

Thermal and Current Noise in Carbon Black-Filled Polystyrene and Polyethylene in the Vicinity of T_g and T_m

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Synopsis

Thermal and current noise in carbon black-filled polystyrene and polyethylene was studied in the vicinity of T_g and T_m . A highly conductive grade of carbon black was used (Ketjenblack EC): 4% for PS and 6.5% for PE. Pronounced maxima in noise voltage were found at T_g for PS and T_m for PE. Prolonged storage at T lower than T_g enhanced the intensity of the noise peak at T_g for PS. A hysteresis occurred on cooling after a heating cycle, with the current and thermal noise being lower on the cooling cycle (no maximum in the case of PS). The peak temperature was lower for PE on the cooling cycle. Good agreement was found between experimental and calculated thermal noise values. The thermal noise spectra were white within the temperature range of 20° to 140°C. The appearance of the current noise peaks could be associated with a conduction model where a decrease in the number of contact points in the carbon black network occurs in the transition regions. This is in accordance with the concept proposed earlier that the carbon black network existing in a polymer undergoes a rearrangement when the polymer melts (softens) or solidifies.

INTRODUCTION

Carbon black-filled polymers are known to exhibit a maximum in resistivity in the T_m region¹⁻⁴ and often also in the vicinity of T_g .^{1,5} In a previous paper, some factors controlling the height of the resistivity peaks at T_g and T_m were investigated.¹ It was found that the T_g peak is highly time dependent, appearing only with samples annealed at $T < T_g$, or for heating rates substantially higher than those used in cooling the samples prior to the measurements. Further, the time dependence of the T_g peak manifested itself in pronounced relaxation effects. The T_m peaks appeared to be influenced by annealing to a lesser degree, although certain time effects (resistivity relaxation) were observed also in that case. The resistivity data presented were complemented by some results showing the corresponding variation of the thermal noise level. For references to resistivity anomalies at T_g and T_m in pure and carbon black-filled polymers, the reader is referred to our previous publication.¹

The present paper reports on the variation of thermal and current noise with temperature in the T_g and T_m regions of polystyrene and low-density polyethylene, respectively. The resistivity peaks are shown to have their

counterpart in the behavior of thermal and current noise. While thermal noise and resistivity follow each other quantitatively (Nyquist's formula), some discrepancies are observed in correlating current noise with the corresponding resistivity values. The spectral distribution is shown to be independent of temperature for both types of noise ($1/f$ spectrum for current noise).

Except for the results published by the present authors for certain carbon black-containing polymers¹ and chlorine-doped amorphous selenium,⁶ measurements of thermal or current noise in polymeric systems seem not to have been given serious consideration. The suggestion put forward by Burgess⁷ to use current noise data to determine the homogeneity of carbon black-containing rubbers appears not to have been taken advantage of. For the sake of completeness, we refer here to measurements of random noise pulses generated in films subjected to high electrical fields⁸ or in discharging electrets,⁹ although these topics lie partly outside the scope of the present work. Brophy¹⁰ studied the current noise in pyrolyzed polyacrylonitrile in order to follow certain structural changes such as graphitization. He found a change from a rather uneven to a smooth $1/f$ spectrum when the pyrolysis temperature exceeded 700°C, indicating a structural change at about 700°C. Carbon fibers have been studied by Owston.¹¹

In other areas, noise studies have clearly demonstrated their usefulness. References to the numerous publications on thermal and current noise in conductors and semiconductors of various types may be found in a number of monographs.^{12,13}

Noise measurements have also been used in studying the fluctuations in magnetic and dielectric solids, as the Barkhausen noise and the ferroelectric and ferromagnetic critical fluctuations near the Curie temperature.¹⁴ Thermal noise measurements have been found valuable in investigating the nature of Curie-type transitions as no external voltage is applied which could influence the course of the transition.¹⁴⁻²⁰ Another example are noise effects associated with ionic transport across membranes,²¹ liquid-liquid interfaces,²² chemical reactions,^{23,24} or DNA transitions.²⁵

In general, noise measurements may provide useful information about the mechanism of charge transport as influenced by the structural parameters of the system under study. On the other hand, some care must be taken in interpreting the results, as the theoretical background concerning the current noise is not particularly well understood.

