

Electrical properties of polyester elastomer composites containing metallic fillers*

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The electrical properties, namely d.c. and a.c. conductivity, of polyester elastomer filled with various metallic and ferrite fillers have been investigated as a function of temperature, frequency and filler concentration. The temperature dependence of resistivity exhibited two regions of low and high activation energy (ΔE). The value of ΔE in the lower temperature region (I) decreased while in the higher temperature region (II) it increased with the increase of work function of the metal used. Only in the case of ferrite-filled composites could a positive temperature coefficient of resistance be observed. The frequency dependence of conductivity revealed that there is a very large intergranular capacitance which was even more in the case of ferrite-filled samples than in metal-filled ones. The various results have been explained on the basis of Schottky barrier formation and the depletion regions formed near the polymer–metal interface.

1. Introduction

Conducting or semiconducting polymer composites have attracted much attention in recent years because of their applications in a variety of areas such as electrostatic charge dissipation, electromagnetic interference/radio frequency (EMI/RF) shielding, electrodes for polymer-based batteries and intermediate layers for high-voltage cable [1–5]. Many reports have appeared both on the theory of electrical conduction [6–8] and experimental findings in a number of such composites [9–11]. A few of these systems also show non-linear conduction processes and a positive temperature coefficient of resistance (PTCR). It is generally known that there is a critical composition of the conductive filler at which the electrical resistance of the composite decreases drastically from the insulating range to conductive or semi-conductive ranges. Some authors contend that this is merely a percolation phenomenon and consider only geometric factors such as particle size, type of dispersion or distribution, shape factor etc. On the other hand, the internal charge transport processes are known to depend on interfacial effects at the filler–polymer interface. A theory for the conduction mechanism taking into account these effects was proposed [7] which clearly brought out the important role played by the interfacial barriers, non-linear conduction processes and the nature of the contact in controlling the overall electrical properties of composites containing metallic fillers. The present studies deal with the electrical properties of a single polymer matrix containing different type of filler so as to obtain the systematic variation in work function of the metal and the barrier height at the polymer–filler interface. The frequency

dependence of the conductivity has been studied so as to obtain greater insight into the interfacial polarization as well as the nature of charge transport in such systems.

Thermoplastic elastomers are increasingly being used in electrical applications where these are mostly in composite form (with carbon black, pigments etc.) [12]. Their potential use for flexible magnets has been studied earlier [13]. However, detailed investigations on the electrical properties of filled systems, especially those containing metallic fillers in these polymers, have not been reported earlier. Further, such polymers offer a matrix which is easy to process without any addition of curing, crosslinking or stabilizing agents and which can take a high concentration of different types of filler. Hence we have carried out these studies on polyester-based thermoplastic elastomers.

2. Experimental procedure

The polymer used was a commercial-grade thermoplastic elastomer, a segmented copolyester containing 76% hard segments of polybutylene terephthalate (PBT) and 24% soft segments of polyteremethylene oxide (PTMO) supplied by Du Pont de Nemours, USA (grade Hytrel 5526); it had a melting point of 212 °C. The fillers used were aluminium, copper, nickel, zinc and ferrite (Fe_2BaO_4), all in powder form. The characteristics are shown in Table I. The samples were prepared by first dissolving the polymer in pure tetrachloroethane at 70 °C to give a clear solution. The required amount of filler in fine powder form was then mixed with the solution and stirred well in the hot condition. This was slowly cooled and the solvent

* NCL communication No. 5042.

TABLE I Characteristics of materials

Material	Origin	Grade	Content
Polyester elastomer	Du Pont, USA	Hytrel 5526	76% polybutylene terephthalate, 24% polytetramethylene oxide
Aluminium powder	Metal Powder Corp., Madurai, India	Electrical	99.9% pure, particle size 12–18 μm
Zinc powder	Metal Powder Corp., Madurai, India	Electrolytic	99.9% pure, particle size 6 μm
Copper powder	Metal Powder Corp., Madurai, India	Electrolytic	99.9% pure, particle size 3–6 μm
Nickel powder	Metal Powder Corp., Madurai, India	Electrolytic	99.9% pure, particle size 6–10 μm
Barium ferrite powder	Morris Electronics, Pune, India	Magnetic	Fe_2BaO_4 , particle size 4 μm

