effect and room temperature volume resistivity.

All the composites manufactured at different loadings of high structure (H) carbon black were prepared using the standard mixing conditions of 15 min mixing time and standard mixing speed of 30 rpm. Fig. 3 is a graph of R_2/R_1 against volume resistivity on a log scale for samples of high structure (H) carbon black in HDPE. The points form an approximate straight line, which will be referred to as the "reference line". Analysis of Fig. 3 enables a composite to be selected with specific resistivity characteristics. The reference line for untreated high structure (H) carbon black has been established. Therefore the resistivity data for any subsequent measurements could be superimposed on this reference to establish the relative effect of the change in mixing conditions or modification of the carbon black.

3.3. Gasification carbon black treatments

The reduction in the PTC height and volume resistivity of a composite manufactured from carbon dioxide treated high structure (H) carbon black and incorporated into HDPE has been reported elsewhere (Part I) [9]. Fig. 4 shows though that the reduction in R_2/R_1 and volume resistivity due to the partial gasification treatment does not merely correspond to an increase of weight per cent of carbon black in the polymer composite, but that the actual structure of the carbon black is being changed fundamentally so that it behaves like a different carbon black. Linseed oil adsorption tests (Part I) [9] have supported the hypothesis that as the reaction time of the high structure (H) carbon black in carbon dioxide at 900 °C increases, individual carbon black primary particles within an aggregate are being selectively gasified, via the introduction of porosity into the carbon black primary particles. This change in structure of the carbon black would explain the observation that at a given concentration (wt%) the volume resistivity and R_2/R_1 resistivity values would be less than those corresponding to untreated high structure (H) carbon black mixed at 35 wt% in HDPE.

3.4. Liquid phase carbon black treatments

Extensive resistivity measurements have been performed on samples of high structure (H) carbon black treated with nitric acid for reaction times of 3, 12 and 24 h. Fig. 5 shows the resistivity values for these nitric acid treated carbon black/HDPE composites at

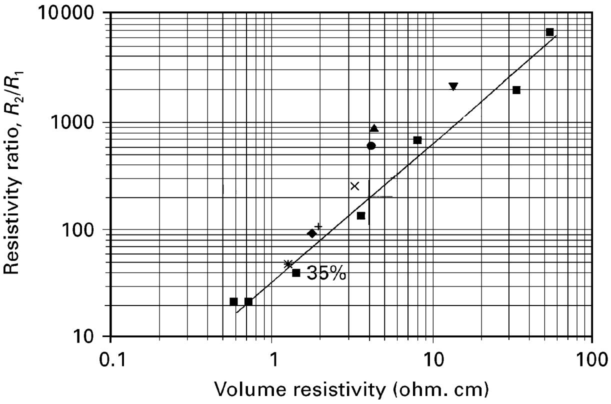

Figure 5 Graph of R_2/R_1 for high structure (H) carbon black nitric acid treated samples in HDPE. Key, (■) untreated carbon black (H), (●) 3 h HNO_3, (▲) 12 h HNO_3, (▼) 24 h HNO_3 (◆) 3 h HNO_3/Ar, (+) 12 h HNO_3/Ar, (×) 24 h HNO_3/Ar and (∗) HTT.

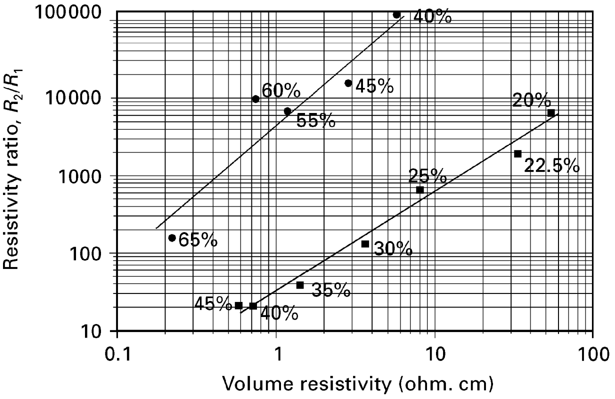

Figure 6 Graph of R_2/R_1 for high structue (H) carbon black and low structure (L) carbon black samples in HDPE. Key (■) carbon black (H) – wt% and (●) carbon black (L) – wt%.

concentration of 35 wt% and superimposed on the reference line formed by untreated high structure (H) carbon black mixed at different weight per cents. As the reaction time in nitric acid increases there is an increase in both the R_2/R_1 and volume resistivities, which move the point up the reference line. The points not only move up the reference line but slightly away from it as well. In an attempt to explain whether this is due to structural or surface effects, the nitric acid treated carbon black samples were heat treated in argon to 1000 °C to remove the majority of the surface functionality. The resistivity values of these samples are still higher than those of the untreated high structure (H) carbon black. It was therefore ascertained that the original increase in resistivity values was due to both structural and surface functionality effects of the carbon black resulting from nitric acid treatment. The oxygen functional groups that had been added to the surface of the carbon black during the nitric acid treatment formed an insulating layer around the high structure (H) carbon black which contributed to part of the increase in observed volume resistivity. The structure of the carbon black must also change due to the nitric acid treatment to explain the increase in resistivities of the composite samples that contain nitric acid treated carbon black with most of its surface functionality removed, by high temperature treatment, compared with the corresponding composites prepared from the untreated carbon black.

