JOURNAL OF MATERIALS SCIENCE **32** (1997) 401–407

Carbon black/high density polyethylene conducting composite materials

Part I *Structural modification of a carbon black by gasification in carbon dioxide and the effect on the electrical and mechanical properties of the composite*

P. J. MATHER, K. M. THOMAS
Northern Carbon Research Laboratories, Bedson Building, Department of Chemistry, University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, UK

Carbon black/polymer composites can be used in a wide variety of applications, such as for antistatic shielding. Some of these applications rely on the enhancement of conductivity that the carbon black filler imparts to the polymer matrix. This study has involved modifying the structure and surface functionality of a high structure (H) carbon black by gasification with carbon dioxide, thereby allowing the properties of the corresponding composite to be modified systematically. Partial gasification of the carbon black decreased the room temperature volume resistivity, at the same concentration (wt%) of carbon black in the composite, and decreased the magnitude of the positive temperature coefficient effect. The results are discussed in terms of a carbon black structure modification and its relation to mechanical and electrical properties.

1. Introduction

An increasingly important use for carbon black is as a filler in polymers in order to enhance the electrical conductivity of the polymer. There have been several papers discussing the conductive nature of polymers containing carbon blacks with varying morphological properties [1–5]. Recently attention has focused on the temperature dependence of these composites [6]. On heating certain carbon black/polymer composites the resistivity of the composite can increase by several orders of magnitude, this effect is known as the positive temperature coefficient (PTC) effect [7]. If the resistivity decreases with increasing temperature, the phenomenon is known as the negative temperature coefficient (NTC) effect.

Carbon blacks vary greatly in their structure. The structural characterization of these materials is difficult because of the very small particle sizes in the materials. In general, the structures are described as being either a "high" structure or a "low" structure. A high structure carbon black usually consists of many primary particles of carbon black fused together in an aciniform ("grape-like") aggregate structure. A low structure carbon black consists of a small number of carbon black particles fused together in an aggregate, generally with a larger primary particle size.

The use of carbon blacks of different structures will affect the conductivity in a given polymer system to varying extents. Normally a polymer loaded with a high structure carbon black or a carbon black with a small particle size, will have a lower electrical resistivity than a carbon black which possesses a low structure or large particle size, at the same carbon black concentration in a composite. Surface functionality of a carbon black can increase the resistivity of a carbon black/polymer composite [8]. In the case of oxygen functionality this is thought to be due to the oxygen forming an insulating layer on the carbon black particles.

The method by which a carbon black is dispersed in a polymer matrix is critical and it is important to accurately control the different processing variables, as small changes may dramatically affect the resistivity of a composite. There have been limited studies on the effect that systematically modifying certain mixing variables such as mixing time and speed have on the resistivity of a given composite [9].

The comparison of carbon black/polymer composites is difficult because of the limited availability of suitable characterization techniques for carbon black and the problem of relating this characterization data to the properties of the composite. The objective of this study was to systematically modify the structure of the carbon black and to prepare the corresponding carbon black/polymer composites. In this way the properties of the composites can be varied systematically by modifying the carbon black structure and the relationships between carbon black structural parameters and carbon black/polymer composites studied.

0022–2461

2. Experimental procedure

The carbon black used in the study – a high structure (H) carbon black was obtained in a beaded form from Cabot Corporation, Special Blacks Division. This carbon black is formed by the oil furnace method. It has a primary particle size of 30 nm and a nitrogen Brunauer-Emmett-Teller (BET) surface area of $254\,m^2\,g^{-1}$ for N_2 at 77K.

The high density polyethylene used, Stamylan HD 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

A 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 30–2880 min. The sample (80 g) of carbon black was heated and cooled in argon so that a precise reaction time in carbon dioxide was attained. A temperature of 900 °C was chosen since this has been found to be the optimum temperature of gasification for most carbon blacks in carbon dioxide [10]. A sample of carbon black was also heated in argon to 1000 °C and held at the heat treatment temperature (HTT) for 960 min.