EXPERIMENTAL

Samples

The amorphous PS samples were dissolved in toluene (analytical grade) and intimately blended with carbon black in a ball mill before film casting with a slowly evaporating solvent. The crystalline PE samples, being more difficult to dissolve and blend in a ball mill at room temperature, were calendered with carbon black between heated rolls until intimate blending occurred.

The mixtures were disintegrated and then given the final shape of a small disc by compression molding. The molding was carried out in a KBr press

TABLE I
Properties of Polymers Used

PS	Polyscience, U.S.A.	$M_w = 227,000$	$M_w/M_n = 3.07$
LDPE	ICI Alkathene 68300	$\rho = 0.924 \text{ g/cm}^3$	$MFI = 8 (190/2.16)$

tool of standard design. The PS samples were heated to 160°C and pressed at 3 kbar, whereas 120°C and 2 kbar was found sufficient for the LDPE samples. Higher temperatures or pressures did not influence the resistivity of the samples.

Samples could also be prepared according to method A in our previous paper,¹ that is, compression molding of an intimate mixture of carbon black with the powdered polymer. The results obtained with these samples will not be given in this paper, since they were in agreement with the results presented below, thus yielding no further information. Details about the sample preparation are given in our previous paper.¹

The dimensions of the disc-shaped samples were 13 mm in diameter and 0.3 to 2.0 mm in thickness (sample resistance adjusted by variation of thickness). The electrodes were applied by painting the two planar surfaces with a thin layer of a colloidal silver dispersion (Acheson type 1415) and heating the sample to 150°C for a few minutes to cure the paint. The electrodes formed in this way were flexible and showed no cracking during the expansion/contraction of the sample upon heating/cooling. The current voltage dependence was ohmic, indicating electrodes with low resistance.

The sample was placed in a holding device of PTFE in which it could be heated to $T > T_g$ or $T > T_m$ without distortion. It was not necessary to use a three- or four-terminal electrode system except during measurements of the capacity of the sample (three-terminal guarded system).

The carbon black used in these experiments was a highly conductive grade (Ketjenblack EC) giving good conduction at low concentrations. This grade had a very large surface area (BET value 800 m²/g), a large pore volume (DBP value 340 ml/100 g), a particle size of 200–300 Å, a volatile matter content of 3.5%, and an ash content of 0.7%. The properties of the polymers used are given in Table I. The carbon black concentration chosen was 4% for the PS samples and 6.5% for the LDPE samples, giving sample resistivity values of the order of 10⁵–10⁷ ohmcm.

Measuring Equipment

The sample mounted in the sample holder was placed in a double-shielded metal cylinder (CoNetic metal, Magnetic Shield Division, U.S.A.) heated by a thermostat-controlled oil bath. The sample temperature was measured with a thin Nichrome–Ni thermocouple attached to a dummy sample placed close to the sample under investigation. This arrangement was necessary to depress spurious rf signals otherwise introduced by the thermocouple wires. The temperature was registered on an X-T recorder giving an accuracy of 1°C. The heating/cooling rate was 1°C/min, with a constancy of 1%. Dry nitrogen was circulated in the sample box. The samples were stored in a desiccator over P₂O₅ between the measurements.

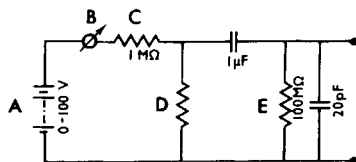


Fig. 1. Circuit for current noise measurements: (A) voltage supply; (B) amperemeter to check the constancy of the direct current; (C) series resistance to prevent signal shortcircuiting by voltage supply; (D) sample; (E) amplifier input resistance (PAR Model 113).

For the description of the electronic equipment, the reader is referred to our previous paper.¹

The current noise measurements were carried out using the conventional technique with a wire-wound resistance (1 M Ω) in series with the current supply to prevent noise signal short-circuiting by the current supply (Fig. 1).

The wire resistance showed negligible current noise compared to the other noise sources. The sample resistance was in the range of 10^3 – 10^5 ohms. The current flowing through the sample was read on a shielded meter and kept constant during the experiment. The usual precautions to eliminate shunting capacitances to earth and spurious noise and hum pickup were taken. Some four-probe noise tests were made giving the samples the shape of a rod (square ends), but the results were the same as for the more convenient two-electrode system.

