Anomalous Behavior of Electrical Conductivity and Thermal Noise in Carbon Black-Containing Polymers at T_g and T_m

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Synopsis

Pronounced maxima in resistivity–temperature curves have been found at or above T_g for a number of amorphous polymers (PS, PMMA, PVC) containing a small percentage of carbon black. The maxima appeared only after a certain period of storage at $T < T_g$ or at heating rates substantially higher than those used in cooling the samples prior to the measurement. For this reason, no maxima were observed during cooling. In crystalline polymers (PE, PP), maxima at T_m appeared both on heating and cooling. Marked relaxation effects (time-dependent resistivity) were recorded in the T_g and T_m regions. Good agreement was found between resistivity and thermal noise data.

INTRODUCTION

The present paper is an account of an experimental study relating to the behavior of electrical conductivity and thermal noise in some amorphous and crystalline polymers rendered conductive by addition of carbon black. Pronounced maxima in the resistance and the noise level of the samples in the vicinity of the T_g and T_m intervals are the main findings of this study. The maxima at T_g were, however, recorded only after a period of storage at $T < T_g$ or at a heating rate higher than that of the preceding experiment. Measurements of thermal noise at T_g and T_m in carbon-filled polymers have, to the authors knowledge, not been reported previously. As no external voltage is applied across the sample, experiments of this type make it possible to exclude some hypotheses adduced earlier in order to explain the maxima in resistivity at T_g and T_m as resulting from polarization effects, orientation of carbon black particles in the field, etc.

The purpose of the addition of carbon black was to increase the conductivity of the polymer to a level easily accessible to normal resistometric techniques including methods for measurement of thermal noise. The amount of carbon black needed was largely dependent on the technique used for sample preparation and on the type of carbon black and polymer. In the majority of the experiments, we used a highly dispersed carbon black, giving sufficient conductivity at comparatively low concentrations. One of the advantages of using this carbon black grade was the reproducible behavior of the samples with regard to conductivity and dependence on thermal treatment.

Among the extensive literature in the field of electrical properties of polymers, the following findings are of particular interest. In pure polymers, the normal dependence of resistivity on temperature can be described as a change in slope of the usual Arrhenius diagram in the vicinity of T_g.[1,2,3]

At the melting temperature, this change is in some cases accompanied by a step-like decrease in resistivity.[4,5,6] A resistivity maximum above T_g superimposed on the broken Arrhenius line has been reported for amorphous polymers with flexible side groups and for PVC.[7,8] Similar results have been observed by the present authors with amorphous selenium.[9] No resistivity peaks seem to have been reported for crystalline polymers, either at T_g or at T_m.

The above results relate to dc measurements. Measurements with ac methods cannot be used for measurements at T_g and T_m because of the well-known dispersion at these temperatures. On the other hand, a number of interesting results have been obtained using intermittent techniques, i.e., by studying the currents through the sample after the dc voltage has been applied for a certain period of time. By applying this method to some amorphous polymers (PVC and several others), peaks at T_g in the current following the voltage step have been recorded.[10,11] The shape of the peaks has been reported to depend on the voltage step pattern.[12] In some cases, the peaks had a rather complicated structure.[13] For some monomers, peaks in the current occured at certain transition points of the monomers.[14]

As regards the behavior of polymers rendered semiconductive by addition of carbon black, the available literature supports the following conclusions. In amorphous materials of this type, the pattern shown by the temperature dependence of resistivity is rather complicated. Both decreasing and increasing resistivity can be observed, depending on the type and amount of the conductive filler used.[15,16] This behavior is largely understood, the decrease or increase in resistivity being related to regions of a broad minimum observed when the temperature range is sufficiently extended.[17] A few publications only make reference to maxima in resistivity at T_g for amorphous polymers.[17,18] Rubbers behave in principle similarly, anomalies at T_g having been reported recently.[19] Due to the comparatively high dc conductivity of materials of this type, dc and ac measurements give similar results, as ac dispersions at T_g and T_m play a minor role only.

Contrary to semiconductive amorphous polymers, crystalline materials containing carbon black always exhibit resistivity peaks at the melting point.[18,20,21,22] The intensity of the peaks depends on the degree of filling and the type of filler used.[18] For instance, coarser carbon black particles appear to produce more pronounced peaks.[18] Another factor determining the peak height seems to be the T_g of the polymer; the lower this value, the higher the peak.[18] In crystalline carbon black-filled materials also it is normal to find an increase in resistivity with temperature in the solid state.[18,20−22]

The influence of storage time on the resistivity peak at T_g has only been recorded for pure unplasticized PVC[8] and for selenium.[9]

The time dependence of the resistivity in the neighborhood of T_g or T_m as discussed in the present paper seems not to have been considered in the available literature. This dependence constitutes a useful tool for explaining the conditions under which the resistivity peaks appear. Finally, the peaks reported in the literature are usually explained in terms of orientation effects induced by the

applied field.[2,7,17,18,19]   In this respect, also, the present results may help to throw some light on this issue, as the thermal noise method used here for following the resistivity works without any external voltage across the sample.