2.2. Mixing and pressing conditions

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

Circular plaques of the high structure (H) 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 radiation dose from an electron beam of 15 MRads at a dose rate of $0.2\,MRads\,min^{-1}$. The Dynatron high energy electron beam was capable of electron energies of 8 MeV, but was tuned to 6 MeV. These crosslinked composite samples were used for the resistivity–temperature and tensile strength measurements. Normally approximately eight samples could be cut from each plaque for characterization experiments.

2.3. Measurements of resistivity

Room temperature volume resistivity measurements were performed on the carbon black/HDPE composite using the four point probe technique based on the BS2044 : 1984, method 2 [11]. 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. The average resistivity for a composite plaque was determined and the standard deviation, which corresponded to variances in resistivity within one plaque, made from one mix in the Brabender plasticorder.

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

2.4. Tensile measurements

*M*100 moduli (modulus at 100% strain) were measured for the crosslinked polymer composites. An Instron laser tensometer was used for the study, using a crosshead speed of 100 mm per min and a sample rate of 20 points s^{-1}. The composite samples were equilibrated at a temperature of 150 °C prior to measurement.

2.5. Linseed oil adsorption test

This test method has been previously described by Sweitzer and Goodrich [12]. 1 g of the carbon black sample was taken and linseed oil added by means of a microburette, the two components were mixed together until a stiff ball of carbon black/linseed oil was formed. The volume of linseed oil required is indicative of the structure of the carbon black, a higher structure carbon black will adsorb more oil than a lower structure carbon black.

2.6. Elemental analysis measurements

A Carlo Erba model 1106 Elemental Analyser coupled to a Shimadzu Chromatopac C-E1B integrator and single channel chart recorder was used to measure the carbon, hydrogen and nitrogen contents in the carbon blacks. A Carlo Erba machine, model 1108 was used to measure the oxygen content.

2.7. Surface area measurements (N_2, 77 K)

Surface area results were obtained using a McBain Spring Gravimetric apparatus. Samples of carbon black of a known weight were outgassed at 373 K prior to adsorption measurements. Isotherm measurements were then performed for N_2 at 77 K at various pressures. The BET surface area was determined by analysis of the adsorption isotherm.

2.8. Thermogravimetric analysis (proximate analysis) measurements

In this procedure 50 mg of carbon black was taken and heated to 110 °C in a nitrogen atmosphere. The weight loss recorded using thermogravimetric analysis equipment represented the amount of moisture present in the carbon black sample. The carbon black was then heated to 900 °C in a nitrogen atmosphere and the weight loss represents the amount of volatile content present in the carbon black. After cooling the sample to 800 °C and gasifying the sample in air the weight recorded at room temperature represents the amount of ash present in the sample.

2.9. Disc centrifuge photosedimentometry (DCP) particle size analysis

The primary aggregate size of various carbon blacks was determined using a BIC-B I-DCP photosedimentometer with data collection/manipulation software version 7.21. The carbon black was dispersed in a surfactant and a scanning optical system was used to track the particle sedimentation after steady state settling had been achieved. The particle size could then be determined from plotting absorbance against sedimentation distance and applying Stokes Law.

3. Results

3.1. Carbon black characterization

The change in the structural characteristics of the carbon black with reaction time was assessed using the stiff paste oil adsorption technique. Fig. 1 shows that as the reaction time in carbon dioxide increases the volume of linseed oil required to form a stiff ball increases. This indicates that either the primary aggregate size of the carbon black is decreasing, primary particles within the aggregate are being selectively gasified, porosity is being introduced into the carbon black particles or a combination of these mechanisms. Disc centrifuge photosedimentometry (DCP) particle analysis results shown in Table I indicated that the primary aggregate diameter of the high structure (H) carbon black was not changing significantly after carbon dioxide gasification. The weight average diameter, D_w, for the untreated high structure (H) carbon black was 238 nm, and that for 1800 min CO_2 treated carbon black was 231 nm.