RESULTS

General Behavior of Thermal and Current Noise at T_g and T_m

It was shown in a previous paper that a minimum time of storage at a temperature lower than T_g is needed for a maximum in resistivity to develop in the T_g region. Alternatively, a heating rate exceeding the previous cooling rate produces a similar resistivity peak at T_g . Prolonged storage enhances the height of the T_g peak compared to the R.T. value of resistivity. No peak is recorded during cooling.¹ It will now be shown that the same applies to the noise data, too. Figure 2 reproduces the peak in thermal and current noise in the T_g region for a PS sample, containing 4% carbon black, stored 4 hr at 70°C prior to the measurement. Corresponding thermal noise values at various temperatures calculated using the Nyquist relation are also shown in the figure. The calculated values are based on the a.c. resistance at 1 kHz of the sample and a bandwidth of 1 kHz. It can be seen that the agreement between experimental and calculated noise values in this frequency range is excellent. The height of the noise peak at T_g is influenced by the combined effect of storage time and heating rate in the same way as demonstrated with regard to resistivity in the previous paper.¹

The peak around T_g exhibited by the current noise appears to be more pronounced than the thermal noise peak.

The results reproduced in Figure 2 are characteristic of the general behavior exhibited by PS samples of various carbon black concentrations and thermal histories.

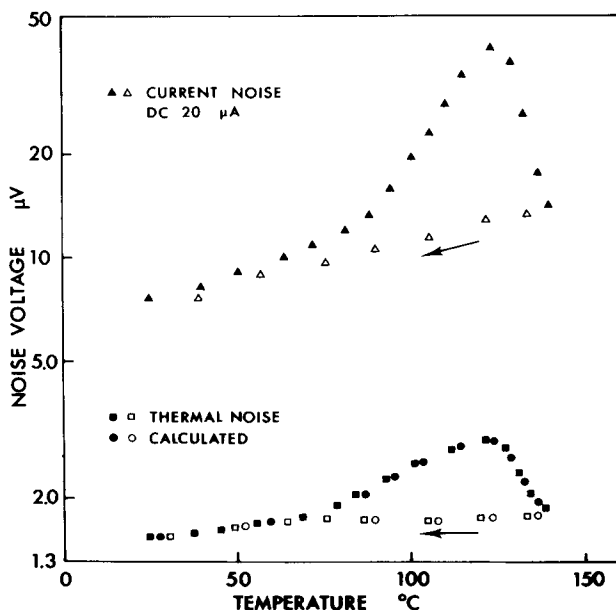


Fig. 2. Thermal and current noise voltage vs. temperature for PS containing 4% carbon black. Corresponding thermal noise values at various temperatures calculated using the Nyquist relation are also shown. Sample stored 4 hr at 70°C prior to measurements. Bandwidth 500–1500 Hz; filled points, heating; unfilled points, cooling.

The crystalline LDPE sample, containing 6.5% carbon black, exhibited a behavior basically similar to that of PS. Figure 3 shows the measured and calculated thermal noise values versus temperature of such a sample. In this case, also, the calculations are based on the Nyquist relation using the 1-kHz resistance values of the sample and a bandwidth of 1 kHz. Figure 3 further illustrates the temperature dependence of current noise in carbon black-filled LDPE. Both types of noise show a pronounced maximum close to the T_m point of the base polymer. Contrary to the amorphous sample, the noise (thermal and current) goes through a maximum at T_m during cooling, even though a hysteresis effect can be seen. As with the amorphous PS sample, the height of the current noise peak at T_m is larger than that of the thermal noise peak. Again, the agreement between experimental and calculated thermal noise values is excellent.

Noise Level versus Sample Resistance

As illustrated above, Figures 2 and 3, the calculated thermal noise levels at 1 kHz corresponding to a bandwidth of 1 kHz agreed well with the measured values. It may be noted that the agreement was not confined to those frequency characteristics, but was rather general within the frequency range studied, that is, 20 Hz–10 kHz. Further, there was no difference in the a.c. and d.c. behavior, the a.c. resistance of the samples used being practically independent of frequency.

