ELECTROTHERMAL ANALYSIS OF CARBON BLACK LOADED POLYMERS *

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ABSTRACT

A Du Pont DSC cell has been modified, without any permanent alteration, to measure absolute values of resistivity of polymer compounds.

Carbon filled polymer compounds show transitions not observed by other thermal methods. Electrothermal analysis (ETA) can predict thermal stability of amorphous polymers. This approach has advantages over other existing methods in the case of PVC.

For semi-crystalline polymers, ETA can be used as a scanning tool for temperature sensitivity of resistivity of compounds for uses such as cable or PTC materials.

INTRODUCTION

The determination of the electrical properties of polymers as a function of temperature has generally involved discrete electrical readings on samples heated in an oven. Such tests are tedious, time-consuming, and require fairly large polymer samples. More recently, Chiu [1] demonstrated that Du Pont DTA equipment can be modified to simultaneously record resistivities and heat transitions at a programmed scanning rate. This dynamic method has proved valuable in scanning polymers to determine resistivity as a function of temperature, and was termed electrothermal analysis (ETA). ETA revealed additional transitions not detected by DTA. The simultaneous DTA—ETA method, however, is restricted by the shape of the electrodes, limiting it to powdered materials and plugs of similar shape to the electrodes. Resistivity values so determined are relative rather than absolute; also, it involves rigorous cleaning of the thermocouples and electrodes after each run. Carroll and Mangravite [2] modified a Perkin—Elmer DSC cell for simultaneously measuring heat transition and electrical conductivity (DSC—ETA). However, this required permanent alteration of the cell and could be a drawback to this approach.

In the method described below, a Du Pont 900 DSC cell is used without any permanent alterations to the cell. Measurements can be determined at programmed scanning rates from —120 to 500°C with the Du Pont 900, or

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from —160 to 660°C with the 990 unit. Absolute resistivity values can be calculated from sample dimensions and current readings at each temperature.

Most of the earlier studies [1,2] on ETA dealt with pure polymers. In this study, the equipment was used to determine the resistivities of carbon black filled polymers. Such materials have resistivities in the range 10^{-1}—10^{1} ohm-cm [3] compared with resistivities of 10^{10}—10^{17} ohm-cm for unfilled polymers. For black filled compounds the current, therefore, is transported largely through the semi-continuous carbon black chains. The larger current permits accurate measurements with less sensitive equipment. Carbon black has a negative temperature coefficient of resistance of 0.5% °C^{-1} [4] and is more or less unaffected by temperature changes up to around 400—500°C in nitrogen, where most polymers decompose. Thus, discontinuities in resistivity with temperature of carbon black loaded polymers are due mainly to transitions in the polymeric phase.

Aside from the experimental advantages discussed above, carbon black filled polymers have significant interest due to their technical usage: e.g. semi-conductive compounds for use in cables, and as antistats to prevent damage to sensitive components by static electricity. In semi-crystalline polymers, black filled compounds exhibit a positive temperature coefficient (PTC) of resistance [5]. Because of this property these compounds are finding increased usage as microswitches, self-controlled heaters, current limitors or sensors, etc. On the other hand, the large increase in resistivity with temperature is an undesirable feature in cable compounds. The approach described herein may therefore be used as a scanning tool for determining the temperature sensitivity of resistance of black filled semi-crystalline or amorphous polymers which are used in various applications.

