Dielectric and Mechanical Properties of Poly(vinyl Chloride)–Dioctylphthalate Systems

A. M. BISHAI, *Microwave Physics Laboratory, National Research Centre, Dokki, Cairo, Egypt,* F. A. GAMIL, *Petroleum Research Centre, Baghdad, Iraq,* and F. A. AWNI and B. H. F. AL-KHAYAT, *College of Education, University of Baghdad, Iraq*

Synopsis

The mechanical properties, tensile strength, and elongation were investigated for poly(vinyl chloride) (PVC) samples mixed with dioctylphthalate (DOP) at concentrations from 0 to 100 parts per hundred parts PVC at 23°C. It was found that the tensile strength decreased with the increase of concentration, and the elongation was increased until a concentration of 30 DOP content, and then decreased. This leads to the suggestion that intermolecular plasticization is dominant until 30 DOP content, while interstructural plasticization is prevailing for higher concentrations. The permittivity ϵ' and the dielectric loss factor ϵ'' of the same samples have been measured in the frequency range 10^2–10^5 Hz at temperatures from 3 to 96°C. Results show that as the DOP content increases in PVC, the dielectric absorption becomes broader, and the glass transition temperature T_g is lowered. The magnitude of the loss peak decreases with an increase of DOP content to a minimum at concentrations from 40 to 60 DOP content. At higher concentrations the loss peak is increased and T_g is unaltered. Another absorption was observed at 100 Hz and at high temperatures, which was attributed to Maxwell–Wagner effect or direct current conductivity or both of them. It was found that the sample containing 40 parts DOP in 100 parts PVC possesses the best mechanical and electrical properties.

INTRODUCTION

Study of the effect of plasticizers on the dielectric and mechanical properties of PVC is important from the practical point of view, because plasticized PVC is used extensively in electric insulation and many industrial applications.

PVC is a hard resin which must be modified by addition of plasticizer in order to produce the flexibility desired. Also, plasticizers make the glass transition temperature (T_g) shift to lower temperatures.

Some investigations[1-6] have been published on the effect of plasticizers on the dielectric and mechanical properties of high polymers and their influence on T_g. On the other hand, only few investigations on the effect of polar plasticizers on these properties are available.

The aim of this study is to investigate systematically the effect of adding increasing quantities of a polar plasticizer on the dielectric and mechanical properties of PVC.

EXPERIMENTAL

All samples were prepared by adding 3 g of tribasic lead sulfate and 1 g of dibasic lead stearate (as additive stabilizer and lubricant) to 100 g of PVC. The plasticizer selected for this study is di-2-ethylhexylphthalate gen-

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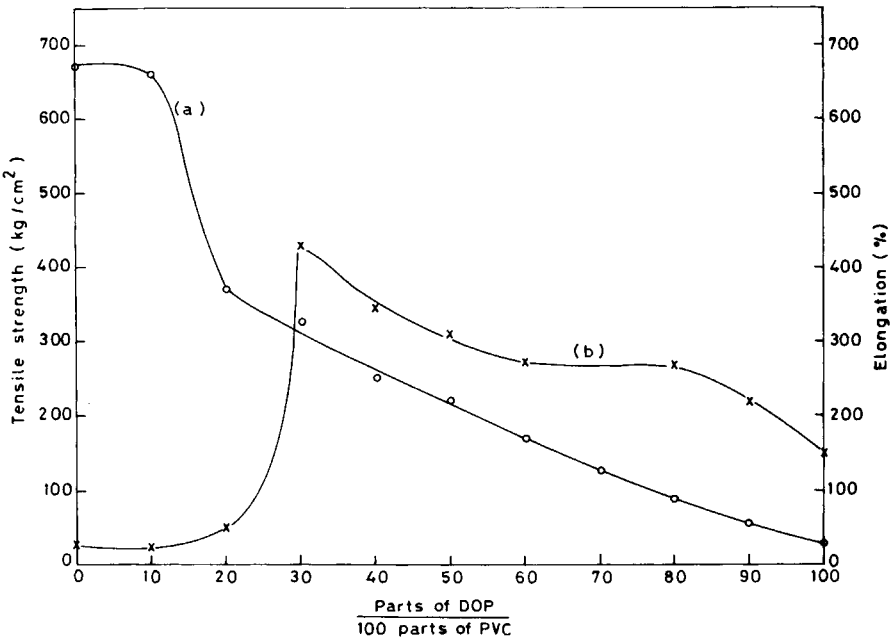

Fig. 1. (a) Tensile strength (○) and (b) elongation (X) versus DOP content in PVC at 23°C.

erally called dioctylphthalate (DOP). Different amounts of the plasticizer were added in steps of 10 g of DOP per 100 g of PVC. The ingredients were treated in a small mixer (Henschel) for 20 min. Sheets of various formulations were prepared using a small laboratory extruder (Brabender type).

