Electrical Properties of Poly(vinyl chloride) Compositions

A. L. G. SAAD,[1,*] A. M. HASSAN,[2] and E. A. M. GAD[2]

[1]Microwave-Physics Department, National Research Centre, Dokki, Cairo, Egypt; [2]Petrochemical Department, Egyptian Petroleum Research Institute, Nasr City, Cairo, Egypt

SYNOPSIS

A sample of poly(vinyl chloride) (PVC) and a polar plasticizer consisting of dioctyl phthalate (DOP) and dibutyl phthalate (DBP) was prepared and found to possess inconvenient electrical properties (permittivity, dielectric loss, and conductivity). Different samples of PVC compositions were formulated from the PVC–DOP–DBP system and also variable proportions of a copolymer of 1-octadecene–maleic anhydride or its hexadecylester. Lead stearate as a heat stabilizer and kaolin as a filler were added. The effect of copolymer structure on the electrical properties of the PVC–DOP–DBP system was studied to obtain a plasticized PVC of good electrical insulation character. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Poly(vinyl chloride) (PVC) is a rigid resin that must be modified by addition of a plasticizer to produce the flexibility desired. Study of the effect of plasticizers on the electrical properties of PVC is important from the practical point of view, because plasticized PVC is used extensively in electric insulation and many industrial purposes. Numerous formulating variables besides the plasticizer have significant effects on the dielectric characteristics; some enhance the dielectric properties and others cause impairment.[1]

Low-molecular plasticizers, namely, organic ester compositions, occupy an increasingly important position in the technology of electrical insulation. When prepared from polyols and dibasic acids, the ester compounds are capable of being polymerized to form solid resinous compositions of engineering importance in structural and electrical insulating applications.[2] PVC has also been compounded with high-molecular plasticizers such as the styrene–maleic anhydride copolymer.[3]

In this investigation, a PVC–dioctyl phthalate (DOP)–dibutyl phthalate (DBP) system was pre-pared and found to have inconvenient electrical properties. The aim of this study was to investigate systematically the effect of adding increasing quantities of a copolymer of 1-octadecene–maleic anhydride or its hexadecylester on the electrical properties of the PVC–DOP–DBP system in an attempt to improve these properties and obtain a good electrical insulating sample for wire covering to suit low voltage.

EXPERIMENTAL

Preparation of 1-Octadecene–Maleic Anhydride and Hexadecylester of 1-Octadecene–Maleic Anhydride Copolymers

1-Octadecene–maleic anhydride copolymer (A) was synthesized by reacting 63 g (0.25 mol) of 1-octadecene with 29.50 g (0.30 mol) of maleic anhydride in the presence of 100 mL xylene as a solvent and 0.125 g benzoyl peroxide as an initiator. The reaction mixture was then refluxed for 6 h with vigorous stirring in the temperature range 120–125°C. The produced 1-octadecene–maleic anhydride copolymer (A) was then esterified with 116 g (0.48 mol) of 1-hexadecanol in the presence of 1 g p-toluene sulfonic acid at 140°C using a Dean and Stark apparatus until no further water of reaction was produced. At the end of esterification process, the reaction mixture was purified and dried to produce hexadecyles-

ter of 1-octadecene–maleic anhydride copolymer (B). The infrared spectra of copolymer (B), measured by a spectrophotometer Perkin-Elmer Model 598, shows two peaks in the 1600–1800 cm^{-1} region (Fig. 1) that correspond to COOH and COOC$_{16}$ H$_{33}$ groups, indicating that only partial esterification has occurred. The specifications of copolymers (A) and (B) are shown in Table I. The reaction can be illustrated in the following scheme:

C$_{16}$H$_{33}$ CH—C$\diagup^O$

| +   ‖ $\diagdown$O   →

HC=CH$_2$ CH—C$\diagdown_O$

1-Octadecene   Maleic anhydride

$\left[\begin{array}{c} \text{CH—CH}_2\text{—CH——CH} \\ | \qquad\qquad | \qquad | \\ \text{C}_{16}\text{H}_{33} \quad \text{C} \quad \text{C} \\ \qquad\qquad \text{O} \quad \text{O} \quad \text{O} \end{array}\right]_n$