EXPERIMENTAL

Resistivity

The apparatus developed for resistivity measurements is somewhat similar to that of Chiu [1] and Carroll and Mangravite [2], but differs in detail. This is exemplified in Figs. 1 and 2. The DSC cell base was covered with a thin piece of glass (I) (microscope slide) to insulate the system from the body of the DSC cell. On the top of the glass plate, a thin piece of asbestos sheet (J) was placed in the reference position to compensate for the thermal capacity of the sample. A 0.05-in. thick platinum foil (K), large enough to cover both the sample and reference positions, was placed on the top of the asbestos piece and extended to the bottom of the sample. Twenty gauge platinum wire electrodes (C), flattened at the bottom, were held in contact with the platinum foil and with the sample top by means of the spring (B) and load (M) (30 g). The spring (B) is attached to a 0.080-in. diameter copper conductor (A), held by a brass screw (P) which rests on a transparent acrylate platform (N) (0.25-in. thick). The platform was machined to fit the top of the steel cylinder (E) which fits the outer steel jacket of the DSC cell.
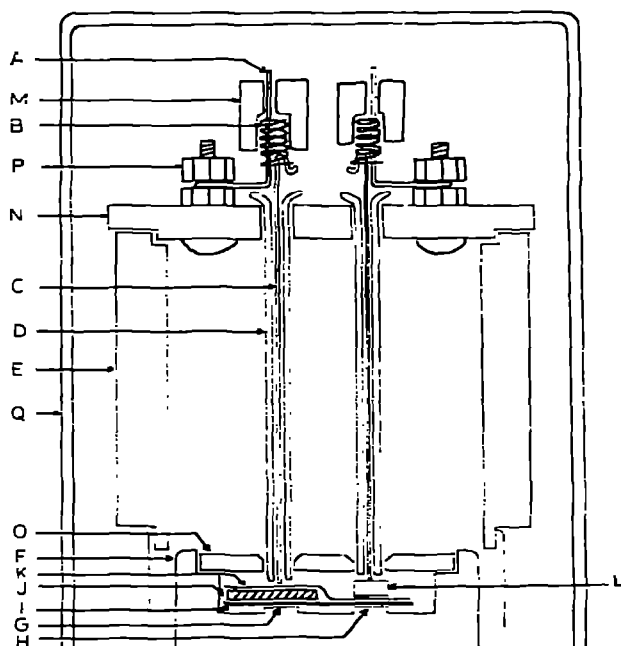
Fig. 1. Cell for ETA measurement. (A) Copper conductor, (B) spring. (C) Pt electrode, (D) glass capillary, (E) extension tube, (F) DSC cell, (G) ref. platform, (H) sample platform, (I) glass slide, (J) asbestos pad, (K) Pt foil, (L) sample, (M) lead weight, (N) clear plexiglass cover, (O) aluminium cover, (P) terminal connection, (Q) glass bell.

An aluminium disc (O), with two holes to accommodate the glass capillary (D) with the electrodes, takes the place of the silver cover of the DSC cell. The disc was marked so that it sits the same way each time. After placing the sample on the platinum foil in alignment with the sample side hole of the
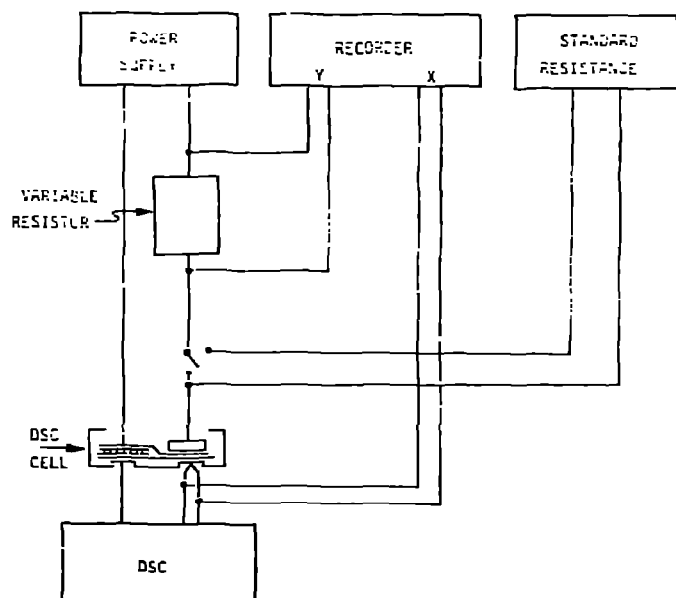
Fig. 2. Schematic for ETA measurements.

