Investigation on the Effect of the Acid Number of the Plasticizer on Some PVC Properties

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Synopsis

The effect of polyester plasticizer of differing acid number on the properties of PVC compositions, to be used for electric insulation purposes, is investigated. It is established that the acid number affects both the temperature dependence of the specific bulk resistance in vitreous and highly elastic state and the process of formation of a polymer matrix with minimum ion diffusion factor. The assumption is made that the effects observed are due both to the different stability of plasticizers of differing acid number towards destruction at thermal processing and to the difference in density of the polymer matrix depending on the acid number of the plasticizer. It is considered that polyester plasticizer (PEP) is a cheap and efficient plasticizer, which, irrespective of the nontraditional high acid number, could successfully be used for PVC plastication.

INTRODUCTION

Use is made in practice of different plasticizers of an acid number below 1.0 mg/g KOH. A high acid number is considered to affect negatively the efficiency of the plasticizer. Certainly, there is a lack of systematic investigations on the effect of the acid number of the plasticizer on PVC properties. This permits the assumption that up to the present moment the problem is solved on an empirical basis only.

The formulation thus adopted restricts the application of products of high acid number from organic synthesis, as PVC plasticizers, independent of the apparent economic advantage. The eventual introduction of similar substances into practice, i.e., lifting of this barrier, is based on a favorable result of the investigations on the effect of the acid number of the plasticizer on PVC properties.

The present investigations, therefore, aim at clarifying some aspects of the effect of the acid number of the plasticizer on the properties of PVC and PVC compositions, to be used for electric insulation purposes.

EXPERIMENTAL

PEP-100 polyester plasticizer is obtained during esterification of a mixture of carboxylic acids, residues from the production of dimethylterephthalate with octyl alcohol depending on the technologic conditions and properties of the initial products; there is a possibility the acid number of the plasticizer obtained to be varied in the range of 1–11 mg/g KOH. The basic properties of PEP-100 are:

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density 1.015 kg/m^3; refractive index n_D^{20} 1.512; viscosity 377.3 × 10^{-3} N·s/m^2; flame point above 225°C and volatile substances (6 h at 100°C) 0.2%. The investigations were carried out with PEP samples of 1.5, 3.5, and 8.0 mg/g KOH acid number. The acid number is determined according to the Bulgarian State Standard 5788-65. The samples were prepared on the basis of suspension PVC with K_f-68 and properties according Bulgarian State Standard 8804-71. The formulations used include tribasis lead sulphate ($3PbO \cdot PbSO_4 \cdot H_2O$), a product of Greiz Dölau (East Germany) as a stabilizer and bisphenol A as an antioxidant. Two compositions are prepared: composition A (75.8 wt % PVC; 22.7 wt % PEP-100 and 1.5 wt % stabilizer) and composition B, differing from the former in that some amount of antioxidant is introduced.

The temperature dependence of the specific bulk resistance ρ_v is thoroughly investigated. The bulk resistance is measured at continuous linear rise of temperature ($T = T_0 + b \cdot t$, where t is time, T_0 = initial temperature, and b = heating speed) at a heating speed of 1 K/min, which ensures thermodynamically quasiequilibrium heating of the samples. Electric field strength is 0.5 MV/m.

The samples to be investigated are of 50 mm diameter and 2 mm thickness. They are normalized at 80°C for 6 h. All other investigations (for physical and mechanical, electrophysical and other properties) on the samples are carried out in accordance with Bulgarian State Standard 5792-76. Investigation was also carried out on the destruction resistance of the plasticizer at 170°C.[1]

RESULTS AND DISCUSSION

It could be expected that the variation in the acid number of the plasticizer will be in correlation with the variation in the electric conductivity of the polymer compositions. The electric conductivity of the polymer materials is determined by the presence of free and loosely bound electric charges. In the field of weak electric fields, with polymer compositions of the investigated type, the so-called ion component of electric conductivity should be expected to predominate. The temperature dependence of the ion component of specific bulk conductivity is

$$\sigma_0(T) = \sigma_0^0 \exp(-W_0/kT) \tag{1}$$

where W_0 is activation energy required for the formation and displacement of the ion, k = Boltzmann's constant, T = temperature, and σ_0^0 = conductivity, extrapolated towards infinitely large temperature values.