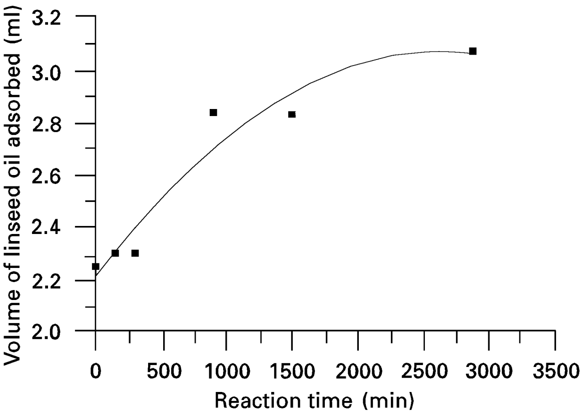

Figure 1 Graph of volume of linseed oil adsorbed versus reaction time in carbon dioxide for the high structure (H) carbon black.

As the reaction time increases there is a dramatic increase in the surface area of the carbon black. Table I shows there is a ten fold increase from 227 m^2g^{-1} for the untreated high structure (H) carbon black to 2170 m^2g^{-1} for the high structure (H) carbon black that has been gasified for 1800 min. There is a systematic increase in the surface area of the carbon black as the burnoff proceeds due to gasification of the carbon black. Table I also shows that the high structure (H) carbon black gasified in carbon dioxide has a typical volatile matter of 1–1.5%. However heat treatment in argon at 1000 °C results in the removal of this volatile matter. These relatively small increases in volatile content can be attributed to the formation of surface complexes which can be removed by heat treating in an inert gas to a higher temperature.

Fig. 2 shows that as the structure of the carbon black increases (i.e., the gasification of primary particles within a primary aggregate), as indicated by an increase in the volume of linseed oil required, the volume resistivity of the composite decreases. After 2880 min reaction time the resistivity of the composite was 0.67 ohm cm compared with 1.09 ohm cm for the composite prepared from the high structure (H) carbon black (HTT 1000 °C). Both composite samples contained the same concentration of carbon black – 35 wt %.

Table I shows that as the reaction time in carbon dioxide increases there is an increase in the oxygen content, from 0.25 wt % for the untreated high

TABLE I Characterization data for carbon black (H)

Sample	Elemental Analysis (wt %)				Thermogravimetric analysis (proximate analysis), (wt %)			Surface area BET (N_2, 77 K)	Particle diameter D_w (μm)
	N	C	H	O	Moisture	Volatiles	Ash		
H	0.00	98.32	0.07	0.25	0.67	1.52	0.90	227	0.238
HTT 1000 °C	0.00	98.53	0.22	0.05	0.00	0.00	1.40	198	–
900 min CO_2	0.00	96.75	0.00	1.60	0.80	1.23	1.82	1223	–
1500 min CO_2	0.00	98.95	0.00	1.40	0.75	1.41	1.82	895	–
1800 min CO_2	0.00	98.55	0.00	1.57	0.67	1.02	2.68	2170	0.231

H is a high structure carbon black

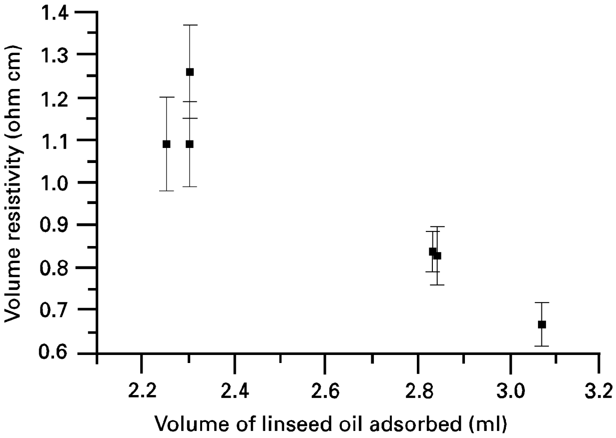

Figure 2 Graph of volume resistivity versus volume of linseed oil adsorbed for the high structure (H) carbon black treated with carbon dioxide for different reaction times.