3.5. Comparison of two carbon blacks

Not only were the high structure (H) carbon black/HDPE composites investigated, but also low structure (L) carbon black/HDPE composite systems. Fig. 6 shows a comparison of the resistivity values for the – high structure (H) carbon black composite system and a low structure (L) carbon black – composite system. Low structure (L) carbon black mixed at different weight per cents forms a reference line similar to that observed for the high structure (H) carbon black system. At any given concentration (wt%) of carbon black, the resistivity values for the high structure (H) carbon black system are lower than for the low structure (L) carbon black composites, since it is a higher structure carbon black and therefore there will be more conducting pathways for a given carbon black concentration.

4. Discussion

High density polyethylene (HDPE) was chosen as the polymer matrix for several reasons. The polymer contains a large amount of crystallinity and therefore will produce a large PTC effect, due to a large volume expansion close to the melting point of the polymer. HDPE is a simple hydrocarbon polymer and it was therefore thought that the polymer would not interact to any great extent with the surface of the carbon black. However there is some interaction between the surface of the carbon black and HDPE. Comparison of the resistivity values for high structure (H) carbon black and high structure (H) carbon black HTT 1000 °C (see Fig. 5) shows that not only was the room temperature volume resistivity value lower for the heat treated (HTT) sample but also that the magnitude of the PTC effect was lower. The room temperature volume resistivity and magnitude of the PTC effect decrease slightly when surface functionality was removed by heat treatment to 1000 °C in argon. This surface functionality may form an "insulating layer" around the carbon black particles and increase the resistivity of the composite. The interaction between the surface of the carbon black and the polymer matrix may also be a factor. The decreases in resistivity values due to treatment with carbon dioxide has been discussed in detail in Part I [9]. It was found that the decrease in resistivity values was due to an increase in structure, corresponding to the selective gasification of primary particles within a primary aggregate, following the introduction of porosity into the carbon black structure. This was characterized by BET. N_2 surface area measurements and linseed oil adsorption measurements. It was found that surface effects after treatment with carbon dioxide did not dramatically affect either the magnitude of the PTC effect or the room temperature volume resistivity. The observation that composites made from a carbon black with a "clean" surface having lower resistivities than the untreated sample has been investigated in other carbon black/polymer systems [10].

Nitric acid treatment increases the resistivities of a HDPE composite due to a change in both surface functionality and structural effects of the carbon black. After a sample was treated with nitric acid and then had the surface functionality removed with argon, the magnitude of the PTC effect and the room temperature volume resistivity values were still higher than that of the untreated carbon black/HDPE composite. This decrease can be attributed to the removal of surface functionality produced by the treatment procedure. The higher resistivity value of the heat treated high structure (H) carbon black corresponds to modification of the original carbon black structure. Surface area measurements and linseed oil adsorption tests revealed a very small difference between the nitric acid treated samples and the untreated high structure (H) carbon black. Other authors have found both increases [11] and decreases [12] in the surface area of carbon blacks treated with nitric acid. The addition of surface functionality, mainly oxygen containing species, also contributes to an increase in the resistivity values of the composite. The shifts in the PTC effect and room temperature volume resistivity follow the reference line reasonably closely.

5. Conclusions

Resistivity–temperature measurements of carbon black/HDPE composites can provide invaluable information regarding the PTC effect and volume resistivity of the composite. The graph of $\log(R_2/R_1)$ against log(volume resistivity) for different concentrations (wt%) of a given carbon black in HDPE establishes a reference line above the percolation threshold limit. The results show that gas phase and liquid phase treatments of the carbon black lead to carbon black/HDPE composites with a range of properties. Modification of the high structure (H) carbon black surface changes the resistivity parameters so that they move along or are close to the reference line formed by the graph of $\log(R_2/R_1)$ and log(volume resistivity). Even severe oxidation with nitric acid modifies the resistivity values so that they move along the reference line to higher values. Heat treatment studies show that these changes are due to a combination of surface functionality and structural changes.

Carbon dioxide treatment for high structure (H) carbon black samples for increasing reaction times decreases the resistivity values of a composite made from the modified carbon black. This is primarily due to the selective gasification of primary particles within the carbon black primary aggregate. Surface functionality modification had little or no effect on the suite of composites prepared from high structure (H) carbon black samples subjected to CO_2 gasification treatment. The interaction between the surface of the carbon black and HDPE polymer backbone is weak.

Nitric acid treatment of the high structure (H) carbon black increases the composite resistivity by primarily adding volatile matter to the surface of the carbon black. Structural changes due to nitric acid treatment are minimal, but they still contribute to an overall increase in the resistivity of the composite.

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