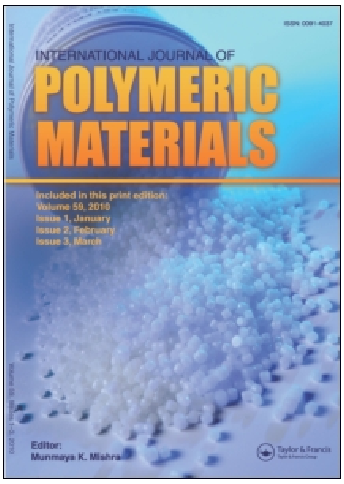

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Electrophysical properties of poly(methyl methacrylate)-polyimide systems

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ELECTROPHYSICAL PROPERTIES OF POLY(METHYL METHACRYLATE) – POLYIMIDE SYSTEMS

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The dielectric response and alternating current conductivity for poly(methyl methacrylate) – polyimide (PMMA – PI) system with different portions of initial components are calculated. The measurements have been done at the frequencies 20 Hz – 20 kHz and temperatures –50 – 50°C. It was shown that the relaxation spectra in PMMA – PI copolymer are determined by the relaxation of PI even for the PMMA : PI system with weight ratio 96 : 4 respectively. The results presented suggest that alternating current conductivity of such systems is very small and decreases with increasing of PI portion in PMMA/PI copolymer.

Keywords: poly(methyl methacrylate)(PMMA), polyimide, blends, electrical conductivity, dielectric

INTRODUCTION

In recent years the study of physical properties of polymer films has been widely used both for a solution of fundamental problems of physics of solids, and for applied aims directed at the usage of polymer materials in modern highly sensitive devices. Now due to theoretical and experimental investigations [1, 2] a thorough understanding has been reached of relaxation mechanisms in polymers under superposition of external effects – thermal and also mechanical, electrical at sound and microwave frequencies. The understanding of the dependence of polymer mobility on structure is complicated by the existence of long-term relaxation processes,

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which, in turn, also depend on temperature, amplitudes and frequencies of external fields of various nature.

The dielectric spectroscopy method is one of the most informative methods, which allows to describe the influence of various structural fragments (from the atoms themselves, group of atoms to a supermolecular organization) and the role of their interactions.

The possibility for study of the mechanisms of transposition and localization charge carriers in polymeric dielectric materials is an advantage of the low-frequency dielectric spectroscopy method.

Polyimides (PI) are a very important class of polymers which is widely used in many modern technologies [3]. Recently, particular attention has been paid to the fluorinated PIs which are highly soluble in various common organic solvents, including acetone, cyclohexanone, MEK, ethyl acetate *etc.* [4]. It was found that such copolyimides containing perfluoroalkylidene bridging groups and cardo fluorene groups are also soluble in some unsaturated monomers, such as methyl methacrylate (MMA). This provides an opportunity to formulate new polymer systems by the polymerization of (meth)acrylates containing dissolved PI [5].

The main purpose of this paper was to study the dielectric characteristics of such new systems as function of frequency and temperature.

EXPERIMENTAL

PMMA, pure PI and their copolymers having initial weight ratio PI : PMMA compositions 4 : 96, 10 : 90, 25 : 75 (copolymers I, II and III, respectively), were studied by low-frequency dielectric dispersion at a frequency range of 20 Hz – 20 kHz and in a temperature range of $-50-50$°C. The copolymers were synthesized by the free-radical polymerization of MMA containing dissolved fluorinated PI. We also studied a PMMA sample containing 4% PI, which was obtained by common mixing of PI and PMMA through joint solution, which will be referred to below as a mechanical PI – PMMA blend.

Copolyimide was synthesized by a one step polycyclization reaction of fluorene dianiline (0.8 mol), Diamine 6F (0.2 mol), and Dianhydride 6F (10 mol) [6]. The formulation of PMMA and PI-based polymeric systems used was earlier described in detail [5].

The films were cast from chloroform solutions of the polymeric systems. They were first dried at room temperature for 1 day and then in vacuum at 70°C.

To determine the complex permittivity $\varepsilon^* = \varepsilon' - \imath\varepsilon''$, the capacity and the dielectric loss tangent were measured with a R551 ac-bridge combined with a null-balance indicator and a sound-frequency generator. An alternating voltage of ~ 0.5 V in amplitude and a frequency of 20 Hz – 20 kHz was applied to the samples. The temperature was varied in the range from -50 to $+50°C$ and checked with an accuracy within 0.01°C.

