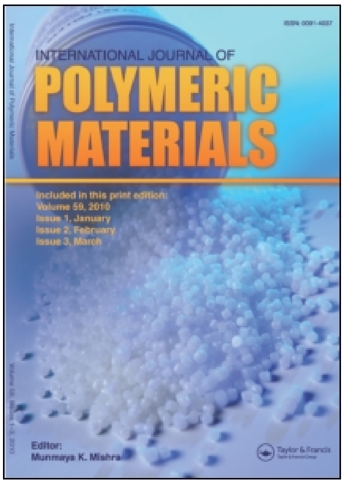

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About Some Potentialities of the Electretic-Thermal Analysis in the Investigation of the Distribution Mechanism of Small Amounts of Additives in Polyvinylchloride

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About Some Potentialities of the Electretic-Thermal Analysis in the Investigation of the Distribution Mechanism of Small Amounts of Additives in Polyvinylchloride

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The electretic-thermal analysis application and especially the magnetic polarization of the dielectrics kind of it gives the possibilities for an investigation of the distribution mechanism of small amounts of additives (dioctylphthalate) in the polyvinylchloride.

The results we received represent an interest for the modification theory of polyvinylchloride, as well as for the theory and the practice of the electretic-thermal analysis.

INTRODUCTION

The Electretic-Thermal Analysis is more and more established as one of the basic methods of the electrophysics for comprehensive observation of the physical and chemical state variations of the polymers and polymers systems.[1,2]

The Electretic-Thermal Analysis is related to a specific temperature and time sequence of the polymer state variations, where the energy communicated to the polymer through the field of force (mechanical, electric or magnetic) a polarization process in the polymer. The character, kinetics and non-equilibrum degree of these processes are determined by the polythermal conditions of temperature variation, the molecular and the supramolecular structure, the polymer thermal history, the relaxation nature of the polarization processes.[2,5] Regardless of the field of force type, the primary data form presentation of the electretic-thermal analysis represents the totality of the thermodepolarization current curves. On the base of polarization curves the polymer state of physical and chemical variations are determined.

The use of different in nature fields of force in the electretic-thermal analysis, based on the polarization or depolarization gives the possibilities of spreading out the analysis ranges. In the present work two types of field of force have been used i.e. electrical and magnetic for realization of the method of thermal-electretic analysis in order to find some aspects of quality level of distribution mechanism of small amounts of additives in polyvinylchloride.

It is well known that the same will be compatible with PVC plasticizer in small concentrations (below 1 wt %) behaves as an intrastructural plasticizer, when in large concentrations the plasticizer behaves as an intramolecular plasticizer. At small plasticizer concentrations the plastication effect greatly depends on the preintroduced additives, quantities and nature.[3]

EXPERIMENTAL PROCEDURE

The investigations are made with K-value 68 suspension PVC. As a plasticizer is used Dioctylphthalate (DOP). The following series of formulations are used (as mentioned and designated in the following figures) curves 1-pure PVC, curves 2-PVC +0.03 wt %, curves 3-PVC +0.25 wt % and curves 4-PVC +15.00 wt % DOP.

The samples of PVC formulations with 1–1.5 mm in thickness and 50 mm diameter are subjected to electretic-thermal analysis and the arrow of action[6] characterizing the kinetic conditions of the experiment is determined: for stationary electric polarization-electric field intensity of 1.2 MV/m, polarization time 3600 s and polarization temperature 100°C (373 K); for stationary magnetic field polarization-magnetic induction 0.2T, polarization time 3600 s and polarization temperature 100°C (373 K). The heating rate at polarization and depolarization is 1 deg/min. After polarization the specimens are cooled at a rate of 12 deg/min, they remain for 24 h in electretic state by the means of short-circuited electrodes and are depolarized when recording the relationship of the thermodepolarization current-temperature or thermodepolarization current-time relationship, respectively as the temperature changes linearly in time: $T = T_0 + bT$, $b = 1$ deg/min.