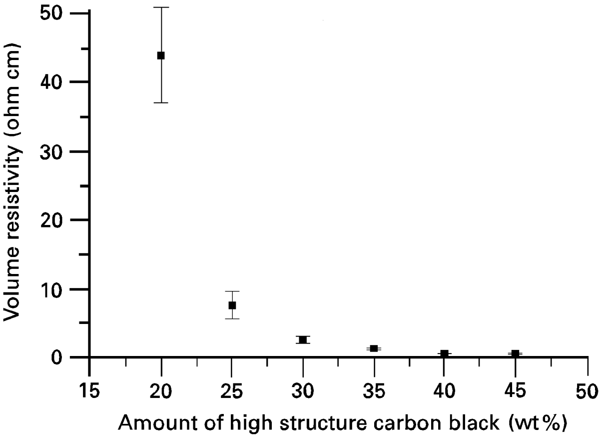

Figure 3 Graph of volume resistivity versus amount of the high structure (H) carbon black mixed in HDPE.

structure (H) carbon black, to 1.57 wt % for the sample gasified for 1800 min, confirming that a limited number of oxygen containing species are added to the surface of the carbon black during the gasification process at 900 °C.

3.2. Assessment of mixing conditions

Fig. 3 shows the loading curve for the high structure (H) carbon black as a function of concentration (wt %) of the carbon black in HDPE. A value of 35 wt % loading was chosen as the standard loading weight for all subsequent mixing trials. At this loading any small changes in the carbon black concentration and distribution in the composite will not dramatically affect the resistivity of the composite, since after about 30 wt % loading there was only a small decrease in the composite resistivity as the concentration (wt %) was further increased.

The effect of mixing time on the resultant resistivity of the composite is shown in Fig. 4. From a mixing time of 2.5 min there was a steady increase in the resistivity of the carbon black/HDPE composite which reached a plateau after about 45 min mixing time. This increase in resistivity can be attributed to a break-up of the agglomerated carbon black network, which leads to fewer conductive pathways. A mixing time of 15 min was chosen to be the standard mixing time for future mixing trials since it was a reasonable compromise between the time taken to perform the experiment, whilst at the same time sufficiently homogeneously distributing the carbon black within the polymer matrix. Any small deviations in mixing time away from 15 min did not result in a large change in the volume resistivity of the resultant composite. Mixing time trials were performed at 14 and 16 min and it was found that the resistivity values of the composite were almost identical to the 15 min mixing time resistivity.

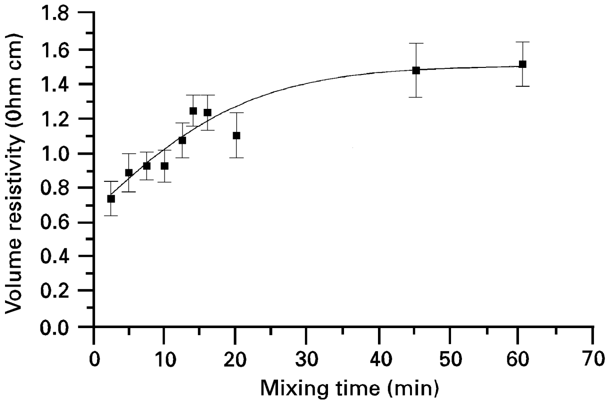

Figure 4 Graph of volume resistivity versus mixing time for the high structure (H) carbon black mixed at a concentration of 35 wt % in HDPE.

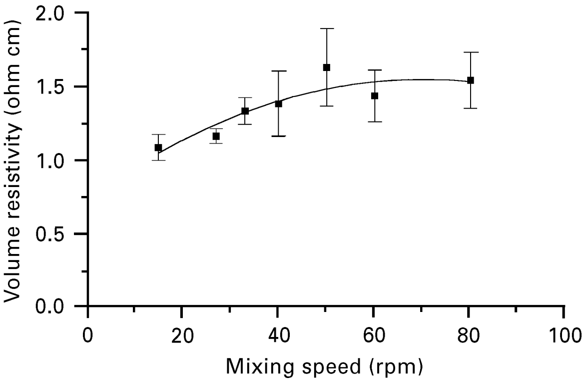

Figure 5 Graph of volume resistivity versus mixing speed for the high structure (H) carbon black mixed at a concentration of 35 wt % in HDPE.