The films of 0.04 ± 0.01 mm thickness and area of $2 \pm 0.5\,\text{cm}^2$ were covered by electrodes (silver paste) with surface area of $0.12 \pm 0.04\,\text{cm}^2$.

RESULTS AND DISCUSSION

The response of matter to an alternating field can be described with the help of complex conductivity

$$\sigma^*(\omega) = \sigma'(\omega) - \iota\sigma''(\omega)$$

or complex dielectric permittivity

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - \iota\varepsilon''(\omega),$$

which are connected by the following relation [2]:

$$\sigma' = \varepsilon''\varepsilon_0\,\omega, \quad \sigma'' = (\varepsilon' - \varepsilon_\infty)\varepsilon_0\,\omega \tag{1}$$

where $\varepsilon_0 = 8.854 \times 10^{-12}$ $(\text{F} \times \text{m}^{-1})$ – is the dielectric constant of vacuum, $\omega = 2\pi f$ – is the circular frequency, ε_∞ – is the dielectric constant at infinite frequency.

The magnitude of the conductivity σ' was calculated using Eq. (1). The numerical data of the dielectric permittivity was taken from Ref. [7].

Depending on the properties of a dielectric matter, the σ magnitude usually increases with the frequency rise and in accordance with the physical nature of charge carriers.

Analysis of experimental data suggests that, as a general rule, for the majority of dielectric materials the so-called universal fractional power law of dielectric response is operative. It was explicitly stated by Jonscher in [8]:

$$\sigma' \sim \omega^k, \quad 0 < k < 1$$

$$\varepsilon' \sim \omega^n, \quad 0 < n < 1$$

It means that the real part of the complex permittivity or conductivity is a linear function of the circular frequency ω when plotted in logarithmic coordinates. Also such dependence is often interpreted within the framework of a hopping model of conductivity in bi- or multipositional approximation, especially in the range of low frequencies. The difference between such two approximations is reduced to difference of the exponent k [9]. Based on available studies of the hopping mechanism of charge transposition, methods can be developed to control the conducting properties of materials.

For all samples, the values of ε' were measured at $\sim 22°C$ and 800, 1300 and 13000 Hz. The relevant data are presented in Table 1. All the films feature, a decrease in ε' with both an increase in the frequency of the applied alternating voltage and increase in the PI content in PMMA (in the case of samples obtained by the free-radical polymerization of MMA with dissolved PI).

Figure 1 demonstrates the fulfillment of the described law. The $\sigma(\omega)$ increase is due to a rule, manifested at low and high frequencies of uni- and

TABLE 1 The values of ε' for the PMMA–PI samples

	ε'		
Polymer sample	0.8 *kHz*	3 *kHz*	13 *kHz*
PMMA	3.49	3.46	3.29
PI	3.64	3.51	3.41
Copolymer I	3.46	3.38	3.35
Copolymer II	3.20	3.06	2.93
Copolymer III	2.96	2.90	2.86
PMMA–PI (96 : 4) mechanical blend	3.59	3.54	3.48

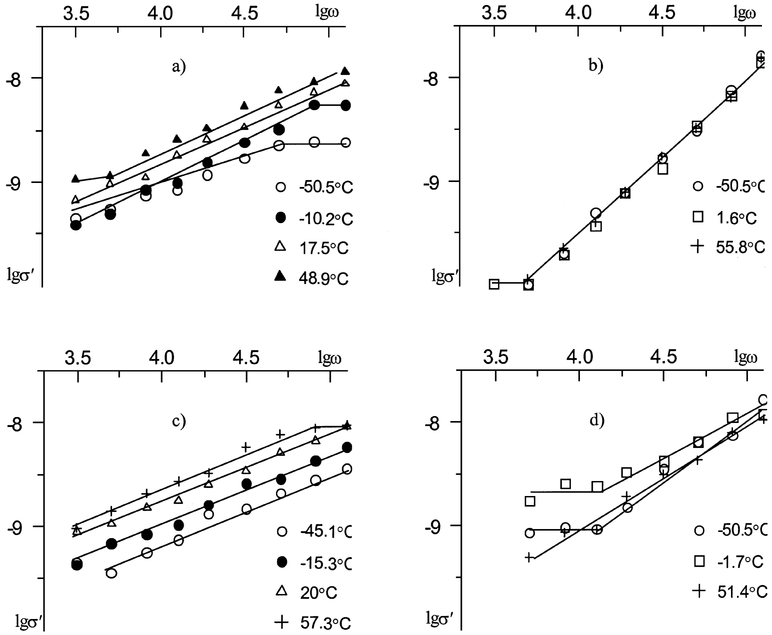

FIGURE 1 Dependence of conductivity σ on circular frequency ω: PI (a), PMMA (b), copolymer I (c), mechanical blend 4%PI (d).

bipositional hops. When the frequency is increased of the overwhelming majority hops of carriers – uni hops are much more numerous than the number of bipositional hops which dominate at low frequencies.