1-Octadecene–maleic
anhydride copolymer

$\left[\begin{array}{c} \text{CH—CH}_2\text{—CH——CH} \\ | \qquad\qquad | \qquad\quad | \\ \text{C}_{16}\text{H}_{33} \quad \text{C} \qquad \text{C=O} \\ \qquad \text{O} | \qquad\quad | \\ \qquad \text{OC}_{16}\text{H}_{33} \quad \text{OH} \end{array}\right]_n$ $\xleftarrow[\text{Partial esterification}]{\text{Cetyl alcohol}\atop\text{C}_{16}\text{H}_{33}\text{OH}}$

Hexadecylester of 1-octadecene–
maleic anhydride copolymer
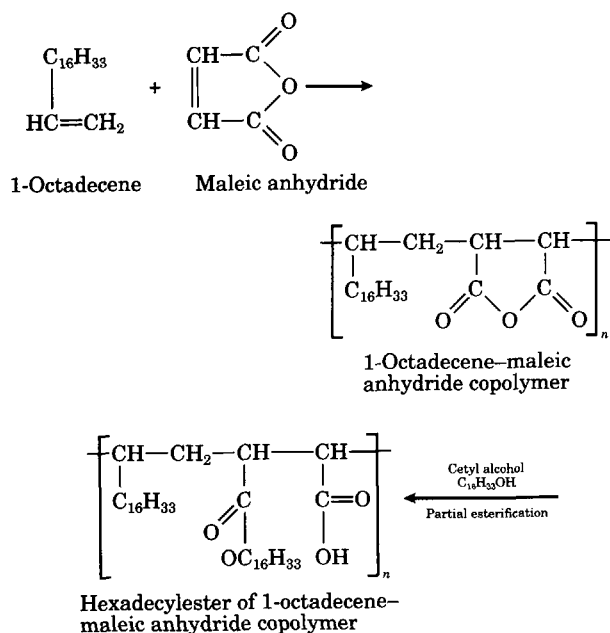
Formulations of the Samples

In the present work, several formulations were obtained by mixing the components in the proportions shown in Table II. The general procedure for formulation is described as follows:

Homogeneous samples were prepared by adding variable proportions of the prepared 1-octadecene–

maleic anhydride copolymer (A) or its hexadecylester copolymer (B) portionwise at room temperature to a composition containing 10 g PVC (K value 70), 5 g DOP, and 2 g DBP plasticizer under stirring. The whole mixtures were then mixed with lead stearate as a heat stabilizer, followed by the addition of kaolin as a filler to give the required samples (gelation temperature at 180°C for 90 s). The obtained samples are denoted by E, E$_1$, E$_2$, ... E$_8$.

Dielectric Measurements

Permittivity ε' and dielectric loss ε'' for the denoted samples were measured at different frequencies ranging from 100 to 50 kHz. A multidekameter (DK05) from WTW (Wissenschaftlich Technische Werkstäten) of the Schering bridge type with the test cell NFM/5T was used. The samples were discs of 58 mm diameter and of 3 mm thickness. Calibration of the apparatus was carried out using standard samples (Trolitul, glass, and air) of thickness 3 mm; the accuracy for ε' was ±1%, and for ε'', ±3%. The measurements were carried out at temperatures 20, 40, and 60°C using an ultrathermostat.

Conductivity Measurements

The electrical conductivity (σ) of the investigated samples was measured by the application of Ohm's law using the test cell NFM/5T. A power supply unit GM 45161/01 from Philips, The Netherlands, was used. The potential difference V between the plates holding the sample and the current I flowing through it was measured by a multimeter type URI 1050 from Rohde and Schwarz, Germany. The electrical conductivity is calculated using the equation
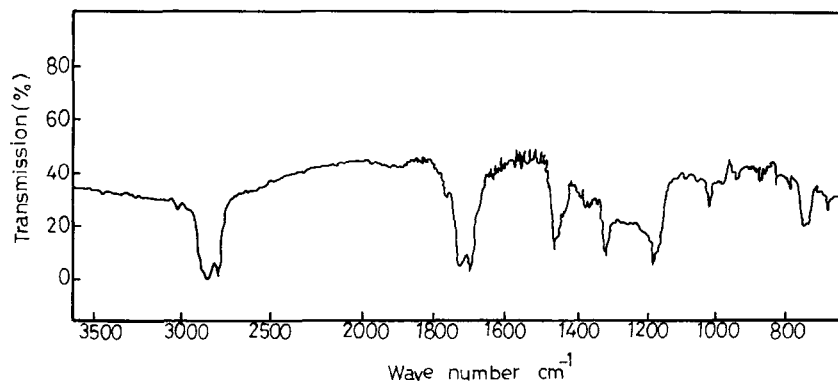

