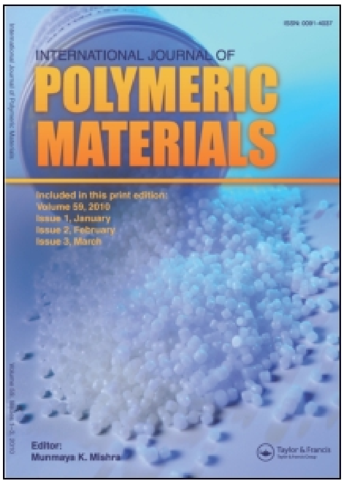

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Dielectric Properties of PVC Plasticized with Dioctyl Sebacate (DOS)

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The dielectric properties of PVC plasticized with dioctyl sebacate (DOS) was studied. The dielectric loss tangent was found to decrease for the plasticized samples which interpreted according to the increase in the intermolecular interactions upon plasticization. The plasticizer contribute to the dielectric strength not only *via* its own polarity but also by markedly changing the nature of the relaxation process. The calculated Frohlich-Kirwood "*g*" factor indicates that there is a strong interaction between the C—Cl group (of the polymer) and the C = O group (of the plasticizer).

Keywords: PVC; dioctyl sebacate; dielectric properties; relaxation process

INTRODUCTION

Polymers are usually plasticized to improve their elasticity, frost resistance and facilitate their processing. Plasticizers are usually liquids with a low volatility to ensure that it is not lost by evaporation, a high boiling point, and a low frezzing point [1]. The free volume in them is larger than that of a polymer. Consequently, the presence of the plasticizer increases the free volume in the system and lowers its glass transition temperature [2]. Also, a growth in the free volume lowers the

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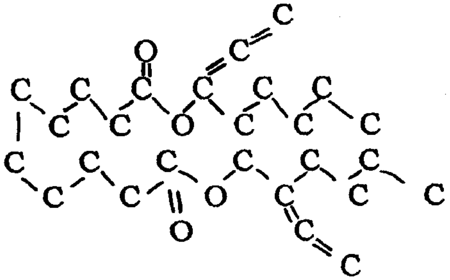
*Corresponding author.

interaction between molecules [3], which is enhanced if a polymer has strong intermolecular bonds, such as hydrogen ones. If the plasticizer has been selected properly, it screens the polymer polar groups, prevents the formation of polymer – polymer bonds, and lowers the glass transition temperature of the polymer. PVC whose T_g is $\sim 354\,\mathrm{K}$, usually contains 30 to 40 mass percent of plasticizer to increase its toughness and flexibility at ambient temperatures [4], which in turn decreases T_g and makes the polymer suitable for plastic raincoats, curtains, and leather-cloth.

The aim of the present work is to study the effect of plasticization of PVC with DOS on its dielectric properties, which has not yet been discussed in the literature.

EXPERIMENTAL PROCEDURE

PVC used in this work is supplied from polymer laboratories Ltd. The weight average molecular weight M_w was 2×10^{5} and M_w/M_n was 1.9, where M_n is the number average molecular weight. Firstly, PVC was dissolved in tetrahydrofuran (THF, Aldrich) and then mixed with 10 wt% dioctyl sebacate (DOS) which has the chemical formula:



The obtained mixture was stirred rapidly. Casting method was used to obtain films with 0.1 mm thick. Gold was used as metal electrode on both sides of the specimen using the evaporation technique.

The dielectric parameters (capacitance, C, and dielectric loss tangent, $\tan\delta$) are measured with the help of philips RLC meter type TM 6304 over the frequency range 1k – 1 MHz and temperatures in the range 300 to 400 K at a heating rate of 1 K/min. The dielectric constant and losses are calculated using the common following equations:

$$\varepsilon' = C\, d \,/ \varepsilon_o\, A$$

and

$$\varepsilon'' = \varepsilon' \ \tan\delta$$

where d is the sample thickness, ε_o is the vacuum permitivity, A is the metallized electrode area.

RESULTS AND DISCUSSION

When PVC is plasticized with DOS, one may expects that the system will consists of different regions. Some of these regions are plasticized and the others are unplasticized [2]. Heterogeneity may exist due to the local distribution of the DOS molecules. Clayden and Howick [3] found by NMR studies that DOS molecules are able to penetrate the crystalline regions of PVC. Thus, it is easy to decide that plasticized PVC consists of two domains one is rich with the plasticizer while the other is poor.

If a polar plasticizer is introduced into a polar polymer, the energy of intermolecular interaction of the polymer decreases if the system polymer-plasticizer is in the rubbery state. When the temperature is lowered to below T_g, the plasticizer molecules act like widely spaced crosslinks on adjacent polymer chains. Then, a more ordered arrangements of the polymer chains is obtained, *i.e.*, a greater effectiveness of intermolecular interactions, that is in the long run leads to an increase in the dielectric losses, Figure 1 .