Plasticized PVC samples were tested using the method for tensile strength and elongation,[7] these were conditional at 23°C for 24 h. Speed of testing was 51 mm/min, and the test was carried out by a universal testing machine (Zwick).

Permittivity ϵ' and dielectric loss factor ϵ'' were measured at frequencies between 10^2 and 10^5 Hz and at temperatures ranging from 3 to 96°C. A WTW dekameter DK05 of the Schering bridge type and a guard ring capacitor type NFM 5T were used. The samples were disks of 59 and 2.6 mm thickness. Ten samples having different plasticizer content (from 0 to 100 g DOP per 100 g PVC) were measured. The accuracy of measurements was 1% in ϵ' and 3% in ϵ''.

RESULTS AND DISCUSSION

Mechanical Properties

The variation of elongation and tensile strength versus plasticizer concentration at room temperature (23°C) is given in Figure 1. From Figure 1(a), it is seen that the tensile strength shows a slight change at concentrations of plasticizer below 10 parts DOP per 100 parts PVC and then it decreases. Such behavior was found before.[8] Figure 1(b) shows that the elongation is small up to 20 DOP content, which may be due to a small increase in crystallinity in PVC as was suggested before by Brown, Musindi,

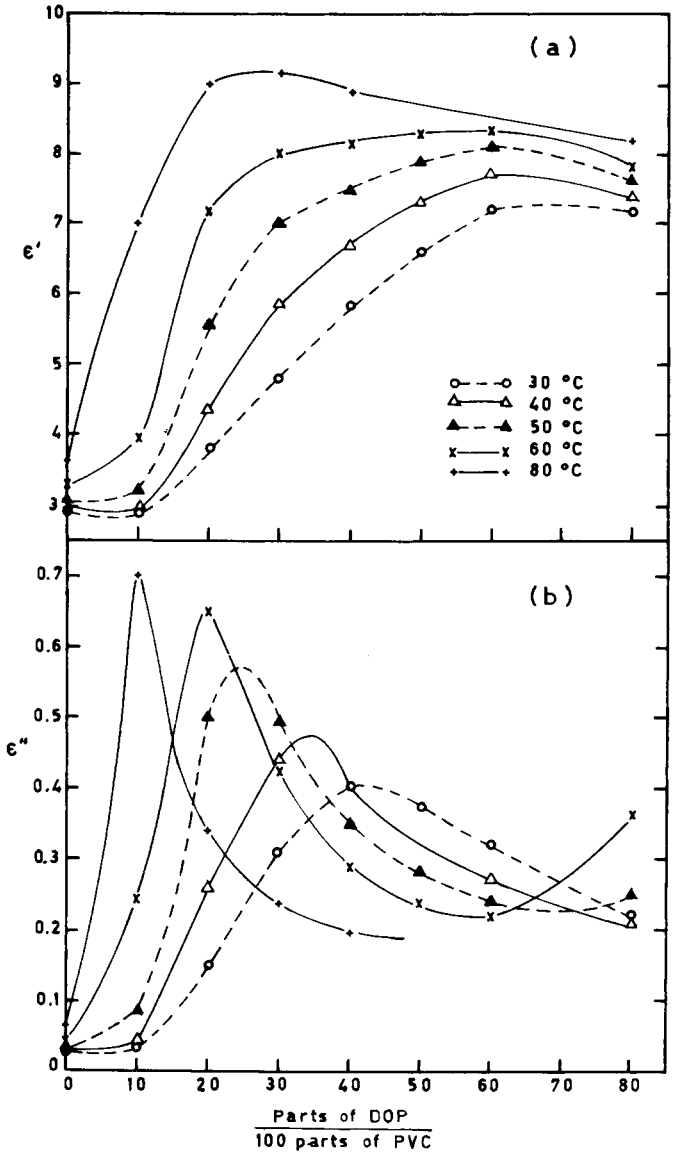

Fig. 2. Permittivity (ϵ') and dielectric loss factor (ϵ'') versus DOP content in PVC at 100 Hz and at various temperatures.