From Figure 1 it can also be seen that for certain temperatures the conductivity becomes constant. So for PMMA and PMMA–PI mechanical blend in a selected range of temperatures and frequencies below 1300 Hz the conductivity does not change with frequency. It is possible to conclude that at these frequencies the conductivity $\sigma(\omega)$ reaches the σ_{dc} value (direct current conductivity) [2]. The same tendency to saturation is observed for pure PI at 48.9°C. But for PI it also saturates at temperature −50.5°C and for copolymer I at temperature 57.3°C. The curves reach constant σ values at higher frequencies (from 8 kHz up to 20 kHz) in contrast to PMMA and PMMA–PI mechanical blend.

It is important to note that with increasing PI fraction in PMMA the conductivity changes sharply with frequency.

It is clear from Figures 1(b, d) that in case of PMMA and mechanical blend the curves practically coincide with temperature growth, *i.e.*, depend on temperature very weakly (Figs. 1d and 1b). It is probably due to tunneling as the mechanism of proton transport.

The power parameter of the "universal" law ($\log\varepsilon' = [1-n]\ \log\omega$) was obtained by fitting the experimental $\log\varepsilon' - \log\omega$ plots. These values are presented in Figure 2. According to [10], such low n values correspond to a low number of charge carriers and their low mobility.

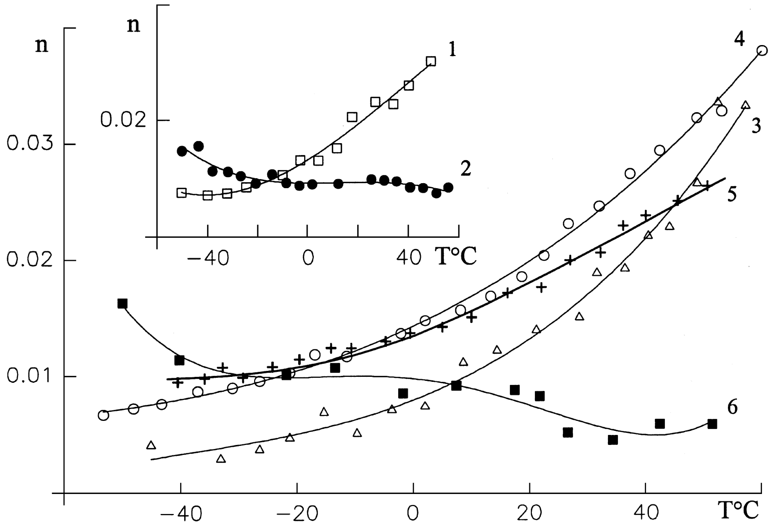

FIGURE 2 The temperature dependence of n for (1) PI, (2) PMMA, (3) **I**, (4) **II**, (5) **III**, and (6) PMMA–PI mechanical blend.

With increased temperature the change of σ PI values at 800 Hz is one order of magnitude (Fig. 3) with a local minimum in σ taking place at -30°C. The conductivity of copolymers I, II, III changes with temperature much more than in the case of pure PI. The increase of PI content in the copolymers promotes a decrease of conductivity value. It may be associated with denser packing of structural elements in the polymer sample. In other words, the value of σ for PI may indicate a "loose" structure then in the case of pure PMMA and copolymers I, II, III.

Three maxima are marked at -43, -15 and 35°C on the σ temperature dependence for the mechanical blend (800 Hz). Similar maxima have been observed for other polymers. Probably they may be explained by the presence of hydrogen bonds [11].

It is possible to evaluate the significance of activation energy of the relaxation processes by estimation of the declination of a linear plot of dependence lg σ on $1/T$. Such evaluation shows, that the transition temperature T_β in copolymers I, II, III increases in accordance with PI fraction growth. Mechanical PMMA mixture having 4%PI is also characterized by a shift of temperature T_β to higher range but less than in copolymer I.