Figure 1 shows that tan δ is diminished with the introducing of the plasticizer. The obtained result can be explained by the fact that the polymer plasticization results in a certain ordering and more dense packing of the PVC macromolecules. A similar effect was observed when PVC was plasticized by diallyl phthalate [5] . The two processes obviously occurred simultaneously when DOS was introduced into the polymer, namely (i) chemical grafting of the plasticizer to the macromolecules of PVC and (ii) usual intermolecular plasticization.

The dielectric strength, $\Delta\varepsilon$, is found to decrease with temperature (see Fig. 2), for both pure and plasticized samples. On the other hand, the quantity $T\Delta\varepsilon$ (which is a measure of the square of the relaxed

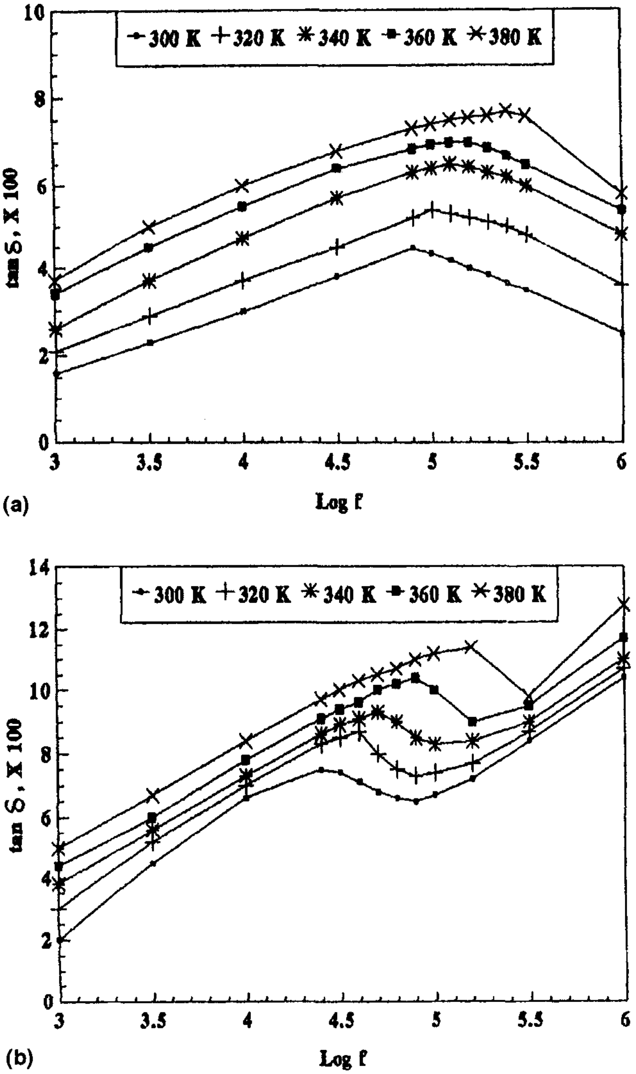


FIGURE 1 Plot of tan δ against the logarithm of frequency for pure PVC (a) and plasticized PVC (b).

dipole moment) was plotted against temperature as shown in Figure 3. It was found that $T\Delta\varepsilon$ progressively increases with increasing temperature. The pure PVC has $T\Delta\varepsilon$ values higher than plasticized

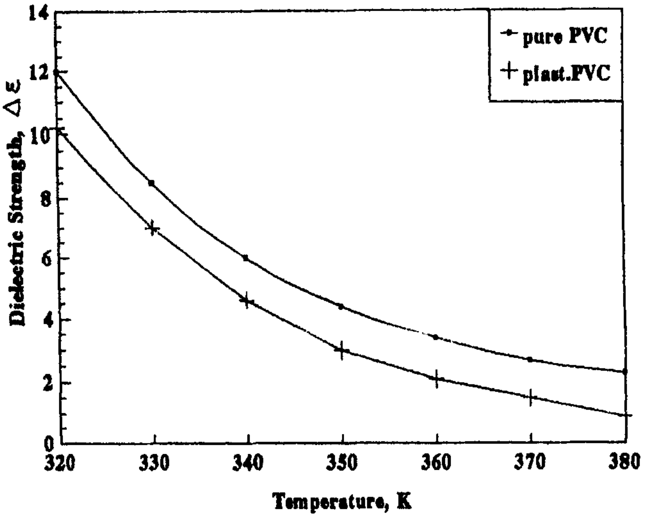


FIGURE 2 The dielectric strength $\Delta\varepsilon$ against temperature in the α-relaxation region of both pure and plasticized PVC.

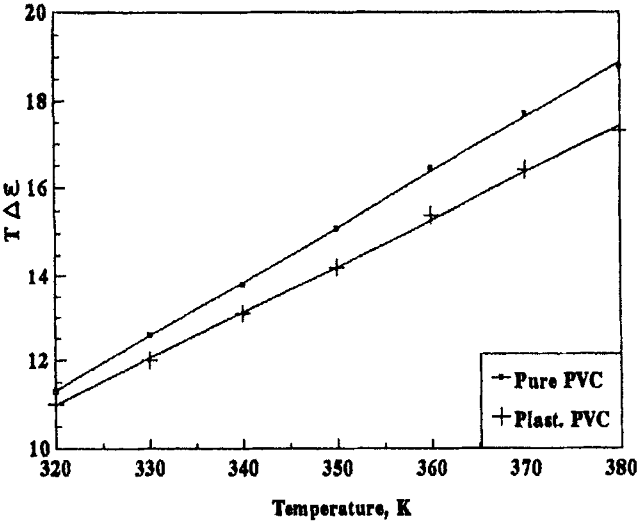


FIGURE 3 Variation of $T\,\Delta\varepsilon$ with temperature for both pure and plasticized PVC.