allowed to evaporate in a Petri dish at 40 °C for 24 h. The polymer granules containing dispersed filler particles were then placed on flat glass plates (microscope-grade slides) or between aluminium foil and heated to 220 °C and then lightly pressed. This was then quenched in water so as to obtain thin sheets (1 mm thick, 25 mm dia.) of the composite from which test specimens (13 mm dia.) were cut for further measurements. The electrical conductivity was studied with respect to temperature, frequency and composition. The details of the measurement of electrical conductivity in the d.c. mode have been described elsewhere [9, 10, 14].

In the case of a.c. measurements, an Audrey 380 dielectric spectrometer (Tetrahedron Associates, USA) was used which gives directly the factor σ/ω , where σ is the conductivity at angular frequency ω , from which σ was estimated. All measurements were carried out using a two-terminal test cell provided with shield, heater and thermocouple assembly as described earlier [14, 15].

3. Results and discussion

3.1. D.c. conductivity

The electrical conductivity for these composites was observed to be in the semiconducting range (10^{-6} Scm^{-1}) even at large filler concentration ($\sim 38 \text{ vol } \%$) which is much higher than the threshold value commonly observed for such composites [1–5]. This may be due either to the elastomeric nature of the polymer causing segregation of the metal filler particles after moulding, or to interfacial effects which are discussed later in the paper. Nevertheless, the resistivity was much lower in the filled system than in the original unfilled polymer ($\approx 10^{14} \Omega \text{ cm}$). The temperature (T) dependence of resistivity (R) in samples containing different metallic fillers for the two concentrations of 15 and 20 vol % is shown in Fig. 1 as graph of $\log R$ versus $1/T$. It is seen that in all cases the temperature dependence of resistivity has mainly two regions, namely region I (300–330 K) in which the change is more gradual and region II ($T > 330 \text{ K}$) in which the decrease in resistivity becomes much faster with increase of temperature. In the case of Al and Zn at higher filler concentration ($> 20 \text{ vol } \%$) an additional transition is observed at about 400 K. The activation energy (ΔE) for electrical conductivity as determined from these graphs is seen to be in the range of 0.15 to 0.4 eV for region I and 0.5 to 0.9 eV for region II. The value of ΔE in each of these regions depends on the actual filler used (see Table II).

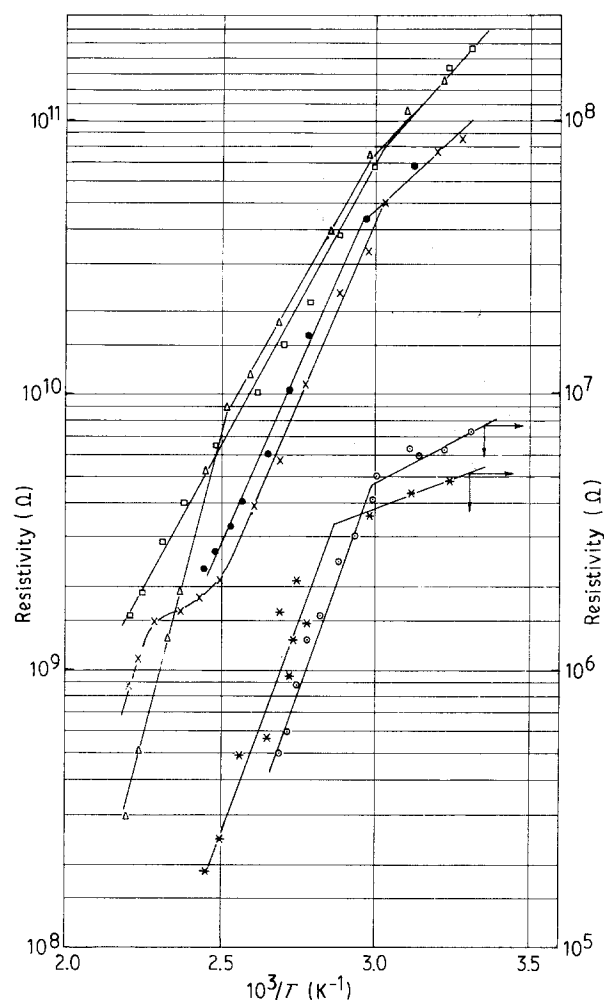


Figure 1 D.c. conductivity versus $1/T$ for different fillers: (○) nickel 15%, (*) nickel 20%, (●) zinc 15%, (×) zinc 20%, (△) aluminium 15%, (□) aluminium 20% by volume.