Figure 1   Infrared spectrum of hexadecylester of 1-octadecene–maleic anhydride copolymer.
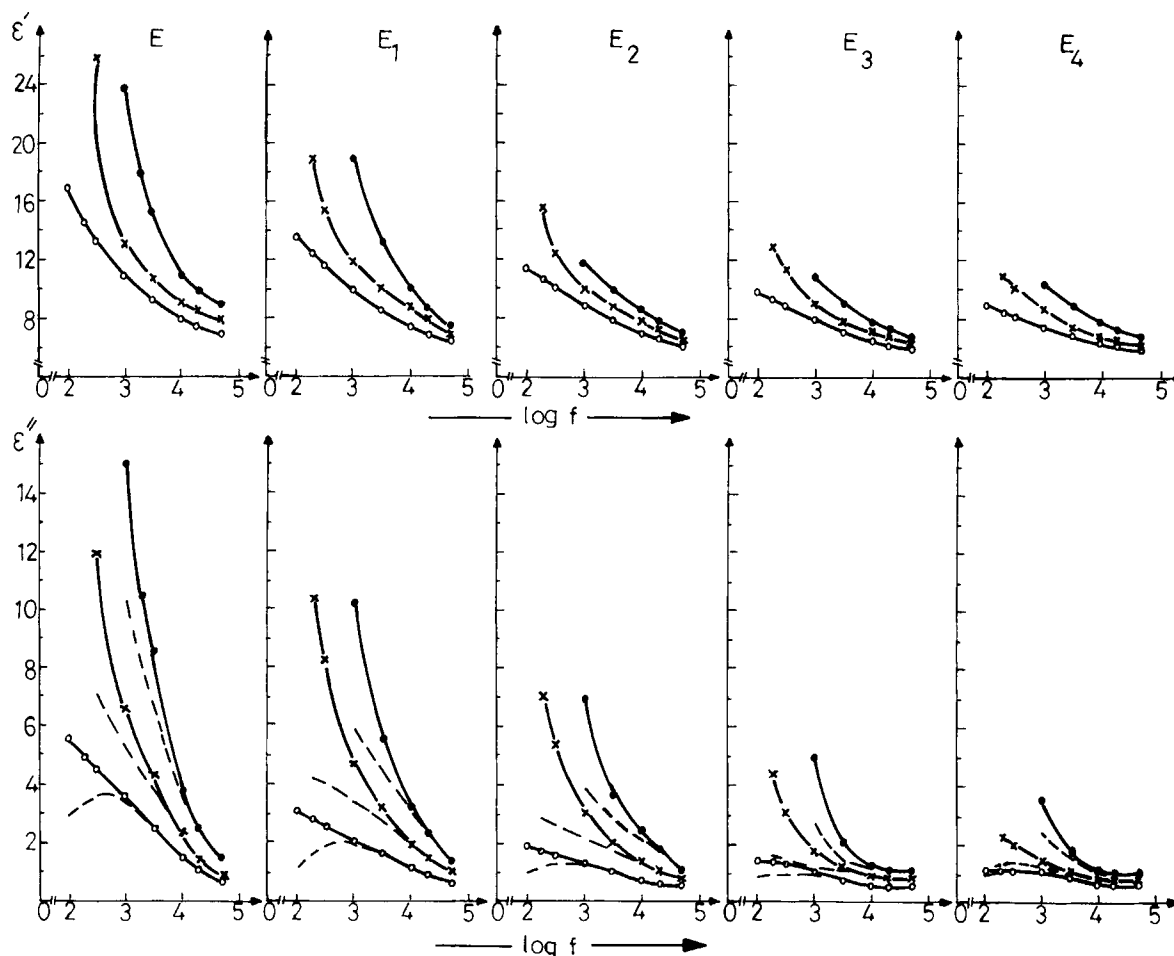
Table I   Specifications of Copolymers (A) and (B)