and Stachurski.[9] The elongation increases abruptly at 30 DOP content and then decreases slowly at higher plasticizer concentrations. So, probably two plasticization processes, namely, intermolecular and interstructural plasticization, are present. At low concentrations, intermolecular plasticization is predominant, where the plasticizer molecules would interact with the active group of the PVC, leading to the breakage of molecular bundles (aggregates), and the chains are separated. At plasticizer concentration higher than 30 DOP, interstructural plasticization is more prevailing, where the plasticizer molecules are distributed in the interaggregate space. In the first process, elongation increases with concentration, whereas in the second process elongation decreases with the increase of plasticizer concentration.

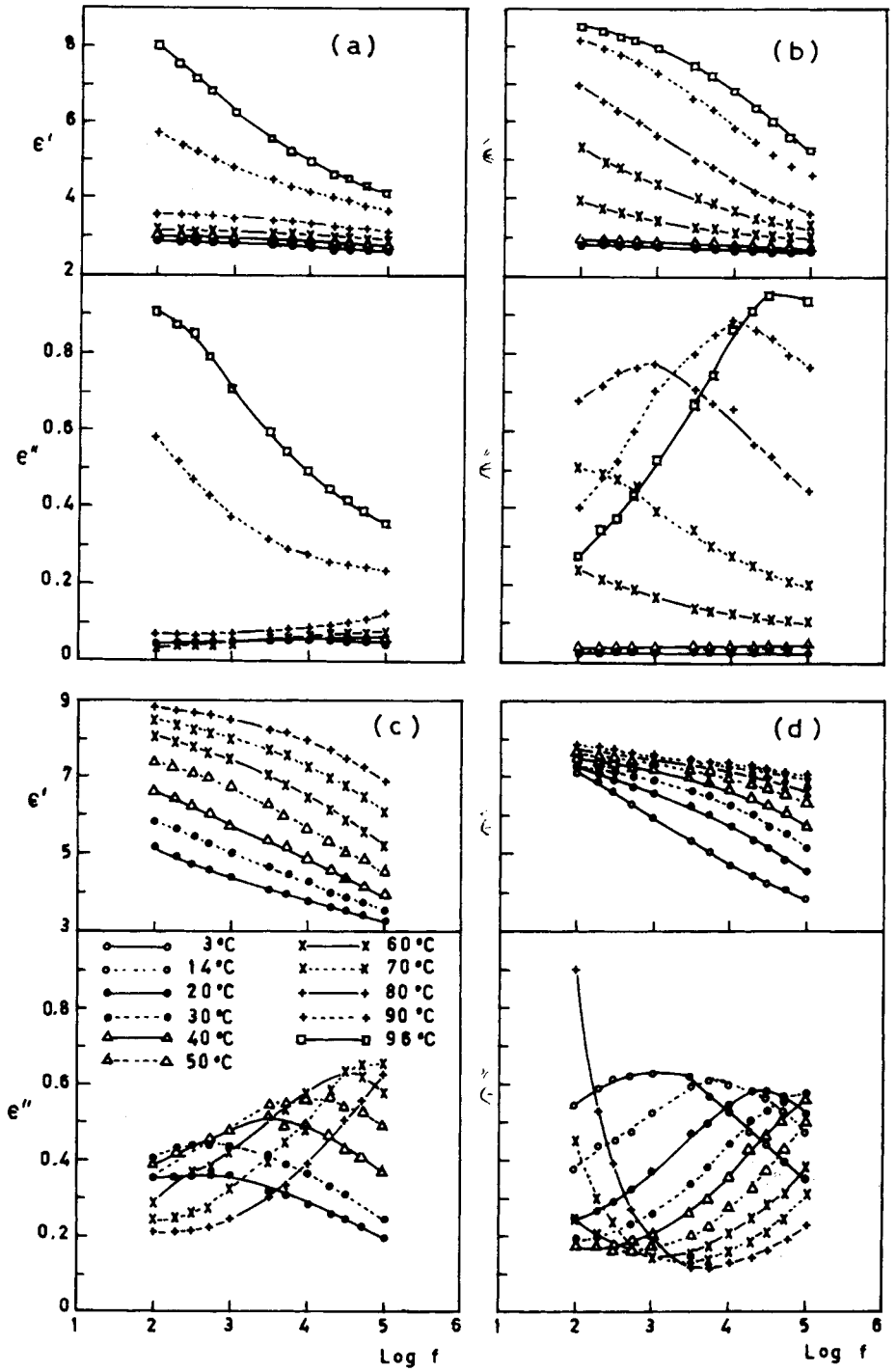

Fig. 3. Permittivity (ϵ') and dielectric loss (ϵ'') versus frequency at different temperatures for (a) unplasticized PVC, (b) 10 parts of DOP, (c) 40 parts of DOP, and (d) 90 parts of DOP in 100 parts of PVC.

