

THE DEPENDENCE OF DIELECTRIC LOSSES OF POLYMERIC COMPOUNDS ON THE CONSTITUTION OF MACROMOLECULES

INTRODUCTION

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ABSTRACT

Concern about the researches of dielectric losses and permittivity of polymers is caused not only by the relevance of these performances for practical use.

Keywords: dielectric losses, polymeric, compounds, macromolecules, polarization.

I. INTRODUCTION

Modern theories of the dielectric polarization and losses allow to bound in some cases the value of ε' and $tg\delta = \frac{\varepsilon''}{\varepsilon}$ and the parameters describing their dependence on temperature and frequencies of an electric field with the constitution of a polymers (and character of thermal motion of macromolecules), i.e. there are possibilities to use the measuring of these values to derive some information about a structure of a polymer.

We shall note, that early theoretical introduction about dipole polarization [1] allow to gain the parameters, describing dipole losses of a polymer by means of which it is possible to forecast the variation of ε' or ε'' qualitatively with temperature and frequency. However in these theories, singularities of a structure of polymeric compounds, specificity of molecular motion in them, determining the processes of relaxation of dipole polarization were not considered.

In the present material the outcomes of probing of dependence of dielectric losses of some polymeric compounds from their molecular structure are presented. Thus, the method of SIMS (Secondary Ion Mass-spectrometry) is used for clearing up the order of a disposition of monomer units in groups of macromolecules.

II. EXPERIMENTAL AND THEORETICAL RESEARCHES.

Earlier in [2], it was shown, that the method of secondary emissive mass – spectrometry can be used for

determination of a microstructure of molecules of polymeric compounds. This method is based on the analyzing of relative ion intensity CX_n^+ in a mass spectrum (where C - carbon, X - depending on type of a polymeric compound - atoms of F, Cl or H), formed when bomb ing polymer substances by atoms of Argon. The mechanism of such formation of ions has been identified and the computational method of the relative ion yields is developed for any of possible microstructures of polytetrafluoroethylene (PTFE) (F-4), polytrifluorochloroethylene (F-3), polyvinylidene fluoride (PVDF) (F-2), polyethylene (F-0), copolymers F-42, F-40, F-32.

In all cases our results about structures of macromolecules of probed polymeric compounds, based on coincidence of calculated and measured intensities of mass-spectral lines, have coincided with the literary data gained with usage of, in essence, diverse methods. The regularity of the tendered mechanism of CX_3^+ type secondary ions formation is confirmed as well by the calculations based on other mechanisms reasonable from the point of view of the physics of interaction of heavy corpuscles with a solid do not yield the outcomes matching to experiment.

It is known, that electric properties of dielectrics (specific conductivity, electric strength, dielectric losses and permittivity) are instituted by availability of the free ions chemically uncombined with macromolecules. These parameters largely depend on availability of low molecular impurities which can be a source of ions. At least, the electric conductivity of polymeric dielectrics approximately equal to $10^{-19} - 10^{-13} \text{ Ohm}^{-1} \text{ cm}^{-1}$, increases with enhancement of monomer units in a molecule [3].

Another unique feature of polymeric compounds is independent movement of the subchains consisting of a major number of monomer links. If such a polymeric compound locates in an electric field, under certain conditions (frequency of a field and a correlation of relaxation times of the orientation moment), variations of orientation

structure of monomer units is observed.

To research the dependence of a dielectric factor (ε) and dielectric losses ($tg \delta$) of polymeric compounds from the orientation of links in them, the distributions of the monomer links grouped in units on m links have been calculated (in some polymeric compounds and by matching calculated and measured relative intensities of ions, instituted their orientation [4]).

Requirements of a synthesis are selected in such a manner that at mole concentrations of tetrafluoroethylene (F-4) and vinylidene fluorides (F-2), equal to $N_A=0,18$ and $N_B=0,82$ accordingly, the copolymer in which the relative concentrations of F-4 and F-2 were equated 0,32 and 0,68 was gained. For this couple of monomers the attitude of kinetic constants of a copolymerization is known: $r_A=0,28$ and $r_B=0,32$ [4]. Here the index A belongs to F-4, and B to F-2.