aluminum cover, the sample was annealed and then cooled with liquid nitrogen to —140°C. The steel cylinder, the plastic platform (which together extends the outer steel cover of the DSC cell) and the electrodes were then quickly placed in position and current recorded at a programmed rate of heating from —100°C. The impressed voltages were kept at 1—3 V to prevent electron tunneling. At this voltage conduction is mostly ohmic. The range of conductivity was adjusted by a Sencore substitution resistor and a 10-turn 20 K potentiometer (Fig. 2). The current was traced using a Houston Instruments X—Y recorder, Model 111-198. The X-axis sensitivity was adjusted to correspond to temperature readings of the DSC. The current was traced between —100 and 250°C for ethylene—vinylacetate copolymer (EVA) and up to around 400°C for elastomers. The samples were annealed at 150°C (100°C for elastomers) for 15 min in a nitrogen stream. The resistivity was calculated from the current reading and dimension of the sample before the experiment. The resistivity was independent of scanning rate between 10 and 30°C min^{-1}, as was also observed by Chiu [6].

Samples

The samples were scooped out from a tensile sheet with a leather punch, covered with colloidal graphite to overcome contact resistance, and rested overnight to release the strain before the experiment. All measurements were done at a programmed rate of 20°C min^{-1} to alleviate any changes due to this factor. Reproducibility of the measurements is illustrated in Fig. 3 with
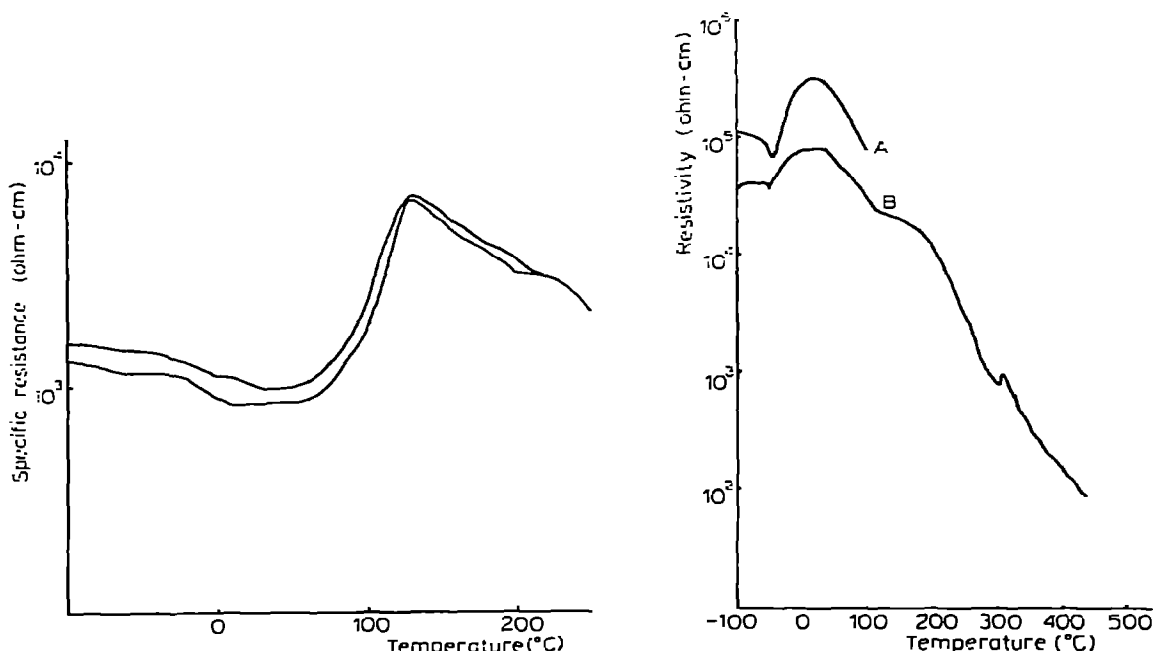

Fig. 3. Reproducibility of ETA measurements.

Fig. 4. ETA curve of IR (A) without graphite coating; (B) with graphite coating, N375, 50 phr.