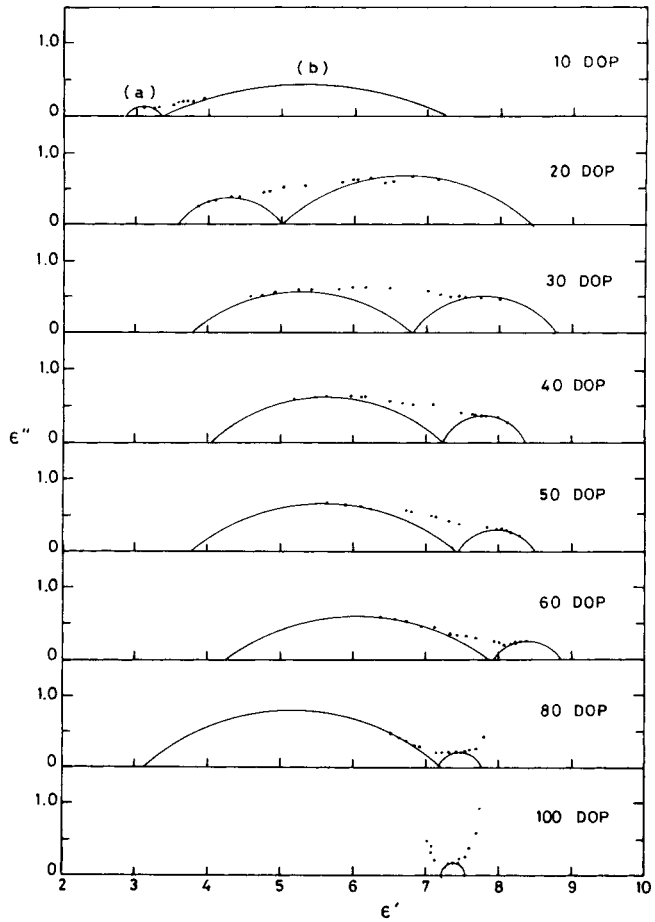

Fig. 4. ϵ'' vs. ϵ' for different concentrations of DOP in PVC at 60°C.

Similar effects were found when PVC interacts with nitrogen containing rubbers.[10]

Dielectric Properties

Effect of Plasticizer Concentration

The results obtained for the permittivity ϵ' and the dielectric loss ϵ'', for samples with increasing DOP content in PVC at different temperatures and at 100 Hz are shown in Figure 2. From Figure 2(a), it can be seen that ϵ' increases with concentration until a certain concentration, which depends upon temperature, and then slightly decreases. Figure 2(b) shows that, at each temperature, ϵ'' increases with the increase of DOP content, goes through maximum at a certain concentration, and then decreases gradually. As the temperature increases, the loss peak increases and becomes sharper. This may indicate that at each temperature there is a certain concentration effective enough to penetrate inside the molecular bundles of PVC and

separate the polymeric chains. Further addition of plasticizer corresponds simply to adding plasticizer molecules, which are distributed between the PVC molecules and are less effective.

Effect of Frequency

The change of the permittivity ϵ' and dielectric loss ϵ'' with frequency for selected PVC samples of different plasticizer content are shown in Figure 3 at the investigated temperatures. From Figure 3(a), for the unplasticized