The $\varepsilon''-\varepsilon'$ curves (Fig. 4) are plotted based on the permittivity measurements at 30°C. These dependencies provide information about the most probable relaxation frequency ω_0. It is interesting that all the samples studied are characterized by one of two types of $\varepsilon''-\varepsilon'$ diagram. The diagram for pure PI and copolymers I–III appear to be similar, while pure PMMA and its mechanical blend with 4%PI exhibit different behavior. For

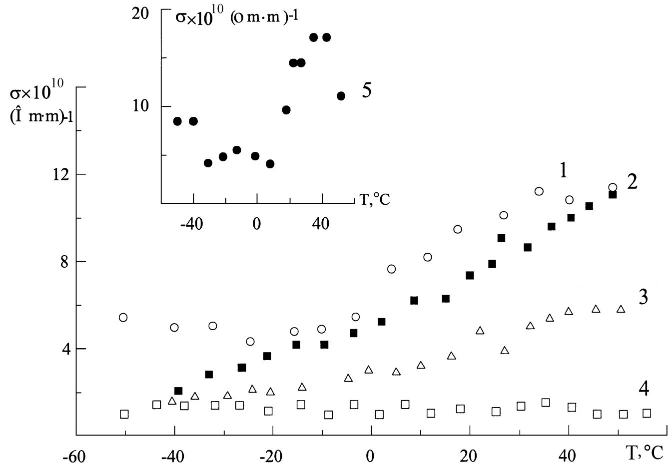

FIGURE 3 Temperature dependence conductivity: 1-PI, 2-copolymer I, 3-copolymer III, 4-PMMA, 5-mechanical blend PMMA–PI. Frequency 800 Hz.

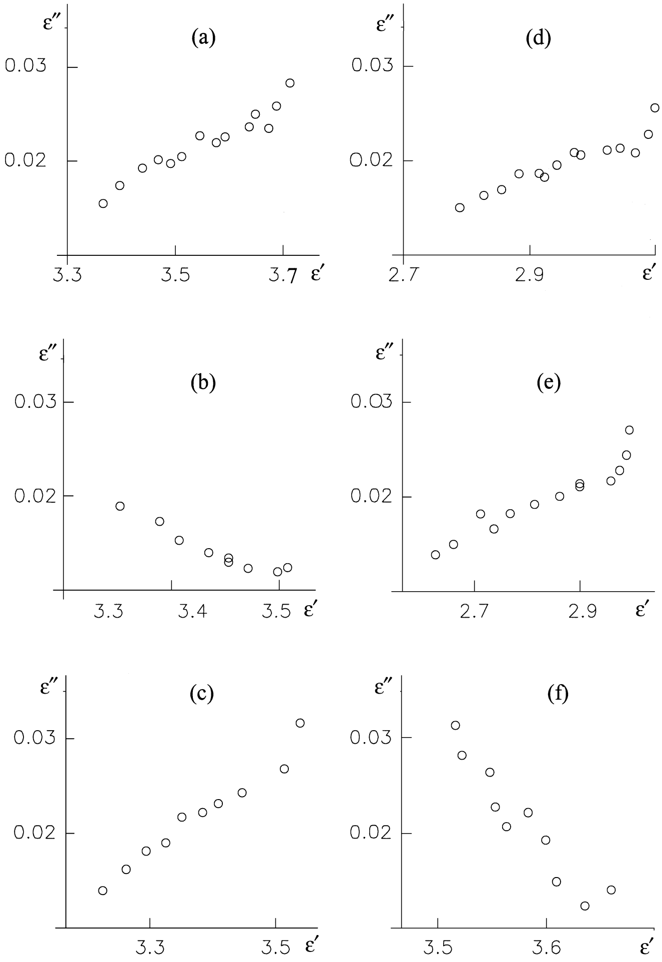

FIGURE 4 Diagrams $\varepsilon''-\varepsilon'$ for (a) PI, (b) PMMA, (c) **I**, (d) **II**, (e) **III**, (f) mechanical blend PMMA–PI.

PI and its copolymers ω_0 lies in the higher frequency region, while for PMMA and the mechanical blend the ω_0 value shifts to lower frequencies. Thus the samples obtained by two different techniques have different dielectric relaxation spectra.

Using data from the diagrams $\varepsilon''-\varepsilon'$ (see Fig. 4) it is possible to evaluate the value of a relaxation parameter λ for some of the studied systems. From Cole–Cole diagrams λ is expected as $\lambda = 2\varepsilon''_{\max}/\Delta\varepsilon$.