Normally, the current noise level (RMS) in resistors of this type is found to vary as a certain power of the resistance and of the current flowing through

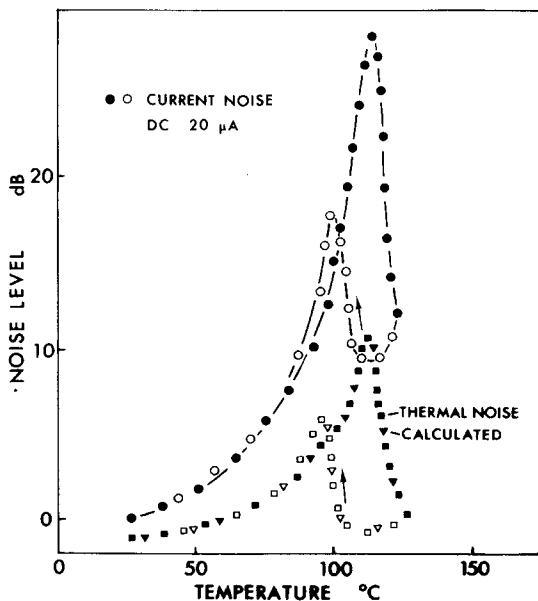


Fig. 3. Temperature dependence of thermal and current noise in LDPE containing 6.5% carbon black. Thermal noise values calculated from the Nyquist relation are also shown. Bandwidth 500–1500 Hz; filled points, heating; unfilled points, cooling.

the sample. As the current was kept constant in the present case, we consider the noise level dependence on the resistance only. Describing this dependence in terms of the d.c. resistance R as R^β , we found the value of β to be between 1 and $\frac{3}{2}$.

Noise Spectra

The noise spectra were determined using a constant bandwidth of 2 Hz within the frequency range 20 Hz–10 kHz. The current used during the current noise experiments had to be large enough to produce a noise magnitude in excess of the background thermal noise even at high frequencies, but still small enough to prevent heating of the samples. Currents of the order of 10 μA were found sufficient. As already mentioned, all the experiments were carried out at constant current through the sample.

The thermal noise spectra of the PS sample were white at all temperatures, as illustrated in Figure 4. The decline of the spectra in the high-frequency region is due to difficulties in correcting properly for the leak capacitance to earth at these frequencies. The current noise spectra at various temperatures (Fig. 4) have the usual $1/f^\alpha$ character, the value of α being 0.6.

Similar results were recorded with the LDPE samples, the thermal noise being white and the current noise showing a $1/f^\alpha$ behavior with α being 0.6, as shown in Figure 5 for some temperatures. The spectra in Figures 4 and 5 were recorded with continuous temperature scanning, no deviations from the described behavior being found at any temperature.

The thermal history of the samples and the value of the current did not in any case influence the character of the spectra at any temperature. Current

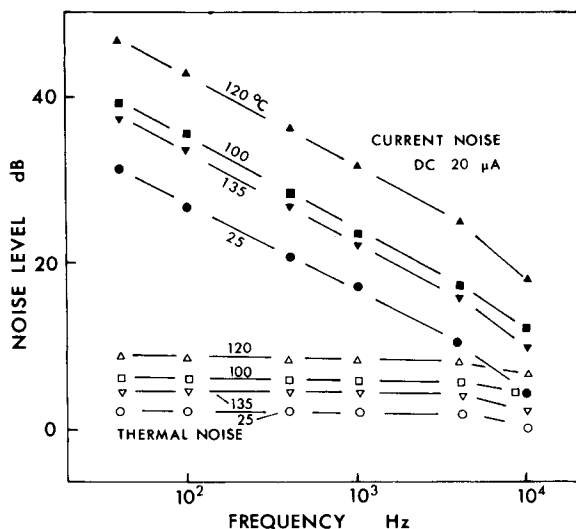


Fig. 4. Frequency dependence of the thermal and current noise at various temperatures for a PS sample similar to that in Fig. 2. Bandwidth 2 Hz.

noise measurements with a four-electrode system did not produce any results differing from those described here.

Sample Capacitance versus Temperature

It is known that the capacitance of a carbon black-containing polymer sample is substantially larger than that of a similar unfilled sample.²⁶ During the capacitance measurements, it was found necessary to use a three-terminal guarded electrode system to eliminate disturbing capacitive effects connected with the wiring and surrounding objects. The calculated dielectric constants were in the range of 50–100. For the PS sample, the effect of temperature was comparatively small, whereas a pronounced minimum was found at T_m with LDPE. Such a minimum accompanied by a hysteresis effect appeared also on cooling the sample from $T > T_m$ (Fig. 6).