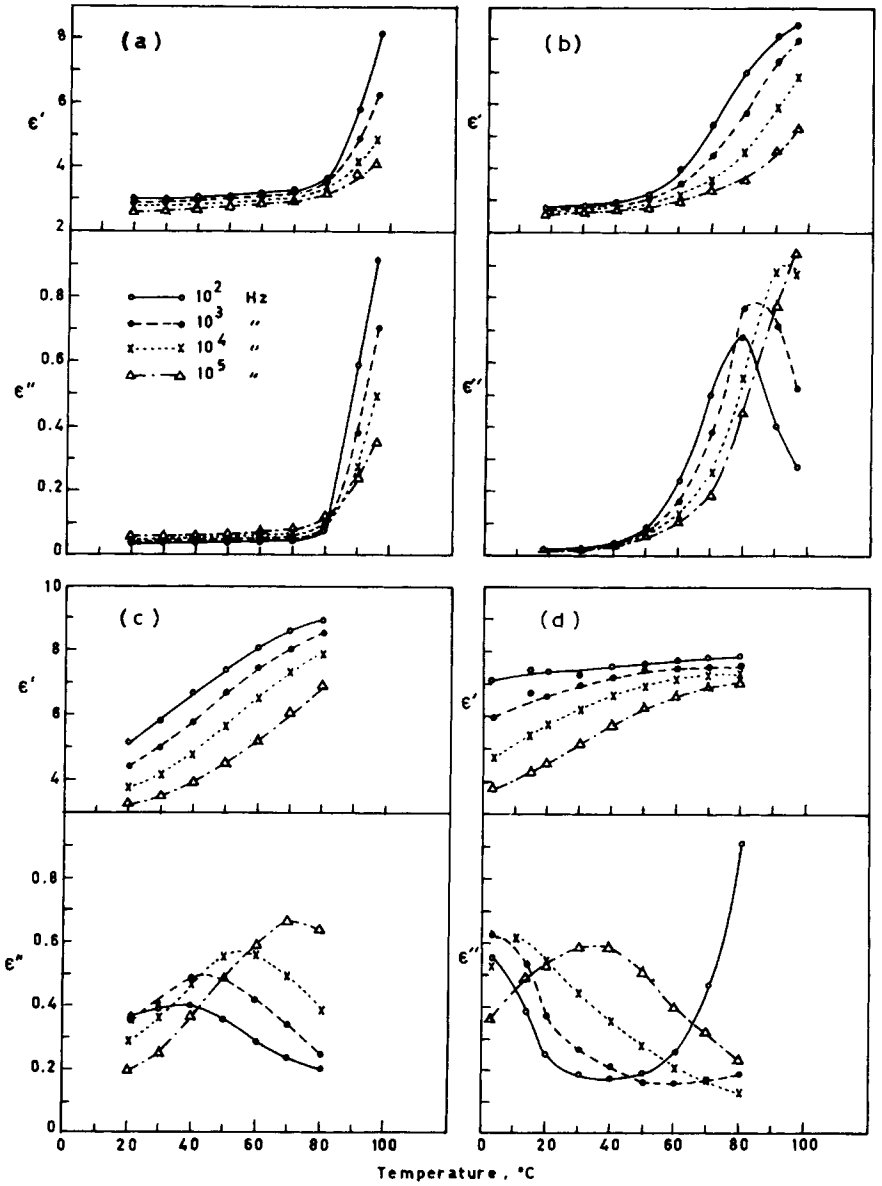

Fig. 5. Permittivity (ϵ') and dielectric loss factor (ϵ'') versus temperature at frequencies 10^2, 10^3, 10^4, and 10^5 Hz for (a) unplasticized PVC, (b) 10 parts of DOP, (c) 40 parts of DOP, and (d) 90 parts of DOP in 100 parts of PVC.