EXPERIMENTAL

Samples

The samples used in this investigation were prepared according to three different methods: (A) compression molding of an intimate mixture of carbon black with the powdered polymer; (B) intimate blending of carbon black with a solution of the polymer in a ball mill, film casting with slowly evaporating solvents, disintegrating the film, and compression molding; and (C) calendering of the carbon black/polymer mixture between heated rolls, disintegrating the product, and giving it the final shape by compression molding.   The influence of the method of preparation on the properties of the samples is discussed below.

The compression molding was carried out in a KBr press tool of standard design.   Samples made according to method A were preheated for 15 min, whereas 5 min was long enough when shaping the samples using methods B and C.   The following temperatures and pressures were used to produce samples with sufficient mechanical strength and reproducible resistivity.   LDPE, 120°C/2 kbar; HDPE, 135°C/3 kbar; PP, 180°C/2 kbar; PVC, 150°C/3 kbar; PS and PMMA, 160°C/3 kbar (for method A, 5 kbar was used to increase strength of the amorphous polymers).   Higher temperatures or pressures did not influence the resistivity of the samples.

The solvent in method B was toluene for PS and PMMA, and acetone/carbon disulfide for PVC.   PE samples could not be produced according to method B. All solvents were of analytical grade.

The calendering machine was a Rapra Micro Mill; processing time, 5 min; processing temperatures, 150°C for the polyolefins, 160°C for PS and PMMA, and 165°C for PVC.   Prolonged calendering often resulted in increased resistivity (oxidation effects).

The dimensions of the disc-shaped samples were: diameter, 13 mm; thickness, 0.5–1.0 mm.   Before and between measurements the samples were kept in a desiccator over phosphorus pentoxide.

The electrodes were applied by painting the two planar surfaces with a thin layer of a colloidal silver dispersion (Acheson type 1415).

The reproducibility of the resistivity values using methods A–C was ±5% for the crystalline and ±10% (±30% for method A) for the amorphous polymers.

It is known that a critical weight concentration, w_1, of carbon black must be reached in order to obtain a transition from a nonconductive to a conductive polymer.[23]   This transition normally extends over a certain range ending at a concentration w_2 corresponding to a mixture whose conductivity remains almost constant when the carbon black concentration is increased above the w_2 value. The concentrations chosen in this case were intermediate between w_1 and w_2. For this reason, the resistivity of the samples was comparatively high.   The noise measurements demanded slightly higher concentrations, in the neighborhood of w_2, in order to match the input impedance of the amplifier (100 MΩ). The critical concentration w_1 depends largely on the carbon black type used, the polymer, and the technique of preparation.

TABLE I
Properties of Different Grades of Carbon Black Used

Type	Classifica-tion	Nitrogen surface area, m^2/g (BET)	Approximate diameter, Å
Ketjenblack EC[a] (AKZO)	conductive	800	10–100
Philblack N220 (Phillips)	ISAF	120	200
Philblack N770 (Phillips)	SRF	25	700–800
Copper powder (ROC/RIC, USA)	—	—	4.000

[a] Volatile matter, 3.5%, ash content 0.7%.

TABLE II
Properties of Polymers Used

Polymer	Manufacturer	M_w or density	M_w/M_n or melt index
PS	Polyscience, USA	227.000	3.07
PMMA	Diakon MG 100 (ICI)	1.18 g/cm³	—
PVC	Pevikon KL-2 (KemaNord)	128.000	2.30
LDPE	Alkathene 68300 (ICI)	0.924 g/cm³	$MFI = 8$ (190/ 2.16)
HDPE	S.N.P.A. Aquitaine (France)	70.300	1.10
PP	Propathene GSE608 (ICI)	0.909 g/cm³	$MFI = 2$ (230/ 2.16)

In the majority of the experiments, a highly conductive grade of carbon black was used (Ketjen Black E-C, KBEC) giving good conduction at very low concentrations. Some of the samples were prepared starting from ordinary grades. The properties of the carbon black grades used are specified in Table I.

The properties of the polymers are listed in Table II. Polystyrene and high-density polyethylene were laboratory grades, while low-density polyethylene, polypropylene, and poly(methylmethacrylate) were commercial products. The poly(vinyl chloride) was a pure resin not containing any additives.

Several other commercial PS, PVC, and LDPE grades were used. No influence of the additives on the results could be detected.

The methods of preparation strongly influenced the properties of the samples. In the first place, there was a marked difference in the lower critical carbon black concentration w_1 for samples prepared according to methods A–C described above.

Compression-molded powder mixtures (method A) gave a very low value of w_1, as illustrated in Figure 1 for PS. This is in accordance with previous findings relating to the dependence of w_1 on the size ratio of the two powder components.[24] In the present case, the KBEC carbon black had an extremely fine structure (10–30 Å by 100 Å). Method A produced samples suitable for the experiments.
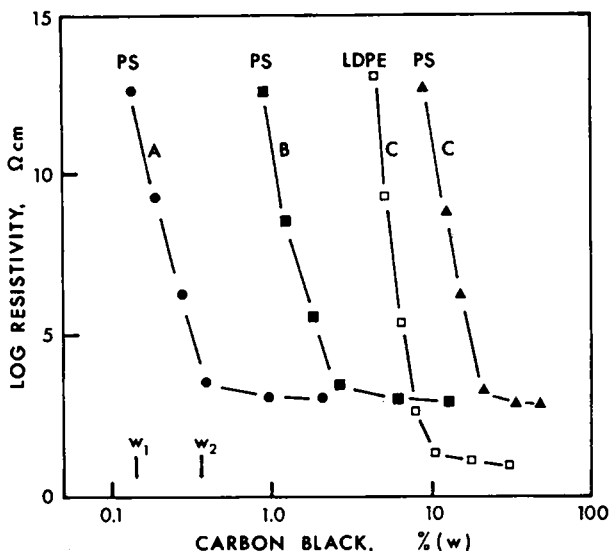
Fig. 1. Resistivity vs. weight per cent of carbon black in PS and LDPE: w_1 and w_2 denote the critical concentrations of the nonconductor–semiconductor transition; (A), (B), (C) method of preparation; applied dc field, 100 V/cm.