DISCUSSION

Thermal Noise

In equilibrium systems, the thermal noise level is given by Nyquist's formula, stating that the square of the mean noise voltage is proportional to the resistance R , as follows:

$$\langle (v)^2 \rangle = 4kTRB \quad (1)$$

where v is the noise voltage, T is the temperature, R is the resistance of the sample within the bandwidth B , and k is the Boltzmann constant. If $S_v(f)$ denotes the spectral density of the open-circuit voltage fluctuations appearing across the sample, eq. (1) can be written as follows:

$$S_v(f) = 4kTR \operatorname{Re}[Z(f)] = 4kTR(f) \quad (2)$$

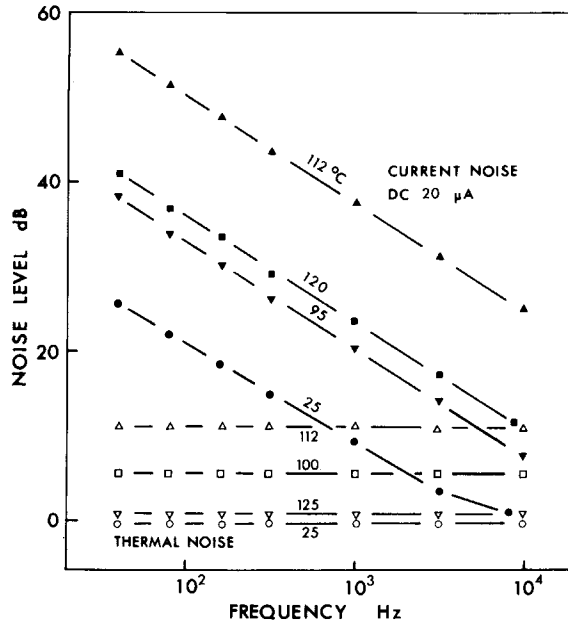


Fig. 5. Frequency dependence of the thermal and current noise at various temperatures for an LDPE sample similar to that in Fig. 3. Bandwidth 2 Hz.

where $R(f)$ is the real part of the sample impedance $Z(f)$ at a frequency f . The thermal noise is thus characterized by a white spectrum (insensitive to frequency) provided that the $Re[Z(f)]$ is frequency independent.

The relation between the measured noise voltage, v , and the sample thermal noise per Hertz, $4kTR(f)$, is given by

$$\langle (v)^2 \rangle = \left(\frac{4kT_S}{R(f)} + \frac{4kT_L}{R_L} \right) / \left[\left(\frac{1}{R(f)} + \frac{1}{R_L} \right)^2 + \omega^2 C^2 \right] \quad (3)$$

where T_S and T_L denote the temperature of the sample and the load, R_L is the amplifier input resistance, $\omega = 2\pi f$, and C is the total sum of the parallel capacitances of sample and load. Equation (3) assumes that the inherent noise of the amplifier is negligible; otherwise, it must be considered in the calculations as shown in a previous paper.⁶ The noise figure of the amplifier used (PAR Model 113) was very small (1 dB) for the chosen sample resistances.

The results of our thermal noise measurements show that no deviation from the spectrum predicted by eq. (1) occurred at any temperature of the sample, including the T_g and T_m regions. The noise level was always in excellent agreement with values calculated from the resistance of the sample. This implies that no fluctuations in excess of those required by eq. (1) are involved in the noise maxima observed at the T_g and T_m transitions of the carbon black-containing PS and LDPE.⁷

Another interesting result is the white character of the noise spectrum, implying a frequency-independent conductivity. Pollak²⁷ has shown that it is possible to distinguish between band-type and hopping-type conduction from the frequency dependence of the conductivity. Hopping or tunnelling

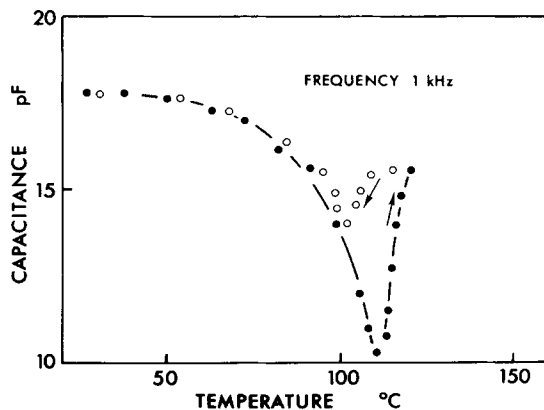


Fig. 6. Variation of sample capacitance with temperature for an LDPE sample identical to that in Fig. 3. Measurements with a dielectric capacitance bridge at 1 kHz.