RESULTS AND DISCUSSION

Figure 1 illustrates the thermodepolarization current curves recorded during the electretic-thermal analysis in stationary electric field. The dioctylphthalate

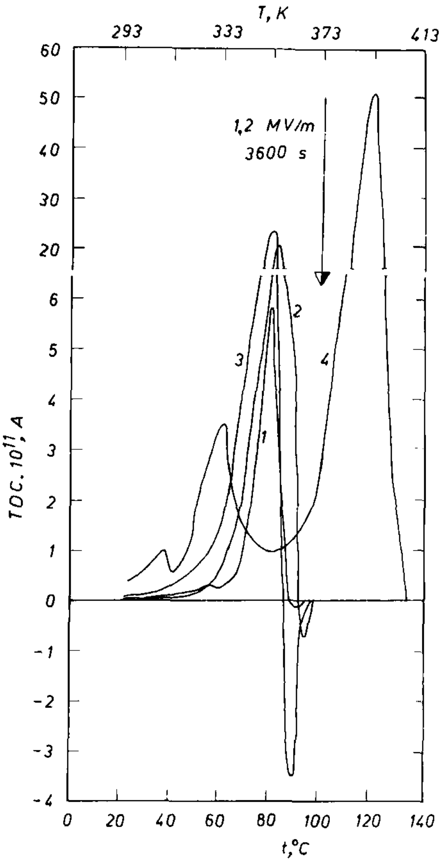

FIGURE 1 Relation of the depolarization current with the temperature in the concentration of DOP (wt %) as follows: 1, zero % DOP; 2, 0.03% DOP; 3, 0.25% DOP; 4, 15.00% DOP.

content changes. The action arrow ensures intensified dipole-segment polarization. The next polarization field intensity increase does not result in considerable polarization increase.

The curves analysis is made on the basis of the following criteria: dependence of the thermodepolarization current from the temperature-thermodepolarization current maximum, respectively density of the thermodepolarization current, location of the maximum in the temperature scale; polarization *P* variation with the temperature, Figure 2; relaxation time variations in the electric charge τ with the temperature, Figure 3; electric charge *W* of the relaxation process activation energy variations with the temperature, Figure 4. The curves are plotted on the basis of the thermodepolarization current curve assuming the presence of the relaxation time distribution spectrum (activation energy, respectively) of the electric charge, i.e. assumption of polyrelaxation polarization process presence (depolarization process). Furthermore, the activation energy reflects the dipole relaxations, whose number is maximum and who have the most probable relaxation time.[2]

The investigations results by the means of the electretic-thermal analysis method are leading to the following suggestions:

In a PVC specimen without a plasticizer a maximum of the thermodepolarization current curves is observed at 80°C, Figure 1. This maximum has an activation energy higher than 130–150 kJ/mol, which determines the dipole-segment nature of the relaxation process. This is in a good correlation with the data from the thermomechanical tests with Kargin's thermomechanical balance—$T_g = 82°C$.[3]

Taking into account that PVC is a difficult-to-crystallize polymer of globular structure organisation, i.e. with clearly expressed supramolecular structure, a maximum should be observed to the thermodepolarization

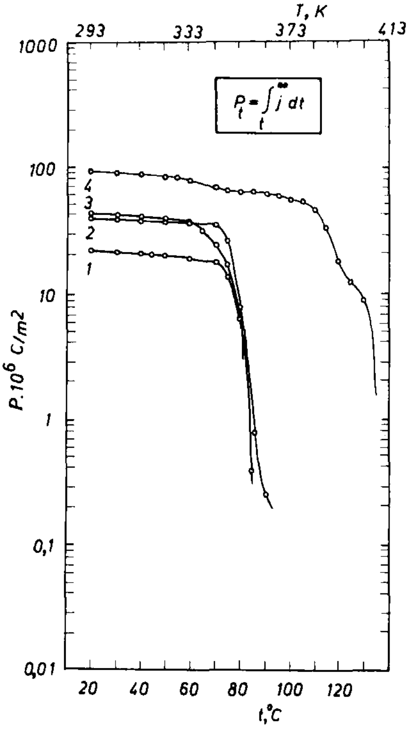

FIGURE 2 Relation of the depolarization with the temperature in the DOP concentrations (in wt %): 1, zero DOP; 2, 0.03% DOP; 3, 0.25% DOP; 4, 15.00% DOP.

current curve determined by dipole-segment polarization of the polymer-α-relaxation process. The dipole-segment polarization is related to the molecular movement, including considerable effective volumes due to the inter- and intramolecular interactions. The α-maximum is most probably due to the segmental mobility in the non-dense and non-array interstructural areas. It is shifted towards lower temperature areas, Figure 4, towards the σ_α-maximum and has an activation energy of 130 up to 150 kJ/mol. The maximum temperature is 76.5°C. When the temperature increases σ_α-maximum appears (at 80°C). In this case these two maxima merge in one, Figure 1, and their separation could be done only on the basis of the activation energy distribution in the terms of the temperatures, Figure 4.