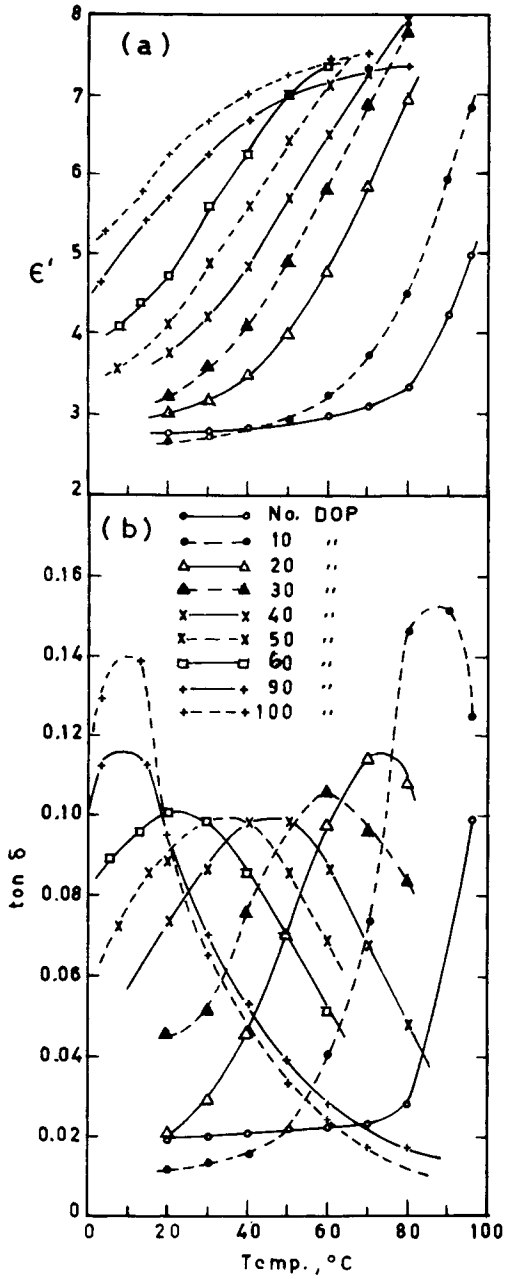

Fig. 6. (a) Permittivity (ϵ') and (b) the loss tangent tanδ versus temperature for samples having different concentrations of DOP in PVC.

samples, it is clear that there is a region of anomalous absorption with a maximum at a frequency less than 10^2 Hz at 96°C. Such behavior was found by Ishida.[11] This absorption region could be attributed to the high-temperature absorption (α absorption), which may be due to the rotation of large segments (aggregates) of the chain. Since the chain of PVC will have a more or less random kinky shape, the size of the segments which tend to rotate

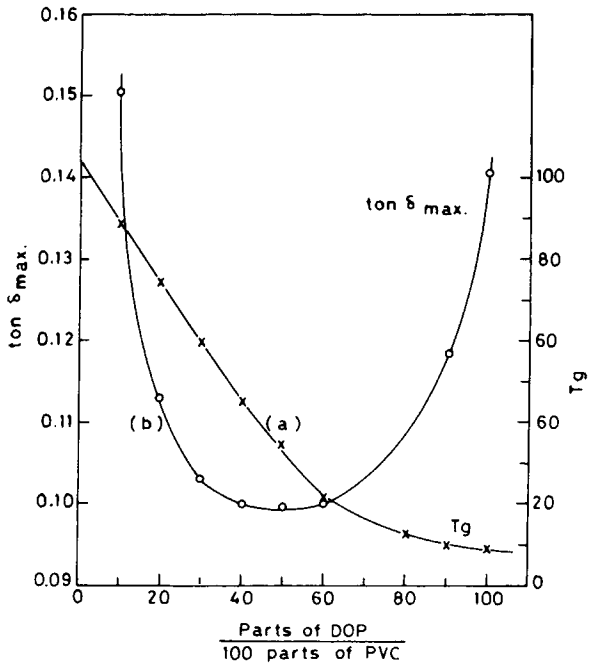

Fig. 7. T_g and tan δ_{max} vs. DOP content in PVC at 10^4 Hz.

as a unit will vary leading to a distribution of relaxation times. As the temperature decreases to 90°C, ϵ'' decreases and the loss peak shifts to lower frequencies. At 80°C a tail of another absorption could be observed at 10^5 Hz, which may be due to low-temperature absorption (β absorption). Adding plasticizer to PVC the α absorption shifts to higher frequencies, and another absorption region appears at the low-frequency region at temperatures higher than 50°C for the 90 DOP content as shown in Figure 3(d). Also the change of permittivity with frequency seems to decreases slowly at temperatures higher than 60°C.

In order to discuss qualitatively the concentration dependance of plasticizer in PVC on the magnitude and shape of the dielectric absorption, the value of ϵ' and ϵ'' obtained at the different frequencies are plotted in a complex plane as shown in Figure 4 for some concentrations of DOP samples at 60°C. The data are represented by two arcs. (a) a high-frequency arc and (b) a low-frequency arc, both with distributions. The low-frequency arc is decreased by the increase of plasticizer concentration, while the high-frequency arc is enlarged by the increase of plasticizer concentration. For samples having 80, 90, and 100 DOP content, it is impossible to represent all the experimental data with one or two arcs, as a result of the high losses noticed around 100 Hz. The low-frequency absorption region may be due to rotation of large aggregates of the chain, while the other absorption may be due to the orientation of smaller aggregates and/or plasticizer molecules.