The ionic conduction is closely related to diffusion, concentration and charge of the ions. Following Nernst–Einstein,

$$\sigma_0(T) = D \cdot n \cdot q^2/kT \tag{2}$$

where D is ion diffusion factor, n = ion concentration, and q = ion charge.

The statements presented so far presume a discontinuity of the specific bulk conductivity in the area of glass transition temperature and presence of an exponential temperature dependence in the area of vitreous and of high elastic state provided that the electric conductivity is of ionic nature.

The experimental results are presented in Figure 1. In the coordinates selected, $\ln \rho_v - 1/T$, the straight line shows the exponential relationship between

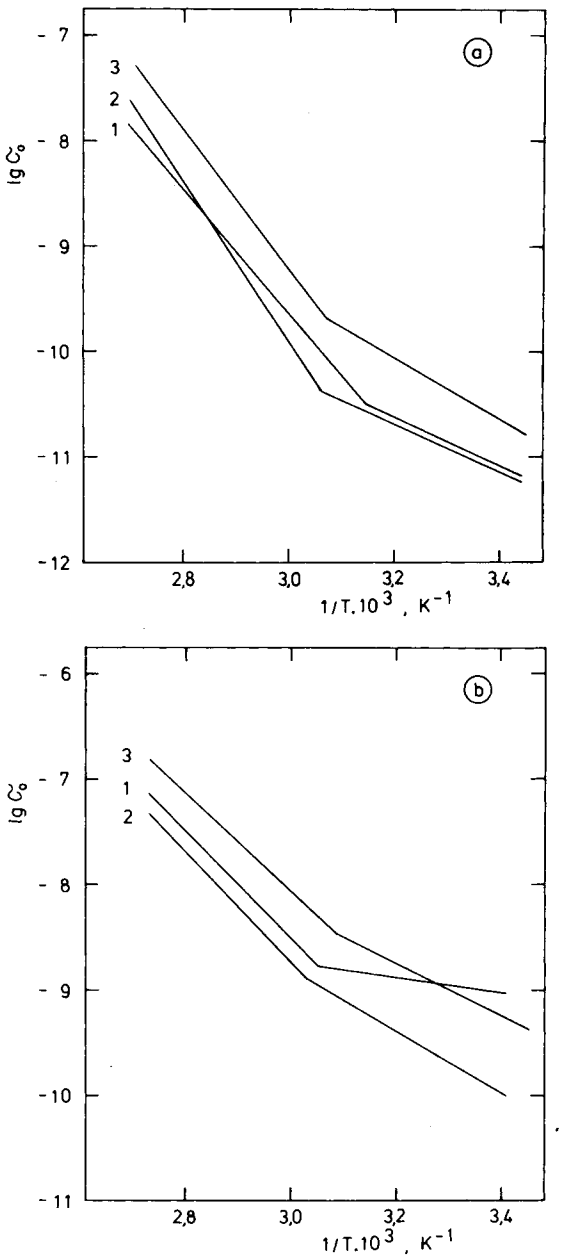

Fig. 1. Temperature dependence of the specific bulk resistance for (a) composition A; (b) composition B. Acid number (mg/g KOH): (1) 1.5; (2) 3.5; (3) 8.0.

electric conductivity and temperature. The correlation relationship between the specific bulk conductivity ($\ln \rho_v$) and temperature ($1/T$) could be statistically evaluated through the linear correlation factor r, on the basis of the correlation analysis of the experimental data.[2]

Quantitatively the relationship is given by the so-called regression equation (2). After changing the coordinates, for the area of vitreous and of high elastic

state relationships are obtained from the type of eq. 1 (Table I). The equations are plotted on Figure 1 in the coordinates $\ln \rho_v - 1/T$. The statistical verification of the individual linear correlation coefficients, in accordance with (2), is made at 0.05 level of significance (Table I). The correlation analysis and the regression equations permit the claim that at exploitation temperature interval of the compositions investigated (from the view point of exploitation at 90°C) the temperature dependence of electric conductivity is of exponential character. Hence, from the physical point of view, conductivity is of ionic nature.

The temperature interval of ionic conductance depends both on the acid number of the plasticizer used and on the composition. The temperature interval of ionic conductance is determined by the amount of experimental data (for the area of high elastic state), for which the correlation factor is considerable at 0.05 level of significance.

The widest temperature interval of ionic conductance is observed at an acid number of 3.5 mg/g KOH: for composition A, up to 130°C, and for composition B, up to 150°C. In the conditions of the experimental investigation depending on the acid number the upper limit of the temperature interval of ionic conductance varies with approximately 20 K.