However, it could only be used with polymers provided as powders (PS, PE, PP, and PVC).

Method B, i.e., the solution technique, gave critical concentration values w_1 higher than in the previous case, as illustrated in Figure 1 for PS. With this method, carbon black conductive networks are probably formed during the evaporation of the solvent, as the samples lost their conductivity upon calendering, unless the carbon black content was increased.

Method C, calendering, yielded conductive polymers with values of w_1 higher than those obtained with methods A and B, as shown in Figure 1 for PE and PS. It may be noted that PE, being a crystalline polymer, required less carbon black to become conductive. This finding has been reported previously,[18] although in the present case the amount of carbon black necessary to reach the w_1 value was substantially lower (ca. 5%) than that reported for normal carbon black grades (about 30%).[18] We found method C to be preferable when preparing conductive samples of crystalline polymers and PVC.

Measuring Equipment

The compression-molded samples were placed in a thermostat-controlled brass cylinder described previously.[9] The sample temperature was measured with a thin Nichrome-Nithermocouple (Philips) attached to the earthed side of the sample. The temperature was recorded with a digital voltmeter (Keithley Model 160). Thermocouples inserted in the samples gave values differing by a maximum of 1°C from the values determined according to the above method. The heating/cooling rates were varied between 0.1° and 20°C/min with a constancy of 1%. Dry nitrogen was circulated in the sample box.

The resistance of the samples was determined using a Keithley Electrometer (voltmeter Model 610B or 160), the accuracy of these measurements being

±1%. The voltage applied to the samples was 0.1–100 V, corresponding to a field strength between 1 and 1000 V/cm.

The noise measurements were carried out with a low-noise preamplifier (Brookdeal Nanovolt 431 with an input impedance R_i of 6, alternatively 16 kΩ, or a Princeton Applied Research amplifier Model 113 with R_i 100 MΩ). The output was fed into an RMS voltmeter (Brüel & Kjaer 2606, with a frequency range of 2–2 × 10⁵ Hz). In some cases, parts of the noise spectrum were processed with a band-pass filter (Krohn-Hite 3550) together with a heterodyne frequency analyzer (Radiometer FRA-1). An RMS level recorder was the last link in the equipment (Brüel & Kjaer 2305). The accuracy of the noise level readings was ±2%. The formulae used for the calculation of the equivalent noise voltages have been given earlier.[9]

The dielectric properties of the samples (conductance and loss factor) were determined with a three-terminal capacity bridge (General Radio 1620, 50–10⁴ Hz) giving an accuracy of ±0.01% for the capacity values and ±0.1% for the conductance.

RESULTS

The findings presented in this section relate primarily to the anomalies in the vicinity of T_g and T_m appearing in the temperature dependence of the resistivity, and manifesting themselves as maxima in the corresponding diagrams. Some of the resistivity data are compared with results calculated from measurements of thermal noise.

Polystyrene and Poly(methyl Methacrylate)

PS samples prepared according to all the three methods described above exhibited resistivity maxima in the T_g region. The highest reproducibility was obtained with samples prepared according to the solution technique (method B). Figure 2 shows the influence of thermal history and heating conditions on the resistivity at T_g for PS rendered conductive according to this method. Note that no maximum is recorded during cooling of the sample.

An important feature of these results is the dependence of the height of the resistivity maxima on the storage time prior to measurement (storage at $T < T_g$). The longer the storage time, the more pronounced is the resistivity anomaly near T_g. On the other hand, the anomaly can appear on heating the sample without any storage prior to the experiment, assuming that the heating rate is substantially higher than that used in the preceding experiment.

The intensity of the anomalies observed, i.e., the height of the resistivity peaks, is thus dependent on the following factors:
(a) time of storage (t) at $T < T_g$ prior to the experiment; (b) heating rate as related to t and the heating rate of the preceding experiment. Increasing the storage time or the heating rate also shifts the resistivity maximum toward higher temperatures. In general, the peaks do not coincide with the dilatometric T_g value in this case, but appear at significantly higher temperatures.