EVA. In earlier experiments without the coating of graphite, reproducibility was extremely poor and a large decrease in resistivity was observed at about the glass transition temperature of various elastomers. This is exemplified in Fig. 4 with an IR compound. Since resistivity was also higher, this must be due to contact resistance which was overcome by the graphite coating. The EVA sample was DQD 1868 from Union Carbide Company, and had a density of 0.94 and typical vinyl acetate content around 18%, as obtained from the supplier's literature. The PVC sample was Geon 101 from B.F. Goodrich Co. Elastomers and additives were commercial samples, used as received.

The EVA compounds were mixed in a preheated Banbury (101.7°C) and dropped after 5 min or at 132°C, whichever came first. A typical recipe was as follows: EVA, 100; black, variable; di-cup R (dicumyl peroxide, 96—99%), 1.3; and agerite resin D (polymerized 1,2-dihydro-2,2,4-trimethyl quinoline), 0.5. The samples were cured for 15 min at 171°C under Mylar. Elastomer compounds were also made in a Banbury following conventional procedures. A typical elastomer recipe was: rubber, 100; carbon black (N-375), 50; stearic acid, 3; ZnO, 5; MBTS, 0.6; and sulfur, 2.5. A Leigh-Dugmore [7] dispersion rating of 93% and above was considered acceptable.

DSC

Although the equipment described is capable of simultaneous DSC—ETA measurements, a substantial amount of DSC sensitivity is lost due to the intervention of the glass slide; therefore separate experiments were carried out for determining the DSC thermograph [8], if necessary.

TG—DTG

The procedure for TG—DTG has been described previously [8].

TMA

Thermomechanical analysis was carried out with both expansion and penetration probes with selected samples with the Du Pont 941 TMA at a programmed scanning rate of $5°C$ min^{-1}, in a nitrogen atmosphere in the range —120 to 100°C for elastomers and —120 to 250°C for semi-crystalline polymers. Penetration experiments did not indicate a significant increase in conductivity in the filled polymers due to penetration of the electrodes in the sample. Both probes show discontinuity at the melting point.

RESULTS AND DISCUSSION

Amorphous polymers

The volume resistivity vs. temperature curve, seen in Fig. 4 for a 50 phr N375 loaded IR compound, is typical for this class of polymers. The incom-

plete upper curve demonstrates the effect of omitting the graphite powder coating used to reduce contact resistance. A sharp drop in resistivity is seen at about the glass transition temperature (—50°C), then resistivity increases to ca. 30°C and then undergoes a steady decline to ca. 400°C, with a transition at around 200°C and a sharp blip at 310°C. A part of this decline can be accounted for by the negative temperature coefficient of resistivity of carbon black, as mentioned above. The resistivity temperature curve is not reversible on samples heated above 200°C, suggesting that non-reversible thermal changes take place around this temperature; also, samples heated above 200°C show transition at the corresponding final temperature of heating. This is undoubtedly the initial stage of carbonization. Additional heat treatment transforms the polymer into a conductive carbon chain by crosslinking and cyclization, which may explain the gradual decrease in resistivity with temperature. The blip in the curve at 310°C indicates where voltalization starts. Neither the TG nor DSC curves [8] show a break around 200°C. Chiu [6] observed similar resistivity decreases for polyacrylonitrile from 180°C to 250°C, long before the 297°C exotherm shown by DTA. This resistivity decrease was attributed to the linking of acrylonitrile groups to form conjugated colored carbon—nitrogen sequences. In oxygen, the change of slope for IR occurred at lower temperature (175°C), and the rate of decrease of resistivity is much higher.