The most interesting observation was made in the case of composites containing ferrite particles. Fig. 2 shows the resistivity as a function of reciprocal temperature for ferrite-filled composites containing 12 (curve A), 18 (curve B) and 22 vol % (curve C) of filler. It may be noted that at room temperature the range of resistivity (10^7 – $10^9 \Omega \text{ cm}$) obtained in these composites is much lower than that in the metal powder-filled system. The distinct feature which is evident from Fig. 2 is that the resistivity increases with increase of temperature, thus showing a positive coefficient rather than a negative one. The sharpness of this transition from low to high resistance value depends on the filler concentration, it being more evident at high concentration. The PTCR transition is followed by the usual decrease of resistivity with increase of

TABLE II Conductivity parameters for metal-filled copolyester elastomer

Filler ^a	Work function (eV) [2,18]	Activation energy (eV), d.c. conducting		A.c. conductive parameters		
		Region I	Region II	α_A	α_B	β_C/ϵ_0
Aluminium (P)	4.36	0.26	0.375, 0.825	1.0	0.05	1×10^5
Zinc (P)	4.3	0.2	0.52	1.0	0.001	1×10^5
Nickel (P)	5.1	0.102	0.61	-	-	-
Ferrite (P), high %	4.3	(PTC)	-	1.0	0.2	7.5×10^5
Ferrite (P), low %	4.3	(PTC)	0.8	1.0	0.1	7.0×10^5
Aluminium (F)	4.36	0.66	-	-	-	-
Copper (F)	4.8	0.17	0.7	-	-	-
Platinum (F)	6.3	0.16	0.79	-	-	-

^a P = particle, F = foil.

temperature (negative coefficient). It is also of interest to note here at low concentrations of ferrite filler the PTCR peak is quite broad and occurs at slightly lower temperature than that noted in other cases.

The above observations clearly show that the conductivity behaviour in the composites depends very much on the filler used. Amongst the various models suggested for explaining the temperature dependence of conductivity, PTCR effects etc. in conducting composites, there are few which consider the phenomena mainly on the basis of thermal expansion of the polymeric matrix [8, 16, 17] leading to breaking of the network of conductive particles, which in turn increases the resistivity with an increase of temperature. If this was the only cause for observing the PTCR or

other non-linear effects, then one should be able to obtain the same in all the conductive particle-filled systems in the range of critical concentration. However, in the present case none of the metal-filled systems showed any PTCR while the ferrite-filled ones exhibited a distinct PTCR peak. This brings out the importance of interfacial phenomena in governing the conductivity behaviour in these composites.

A conductive polymer composite can be considered as a matrix of particles forming a number of metal-polymer-metal (M-P-M) type of junctions which are connected in series and parallel as shown in Fig. 3. The numbers of elements in series (N_s) and parallel (N_p) are given by

$$N_s = \frac{L - d}{D + d} \quad (1)$$

$$N_p = \frac{(B - d)^2}{(D + d)^2} \quad (2)$$

and the interparticle gap d is related to the filler concentration θ by

$$\theta^{1/3} = D(L - d)/(D + d)L \quad (3)$$

where L is the length and B the breadth of the sample, D is the particle size and d the interparticulate distance.