Figure 2 further shows that the anomaly near T_g appears in the thermal noise temperature diagrams as well. Curve a shown in Figure 2 was calculated from noise measurements at 1 kHz. The equivalent noise resistance was determined using Nyquist's formula.[9,25] The resistivity of the samples was found to be
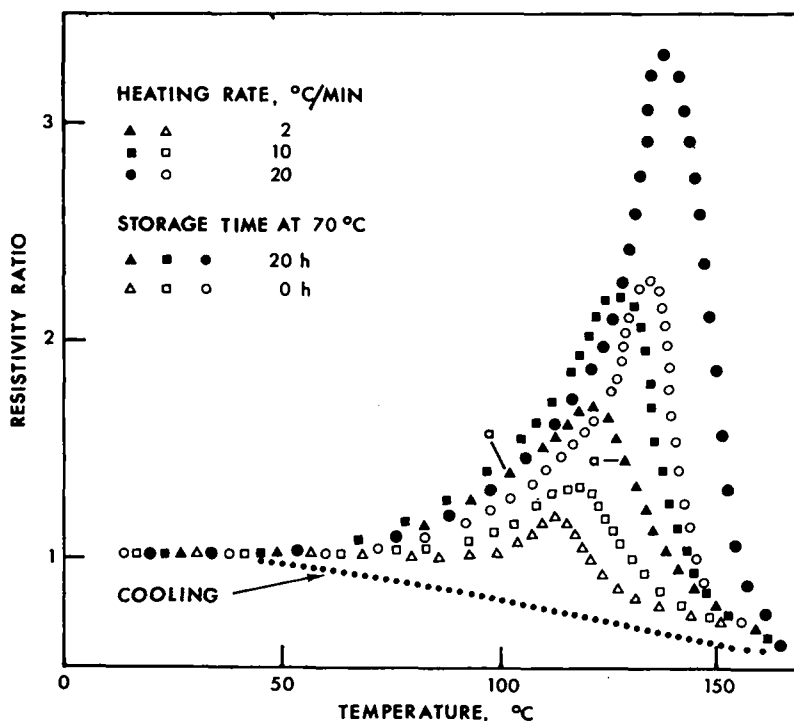
Fig. 2. Resistivity ratio (resistivity/resistivity at room temperature) vs. temperature for PS (4% carbon black, KBEC, method B) for different thermal histories and heating rates. Samples cooled from 160°C → R.T. at 0.5°C/min before storage; R.T. resistivity, 10^5 ohm cm; dc field, 1 V/cm; curve a, coinciding resistivity and thermal noise at 1 kHz, eq. (1).

weakly dependent on frequency, and the relative change in resistivity at T_g was independent of frequency (50–10,000 Hz). It should be noted that no external voltage is applied to the sample in this type of experiment. Consequently, the anomalies reported seem not to be due to polarization effects, as has often been stated.[2,7,17,18,19]

The dependence of the resistivity peaks on storage time and heating rate suggests that the resistivity in the peak region will depend on time when the temperature is kept constant. Such relaxation effects were in fact observed; Figure 3 gives a few examples. This figure shows the resistivity–time curves recorded at four different temperatures, 100°, 110°, 120°, and 130°C. The lowest temperature is below, the two intermediate within (just below the peak), and the highest above the peak region. There is only a slight time dependence of the resistivity before the anomaly region is reached, while a pronounced relaxation effect can be seen at 130°C. At 110°C, i.e., within the region, the resistivity passes through a maximum when followed for a sufficiently long period of time.

Relaxation effects can also be seen at temperatures below the anomaly (peak) region. Figure 4 shows that the relaxation processes involved at 75°C in PS are very slow but significant.

The slow decrease of resistivity with time, Figure 4, curve a, may possibly be related to the volume relaxation of a sample kept at a temperature under T_g.[26] In order to support this assumption, the following experiment was performed. A sample which had been brought into an equilibrium state at RT was rapidly
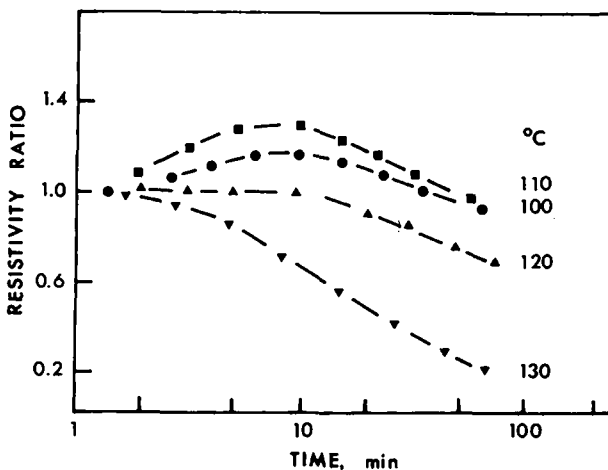
Fig. 3. Resistivity ratio (resistivity/resistivity at 1 min) vs. time at different temperatures in the T_g region: PS, 4% KBEC, method B, storage 4 hr at 70°C; heating rate, 2°C/min; dc field, 1V/cm.
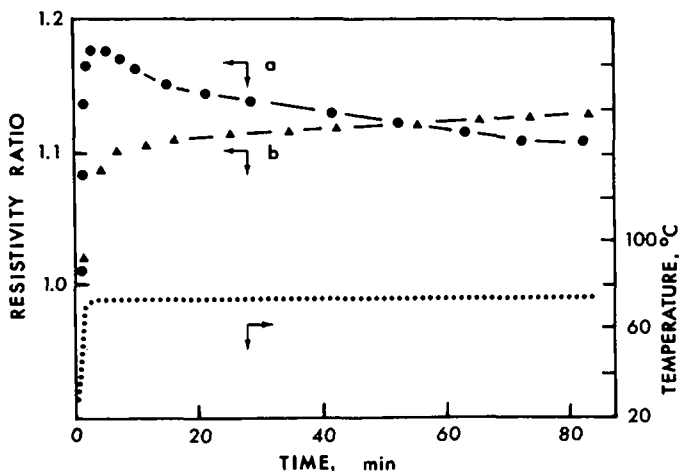