The change in electric conductivity in terms of character above this limit could be related to the growing participation of the electrophoretic (molionnic) conductivity in the conditions of thermal activation of the polymer system, containing a relatively high amount of plasticizer (22.7 wt % PEP-100). The difference in the behavior of both compositions is due mainly to the action of the antioxidant bisphenol A introduced. The acid number of PEP-100 affects essentially the temperature interval of ionic conductance permitting that it be enlarged towards higher temperature areas. The introduction of antioxidant in the composition enables that this effect be considerably intensified. In line with this, the range of variation of the specific bulk conductivity in the exploitation temperature interval is narrower with approximately 28% during introduction of bisphenol A.

The acid number of PEP-100 has a direct effect also on the value of specific bulk conductivity both in vitreous and in high elastic state (Fig. 1). Minimum electric conductivity values are observed at 3.5 mg/g KOH. This fact is valid for the whole exploitation temperature range of composition A and composition B, with the exception of the glass transition area for composition A. The introduction of an antioxidant stabilizes the result obtained in the temperature range investigated.

The acid number of PEP-100 determines the value of electric conductivity in the whole temperature range. Its variation is in correlation both with variation of activation energy of the conductivity and with variation of conductivity, extrapolated towards infinitely large values of temperature (Table I).

In the area of vitreous state the following peculiarities are observed:

—the growth in acid number results in the growth of conductivity, extrapolated towards infinitely high temperatures, that does not depend on temperature;

—the growth in the acid number results in growth of the apparent activation energy of conductivity, and up to 3.5 mg/g KOH it is almost invariable;

—the growth of the acid number of the plasticizer is expressed differently for the two compositions: for composition A the activation energy of conductivity grows in parallel with the growth in conductivity σ_0^0, independent of temperature;

TABLE I
Correlation Analysis Results

PEP-100 acid number, (mg/g KOH)	Vitreous state			Glass T_g		High elastic state		
	Conductivity σ_0^0 (s/m)	energy, W_0 (kJ/mol)	Correlation factor (r)	(°C)	(K)	Conductivity σ_0^0 (s/m)	Activation energy, W_0 (kJ/mol)	Correlation factor (r)
				Composition A				
1.5	5.54×10^{-4}	44.0	0.918	47	320	0.43×10^{9}	116.8	0.981
3.5	2.14×10^{-4}	42.2	0.993	53	326	0.75×10^{13}	145.2	0.982
8.0	0.20	55.8	0.991	53	326	0.34×10^{11}	125.9	0.984
				Composition B				
1.5	2.36	52.8	0.996	53	326	0.36×10^{7}	96.0	0.982
3.5	1.64	57.3	0.997	58	331	0.55×10^{7}	98.6	0.984
8.0	0.11	46.5	0.990	51	324	0.20×10^{7}	91.6	0.988

for composition B the activation energy passes through a maximum at 3.5 mg/g KOH, and σ_0^0 conductivity is reduced;

—the variation of the acid number of the plasticizer in the range of 1.5–3.5 mg/g KOH for composition A does not result in sharply differing values;

—the introduction of bisphenol A increases conductivity of the polymer system but permits that stable results be obtained and a clearly defined effect of reduction in conductivity at 3.5 mg/g KOH.

In the area of highly elastic state the following peculiarities are observed:

—the growth in the acid number of the plasticizer determines the variation in the activation energy of conductivity and of σ_0^0 conductivity, passing through a maximum in the area of 3.5 mg/g KOH;

—the introduction of bisphenol A results in reduction of σ_0^0 conductivity but also in reduction of activation energy and as a result of their mutual variation conductivity increases in the exploitation temperature interval for both compositions.

The experimental facts pointed out impose the general conclusion that there are plasticizers and conditions with which high exploitation properties are obtained at an acid number above 1 mg/g KOH.

The high activation energy value for conductivity is a measure for increased internal friction in the system, for reduction in diffusion of the current carriers in the polymer system. This statement is also favored by the dependence of glass-transition temperature on the acid number (Table I). The maximum shift of the transition temperature towards high temperature areas is established at an acid number of 3.5 mg/g KOH and at the introduction of bisphenol A (T_g = 58°C). The data for the density of the samples for both compositions (Table II) also confirm the higher degree of packing of the polymer system, the increased intermolecular interaction, and the increased internal friction in the samples of 3.5 mg/g KOH acid number. The acid number of the plasticizer is a factor changing the internal friction in the system and the diffusion of the charge carriers in it.