Another important mixing variable is the mixing speed of the blades in the mixing chamber. Fig. 5 shows that as observed with the mixing time curve, as the speed increased, there was an increase in the volume resistivity of the resultant composite. This can be attributed to an increase in shear applied to the polymer composite as the speed increases, which in turn breaks up the conducting carbon black agglomerated network to a greater extent. From this mixing speed curve a standard mixing speed of 30 rpm was chosen for subsequent mixing trials on modified carbon blacks. At this mixing speed the properties of the composite were relatively insensitive to small variations in the mixing speed away from 30 rpm.

3.3. Resistivity measurements

After the high structure (H) carbon black was treated with carbon dioxide and mixed at 35 wt % in high density polyethylene using standard mixing conditions, the volume resistivities of the composites were measured. Fig. 6 shows a graph of volume resistivity versus reaction time in carbon dioxide for the high structure (H) carbon black in HDPE. There was an overall decrease in the resistivity as the reaction time increased. After a reaction time of 2880 min in carbon dioxide the room temperature volume resistivity decreased to 0.67 ohm cm from the original value of 1.09 ohm cm.

Fig. 7 shows a typical resistivity–temperature profile for 35 wt % high structure (H) carbon black mixed in HDPE, and radiation crosslinked. The composite samples were irradiated with a 15 MRads dose at a rate of 0.2 MRads min^{-1} before any measurements were performed. This radiation treatment crosslinks the polymers and after the composite has shown a PTC effect there is a slight NTC effect, which would have been much greater if the polymer had not been crosslinked, as the temperature was further increased. The PTC effect occurs in a relatively narrow temperature range, between 125–140 °C. This dramatic rise in resistance occurs close to the melting point of the polymer matrix (HDPE), which would be expected due to the HDPE having a larger thermal expansion coefficient than the carbon black. A volume increase in the polymer matrix will therefore push the carbon black agglomerates apart, which in turn will decrease the number of carbon black conducting networks.

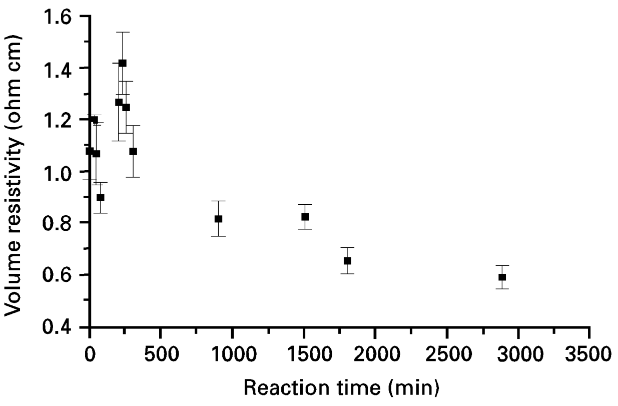

Figure 6 Graph of resistivity versus reaction time in CO_2 for the high structure (H) carbon black mixed at a concentration of 35 wt % in HDPE.

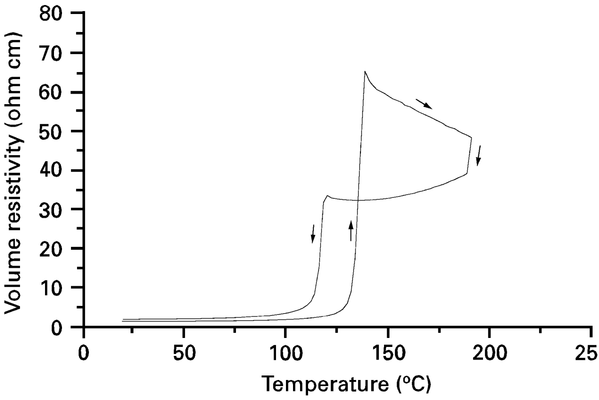

Figure 7 Graph of volume resistivity versus temperature for 35 wt % high structure (H) carbon black mixed in HDPE.