Fig. 4. Resistivity ratio (cf. Fig. 3) vs. time in the glassy state of PS. Samples similar to those in Fig. 2 (4% KBEC). Sample a cooled from 160°C → R.T. at 20°C/min; sample b, from 70°C (storage 20 hr) → R.T. at 0.1°C/min. Both samples then heated to 75°C at 10°C/min; dotted line denotes the temperature–time course; dc field, 1 V/cm.

heated to 75°C and the resistivity recorded simultaneously. It may be seen from Figure 4 (curve b) that the resistivity does not reach a constant value when the sample temperature is 75°C, but increases with time. This is in qualitative agreement with the volume relaxation behavior,[26] assuming that an increase in volume is associated with an increase in resistivity due to greater distance between the carbon black particles.

PMMA prepared according to method B (solution) showed peaks in the resistivity–temperature curves for samples having appropriate thermal history, Figure 5. As for PS, no resistivity peak was recorded during cooling. The influence of storage time and heating rate was similar to that recorded with PS samples.
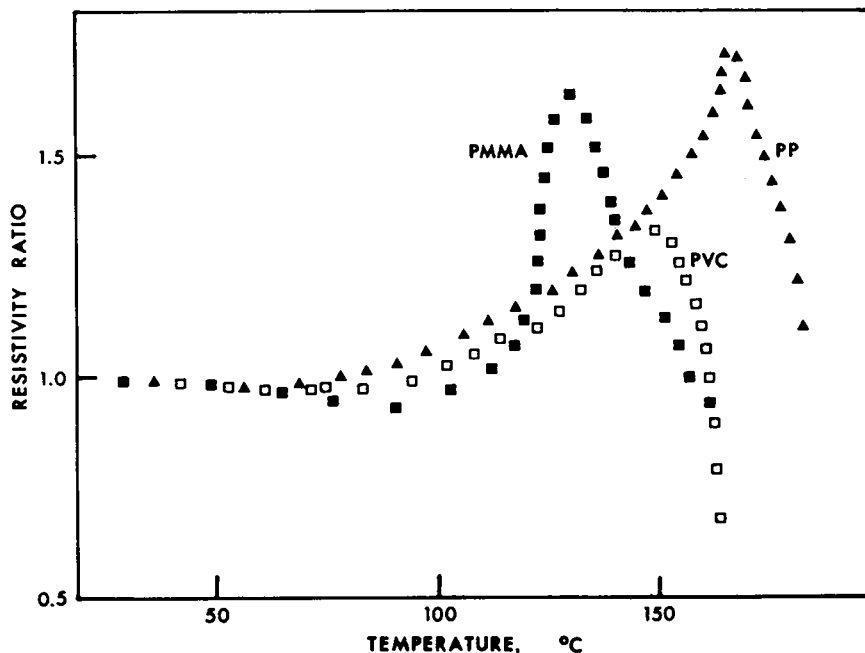
Fig. 5. Resistivity ratio (cf. Fig. 2) vs. temperature for PMMA, PVC, and PP. PMMA: 4% KBEC; method B; R.T. resistivity, 10^6 ohm cm; storage, 20 hr at 70°C. PVC: 2% KBEC; method A; resin particle size, 1 μm, R.T. resistivity, 10^4 ohm cm; storage, 20 hr at 65°C. PP: 0.5% KBEC; method A; R.T. resistivity, 10^3 ohm cm; peak not influenced by storage at R.T., heating rate, 2°C/min; dc field, 1 V/cm.

Poly(vinyl Chloride)

PVC samples showed a somewhat different behavior in the temperature region investigated. The resistivity–temperature curves had, contrary to the polymers discussed above, a high positive slope, that is to say, the resistivity increased sharply with temperature. For PS and PMMA, there was a slight decrease. The anomalies recorded with PVC samples were also different, as they could not be considered as resulting from a simple superimposition of a peak onto the R-T curve. The resistivity peaks were followed by deep minima lying below the parent R-T curve, i.e., the curve which did not show any anomaly and which could be obtained by measuring on samples not stored prior to the experiment, Figure 6. On increasing the storage time at $T < T_g$, this effect became more pronounced. Figure 6 also clearly shows the influence of the storage time on the intensity of the peaks, which in this case are close to the dilatometric T_g value.

The results shown in Figure 6 relate to calendered samples, which basically behaved similarly to samples of PS and PMMA. On the other hand, PVC samples prepared according to method A (compression molding of powder mixture) showed a resistivity peak close to the molding temperature, Figure 5. The reason underlying this peculiar behavior is not known.