Figure 5 shows electrothermographs of NR, BR, and a 40 : 60 NR/BR blend. The curves are similar to that of IR. The BR curve shows a sharp, reproducible dip in resistivity at around 130°C. The reason for this transition
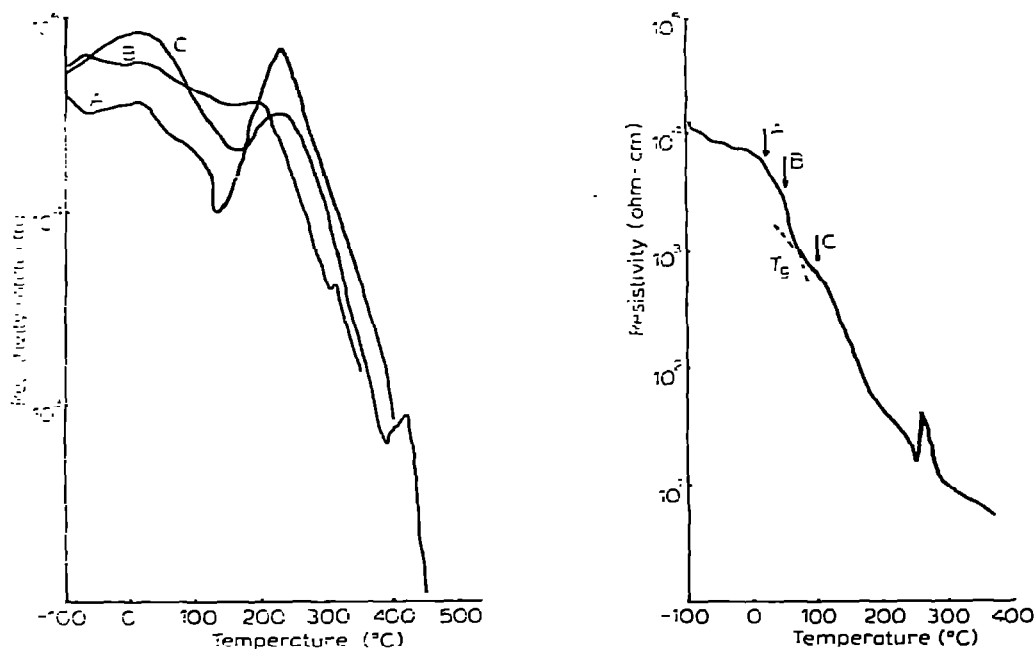

Fig. 5. ETA curve of (A) NR, (B) Br, and (C) 40 : 60, NR : BR, N375, 60 phr.

Fig. 6. ETA of PVC compound, N472, 60 phr.

is not apparent, indicating that ETA curves reveal transitions not recorded by other methods, as was also found by Chiu [1,6]. The BR/NR blend shows an average pattern of the two components. The reversion temperatures are 200°, 230°, and 235°C for NR, BR, and NR/BR, respectively.

Figure 6 shows ETA thermographs of PVC, a largely amorphous polymer which contains a small proportion (about 5%) of small and imperfect crystallites. The arrow markers on the curve show the points at which resistivities are measured by ASTM method D257 [9] (A, 23°C) and the British Standard Method [10] (B, 50°C). The T_g at 75°C agrees with the values published for the commercial materials [11]. The slope change at 100°C (C) corresponds to the temperature at which dehydrochlorination starts and a change in color of the polymer is observed. The International Standards Organization test for thermal stability of PVC depends upon the assessment of color changes occurring in specimen discs heated from 120 to 200°C [12]. Such assessment, of course, is difficult for colored compounds. The evolution of hydrogen chloride has also been used for assessing the stability of PVC [13]. However, in practical compounds the evolved hydrogen chloride is frequently neutralized by the stabilizers and only becomes detectable when these stabilizers are exhausted. Color and melt viscosity then undergo rapid changes due to polymer crosslinking [13]. It is evident that ETA can be used to predict the thermal stability of PVC and that this approach is free of the limitations of the other tests. The final temperature for dehydrochlorination is around 250°C, in agreement with other literature values [13]. Above this temperature, decomposition of the residual hydrocarbon occurs with the evolution of benzene. The slope changes between 100 and 250°C are due to the production of metastable states. Figure 7 shows the DSC, TG, and DTG curves of PVC. It is evident that the ETA curve records dehydrochlorination long before it is evident in other thermal curves and is of considerable significance in interpreting the decomposition reactions which take place.