Due to the volume charge polarization there is no observation of the so-called σ_π-maximum.[3] Such a maximum is observed only on the thermo-depolarization current curve at 15 wt % of DOP. This is due to the movement of ions, ion associates and aggregates and other difficult-to-move elements as a result of the presence of a free unsolved plasticizer quantity in the polymer volume.

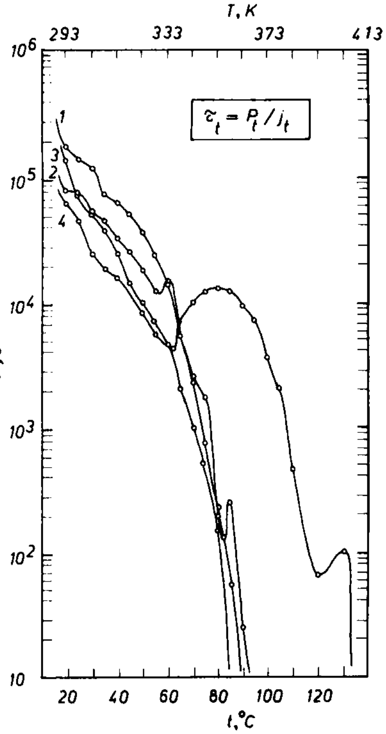

FIGURE 3 Relation of the relaxation time of the dielectric polarization with the temperature in the DOP concentration (wt %): 1, zero DOP; 2, 0.03% DOP; 3, 0.25% DOP; 4, 15.00% DOP.

The addition of 0.03 wt % of DOP does not result in the separation of α and σ_α maxima but only to an increase of the activation energy. The cooperative character movement increases as a result of the dipole solvation in the intraglobular areas. Complete separation of these two maxima is observed only at 15 wt %. The second maximum corresponds to T_g and the screening effect, the effect resulting from segment length reduction and the effect from the presence of a free plasticizer appear here—the activation energy of this maxima being 10 kJ/mol. The first maximum with activation energy of 2.75 kJ/mol is assumed to be due to the free plasticizer. The position of the three maxima suggests that the plasticizer of good compatibility with the polymer was diffused in the polymer volume and has partially destroyed its supramolecular structure-intrastructural plastication. At 0.03 and 0.25 wt % the activation energy value for σ_α-max is larger than 130–450 kJ/mol suggesting a dipole-segmental character of the polarization.

This fact is also confirmed by the character of polarization change depending on the temperature, Figure 2. With the introduction of 0.03 wt %

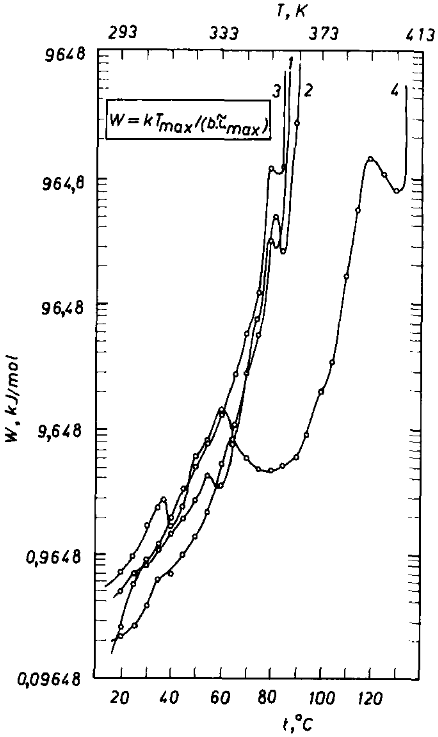

FIGURE 4 Relation of the energy of activation of the dielectric polarization with the temperature in the concentration of DOP (wt %): 1, zero DOP; 2, 0.03% DOP; 3, 0.25% DOP; 4, 15.00% DOP.

DOP polarization sharply increases in comparison to the pure PVC, nearly two times. At 0.25 wt % DOP, the increase is negligible as compared to 0.03 wt % DOP and polarization grows considerably more smoothly with the temperature decrease. The introduction of 15 wt % DOP results in increasing the polarization value approximately two times as compared to 0.03 wt % DOP. The curve illustrates that polarization growth is due to the volume charge polarization which occurs above the verification temperature—σ_π max. The polarization increases at a leap by introduction of 0.03 wt % DOP, which confirms the interstructural character of the polarization when introducing small amounts of additives.