PVC, Figure 3. This can be attributed to the increase in the dipole concentration as the plasticizer is added to the polymer. This behavior can be interpreted as: the plasticizer molecules contributes to the dielectric strength not only *via* its own polarity but also by markedly changing the nature of the relaxation process, *i.e.*, enhancement of its α-relaxation. The nature of this relaxation process was represented by plotting the peak frequency obtained from Figure 1 against the reciprocal temperature as shown in Figure 4. The obtained data were fitted to Vogel–Fulcher–Tamman equation [7]

$$f_m = f_o \exp(-B/(T - T_o)) \tag{1}$$

where f_m is the apparent peak frequency of the loss curve, and f_o, B and T_o are adjustable parameters. The obtained values of the adjustable parameters are given in Table I .

During cooling the specimen to temperature below T_g, the high energy conformations will freeze into the glass. To reach a lower energy conformations, the polymer chain must rotate and thereby absorb energy. There must be sufficient free volume available to allow these motions to occur. The existence of these two conditions enables the relaxation processes associated with the transition to occur.

When energy is introduced into a quenched sample, a large portion of this energy may be absorbed by conformational changes involving

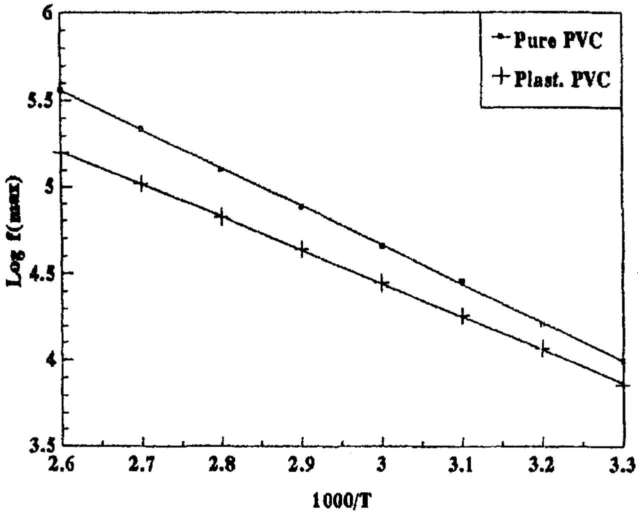


FIGURE 4 The logarithm of maximum frequency losses against the reciprocal temperature in the α-relaxation region for both pure and plasticized PVC.

TABLE I The various parameters of the α-relaxation process of PVC and PVC plasticized with DOS

Sample	T_o, *K*	*A, Hz*	*B, K*
Pure PVC	350	18.60	640
PVC + DOS	380	25.45	1603

the C—Cl and C=O groups. As the system is annealed, the free volume decreases, packing increases, and the ability for a conformational change to occur decreases due to the fact that the chains are in thier lowest energy conformation [8]. Thus, only a small fraction of the energy introduced into the specimen can be absorbed. It is also plausible to assume that the rate at which the polymer chain deforms is decreases as well.

The increase in the peak height of tan δ upon plasticization must parallel an increase in the activity of a particular motion and/or the population of relaxation associated with motion. This activity is attributed to an increase in relaxation associated with the C—Cl groups in the polymer. The strained segments cause the C=O groups (of the DOS) to interfere with the C—Cl groups.

The number and orientation correlation of the dipole moments along the polymer chains can be determined from the relaxation strength. The Frohlich-Kirkwood "*g*" factor is given by [7],

$$\Delta\varepsilon = \varepsilon_o - \varepsilon_\infty = (3\varepsilon_o/(2\varepsilon_o - \varepsilon_\infty))(4\pi N/3kT)((\varepsilon_\infty + 2)/2)\, g\mu_o^2 \quad (2)$$

where ε_o is the vacuum permitivity, ε_∞ is the high frequency dielectric constant, k is Boltzmann's constant, T absolute temperature, N the number of dipoles per unit volume and μ_o is the effective moment of one molecule surrounded by vacuum. Equation (2) indicates that the extent of the correlation of the dipolar motions is involved in the relaxation process. Using the values of 1.2 D and 2.3 D for μ_o[9] were employed for the C—Cl and C=O groups, the obtained values of "*g*" are 0.1882 and 2.15 for the higher frequency processes is found to be reasonable. Also, the value of "*g*" is increased with increasing temperature due to the correlation of dipole moments which becomes less significant with increasing temperature. However, higher value of "*g*" in case of the low frequencies indicates that there is a strong interaction between the C—Cl and the C=O groups.

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