is normally accepted to be the predominant mechanism of charge transport through carbon black-filled rubber and polymers.^{4,5,26,28,29} The temperature dependence of the resistivity has been difficult to explain. Ferralli and Lewis⁵ assumed a two-mechanism charge process and expressed the resistance by a two-term relation taking account of both the intrinsic resistance of the carbon elements and the interparticle gap resistance (tunnelling model). A correlation with the linear expansion of the polymer was introduced into the gap quantity in the tunnelling term whereby reasonable agreement with experimental data at $T < T_g$ was reached. Crystalline polymers were not treated in that study. At T_g the model failed. This was also the case with similar models for crystalline polymers at T_m .⁴

The frequency independence of the thermal noise results shown above seems to imply that the hopping-type conduction is less dominant in the carbon black-filled polymers used in this study. The glassy and crystalline polymers behave in a similar way, suggesting that a band-type conduction takes place.^{26,27}

The dielectric constants calculated from the capacitances of the samples showed rather high values in agreement with previous findings.^{26,30} Dielectric materials interspersed with conducting spheres show unusually high values of the dielectric constant. In this respect, there are some differences between our results and those reported by Bueche³⁰ concerning electrical properties of carbon black-filled waxes (SBR-tetracosane systems) close to T_m . Bueche noticed a frequency dependence of the resistivity and capacitance of the samples at temperatures exceeding T_m whereas no dependence was found in the solid state. The resistivity of his samples did not decrease when T exceeded T_m . Bueche further found a sharp drop in resistivity at $T > T_m$ at large d.c. voltages. He proposed a theory similar to the theory of gel formation in polymers. This similarity was used to explain the sudden onset of conductivity at a critical concentration of carbon black, where the particles tend to form a conducting three-dimensional network. The theory of Bueche is not applicable to polymers like our PS and LDPE samples since the appearance of the noise peaks at T_g and T_m is not sensitive to smaller variations in the carbon black concentration. An explanation to this is the fact

that the critical range where the polymer changes from nonconductor to a semiconductor covers a rather broad range of carbon black concentration.²⁹

Current Noise

A current flowing through a conductor gives rise to a current noise in excess of the thermal noise level. Normally, current noise is characterized by (i) a power spectrum proportional to $1/f^\alpha$, with α approximately equal to unity,^{12,13} and (ii) an RMS voltage value proportional to the steady current.^{12,13} One of the main problems in explaining the nature of the $1/f$ noise is its unusually broad frequency range.

The hypothesis has been put forward that the current noise is due to cooperative phenomena.³¹ Burgess⁷ postulated that if critical fluctuations in a polymer occurred in the neighborhood of transition temperature such as T_g , they would be associated with the appearance of an excess current noise. The magnitude and spectrum of this excess current noise would provide some information concerning the kinetics and the range of spatial order involved in the transition. Up to now, no excess noise of this type seems to have been recorded.

Similar to the thermal noise behavior, our current noise spectra show no deviations from the average temperature behavior when T approaches T_g or T_m , thus confirming that no critical fluctuations of measurable size are involved in the current noise maxima observed at the transition points of the carbon black-filled PS and LDPE.

Despite the numerous theories in this area, it now appears established that current noise is associated with fluctuations in the number of free carriers.³² Without considering the basic mechanisms of the phenomena involved, we have chosen to discuss our results in terms of a simple empirical model proposed by Hooge,³² who found the following relation to describe the magnitude of the current noise

$$\left\langle \left(\frac{\Delta G}{G} \right)^2 \right\rangle = \frac{c}{N} \cdot \frac{\Delta f}{f} \quad (4)$$

In this formula, G is the conductance, N is the number of mobile carriers in the sample, c is a dimensionless constant, and f is the frequency. This relation holds for most materials.

According to eq. (4), the appearance of the current noise peaks could be associated with a conduction model where the total number of charge carriers decreases as the transition point is approached. Such a model could be based on electrons passing through contacts formed by the carbon black particles, the number of such contacts decreasing due to the thermal expansion or enhanced thermal motion when T approaches T_g or T_m .