The dielectric permeability increment calculated on the basis of the electric charges, liberated at depolarization for each relaxation process could also serve as a criterion for the dipole nature of the respective maximum. The size of the generalized charge in the temperature range investigated is a sum of all the increments $\Delta\xi_i$:[2]

$$Q_g = \sum \Delta\xi_i = \sum Q/(\xi_0 \cdot S \cdot E_p) \qquad (1)$$

The calculations made for pure PVC are giving $\Delta\xi = 9.7$ for the total charge which corresponds to that obtained by other authors.[3]

It could be assumed, with an accuracy up to the homocharge recording that the total increment for the 20–100°C range is proportional to the polarization at 20°C. For the three formulations and the pure PVC (pure PVC, PVC +0.03 wt %, PVC +0.25 wt % and PVC +15 wt % dioctylphthalate) the polarization values are 20.63×10^{-6}, 39.59×10^{-6}, 40.28×10^{-6} and $94.02 \times 10^{-6}\,\mathrm{c/m^2}$, respectively. At small amounts of additives polarization increases at a leap indicating the interstructural character of the plastication of these DOP concentrations. Furthermore, the relaxation time corresponding to this polarization also increases at leaps from 22.49 h for the pure PVC sample up to 53.97 h for the sample of 0.03 wt % DOP addition after which a decrease is observed—43.93 h for the sample with 0.25 wt % DOP and 17.09 h for the sample with 15 wt % DOP. The charge relaxation time for the large amounts of additives is lower than that of the pure PVC which proves again the principal thesis of the present work.

The statements made so far are giving the possibilities for a verification by the means of the electretic-thermal analysis of the already established fact,[3] i.e. that the same plasticizer well compatible with the PVC at small concentrations is distributed interstructurally, and at large concentrations intermolecularly. Furthermore, in small concentrations it is mainly distributed in the free volume of the non-dense interglobular areas, increasing the segmental mobility of the non-array macromolecules and passage chains. As the total volume of these areas is negligible, small amounts of the additive fill these areas and change to a considerable extent the relaxation transition of the system.

The increased segmental mobility of the non-array macromolecules and passage chains is not the only result of the introduction of small amounts of thermodynamically compatible plasticizer—an increase in the homocharge is observed. From 0.12×10^{-6} c/m^2 for the pure PVC sample, at 0.03 wt% DOP it becomes 0.72×10^{-6} c/m^2 and at 0.25 wt% DOP it is 5.1×10^{-6} c/m^2. There is a departure from this tendency for large amounts of additives—15 wt% DOP. There the homocharge is zero. This could be explained by the reduced specific bulk resistance of the polymer—$\rho_v = 10^{11}\,\Omega$m, where the homocharge is quickly neutralized.

The introduction of small concentrations of a plasticizer thermodynamically compatible with the PVC resin results in a change of the surface condition, i.e. its density and energy spectrum. In this case the surface condition is most likely of its own type with impurities. A part of the plasticizer is distributed on the surface and changes the self type of PVC surface condition.

The homocharge could serve as a criterion for the distribution of the small amounts of additives in the polymer surface layer.

The electretic-thermal analysis with a magnetic field[4] gives the possibilities for looking at these changes from another point of view.

Although the hard-chain molecules are diamagnetic, due to the fact that in one domain they are in the order of 10^6–10^8, the domain could be regarded as a paramagnetic superparticle. The magnetic field effect results in the orientation of all the domains in the direction of the field to a specific extent.[6] According to this hypothesis the orientation effects to be observed in the PVC are due to the domain as a structural element. They have certain independence in movement which is expressed both at the introduction of solvents and plasticizers and at the impact of mechanical, electric and magnetic fields. The domains are characteristic for the hard-chain polymers (to which PVC also belongs) and are regarded as fluctuation structural elements.[6] On the basis of the above mentioned, the following working hypothesis has been developed for the potentialities of the electretic-thermal analysis with a magnetic field in revealing the plastication mechanism.

The occurrence of anisotropy in the dielectric properties of PVC compositions under the magnetic field action is an evidence to the presence of domains with paramagnetic properties and the irrigation of liquid crystal structure in PVC.[5] The degree of anisotropy at other equal conditions is affected by specific thermodynamic factors amongst which are the plasticizers. The residual polarization after the effects of mechanical, electric and magnetic field could serve as a measure of the anisotropy in the polymer properties. There is no difference in terms of external manifestations of the electric charge for the three cases—hetero- and homocharge appear. Data shows that for the effect of the magnetic field the charge is about one order of magnitude smaller than that of the electric field effect. Depolarization observed through the thermodepolarization current supplies information about the movement of the dipoles and charges in the polymer. The difference from electric-thermal analysis with electric field consists in fact that the polarization in this case runs through impact on the domain as a structural element of paramagnetic properties which carries additional information.