Fig. 8 shows the variation of volume resistivity with temperature for the high structure (H) carbon black samples mixed over a concentration range in HDPE. As the carbon black concentration increases there is a decrease in both the room temperature volume resistivity and the magnitude of the PTC effect. This is attributed to an increase in the number of conductive pathways. The initial PTC effect is due to a volume expansion of the polymer, forcing the carbon black agglomerates further apart and increasing the resistivity of the composite. If the composite had not been crosslinked there would have been a significant NTC effect, because after the initial volume expansion of the polymer the carbon black would rearrange in the polymer melt and form new conductive pathways. As the degree of crosslinking is increased, the NTC effect is gradually reduced. Only the heating cycle is shown in Fig. 8 to simplify the graph.

Fig. 9 shows the variation in resistivities of composites prepared from the high structure (H) carbon black gasified in CO_2 for reaction times between

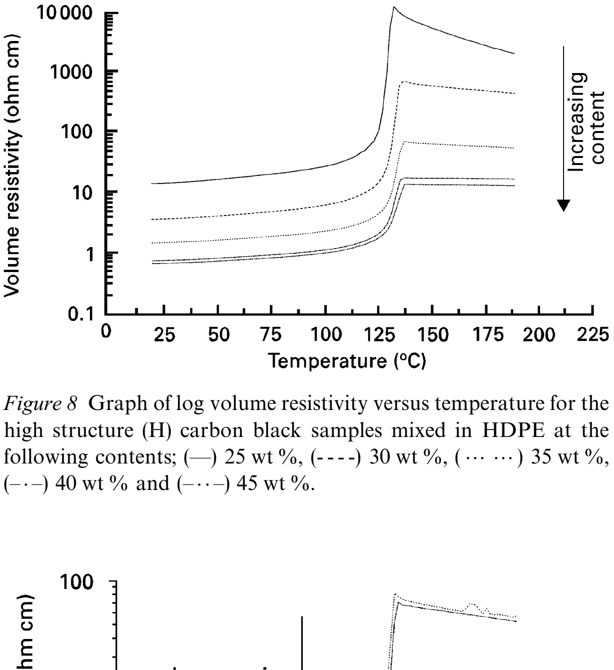

Figure 8 Graph of log volume resistivity versus temperature for the high structure (H) carbon black samples mixed in HDPE at the following contents; (—) 25 wt %, (----) 30 wt %, (··· ···) 35 wt %, (–·–) 40 wt % and (–··–) 45 wt %.

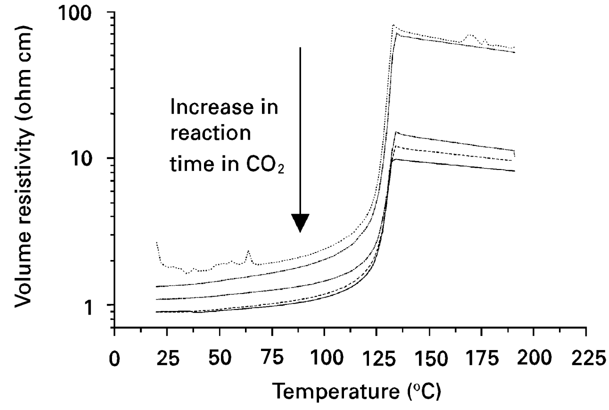

Figure 9 Graph showing the log volume resistivity versus temperature for the high structure (H) carbon black samples treated with carbon dioxide, mixed at 35 wt % in HDPE. Data shown for reaction times in CO_2 of; (–) 1800 min, (---) 1500 min, (–·–) 900 min, (–··–) 150 min; also shown (··· ···) HTT.

150–1800 min and mixed at a 35 wt % concentration in HDPE. As the reaction time is increased there is a decrease in the room temperature volume resistivity of the composites and a decrease in the magnitude of the PTC effect. This decrease in resistivity can be attributed to a change in the structure of the high structure (H) carbon black, corresponding to the selective gasification of carbon black primary particles within carbon black aggregates.