Some features of the behavior of carbon black-filled PVC may possibly be associated with the slight degree of crystallinity of this polymer.
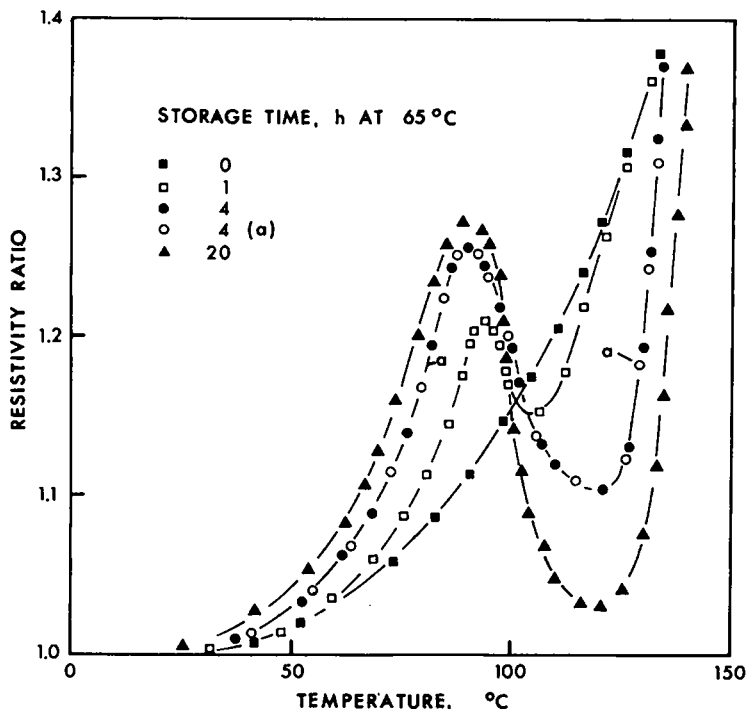
Fig. 6. Storage time dependence of the resistivity ratio (cf. Fig. 2) vs. temperature in the T_g region for PVC (7.5% KBEC; method C; R.T. resistivity, 10^4 ohm cm; heating rate, 2°C/min); dc field, 1/cm; curve a, identical resistivity and thermal noise data at 1 kHz, cf. eq. (1).

Polyethylene and Polypropylene

Contrary to the amorphous polymers discussed above, carbon black-containing samples of PE and PP did not exhibit any anomalous behavior in the vicinity of T_g, the resistivity–temperature curves being smooth in the glass transition region. On the other hand, marked peaks were recorded in such diagrams within a region centered around the melting point of the polymer.

A typical result obtained with LDPE samples containing carbon black (high-structure grade) is shown in Figure 7. The well-known difference in the course of melting and crystallization is reflected in the curves shown. Similar results were obtained with a number of other samples differing, for example, in the carbon black content, structure of carbon black, preparation, etc.

The hysteresis between the R-T curve portions obtained on heating and cooling of polyethylene seems to be limited to the melting region only. At lower temperatures, the heating and cooling curves almost coincide. In this respect, there is a distinct difference between the T_m peaks in resistivity and those recorded near T_g. Further, the temperature at which the peak maxima obtained on heating the sample are situated always coincides, within a few degrees, with the melting point of the polymer. On the other hand, peaks recorded during cooling appear at significantly lower temperatures.

A further difference compared to amorphous polymer is the reappearance of the peaks on repeated heating; storage of the samples below T_m is not necessary.
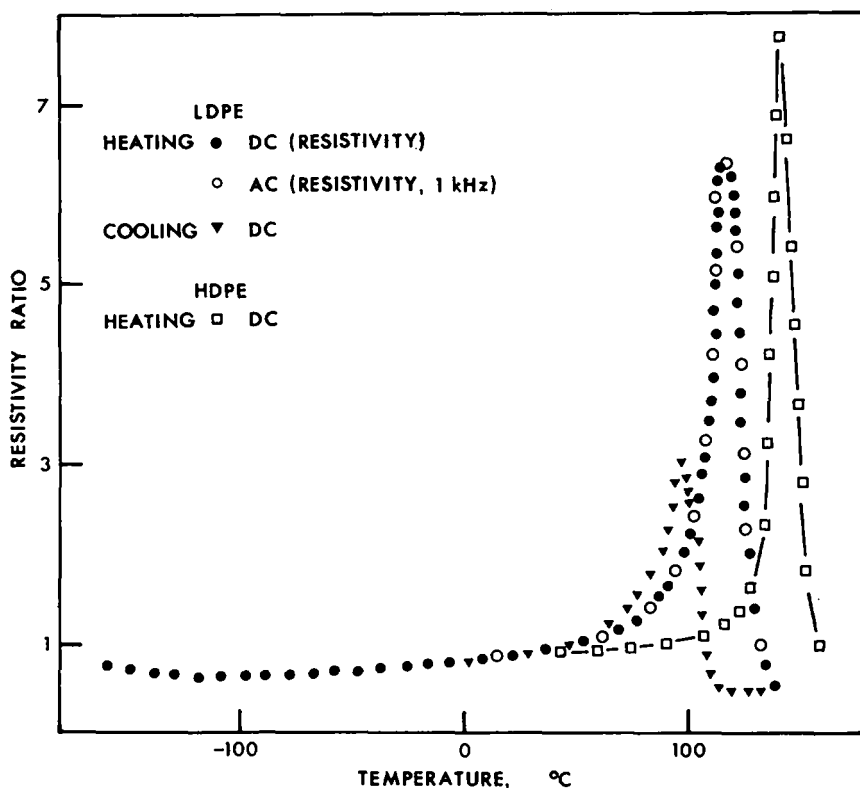
Fig. 7. Resistivity ratio (cf. Fig. 2) vs. temperature for LDPE (6.5% KBEC; method C) and HDPE (3.0% KBEC; method C); R.T. resistivity, 10^5 ohm cm for LDPE and 3×10^3 ohm cm for HDPE; heating (cooling) rate, 1°C/min; dc field, 1 V/cm.