Polarization, relaxation time of the electric charges and the activation energy of the relaxation process could be calculated on the basis of the thermodepolarization current curve. For pure PVC, Figure 5, has three characteristics maxima: at 77°C, 50°C and 25°C. The calculation of the depolarization process activation energy determines the first maximum to be related to the dipole segmental mobility and the remaining to be related to the dipole segmental mobility which is most likely. σ_α-maximum is divided into two: α-maximum at 77°C and σ_α maximum at 82°C.

The reduction in polymerization at small additions of DOP being about five

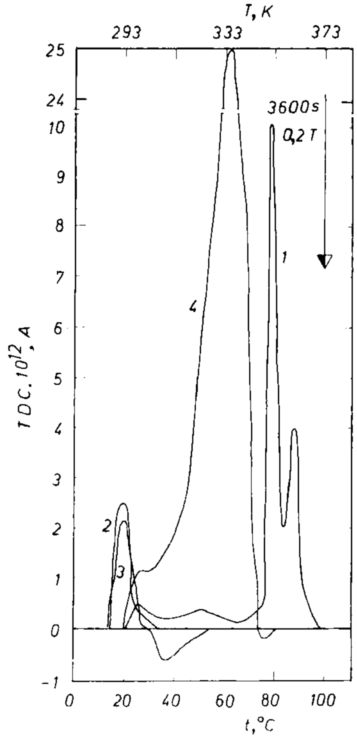

FIGURE 5 Relation of depolarization current with the temperature in the conditions of the magnetic polarization and DOP concentrations (wt%): 1, zero DOP; 2, 0.03% DOP; 3, 0.25% DOP; 4, 15.00% DOP.

times lower for 0.03 wt % compared to the pure PVC resin is most likely to be interpreted as a reduction in the probability for domain structure formation. Furthermore, the plasticizer evidently is distributed in the interstructural areas as the dipole-segmental process shifts towards the lower temperature. It could be assumed that the introduction of the thermodynamically compatible plasticizer in small concentrations obstructs the formation of a domain structure of paramagnetic properties. It is not until the action of the magnetic field being superimposed on the action of the plasticizer that the system acquires domain structure and is able to be orientated under the field effect. For small amounts of additives it could be assumed, that the field plays not only a role in the orientation of the paramagnetic super particle but also increases the difference in the free energies of the local flexible and inflexible conformation.

At high DOP concentrations the magnetic field plays the only role of a factor of external effect resulting in the orientation of the paramagnetic super particles. An evidence to this is the coincidence of the two areas of the dipole-segmental mobility—around 51°C for the electric-thermal analysis with a magnetic and electric field. Besides that the polarization at high concentrations of DOP plasticizer is higher than that of a pure PVC resin which is explainable with the effect of the plasticizer as thermodynamic factor for the change in the polymer structure, on one hand, and as a factor facilitating the internal friction in the orientation under the action of the field of force.

The electretic-thermal analysis with magnetic field gives the possibilities for distinguishing the two types of plastication.

The hypothesis pointed out for the application of the electretic-thermal analysis with a magnetic field as a method of assessing the polymer structure changes is confirmed by the facts known in the field of using small additions of a plasticizer thermodynamically compatible with PVC. In case of small additions of DOP plasticizer the results sharply differ from these of the electretic-thermal analysis with an electric field because the magnetic field plays a principal role in the formation of the paramagnetic super particles—the domains. The polarization is much lower than that of pure PVC. In case of large amounts of plasticizer additions the results coincide with those of electretic-thermal analysis with an electric field as the magnetic field of force where orientation of the existing structure formation action of the magnetic field is negligible in comparison with the action of the plasticizer. The polarization is higher than that of the pure PVC.

CONCLUSIONS

In conclusion it should be emphasized that the method of electretic-thermal analysis could be successfully used in the investigation of the PVC plastication. The occurrence of α and σ_α polarization processes in the PVC-compositions, regardless of the fact whether large or small amounts of a plasticizer thermodynamically compatible with the polymer are introduced equally confirms that the method of electretic-thermal analysis gives possibilities for determination of the specific features of small and high plasticizer amounts introduction in the polymer.

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