3.4. Mechanical properties

*M*100 modulus measurements for the high structure (H) carbon black/HDPE composites mixed at different concentrations in HDPE and then radiation crosslinked are shown in Fig. 10. The *M*100 modulus is the modulus measured at 100% strain. As the concentration of the high structure (H) carbon black was increased there was an increase in the *M*100 modulus as the carbon black reinforces the polymer composite. A similar effect has been observed for the reinforcement of rubber using carbon black as a filler.

Fig. 11 shows that, after the high structure (H) carbon black was treated with carbon dioxide and the *M*100 modulus for the corresponding radiation crosslinked composite measured there was an increase in the *M*100 modulus as the reaction time increases. This increase in the *M*100 modulus with extent of gasification supports the hypothesis that the corresponding decrease in the volume resistivity results from the selective gasification of carbon black primary particles within a carbon black aggregate by the development of porosity within the carbon black.

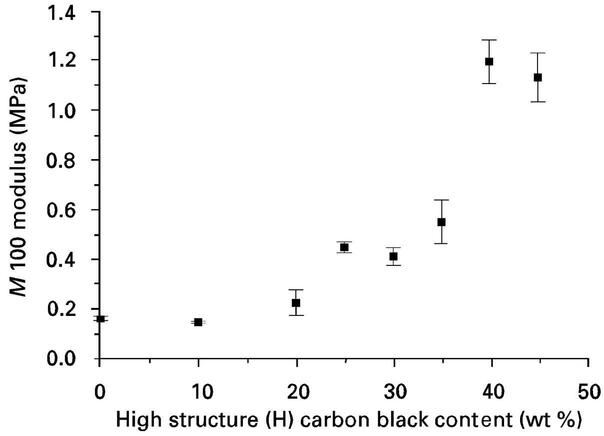

Figure 10 Graph of *M*100 modulus versus the high structure (H) carbon black content in HDPE.

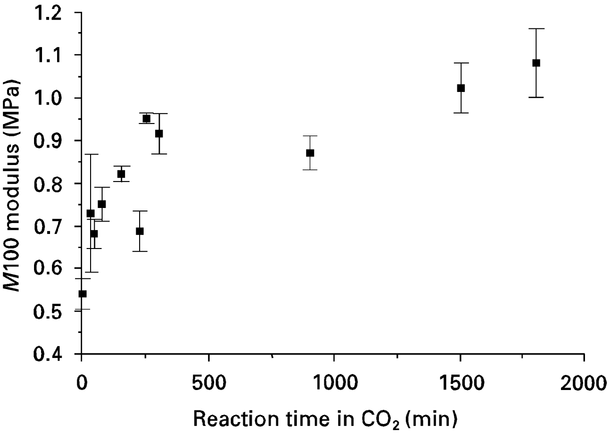

Figure 11 Graph of *M*100 modulus versus reaction time in CO_2 for the high structure (H) carbon black mixed at a concentration of 35 wt % in HDPE.

4. Discussion

The manufacture of carbon black/polymer conducting composites has been limited to commercially available materials. As a result this has placed a limit on the properties of the composites. In this investigation the effect of the modification of carbon black structure and surface functionality by partial gasification and the incorporation of these modified carbon blacks into the composites has been investigated. The rigorous mixing trials performed on the high structure (H) carbon black/HDPE system to establish standard mixing conditions were extremely important prior to the preparation of carbon black/polymer composites involving the modified high structure (H) carbon black. Although the modified high structure (H) carbon black/HDPE composites will have their own mixing time and mixing speed curves it was found [13] that a mixing time of 15 min at a speed of 30 rpm was suitable for all the modified carbon blacks and untreated carbon black polymer systems. A direct comparison of resistivity values between HDPE composites made from the high structure (H) carbon black and high structure (H) carbon black modified by gasification in carbon dioxide can therefore be made with confidence, and that the observed changes were due to modification of the carbon black and not a function of erroneous mixing conditions.