Figure 7A shows that different DSC thermographs are obtained for carbon black, filled (b) and unfilled (a) PVC. An exotherm in the former, with peak
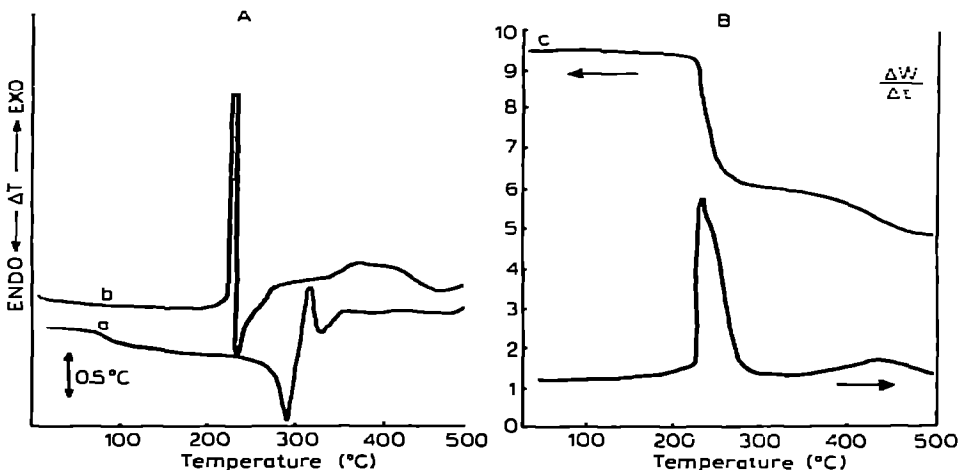

Fig. 7. DSC (A), TG, DTG (B) Curves for PVC. a, 8.21 mg; b, 10.53 mg; c, 9.55 mg.

at 239°C, indicates a crosslinking reaction of sulfur cured PVC in the presence of carbon black. The peak coincides with the DTG peak temperature (7B), indicating that the crosslinking is preceded by the evolution of hydrogen chloride. These results are similar to those observed for polychloroprene (CR) [14].

Semi-crystalline polymers

The electrothermograms of black loaded semi-crystalline polymers differ significantly from those of amorphous polymers due to the effects associated with the crystallite melting. Figure 8 shows a schematic of the relationship of resistivity with temperature and volume concentration of carbon black. Room temperature resistivity decreases sharply with carbon black concentration, as an increase in conductivity takes place through the carbon black networks (Fig. 8A). Finally, the black concentration is high enough to establish interparticle contacts, at which point resistivity decreases only slightly with increased loading. Resistivity at the crystallite melting temperature shows a peak at all black concentrations, but at both very high and very low concentrations the peak intensity (R_p/R_t), calculated as the ratio of the resistivity at the peak to that at room temperature, is very low (Fig. 8B). For maximum peak intensity there is an optimum concentration of carbon black, which depends upon the black parameters [15,16]. Although a universally accepted mechanism to account for the PTC effect of semi-crystalline polymers has not been developed, expansion of the polymer appears to play a role [17]. At low volume concentrations of black (or pure polymer), resistivity is very high and further separation of the chains increases the resistivity only slightly. As the black concentration increases, an increasingly large proportion of the current is carried by the carbon chains. Partial separation of the chains at the crystalline melting point at the optimum loading results in a significant increase in resistivity. At very high concentrations, carbon chains are numerous and expansion of the polymer does not effectively reduce the number of continuous carbon networks or
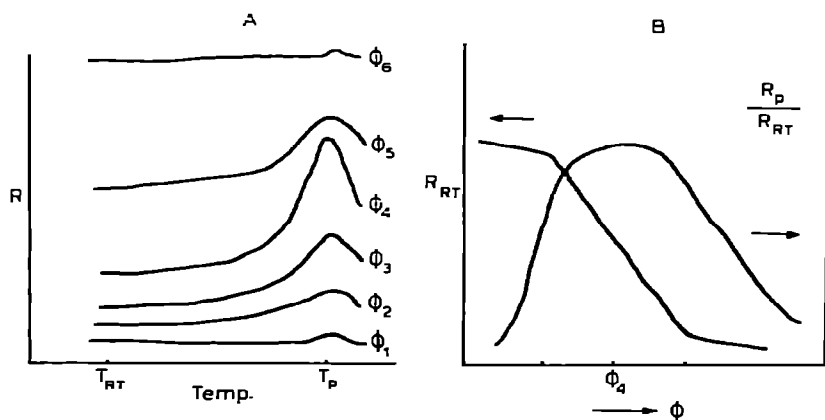