Product	1-Octadecene–Maleic Anhydride Copolymer (A)	Hexadecylester of 1-Octadecene–Maleic Anhydride Copolymer (B)
Appearance	Solid, transparent	Solid, apaque
Color	Pale orange	Yellow
Average molecular weight	—	2959
Melting range (°C)	55–63	47–50
Acid number (mg KOH/g)	—	43
Density at 30°C (g/cm³)	1.4779	1.1015
Solubility at 30°C (g/100 mL)	Cyclohexanone, MEK, xylene, and ester	Cyclohexanone, MEK, xylene, ester, and methanol

$$\sigma = \frac{dI}{AV} \text{ mho } \text{ m}^{-1}$$

where d is the thickness of the sample in m and A is its surface area in m².

RESULTS AND DISCUSSION

Polymers such as PVC are known to have kinetically rigid chains. On the addition of low-molecular admixtures, particularly, polar plasticizers such as DOP and DBP, they are effective enough to penetrate inside the molecular bundles of PVC and to separate the polymeric chains. Accordingly, the mutual interaction between plasticizer and PVC becomes appreciable, leading to aggregates or segments having sizes smaller than that of PVC, i.e., segments of higher molecular mobility. Since the appearance of dipole–segments and dipole–groups in polymers is associated with the mobility of the kinetic units of the macromolecular chain, therefore, the PVC–DOP–DBP system should exhibit higher mobilities.[4]

In this investigation, the treatment of PVC with a polar plasticizer consisting of DOP and DBP produces a PVC–DOP–DBP system (sample E) that is found to have inconvenient electrical properties. In an attempt to improve the electrical properties of sample E and directing it to be a good electrical insulator, 1-octadecene–maleic anhydride copolymer (A) or its hexadecylester copolymer (B) are formulated together in different concentrations (Table II). The permittivity (ε') and dielectric loss (ε'') for the prepared samples (E, E_1, E_2, ..., E_8) over the frequency range from 100 to 50 kHz at different temperatures from 20 to 60°C were studied. The results obtained for ε' and ε'' vs. the frequency for these samples at the different temperatures are shown in Figures 2 and 3.

It is evident from Figures 2 and 3 that ε' increases with increasing temperature and decreases with increasing frequency. Similar behavior was noticed before in the literature.[5] The increase of ε' with temperature can be explained by the increase in the mobility of polar groups, decrease in density, and, hence, a decrease in the effect of the environment

Table II   Formulations of the Samples

Constituents; Parts by Weight (g)	Sample Notation								
	E	E_1	E_2	E_3	E_4	E_5	E_6	E_7	E_8
Poly (vinyl chloride) (PVC)	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
Dioctyl phthalate (DOP)	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Dibutyl phthalate (DBP)	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
1-Octadecene–maleic anhydride copolymer (A)	—	1.0	2.0	3.0	4.0	—	—	—	—
Hexadecylester of 1-octadecene–maleic anhydride copolymer (B)	—	—	—	—	—	1.0	2.0	3.0	4.0
Lead stearate	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Kaolin	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0

Figure 2 The permittivity (ε') and dielectric loss (ε'') vs. frequency at different temperatures—(○) 20; (×) 40; (●) 60°C—for the PVC-DOP-DBP system mixed with variable proportions of 1-octadecene–maleic anhydride copolymer (A) (E, E_1, E_2, E_3, and E_4; see Table II). The dashed line represents the measured $\varepsilon'' - \varepsilon''_{d.c}$.

that facilitates the orientation of the mobile groups. The decrease of ε' with frequency shows an anomalous dispersion. Moreover, Figures 2 and 3 show that the value of ε' decreases with increase in copolymer (A) or copolymer (B) content, especially at the very low frequency region. This could be attributed to steric hindrance due to the presence of large alkyl radicals in copolymer (A) or copolymer (B) despite the presence of a number of polar groups that are capable of orientation in an electric field. This restricts the rotation of the large aggregates of the polymeric chain. It is significant to point out that the presence of one C_{16} H_{33} group in copolymer (A) may lead to less steric hindrance than does the presence of two C_{16} H_{33} groups in copolymer (B) and, accordingly, the decrease of ε' is more pronounced when copolymer (B) is introduced (samples E_5, E_6, E_7, and E_8), especially at 20°C, and reaches

6.4 at 1 kHz for sample E_8. This result is in agreement with the data of standard plasticized PVC insulated wire[2] ($\varepsilon' = 5$–7 at 1 kHz and 25°C) and supported by the results of PVC–DOP systems[5] ($\varepsilon' = 4.5$–6.5 at 1 kHz and 20°C).