The effect that surface functionality has on the resistivity of a composite made from carbon dioxide modified carbon blacks is not large. This can be concluded from comparison of the resistivity value of 1.17 ± 0.11 ohm cm for 35 wt % untreated high structure (H) carbon black mixed in HDPE, compared with 1.09 ± 0.10 ohm cm for the corresponding high structure (H) carbon black (HTT 1000 °C – surface functionality removed). These values of resistivity are very close and therefore any effect of surface functional groups must be small, since the volatile content of the untreated high structure (H) carbon black and the carbon dioxide treated carbon blacks are very similar; see Table I.

It was evident that the change in structure of the high structure (H) carbon black during gasification in carbon dioxide contributed to an overall decrease in the volume resistivity of a composite made from the modified carbon black and high density polyethylene. The oil adsorption results confirmed that the structure was modified so that carbon black particles within the carbon black aggregates were gasified, leading to a higher structure with respect to reaction time in carbon dioxide. Heckman and Harling [14] have studied the gasification of carbon black using transmission electron microscopy and discovered that when a carbon black aggregate was gasified individual carbon black primary particles collapsed within the aggregate as gasification proceeded. It is thought that as gasification proceeds, individual carbon black primary particles are gasified completely within the aciniform aggregate structure of the carbon black. Therefore when a HDPE composite is made from a high structure (H) carbon black and high structure (H) carbon black (CO_2 treated) at 35 wt % carbon black loading, the modified carbon black composite will have a lower volume resistivity, since there are more conductive pathways, due to a change in structure of the carbon black i.e., a greater number of primary aggregates in a given concentration of the treated carbon black.

5. Conclusions

The modification of the carbon black structure by controlled gasification and the incorporation of the modified carbon blacks into HDPE composites has allowed a series of conducting polymers to be prepared which have a range of volume resistivity values and PTC effects. An increase in the reaction time of the high structure (H) carbon black in carbon dioxide resulted in an increase in the structure of the carbon black and a decrease in the volume resistivity and magnitude of the PTC effect of the corresponding high density polyethylene composite. This effect has been attributed to the larger number of conductive pathways due to an increase in the number of particles for a given concentration of carbon black.

Acknowledgements

The provision of an EPSRC Case studentship with Raychem for P.J. Mather is gratefully acknowledged. The authors would also like to thank S. Baigrie for his help.

References

1. W. F. VERHELST, K. G. WOLTHIUS, A. VOET, P. EHRBURGER and J. B. DONNET, *Rubber Chem. Technol.* **50** (1977) 735.
2. D. BULGIN, *ibid* **19** (1947) 667.
3. F. BUECHE, *J. Appl. Phys.* **43** (1972) 4837.
4. *Idem, ibid* **44** (1973) 532.
5. M. H. POLLEY and B. B. S. T. BOONSTRA, *Rubber Chem. Technol.* **30** (1957) 170.
6. Y. HUALI, T. HAO, P. JIANHUI and C. XINFANG, *Radiation Phys. Chem.* **42** (1993) 135.
7. A. VOET, *Rubber Chem. Technol.* **54** (1980) 42.
8. E. K. SICHEL, "Carbon Black Polymer Composites" (Marcel Dekker, New York, 1982).
9. D. M. BIGG, *Journal of Rheology* **28** (1984) 501.
10. P. L. WALKER, Jr., F. RUSNINKO, Jr. and L. G. AUSTIN, *Chem. Phys. Carbon* **2** (1966) 275.
11. BRITISH STANDARD INSTITUTE: Determination of resistivity of conductive and antistatic plastics and rubber, B.S. 2044: 1984 Part 2 (British Standards Institute, London, 1984).
12. C. W. SWEITZER and W. C. GOODRICH, *Rubber Age* **55** (1944) 469.
13. P. J. MATHER, (unpublished results).
14. F. A. HECKMAN and D. F. HARLING, *Rubber Chem. Technol.* **39** (1966) 1.

Received 23 February
and accepted 5 July 1996