Fig. 8. Schematic of (A) resistivity—temperature curves at various concentrations ϕ of a conductive filler; (B) room temperature resistivity and PTC intensity—ϕ curve.
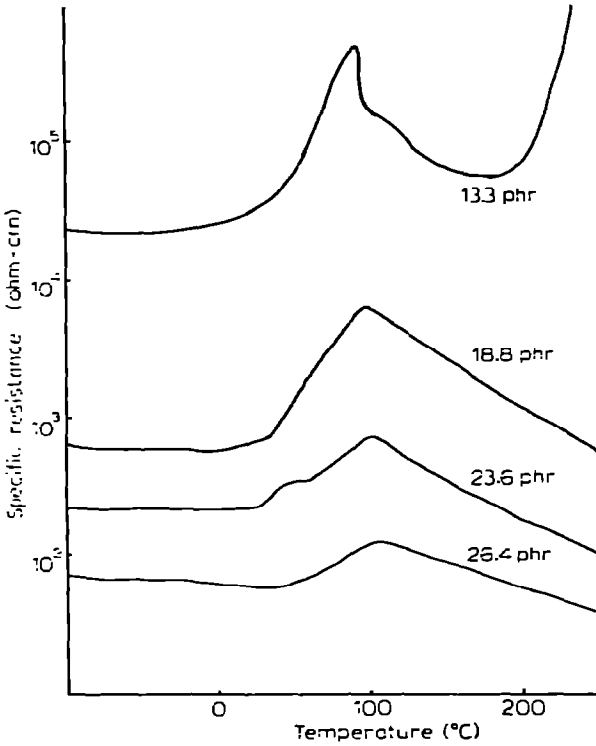
Fig. 9. Resistivity vs. concentration of N472 carbon black in EVA.

electron tunneling. Figure 9 shows the resistivity vs. temperature curves of EVA containing varying concentrations of N472 black. Figure 10 shows the PTC intensity vs. concentration of N472 in EVA. Both figures demonstrate the advantage of ETA for scanning black loaded semicrystalline polymers for applications requiring both high and low PTC intensity compounds. The effect of black parameters on room temperature resistivity and PTC intensity of semi-crystalline polymers is the subject of another communication [18].
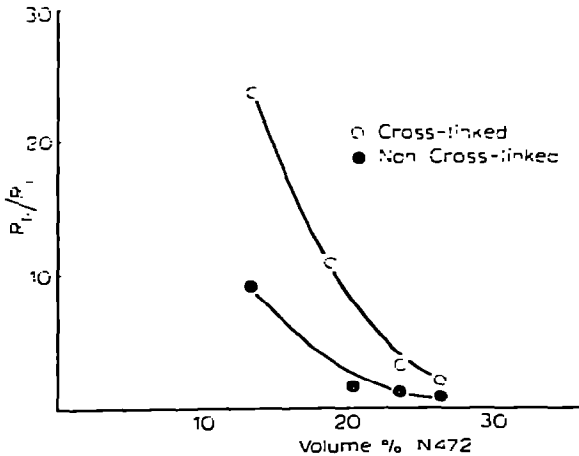

Fig. 10. PTC intensity vs. concentration of N472 black in crosslinked EVA.

CONCLUSION

ETA thermographs show features not observed by other thermal methods. Transitions are seen at the point of reversion of amorphous polymers and should provide useful indicators of limiting service temperatures. In PVC compounds, the approach has advantages over existing stability tests.

ETA is an improved scanning tool for PTC materials and for other applications of carbon filled semicrystalline or amorphous polymers where the temperature sensitivity of resistivity is important.

ACKNOWLEDGEMENT

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