There is no basic difference in the behavior of the samples when the dc or the ac resistivity is measured. Actually, the reheating curve in Figure 7 represents the ac resistance values at 1 kHz. The ac measurements showed that the resistivity was independent of frequency.

As the behavior of HDPE and PP was in all the above discussed respects similar to that of LDPE, only single curves showing the R–T curve are reproduced here, in Figure 7 for HDPE and in Figure 5 for PP. Again, the curves shown here are typical of a large number of similar results.

In a series of experiments, the time dependence of the resistance in the T_m region was studied, Figure 8. An LDPE sample was heated at 2°C/min to the four temperatures indicated, three below and one above the peak temperature (84°, 102°, 106°, and 118°C). The sample was similar to that used in Figure 7. At 84°C, well before melting started, there was no time dependence of the resistance within the time period investigated (20 min); at 102° and 106°C, a slight increase was observed, while at 118°C, a marked relaxation became evident. In this respect, the behavior above the critical temperature, i.e., above T_m and T_g, was similar.

The time dependence was studied with a large number of samples of varying purity and carbon black content as well as varying carbon black type and different measuring methods (dc, ac, noise measurements). In all cases, the typical behavior shown in Figure 8 was recorded.

TABLE III

Influence of Carbon Black Particle Size on Ratio of Resistivity at T_m to Resistivity at R.T.
(Logarithmic Ratio, R_p)[a]

Particle size, Å	log ratio R_p[b]	Resistivity at R.T., ohm cm	Carbon black, % by weight
10–100	1.8	10^5	6.25% Ketjen Black EC
200	2.8	10^2	10% ISAF
700–800	3.7	10^2	15% SRF
4000	4.5	10^5	35% CU-powder (by volume)

[a] Calendered samples of LDPE with carbon black concentration approximately equal to the higher critical concentration w_2. Calendering temperature, 150°C.
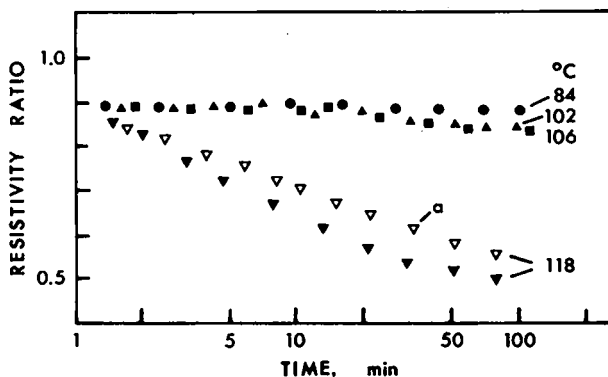
[b] According to ref. 18.

Fig. 8. Resistivity ratio (cf. Fig. 3) at different temperatures in the T_m region for LDPE. Same samples as in Fig. 7. Heating rate, 2°C/min; dc field, 1 V/cm; curve a, thermal noise values (1 kHz).

The height of the resistivity peaks, measured as the ratio of maximum to room temperature resistivity, was found to be low for the carbon black type used (KBEC). This is due to the fact that the peak height depends on the size of the carbon black particles, as shown in Table III. In general, the peak height increases with particle size.

FINAL REMARKS

The main results of this investigation can be summarized as follows. For amorphous polymers rendered conductive by addition of a few per cent carbon black, pronounced peaks appear at or above T_g for samples which have been stored for a period of time at $T < T_g$. The intensity of the peaks and the temperature at which they appear both increase with storage time. The peak appears only during heating of the sample; during cooling, the resistivity changes monotonously with temperature. The resistivity within the peak region shows pronounced relaxation effects.

The behavior of crystalline polymers is similar. However, the peaks appear at T_m, not significantly above as in the preceding case, and the R–T curves during heating and cooling are largely symmetrical, no storage time being needed

for the peaks to develop, although there is a hysteresis effect between heating and cooling peaks associated with the peak shape and their temperature position.

An important feature of the resistivity peaks is their dependence on time, as reflected in the influence of storage time, heating rate, and also as manifested by the time dependence of the resistivity within or above the T_g or T_m region. This dependence appears to have escaped notice in the works published hitherto. It may, at least partly, explain the widely differing results obtained by other authors. It may also account for the fact that in some cases resistivity peaks have not been found.

The literature does not provide any explanation of the effects observed. Qualitatively, such effects may be related to a structure formed by the carbon black particles. Let us assume that such a structure in its consolidated state has a lower resistivity than when it is disturbed. Such disturbances are likely to occur at temperatures at which the polymer matrix undergoes a change of state, that is to say, at or above T_g or T_m.