It is interesting to note that the decrease in the number of contact points in the carbon black network according to eq. (4) fits well the concept proposed by the present authors in order to explain the occurrence of resistance and noise peaks at T_g and T_m in carbon black-filled polymers.¹ According to this concept, the carbon black network existing, for instance, in a crystalline polymer undergoes a rearrangement when the polymer melts or solidifies. In the region around T_m , the number of contacts should be lower than below or

above the melting point where consolidated and therefore more conductive structures exist. This picture also explains, though only qualitatively, the time effects involved in phenomena of this type. Further studies aiming at a more careful analysis of current noise data at T_g and T_m in carbon black-filled amorphous and crystalline polymers may improve the picture of the conduction mechanisms in such systems. The method also appears promising in studies of flow and transition mechanisms in carbon black-filled liquid or solid systems, the rearrangement of the carbon black network being an indicator of the flow or transition processes taking place in such systems.

Results pertaining to the time dependence of the resistance and, consequently, also of the noise level have been presented earlier.¹

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References

1. C. Klason and J. Kubát, *J. Appl. Polym. Sci.*, **19**, 831 (1975).
2. K. Ohe and Y. Naito, *Jap. J. Appl. Phys.*, **10**, 99 (1971).
3. B. Wargotz and W. M. Alvino, *Polym. Eng. Sci.*, **7**, 63 (1973).
4. J. Meyer, *Polym. Eng. Sci.*, **13**, 462 (1973).
5. M. W. Ferralli and A. F. Lewis, *Phase Transitions—1973*, 409, L. E. Cross, Ed., Pergamon Press, New York, 1974.
6. C. Klason, J. Kubát, and Ch. Söremark, *Kolloid-Z. Z. Polym.*, **245**, 465 (1971).
7. R. E. Burgess, *J. Polym. Sci., C*, **17**, 51 (1967).
8. R. F. Boyer, *J. Appl. Phys.*, **21**, 469 (1950).
9. N. P. Baumann and G. G. Wiseman, *J. Appl. Phys.*, **25**, 1391 (1954).
10. J. J. Brophy, *J. Appl. Phys.*, **33**, 114 (1962).
11. C. N. Owston, *J. Phys. D*, **3**, 1615 (1970).
12. H. Bittel and L. Storm, *Rauschen*, Springer-Verlag, Berlin, New York, 1971.
13. A. van der Ziel, *Proc. I.E.E.E.*, **58**, 1178 (1970).
14. J. J. Brophy, *Fluctuation Phenomena in Solids*, R. E. Burgess, Ed., Academic Press, New York, 1965.
15. M. M. Jannin, *C. R. Acad. Sci. B*, **270**, 411 (1970).
16. F. Micheron and L. Godefroy, *Rev. Sci. Instrum.*, **43**, 1460 (1972).
17. Y. Tominaga, S. Wada, and S. Iida, *J. Phys. Soc. Japan*, **32**, 1675 (1972).
18. Y. Tominaga and S. Iida, *J. Phys. Soc. Japan*, **32**, 1437 (1972).
19. H. Bittel, H. G. Unruh, and G. Hellmiss, *Z. Phys.*, **184**, 1 (1965).
20. J. Petersson, *Z. Angew. Phys.*, **28**, 261 (1970).
21. M. E. Green and M. Yafuso, *J. Phys. Chem.*, **72**, 4072 (1968).
22. B. A. Sokol and M. E. Green, *J. Electroanal. Chem.*, **41**, App. 27, (1973).
23. M. Fleischmann and J. W. Oldfield, *J. Electroanal. Chem.*, **27**, 207 (1970).
24. G. Feher and M. Weissman, *Proc. Nat. Acad. Sci. U.S.*, **70**, 870 (1973).
25. D. Vasilescu, M. Teboul, H. Kranck, and B. Camous, *Biopolymers*, **12**, 341 (1973).
26. R. E. Carley Read and C. D. Stow, *J. Phys. D*, **2**, 567 (1969).
27. M. Pollack, *Phys. Rev.*, **138**, A1822 (1965).
28. E. O. Forster, *I.E.E.E. Trans. Power Apparatus and Systems*, **PAS-90**, 913 (1971).
29. R. H. Norman, *Conductive Rubbers and Plastics*, Elsevier, London, 1970, p. 167.
30. F. Bueche, *J. Polym. Sci. A-2*, **11**, 1319 (1973).
31. D. A. Bell, *Electrical Noise*, Van Nostrand, London, 1960, p. 210.
32. F. N. Hooge, *Physica*, **60**, 130 (1972).

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