The dipole-group mechanism of a relaxation takes place (Fig. 5) in the above cited frequency and temperature regions [7, 12].

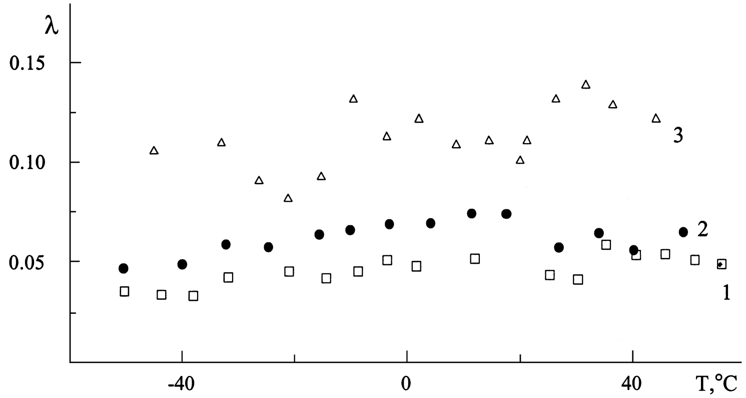

FIGURE 5 Temperature behavior of relaxation parameter λ: 1-PMMA, 2-PI, 3-copolymer I.

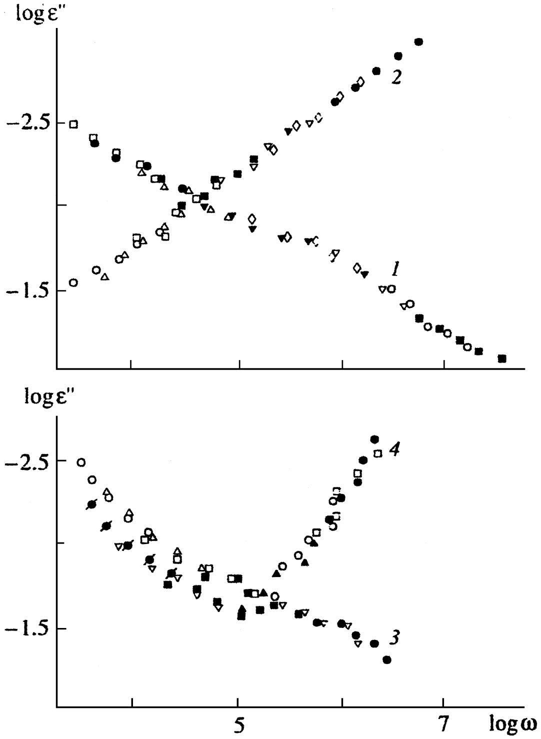

FIGURE 6 Reduced curves for (1) PI, (2) PMMA, (3) copolymer I, and (4) PMMA–PI mechanical blend. Different points correspond to different temperatures. See text for explanation.

The maxima on curve 3 in Figure 5 are distinctive at temperatures −40, −15 and 35°C. It is necessary to note that presence of PI in the mechanical blend and copolymer I (see Fig. 3 curve 5 and Fig. 5 curve 3) results in anomalies at the same temperatures. Such behavior is probably caused by hydrogen bonds, for which such temperature areas are specific [13, 14].

Reduced curves (Fig. 6) were obtained from $\log\varepsilon'' - \log\omega$ diagrams plotted at each temperature [15].

It is evident that for PMMA and the mechanical blend the probable relaxation time τ_0 value lies at high frequencies. On the contrary, for PI and copolymer with 4%PI this value lies in the range of lower frequencies. This may by related to the "activation" of small (in the first case) and large (in the second case) fragments in the given frequency interval.

CONCLUSIONS

The results presented above suggest that for the PMMA – PI system obtained by free-radical polymerization of MMA containing dissolved fluorinated PI the nature of the relaxation process is determined only by PI even when its content is as low as 4%.

Polymer films based on PMMA and PI systems in the given interval of frequencies and temperatures differ by small conductivity values of the order of 10^{-10} $(\mathrm{Ohm} \times \mathrm{m})^{-1}$. It may by due to both polarization and the charge carriers (probably ions). The dipole-group mechanism of polymer chain mobility is more probable. The σ values decrease with the growth of PI fraction in the film and the changes with temperature are higher than the σ values for pure PI.

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