Effect of Temperature

The variation of ϵ' and ϵ'' versus temperature at frequencies of 10^2, 10^3, 10^4, and 10^5 Hz are shown in Figure 5. ϵ' increases with temperature while it decreases with the increase of frequency. By addition of plasticizer the

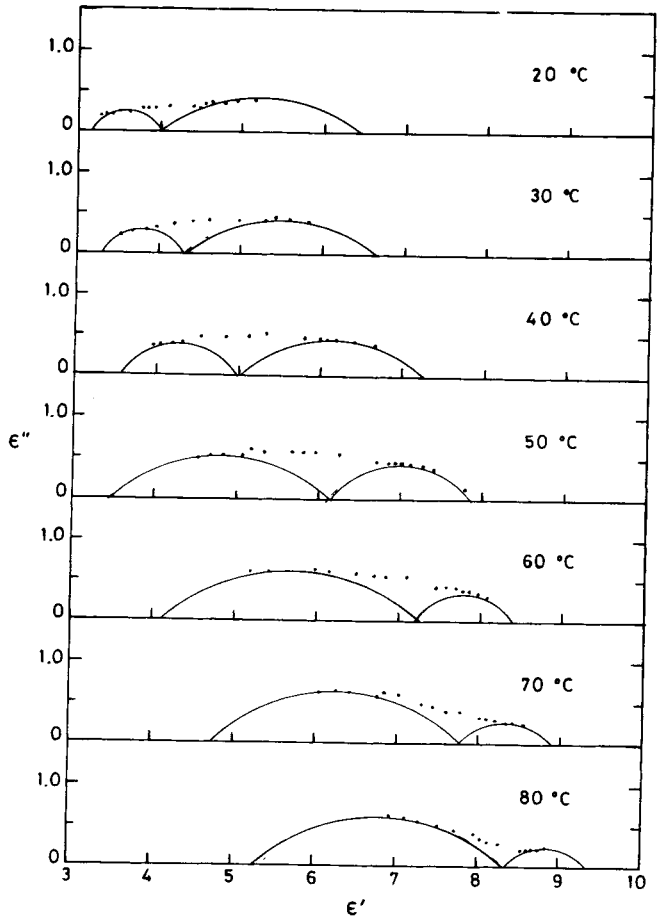

Fig. 8. ϵ'' vs. ϵ' for samples having 40 parts of DOP in 100 parts of PVC at various temperatures.

absorption curves are broadened and the maximum shift to lower temperatures. At 90 DOP content another absorption region is found at high temperature and 100 Hz. This may be due to contribution from steady-state dc conductivity,[12,13] because at high temperature it is probable that hydrogen chloride is evolved from PVC and the chlorine ions are free to follow the external field. Besides, it may also be due to Maxwell–Wagner effect as a result of the heterogeneity of DOP–PVC systems at high concentrations.

The temperature dependence of ϵ' and $\tan\delta$ for most of the samples tested at 10^4 Hz is illustrated in Figure 6. At higher concentrations of DOP in PVC, the dispersion step seems to decrease, which is probably a result of the decrease of the effective dipole moment. From the variation of $\tan\delta$ versus temperature shown in Figure 6(b), it can be seen that as the concentration of the plasticizer increases until 60 DOP content the absorption peak becomes broader and its position shifts to lower temperatures, i.e., the T_g is lowered. At concentrations of 90 and 100 DOP content the T_g is approximately unaltered which is clearly shown in Figure 7(a). The height of the loss peak decreases with increase in concentration to a minimum at concentrations between 40 and 60 DOP content, then increases again by further increase of plasticizer [Fig. 7(b)]. This can be explained by the fact