The behavior of such a structure in the melting region is easy to understand. Below T_m, the carbon black structure is highly dependent on the crystalline structure of the polymer, the carbon black particles being incompatible with the crystalline parts. At T_m, this structure is destroyed due to a more homogeneous distribution of the particles. This in turn results in increased resistivity. When increasing the temperature above T_m, a new structure is formed, with a higher heterogeneity and thus lower resistivity. Consequently, the resistivity peaks could be associated with the transition between two carbon black structures adapted to the state of the polymer below and above T_m. According to this assumption, the resistivity in the T_m region should be time dependent. The results given in Figure 8 support this hypothesis.

With regard to T_g, a similar reason appears plausible. In this case, it may be expected that the formation of a carbon black structure will require a substantial period of time, especially at $T < T_g$. This possibly explains the dominant role played by the storage time in this temperature region, where T must not be too far removed from T_g, as otherwise the formation of a structure with lower resistivity would be inhibited. Our hypothesis also explains the influence of heating rate, the disappearance of the peaks on cooling from $T > T_g$ and finally the important observation that the peak does not appear at T_g but at signficantly higher temperatures, at which, owing to lower viscosity, the change of the carbon black structure can take place within reasonable time periods.

It should be noted that the effects reported here are not due to the applied field. This is clearly borne out by the results of the measurements of the thermal noise, such measurements being performed without any external field. The results are found in Figures 2, 6, and 8.

Another illustration is given in Figure 9, showing the excellent agreement between thermal noise levels and resistance values around T_g for PS and around T_m for LDPE. The noise level was related to the resistance of the sample through the Nyquist formula

$$\bar{v}^2 = 4\,k\,T\,R\,B \tag{1}$$

where $(\bar{v}^2)^{1/2}$ is the RMS value of the thermal noise voltage within a bandwidth B at temperature T for a sample having a resistance R at frequencies within B; k is
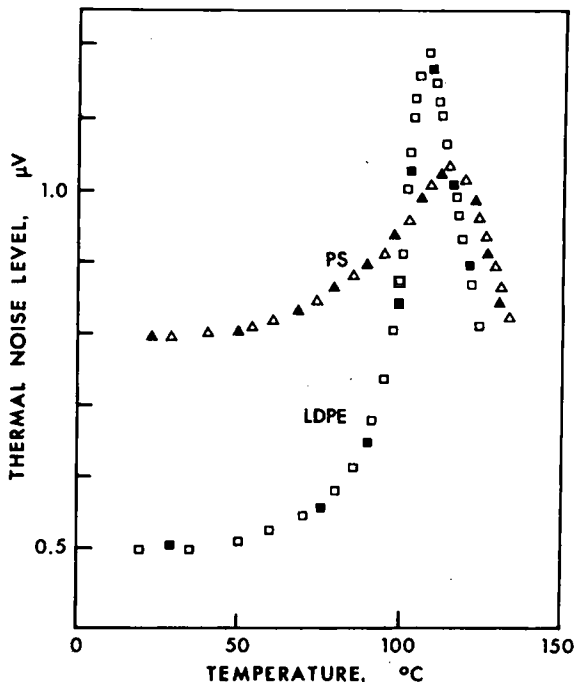
Fig. 9. Measured thermal noise (open dots) vs. temperature in the T_g region for PS and in the T_m region for LDPE. Solid dots, thermal noise calculated from resistivity values at 1 kHz; bandwidth, 500–1500 Hz. PS: R.T. resistance, 38 kohm; same sample as in Fig. 2; storage, 10 hr at 70°C; heating rate, 10°C/min. LDPE: R.T. resistance, 15 kohm; same sample as in Fig. 7; heating rate, 1°C/min.

the Boltzmann constant. When R is independent of frequency, it can be measured at any frequency within the frequency band B. When R is frequency dependent, a narrow frequency band is to be used and eq. (1) integrated over B. Details relating to corrections of the measured noise values for the input resistance of the amplifier have been given elsewhere.[9]

In eq. (1), R was determined by conventional methods, i.e., using a capacity and conductance bridge at different frequencies. The fact that the ac resistivity coincided, within the limits of measuring error, with the R value determined from the noise level shows that there were no fluctuations at T_g or T_m in excess of the normal thermal noise. Similarly to the behavior of resistivity, the thermal noise level exhibited all the time effects described above, cf. Figure 8, without any noise in excess of that given by eq (1). The field strength used in determining the resistivity were in the range of 0.1–100 V/cm.

We do not attempt to go into a closer examination of the physical background to the phenomena encountered here. No doubt the resistivity peaks and their dependence on time are reminiscent of the C_p peaks recorded using DSC or DTA method and explained in terms of enthalpy relaxation. This applies especially to the differences between PS and PMMA on the one hand and PVC on the other.[27]

It may suffice here to present the idea of a carbon black structure transition at the critical points as a qualitative explanation of the resistivity and noise peaks, even though such an explanation may appear to conflict with some recent results

relating to carbon black-filled tetracosan $(C_{24}H_{50})$.[28] Such a system shows a step-like resistivity increase at T_m. There is no peak, as the resistivity does not return to the corresponding lower level above T_m. In order to explain this behavior, it has to be assumed that the carbon black structure is destroyed at T_m, whereafter no reformation of a new, more conductive structure takes place. This would mean that in PE above T_m, the formation of a carbon black structure is favored as compared to the behavior of tetracosan. Considering the long-range interaction in a polymer melt and its possible influence on the dispersed carbon black particles, such an assumption does not appear implausible.

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