Knowing these coefficients, we calculate allocations of monomers in an area of each type on blocks in a molecule of a copolymer by the formula:

$$\delta_{Am} = \frac{m \lambda_A^{m-1}}{(1 + \lambda_A)^{m+1}} \quad \text{and} \quad \delta_{Bm} = \frac{m \lambda_B^{m-1}}{(1 + \lambda_B)^{m+1}}, \quad (1)$$

Where δ_{Am} and δ_{Bm} - a relative quantity of monomer units of F-4 and F-2 are grouped in blocks on m links, $\lambda_A = r_A (N_A / N_B)$ and $\lambda_B = r_B (N_A / N_B)$. At $\lambda_A=1,46$ and $\lambda_B=0,061$, it is possible to determine allocation of monomer links in molecules of copolymer. In tab. 1 allocation of monomer links for several polymeric compounds and copolymers are shown. Apparently from the table, in molecules of polymeric compound F-4 links in the core are proportioned on one (84,2 %) and on two (13,7 %), at the same time the links of F-2 are arranged on all units. For a microstructure analysis of a copolymer measured of value (fig.3) of intensity of ions CF_3^+ , CF_2H^+ , CFH_2^+ were compared to calculated output of the same ions from each type of structural sections and were summarized on links. Thus summarized yield for copolymer F-42 was calculated by the formula:

$$i_{CF_3^+} = C_A \left(8 - \frac{3}{1 + \lambda_A} \right) + C_B \left(2 + \frac{1}{1 + \lambda_B} \right)$$

$$i_{CFH_2^+} = C_A \frac{3}{1 + \lambda_A} + C_B \left(2 - \frac{1}{1 + \lambda_B} \right);$$

$$i_{CF_2H^+} = C_B \left(1 + \frac{1}{1 + \lambda_B} \right)$$

Summarized yields of ions and other probed polymeric compounds and the copolymers, depicted in Table 1 have been calculated analogously.

The research of total contribution of each monomer link in a mass spectrum of ions of copolymer F-42

and their matching with measured others have shown a correctness of calculation on an order of value. Therefore the information from the Table served as a basis for study of the influence of a constitution of molecules of polymeric compounds (copolymers) on their electric properties.

For determination of a dielectric factor of above-stated exemplars the UHF method has been used. For this purpose exemplars were interposed into a waveguide of the rectangular cross section, and the variation of wavelength in the waveguide with the introduction of a dielectric was measured.

It is known that the dielectric constant of matter is generally determined by

$$\varepsilon = \varepsilon' - j \varepsilon'' = \varepsilon' (1 - j tg \delta),$$

Where $tg \delta = \frac{\varepsilon''}{\varepsilon'}$ - dielectric losses. In lack of losses ($\varepsilon = \varepsilon'$) the guide wavelength at availability of a dielectric is determined by a correlation:

$$\lambda_g = \frac{\lambda_0}{\sqrt{\varepsilon \mu - \left(\frac{\lambda_0}{\lambda_{kp}} \right)^2}}, \quad (2)$$

Where λ_0 - a free-space wavelength, $\lambda_{kp} = 2a$ - critical wavelength in the waveguide (at $\varepsilon=1$), a - width of a common leg of a waveguide (3,2 cm). Being restricted to a case $\mu=1$ from (2) we shall gain:

$$\varepsilon = \frac{\left(\frac{a}{\pi} \right)^2 \beta_\varepsilon + 1}{\left(\frac{2a}{\lambda_g} \right) + 1}, \quad (3)$$

Here $\beta_\varepsilon = \frac{2\pi}{\lambda_g}$ - a phase constant of a wave in the waveguide at availability a dielectric in it.

Dielectric losses of considered dielectrics are instituted from a correlation:

$$k = \frac{tg \beta_\varepsilon d}{\beta_\varepsilon d}, \quad (4)$$

Where d - the width of a dielectric. The equation (4) is transcendental the equation having the infinite solution. Therefore, for determination (β_ε) made measuring ε for two samples of the same dielectrics of various width d_1 and d_2 . Thus required magnitude β_ε was what fulfils the equation (4) for d_1 and d_2 .

Thus, ε' and ε'' have been measured for dielectrics F-4, F-3, F-2, F-0, and also F-32 and F-42 at various frequencies of UHF of a field. On fig. 1 and 2 the typical

dependences of ε' and ε'' from the frequency are presented, which are characteristic of polymeric compounds for which one area is dipole-segmental and two areas are dipole-group attitudes are observed. As a rule high-frequency magnitude for these polymeric compounds amounts to 2,2 - 2,5. However static value of a dielectric factor can have the most different values depending on a molecular structure of a polymeric compound. So, for example, for polyethylene (F-0) $\varepsilon_0 = 2,25$, and for polymeric compound F-32 at the temperatures 140°C $\varepsilon_0 = 5$

The meanings of maximum values ε'' of dipole-segmental and dipole - group losses of polymeric compounds are shown in Tab. 2.

III. DISCUSSION OF RESULTS

It's apparent from the table, first of all, that losses in all cases monotonically diminish with increment of number of links in units. Secondly, the least values of ε'' have non-polar polymers of polyethylene and copolymer F-42. Calculations show that dielectric losses of fluoroplastics are caused mainly by two reasons: dipole polarization and electrical conductance. However, non-polar polymeric compounds have noticeably less value, than polar others.