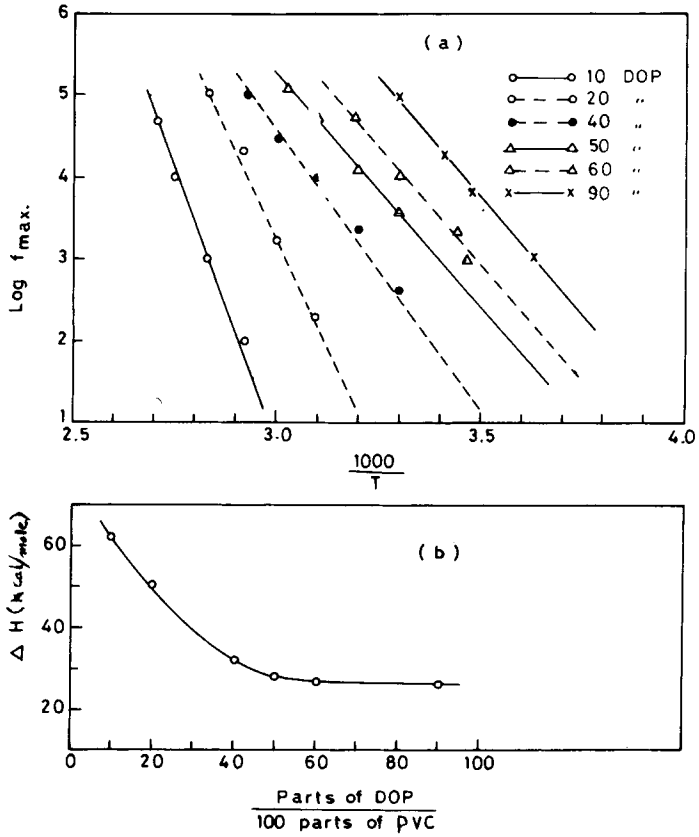

Fig. 9. (a) log f_{max} vs. $1/T$ for samples having different concentrations of DOP in PVC. (b) The apparent activation energy (ΔH) vs DOP content in PVC.

that at low concentrations the loss peak observed is due to the relaxations of PVC segments slightly modified by the presence of plasticizer molecules. At concentrations between 40 and 60 DOP content, the mutual interaction between plasticizer and PVC becomes appreciable leading to aggregates or segments having sizes smaller than that of PVC and not differing much from each other. This is seen from the broadness of the absorption curves and the shift of the loss peaks to lower temperatures. This suggests that at concentrations from 40 to 60 DOP content an optimum compatibility is attained. At higher concentrations the absorption curves may be due to relaxation of excess plasticizer not compatible with the PVC. This excess plasticizer leads also to Maxwell–Wagner effect due to heterogeneity in the system.[14]

On the grounds of experimental evidence we can say that samples having plasticizer from 40 to 60 DOP content in PVC are considered to be good insulators. But because the increase of plasticizer leads to degradation in mechanical properties,[15] the sample containing 40 DOP content is preferable. It is worthy to analyze the data obtained for this sample at different temperatures using the cole–cole method. From Figure 8, it is found that the data are better represented by two arcs, a high-frequency arc and a low-frequency one, both with distributions. The lower-frequency arc is de-

creased with the increase of temperature, while the higher-frequency arc is enlarged with the increase of temperature until 60°C, and after that temperature they remain unchanged. We can conclude that the dielectric properties of the sample containing 40 DOP content does not change by increasing the temperature higher than 60°C.

To calculate the apparent activation energy for some samples, the logarithm of the frequency corresponding to ϵ''_{max} was plotted against the reciprocal of the absolute temperature. This is shown in Figure 9(a) where a straight line was obtained for each concentration. From the slope of the straight line, the apparent activation energy was calculated using the equation

$$T = A\, e^{-(\Delta H/RT)}$$

where $T = 1/2\pi f_{max}$ is the relaxation time at the frequency of maximum loss, R is the gas constant, and T is the absolute temperature. The apparent activation energy ΔH obtained for samples having concentrations from 10 to 90 DOP content was found to have a value from 63 to 27 kcal/mol. It was found by Ishida[11] that the activation energy for α absorption of unplasticized PVC was 87 kcal/mol. This confirms the suggestion that the dielectric absorption observed is the α absorption, and T_g is the α transition $T_{g\alpha}$, ΔH is plotted versus DOP content in Figure 9(b), where it can be seen that the apparent activation energy decreases with the increase of concentration. Such decrease was found before.[12,16] This may be attributed to the change in the internal viscosity of the medium which was found before by Fuoss.[17]

It could be concluded that samples having 40 parts DOP in 100 parts PVC possess the best mechanical and electrical properties. The glass transition temperature $T_{g\alpha}$ shifts from higher than 96°C at 100 Hz for the unplasticized PVC to about 35°C for the mentioned sample. Also the absorption curve is broadened and covers a wide range of temperatures, making it of interest as a practical wire insulator.

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