It is apparent from Figures 2 and 3 that ε'' is greatly increased at higher temperatures, especially in the lower-frequency region. Moreover, Figures 2 and 3 reveal that the value of ε'' in the lower-frequency region decreases with increasing copolymer (A) or copolymer (B) content and is slightly changed at frequencies after 10 kHz, where it becomes approximately the same for all samples. It reaches 0.7 at 1 kHz and 20°C for sample E_8. Similar results have been found in Ref. 2 ($\varepsilon'' = 0.35$–0.6 at 1 kHz and 25°C) and Ref. 5 ($\varepsilon'' = 0.35$–0.4 at 1 kHz and 20°C). The decrease in the ε'' value may be due to the presence of very bulky substituents (the
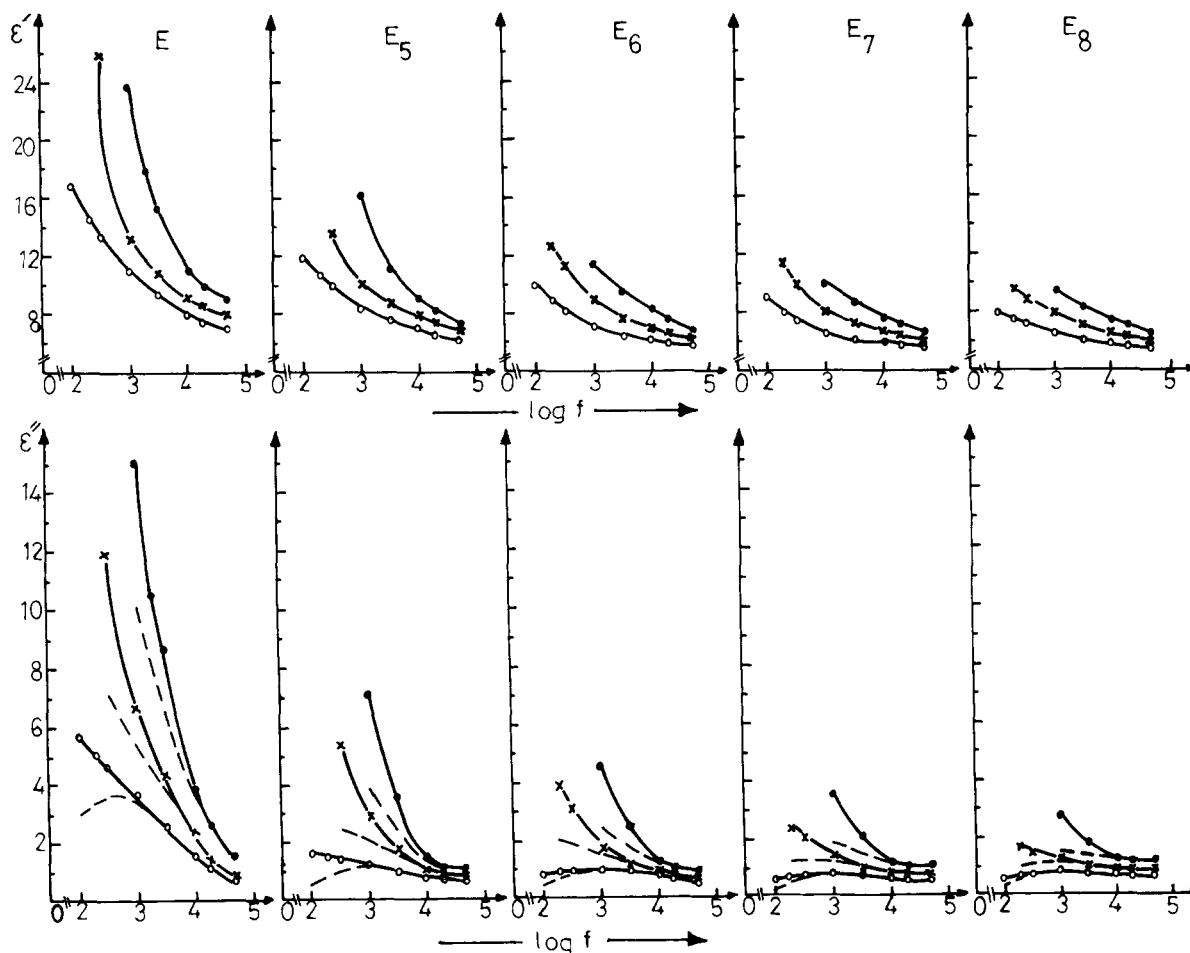
Figure 3 The permittivity (ε') and dielectric loss (ε'') vs. frequency at different temperatures—($\bigcirc$) 20; ($\times$) 40; ($\bullet$) 60°C—for the PVC–DOP–DBP system mixed with variable proportions of hexadecylester of 1-octadecene–maleic anhydride copolymer (B) (E, E_5, E_6, E_7, and E_8; see Table III). The dashed line represents the measured $\varepsilon'' - \varepsilon''_{d.c.}$.