At each of these junctions the charge transport is strongly dependent on the nature of the contact, trapping centres, the various energy levels involved, the interparticle gap etc. The theory of the conduction process taking into consideration all these factors has been described elsewhere [7]. The salient features which emerge from it are that when an M-P-M structure has Schottky barrier formation the overall resistivity of the composite is given by

$$R_{sc} = A \exp(\Delta/kT) \times \exp \left[- \frac{\beta}{kT} \left(\frac{V^{1/2}}{L\theta^{1/6}} \right) \frac{[1 + L/D]\theta^{1/3}}{1 - \theta^{1/3}} \right] \quad (4)$$

where Δ is the barrier height at the interface due to the difference in work function (ϕ_m) of the two materials, k is the Boltzmann constant, V is the applied potential (constant in present case), β is the Schottky parameter and A is a constant. It is seen from the above equation that (a) the "activation energy" obtained from the log R versus $1/T$ plot would depend on the work

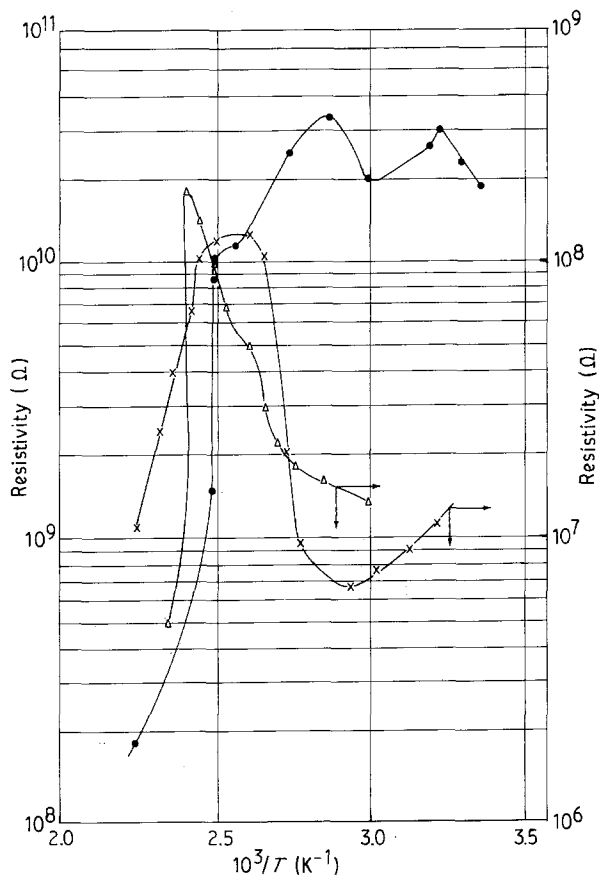
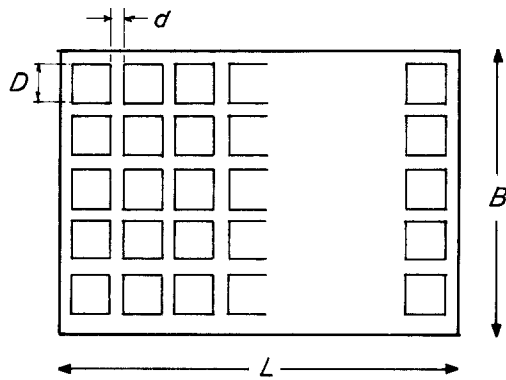
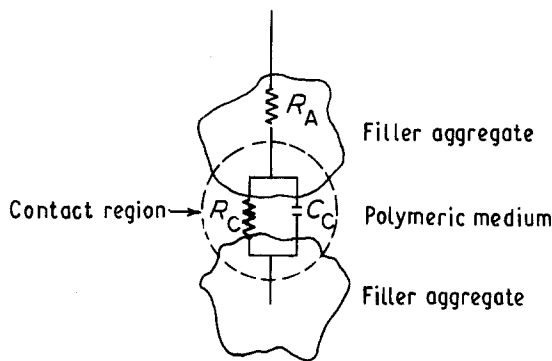


Figure 2 D.c. conductivity versus $1/T$ for barium ferrite composites for different volume fractions: (●) 12%, (Δ) 18%, (×) 22%.