In the strict case, electric properties of polymeric compounds in alternating fields are instituted by process of establishment of polarization in a time. The motion of electron, ions, dipoles or more complex corpuscles in an exterior electric field is accompanied by variation of interacting of these corpuscles, resulting in a power dissipation of an exterior field in a dielectric. So-called resonance dielectric losses are bound with the process of establishment of polarization of electronic and ion displacement. For identification of process of the dipole polarization determined by loosely bounded ions (in our case CF^+ and CF_3^+ in F-4; CF^+ and CF_2Cl^+ in F-3; CF_2H^+ in F-2; and also CF^+ and $C_2F_2^+$ in F-42), relaxation dielectric losses are characteristic. At low frequencies, the losses bound with an electrical conductance $tg\delta \approx \frac{4\pi\gamma}{\omega}$ [2] make a substantial contribution to dielectric absorption.

In actual polymeric compounds the superposition of resonance and relaxation losses is possible. We shall notice, that relaxation losses as a rule are evident over the range $10^5 - 10^{10}$ Hz (fig.2), and resonance over the range $10^{12} - 10^{14}$ Hz [3]. Obviously for this reason, for some dielectrics (especially with the strong intermolecular interaction) the considerable discrepancy between calculated and experimental data is to be observed. As a rule, the dependences of dielectric permittivity (ε') and losses

(ε'') in the field of dispersion, covers a broader band of corpuscles.

The experiments show that a diminution of dipole losses for non-polar polymeric compounds promotes careful clearing of monomers and stabilization of a material from oxidizing agents the induction of which does not result in noticeable magnifying of $tg\delta$. Apparently from the table at observance of the above-stated process technology of a synthesis of polymeric dielectrics it is possible to attain $tg\delta \leq 1,5 \cdot 10^{-4}$.

IV. CONCLUSION

1. The calculations have shown, that at the temperature of 293 K, the value of dielectric losses stipulated by resonance losses in polytetrafluoroethylene (PTFE) (F-4) at frequency of $6 \cdot 10^9$ Hz amounted to $1,64 \cdot 10^{-6}$

2. A relatively high level of losses in polytetrafluoroethylene (PTFE) leads to the conclusion, that at low temperatures in this polymeric compound alongside resonance, the relaxation dipole losses occur with rather low activation energy. The last also result in the overestimated values of $tg\delta$ on matching with calculated.

3. The assaying of temperature dependence of $tg\delta$ displays that the experimental data are well featured by a straight line $\lg(\varepsilon''T) = \lg\left(\frac{1}{T}\right)$.

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Table. 1

Polymers	Measured intensity of ions	Calculated subscript of links				
		$m=1$	$m=2$	$m=3$	$m=4$	$m=5$
F-4	CF_3^+ --- 75%	$84,2 \pm 0,05$	$13,7 \pm 0,09$	-	-	-
F-3	CF^+ --- 70%	$76,1 \pm 0,02$	$18,9 \pm 0,04$	$5,1 \pm 0,04$	-	-
F-2	CF_2H^+ ---52%	$22,1 \pm 0,09$	$23,1 \pm 0,02$	$18,2 \pm 0,07$	$17,6 \pm 0,04$	$7,7 \ 0,06$
F-0	CH_2^+ --- 48%	$22,7 \pm 0,03$	$50,1 \pm 0,05$	$21,3 \pm 0,05$	-	-
F-42	CF^+ --- 20%	$32,1 \pm 0,05$	$41,3 \pm 0,05$	$9,2 \pm 0,04$	$17,4 \pm 0$	-
F-40	CH_2^+ --- 30%	$25,1 \pm 0,04$	$23,5 \pm 0,7$	$28,4 \pm 0,03$	$22,5 \pm 0,07$	-

Table. 2

Polymers	Measured intensity of ions	Calculated subscript of links				
		$m=1$	$m=2$	$m=3$	$m=4$	$m=5$
F-4	CF_3^+ --- 75%	$84,2 \pm 0,05$	$13,7 \pm 0,09$	-	-	-
F-3	CF^+ --- 70%	$76,1 \pm 0,02$	$18,9 \pm 0,04$	$5,1 \pm 0,04$	-	-
F-2	CF_2H^+ ---52%	$22,1 \pm 0,09$	$23,1 \pm 0,02$	$18,2 \pm 0,07$	$17,6 \pm 0,04$	$7,7 \ 0,06$
F-0	CH_2^+ --- 48%	$22,7 \pm 0,03$	$50,1 \pm 0,05$	$21,3 \pm 0,05$	-	-
F-42	CF^+ --- 20%	$32,1 \pm 0,05$	$41,3 \pm 0,05$	$9,2 \pm 0,04$	$17,4 \pm 0$	-
F-40	CH_2^+ --- 30%	$25,1 \pm 0,04$	$23,5 \pm 0,7$	$28,4 \pm 0,03$	$22,5 \pm 0,07$	-