$C_{16} H_{33}$ groups) in the polymeric chain of copolymer (A) or copolymer (B), which reduces the molecular mobility.

The low-frequency losses may be due to either d.c. conductivity[6,7] resulting from the increase of ion mobility or the Maxwell–Wagner effect[8] as a result of an a.c. current in phase with the applied potential, or to both. To confirm this, the d.c. conductivities of the investigated samples were measured by application of Ohm's law to the direct current flowing through the samples at 200 V and at temperatures from 20 to 60°C. All investigated samples showed appreciable d.c. conductivity. The dielectric losses due to the d.c. conductivity (σ) at the different frequencies (W) are calculated using the equation[9]

$$\varepsilon''_{d.c.} = \frac{9 \times 10^{11} 4\pi\sigma}{W}$$

and subtracted from the values of ε'' in the low-frequency region. The data of ε'' after subtracting $\varepsilon''_{d.c.}$ are plotted vs. log f and represented by dashed lines as shown in Figures 2 and 3. From these figures, it is clear that at 20°C for samples E and E_1 (having 0 and 1 g of copolymer A) or samples E and E_5 (having 0 and 1 g of copolymer B), there is an absorption region with a maximum at about 1 kHz. Also, for samples E_2, E_3, and E_4 (having 2, 3, and 4 g of copolymer A) or samples E_6, E_7, and E_8 (having 2, 3, and 4 g of copolymer B), the curves are broad, indicating an overlapping of more than one absorption region. At 40 and 60°C, we obtain an absorption region extending below 100 Hz that may be due to rotation of large aggregates of the chain. Unfortunately, we cannot give further interpretation of this region since we have no measurement below 100 Hz.
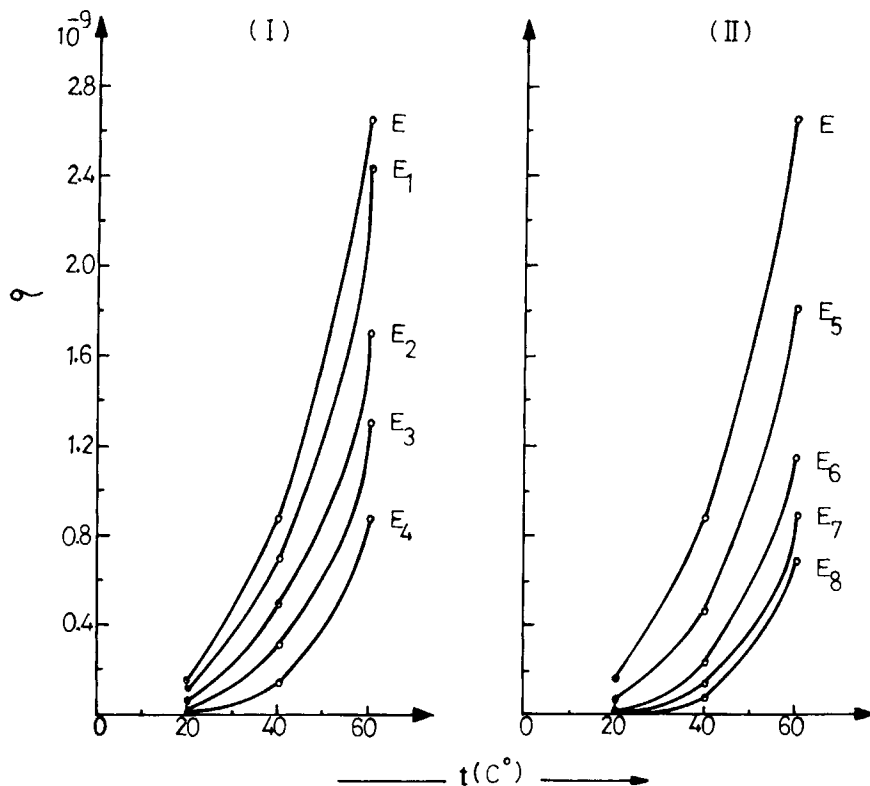
It may be concluded that the low-frequency losses