(a)



(b)

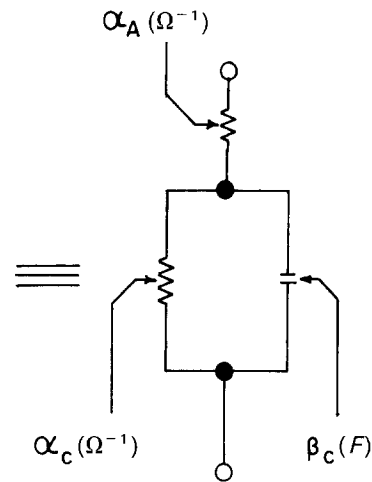


Figure 3 (a) Model of polymer containing uniformly dispersed filler of dimension D . The arrangement is shown on the x - y plane but extends in three dimensions. (b) Equivalent resistor-capacitor circuit in the contact region of filler aggregates. Net d.c. resistance = $R_A + R_C$; net resistance at high frequency = σ_{ac} .

function of the metal used, (b) unless there is a sufficiently large interfacial barrier one would not observe positive coefficients, and (c) the filler concentration which decides the interparticle distance d also affects the temperature coefficient of resistance since it occurs in the second exponential term.

In order to study the effect of metal-polymer contact on the activation energy for conduction, a few experiments were carried out with an M-P-M structure in which the metal M was changed from Al to Cu and Pt so as to vary the ϕ_m value. The temperature dependence of the resistivity in such junctions is shown in Fig. 4. It is evident from the figure that in this case also the temperature dependence is similar to that observed in the composites, wherein two regions of temperature having low and high values of activation energy are noted.

Fig. 5 shows the activation energy (ΔE) in the two regions obtained from these various experiments as a function of ϕ_m value of the metal in contact with the polymer. It is interesting to note that the data derived from composites as well as single junctions follow nearly the same trend. It may be seen that in region I, ΔE decreases with increase of ϕ_m while in region II ΔE increases with increase of ϕ_m . The former result is expected for contact barrier formation at a metal-p-type (in the present case polymer) insulator or semi-

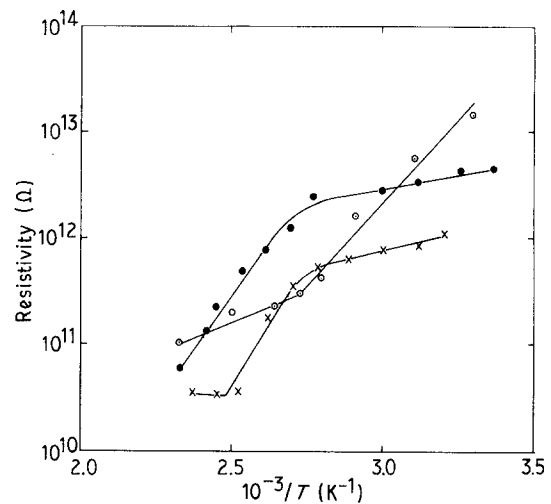


Figure 4 D.c. conductivity versus $1/T$ for different metallic foil polyester-elastomer sandwiches: (x) copper foil, (●) platinum foil, (○) aluminium foil.

conductor interface. Since insulating polymers usually have valence bands at about 6.0 eV below the vacuum level [18] one would find a decrease in ΔE with increase of ϕ_m . This will cause a decrease in the barrier height and hence a lowering of the activation energy. On the other hand, the increase of activation energy