The measurements of the specific bulk resistance at 20°C (vitreous state) and at 60°C (highly elastic state) carried out in accordance with Bulgarian State Standard 5792-76 are again in good correlation with the data for the density of the samples (Table III).

The test for resistance to moisture and heat strongly confirms the reduced diffusion of the samples with 3.5 mg/g KOH acid number (Table III).

The physical and mechanical tests on the different samples (Table IV) show that the effect of the acid number of the plasticizer on the physical and mechanical properties is inessential.

The weight losses of the samples investigated (Table IV) could be related also to the destruction resistance of PEP-100 at thermal activation. The investigations carried out at 170°C permit the claim that PEP-100 plasticizer of 3.5 mg/g

TABLE II
Density at 20°C (kg/m³)

PEP-100 acid number (mg/g KOH)	1.5	3.5	8.0
Composition A	1319	1327	1306
Composition B	1356	1360	1332

TABLE III
Electrical and Physical Properties

PEP-100 acid number (mg/g KOH)			1.5	3.5	8.0
1. Specific bulk resistance (Ω·m)	at 20°C	Composition A	2.00×10^{13}	5.20×10^{13}	0.31×10^{13}
		Composition B	0.16×10^{13}	1.00×10^{13}	1.00×10^{13}
	at 70°C	Composition A	2.20×10^{10}	5.70×10^{10}	2.00×10^{10}
		Composition B	2.20×10^{10}	8.80×10^{10}	2.00×10^{10}
2. Electric strength (MV/m)		Composition A	22	21	21
		Composition B	24	23	24
3. Moisture and heat resistance					
Specific bulk resistance at 20°C (Ωm)		Composition A	1.50×10^{13}	5.10×10^{13}	3.5×10^{13}
		Composition B	0.086×10^{13}	0.51×10^{13}	0.058×10^{13}
Electric strength (MV/m)		Composition A	21	20	18
		Composition B	24	20	24

TABLE IV
Physical and Mechanical Properties

PEP-100 acid number (mg/g KOH)		1.5	3.5	8.0
Tensile strength (MPa)	Composition A	23.0	23.0	24.0
	Composition B	20.0	21.4	20.0
Relative rupture elongation (%)	Composition A	280	260	270
	Composition B	260	270	276
Thermal deformation (%)	Composition A	22	22	26
	Composition B	26	25	26
Cold resistance (°C)	Composition A	−33	−34	−35
	Composition B	−41	−41	−39
Weight losses (%)	Composition A	0.35	0.36	0.80
	Composition B	0.42	0.41	0.47

KOH acid number has the highest destruction resistance (Fig. 2). This could explain the improved dielectric properties in the area of low intensity electric fields, and the tendency towards realization of a polymer matrix with minimum ion diffusion factor.

The data for electric strength of the individual samples show that in the area of strong electric fields, where conductivity of electron character dominates, the acid number does not result in essential change of this factor.

CONCLUSIONS

The acid number of PEP-100 plasticizer has an essential influence on the ionic conductance of the polymer system; it changes its temperature dependence, its temperature interval, and its value. These effects are due to the variations in destruction resistance of the plasticizer and to the changes of the ion diffusion in the polymer system.

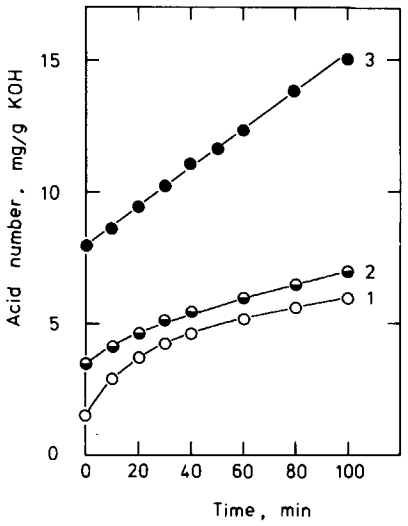

Fig. 2. Destruction resistance of PEP-100 polyester plasticizer at an acid number (mg/g KOH): (1) 1.5; (2) 3.5; (3) 8.0.

The problem for the influence of the plasticizer used, on the properties of the polymer system, should be treated individually for each specific case of application of the plasticizers.

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