Figure 4   The relation between conductivity (σ) and temperature (t) for PVC–DOP–DBP system mixed with the copolymer A(I) or B(II).

are not totally d.c. losses and that they may comprise Maxwell–Wagner losses, as the difference between the permittivities of the different ingredients in the investigated samples are relatively large.

On the other hand, the change of the electrical conductivity (σ) of samples E, E_1, E_2, E_3, . . ., E_8 with temperature is shown in Figure 4. It is evident that, at lower temperatures, σ of these samples is low and increases as the temperature is increased. This may be due to the increase of the mobility of the ionic bodies that takes place as a result of the excitation by heat, leading to an increase in the conductivity of the investigated samples. Figure 4 also shows a pronounced increase in σ of sample E with increasing temperature. This may be attributed to the rupture of the double bonds (the π bonds) due to the excitation by heat with the formation of free electrons that are mobile under the influence of an electric field and, thus, greatly increase the degree of electrical conductivity in this sample. At the higher temperatures, it is also probable that hydrogen chloride is evolved from PVC and that the chlorine ions are free to follow the external field. With respect to sample E mixed with copolymer (A)

(samples E_1, E_2, E_3, and E_4) or copolymer (B) (samples E_5, E_6, E_7, and E_8), Figure 4 also shows that the value of σ decreases with increasing copolymer (A) content and decreases to a greater extent with the increase in copolymer (B) content, especially at higher temperatures. This may be attributed to steric hindrances due to the presence of the large C_{16} H_{33} groups that play a great role in decreasing the mobility of the electric charges and, accordingly, the conductivity of these samples decreases.

It can be concluded that a prepared sample having 10 parts PVC, 5 parts DOP, and 2 parts DBP possesses inconvenient electrical properties (permittivity, dielectric loss, and electrical conductivity). These electrical properties are improved by the addition of 1-octadecene–maleic anhydride copolymer (A) and to a greater extent by adding hexadecylester of 1-octadecene–maleic anhydride copolymer (B) to the PVC–DOP–DBP system, especially at frequencies higher than 10^4 Hz. Therefore, plasticized PVC formulated with 4 parts of copolymer B (sample E_8) possesses the best electrical properties, making it of interest as a practical wire insulator.

REFERENCES

1. I. G. Krauskopf, In *Encyclopedia of PVC*, L. I. Nass, Ed., 1977, Vol. 2, Chap. 11, p. 582.
2. F. M. Clark, *Insulating Materials for Design and Engineering Practice*, Wiley, New York, London, 1962, pp. 716, 559.
3. T. Mitsui, *PVC Compositions with High Volume Resistivity, Inc. Jpn. Kokai Tokyo Koho Jp*, 1982, Vol. 57, pp. 119, 944.
4. A. A. Tager, *Physical Chemistry of Polymers*, Mir, Moscow, 1978, Chap. 11, p. 325.
5. A. M. Bishai, F. A. Gamil, F. A. Awni, and B. H. F. Al-Khayat, *J. Appl. Polym. Sci.*, **30**, 2009 (1985).
6. J. M. Davies, R. F. Miller, and W. F. Busse, *J. Am. Chem. Soc.*, **63**, 361 (1941).
7. H. Sasabe and S. J. Saito, *J. Polym. Sci. A.2*, **7**, 1405 (1969).
8. F. F. Hanna, A. A. Yehia, and A. Abou Bakr, *Br. Polym. J.*, **5**, 83 (1973).
9. C. P. Smyth, *Dielectric Behaviour and Structure*, McGraw-Hill, New York, 1955.