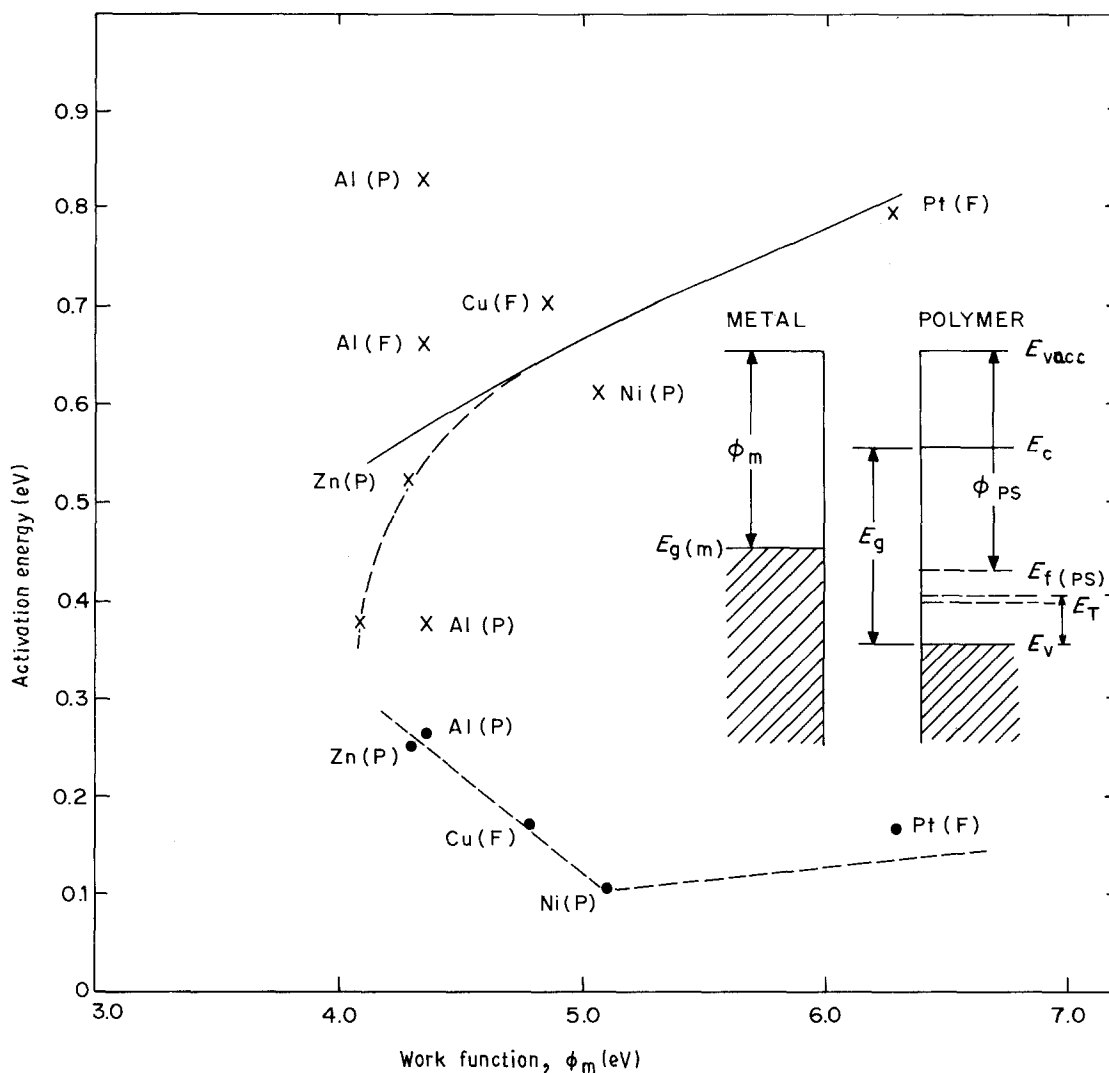


Figure 5 Activation energy variation with work function ϕ_m (eV) for various filler particles (P) and different foils (F) for low and high temperature regions. The inset shows a typical energy-band diagram for the metal-polymer (p-type) function. (---) Region I, (—) Region II

with increase of ϕ_m in the high temperature region is a little unusual. However this can be explained as follows. It is generally known that polymers, being disordered solids, have a number of trapping centres and the charge carriers get localized in these. The energy level for these trapping centres can extend deep into the band gap region and also be distributed exponentially. By varying the work function of the electrode it is possible to scan these, as for example in contact charging [19]. In the present case, it is the difference between the trap depth (E_T) and the ϕ_m value of the electrode that is being determined as the activation energy for region II. If the trapping levels for holes (for p-type) are much above the valence band, then with an increase of ϕ_m the difference between E_T and ϕ_m would increase and hence the activation energy as determined in conductivity measurement would increase. Thus one may consider region I as that where charge transport from metal to polymer is taking place, while in region II the trapped charges are being thermally excited from deep levels to the conduction level/counter-electrode.

3.2. A.c. conduction

The frequency dependences of conductivity, capacitance, loss factor etc. are often used to investigate various types of conduction process, interfacial polarization, junction characteristics etc. In conducting polymer composites the intergranular capacitance (see Fig. 3b) can be high and an important factor in controlling the frequency-dependent behaviour. The a.c. conductivity for the various composites studied in the present case as a function of applied frequency is shown in Fig. 6. Curves A, B, C, D and E correspond to polymer-filled zinc, aluminium, nickel, ferrite low concentration and ferrite high concentration, respectively. It is seen that the conductivity is constant up to a certain frequency (7 kHz) but for higher frequencies it increases sharply. The extent to which this change occurs depends on the actual filler used. In the case of the nickel-filled composite no change in conductivity could be observed within the range of frequencies studied. The frequency (ω) dependence of conductivity (σ) has been studied earlier for conducting polymers and it has been mostly associated with hopping of

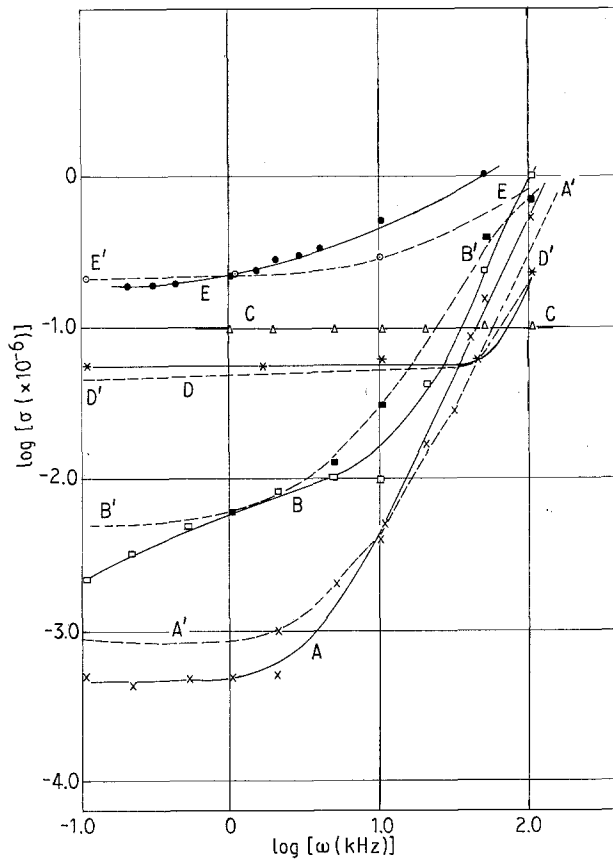


Figure 6 A.c. conductivity with frequency for various fillers. (x) 12 vol % ferrite (curves A, A'); (□, ■) 20 vol % Al (curves B, B'); (Δ) 20 vol % Ni (curve C); (*) 22 vol % Zn (curves D, D'); (●, ○) 20 vol % ferrite (curves E, E'). The dotted curves with primed symbols correspond to theoretically estimated ones according to Equation 5 with various values of parameters given in Table II.

charge carriers wherein $\sigma \propto \omega^n$ ($0.5 < n < 1$) type of behaviour has been observed [20–22]. In the present case such analysis is not possible since the exponent n appears to be quite high and it depends very much on the type of filler used. Alternatively, if one considers the equivalent circuit shown in Fig. 3, the conductivity is given by [3, 23]

$$\sigma_{ac} = \alpha_A \frac{\alpha_c(\alpha_A + \alpha_c) + (\omega\beta_c)^2}{(\alpha_A + \alpha_c)^2 + (\omega\beta_c)^2} \quad (5)$$

where α_A is the net conductance of the particles, α_c is the conductance due to the junction/interparticle gap and β_c is the equivalent capacitance due to the junction. The dotted curves A', B', D' and E' in Fig. 6 are obtained from the above equation using the values of α_A , α_c and β_c/ϵ_0 (where ϵ_0 is the permittivity of free

space) indicated in Table II for the corresponding systems. It is seen that the observed data fall close to these curves, especially in the high frequency region. These values of β_c/ϵ_0 are much higher than those reported for carbon black conductive composites in which β_c/ϵ_0 is in the range of 10^3 to 10^4 . This clearly suggests that there is a very larger intergranular capacitance in the metal-filled systems as compared to other conductive composites. Now, if one considers the metal-polymer junction, the depletion layer thickness (δ) is given by [24]

$$\delta = \left(\frac{2\epsilon\epsilon_0\Delta\phi}{eN_d} \right) \quad (6)$$

where ϵ is the dielectric constant of the material, $\Delta\phi$ the difference between the work function of the metal (ϕ_m) and that of polymer (ϕ_p), N_d is the donor density (here the number of defect states) and e is the electronic charge.

One can estimate the junction capacitance (C_j) for an individual M-P-M unit and then derive the value of the total effective capacitance due to all such junctions in the whole matrix, taking into account the number of series and parallel elements. The value of C_j (per unit area) is given by

$$C_j = \frac{\epsilon\epsilon_0}{\delta} \quad (7)$$

and the total capacitance would be

$$C_{int} = \frac{N_p}{N_s} C_j = \frac{\epsilon\epsilon_0 N_p}{N_s} \quad (8)$$

which is also equal to the factor β_c mentioned earlier. The various values of C_{int}/ϵ_0 were estimated from the above equation with the various parameters assigned the following values: $\epsilon = 3.0$, $L = 1$, $B = 1$, $N_d = 10^{12} \text{ cm}^{-3}$, $\Delta\phi = 0.1, 0.4$ and 0.7 eV and particle size $D = 4, 10$ and $20 \mu\text{m}$. Table III shows the sets of values of C_{int}/ϵ_0 for filler concentrations of 50 and 25 vol %. It is interesting to note that for any filler concentration, the particle size as well as the $\Delta\phi$ value affect the intergranular capacitance in more or less the same order of magnitude. Comparing these values for C_{int}/ϵ_0 with those of β_c/ϵ_0 given in Table II, it becomes evident that for a filler fraction of 25 vol % these are in the same range of magnitude. Exact agreement of the values would be difficult to achieve and it may not be reasonable to expect this, since the distribution of the filler particles and their size have been assumed to be perfectly uniform in the theoretical

TABLE III Effective intergranular capacitance C_{int}/ϵ_0 , for different particle sizes, D^a

$\Delta\phi$ (eV)	C_{int}/ϵ_0					
	Filler volume fraction 0.5			Filler volume fraction 0.25		
	$D = 4 \mu\text{m}$	$D = 10 \mu\text{m}$	$D = 20 \mu\text{m}$	$D = 4 \mu\text{m}$	$D = 10 \mu\text{m}$	$D = 20 \mu\text{m}$
0.1	1.03×10^7	4.15×10^6	2.07×10^6	8.00×10^6	3.26×10^6	1.66×10^6
0.4	5.13×10^6	2.05×10^6	1.03×10^6	3.95×10^6	1.66×10^6	8.26×10^5
0.7	3.88×10^6	1.55×10^6	7.78×10^5	2.99×10^6	1.22×10^6	6.21×10^5

^a $\epsilon = 3.0$, $\epsilon_0 = 8.86 \times 10^{-14} \text{ F cm}^{-1}$, $e = 1.6 \times 10^{-14} \text{ C}$, $N_d = 10^{12} \text{ cm}^{-3}$, $L = 1.0 \text{ cm}$, $B = 1.0 \text{ cm}$.

calculations, while in practice, these are known to be quite irregular. Nevertheless, these estimates of the intergranular capacitance clearly indicate that in the case of ferrite there is a large interfacial effect as compared to metal-filled composites. This appears to be the most likely source of different types of conductivity behaviour or PTCR effect. This is especially true because the filler concentration, thermal expansion coefficient of filler and the polymer matrix used are the same in all cases, so that other possible mechanisms cannot explain the observed differences.

It may be noted that the above analysis is quite different from the usual Maxwell–Wagner–Sillars (MWS) theory for interfacial polarization, formulated for conductive particles dispersed in a dielectric medium [18, 23]. We have estimated the relaxation frequency and $\tan\delta$ values according to the MWS equations in the present case, taking the spherical size of the particles given in Table I, a volume fraction of 0.25, dielectric constant of polymer = 3.0, conductivity of polymer = 10^{-14} S cm $^{-1}$ and conductivity of particles 10^4 S cm $^{-1}$. With these values, there is very little frequency dependence expected for $\tan\delta$ and/or ϵ'' below 10^6 Hz for these composites. Thus, the MWS effect is not likely to contribute to the observed phenomena.

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Received 25 October 1990
and accepted 25 February 1991