CHARGE RELAXATION IN PARTIALLY CRYSTALLINE R-BAPB POLYIMIDES UNDER CONDITIONS OF ELEVATED HUMIDITY

M.E. Borisova[1], A.M. Kamalov[1], I.D. Orlov[1], V.E. Smirnova[2]

[1] Peter the Great St. Petersburg Polytechnic University, St. Petersburg, Russian Federation;

[2] Institute of Macromolecular Compounds of RAS, St. Petersburg, Russian Federation

The charge relaxation processes in the films based on R-BAPB polyimide with different degree of crystallinity have been studied. The supramolecular structure effect on the charge relaxation processes in the films under elevated humidity conditions was revealed. The obtained experimental data was analyzed in the context of the present-day knowledge of the charge relaxation mechanism. The complex spectra of the thermally stimulated depolarization currents (TSDC) were resolved into individual components and described by the first-order kinetics equations using computer simulation. The TSDC activation energies were calculated and interpreted in terms of the mechanism of release of charge carriers. It was shown that the increment of crystallinity degree of the polyimide films lead to a decrease in the electret state stability at elevated temperature and high humidity.

Key words: polyimide; crystallinity; hygroscopicity; trap; simulation; coronoelectret

Introduction

As polymer electrets are gaining wider applications, there is a continued effort to find methods for slowing down the charge relaxation processes in dielectrics and for increasing the stability of the electret state. The properties of polymers are typically adjusted by modifying their surface and structure and by introducing various fillers into the polymer [1 − 3]. The study of charge relaxation processes in polymer films presents an additional interest because the field of a charged dielectric affects the electrical properties of the entire insulation system in which it is used.

Polyimides are a class of polymers that has been in demand in industry for many years. Despite their high costs, polyimide films are widely used due to their heat resistance, high electrical and mechanical characteristics [4]. New types of polyimides are constantly developed, and the existing types are modified to enhance certain characteristics of the material.

One of the main problems of using polyimides in electrical insulators and electret devices is their low resistance to moisture [5, 6]. If polyimide insulation is in a humid environment for a long time, its electrical insulation properties deteriorate rapidly, increasing the conductivity of the insulation and the instability of the dielectric capacitance. A great deal of studies have been dedicated to investigating and improving the moisture-resistant characteristics of polyimides.

The goal of this study is to determine the effect of moisture on the charge relaxation process in R-BAPB polyimide films with different degrees of crystallinity, developed at the Institute of Macromolecular Compounds of the Russian Academy of Sciences in order to create thermally stable thermoplastic polyimides that compare favorably to foreign equivalents (PEEK, ULTEM, PPS).

Experimental procedure

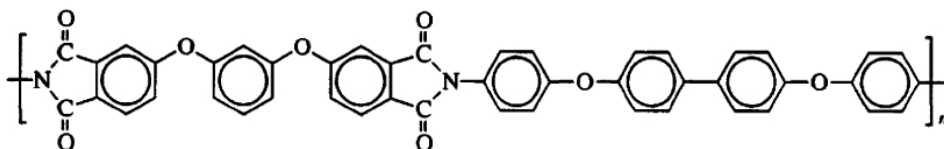The experimental samples were the films of

Fig. 1. The chemical formula of R-BAPB polyimide

R-BAPB polyimide (Fig. 1) based on 1,3-bis (3,3'-4,4'-dicarboxyphenoxy) benzene (R dianhydride) and 4,4'-bis (4-aminophenoxy) biphenyl (BAPB diamine) with the degrees of crystallinity of 0, 20 and 40%.

The effect of supramolecular structure of the R-BAPB material on the stability of the electret state under elevated humidity was studied in this paper.

A series of R-BAPB polyimide films with different degrees of crystallinity were heated to remove moisture and residual static charge for one hour at a temperature of 160 °C, and then kept in a desiccator at a humidity of 98% for 24 h. The second series of control samples were not hydrated. The films were then charged in air with a negative corona discharge under normal environmental conditions. An electret with a homocharge, where the charge carriers are localized at energy levels (traps) in the thin near-surface layer of the dielectric, is formed as a result of such charging [7, 8].

We studied electric charge relaxation in the resulting electrets by the method of thermally stimulated depolarization currents (TSDC) with a constant heating rate $\beta = dT/dt = 2$ K/min maintained for the samples. The measurements were carried out with a blocking contact between the electrode and the sample. To achieve a blocking contact, an insulating layer made of a 40-μm-thick polytetrafluoroethylene film was placed on the charged surface of the film. In this case, the direction of the depolarization current coincided with the direction of motion of charged particles through the bulk of the sample.

The degree of hydration Γ of the samples was calculated from the increase in their mass (in percent) after exposure to 98% humidity for a certain time according to the following formula:

$$\tilde{A} = \frac{m - m_0}{m_0} \cdot 100\%,$$

where m_0 is the initial mass of the sample, m is the mass of the sample after hydration.
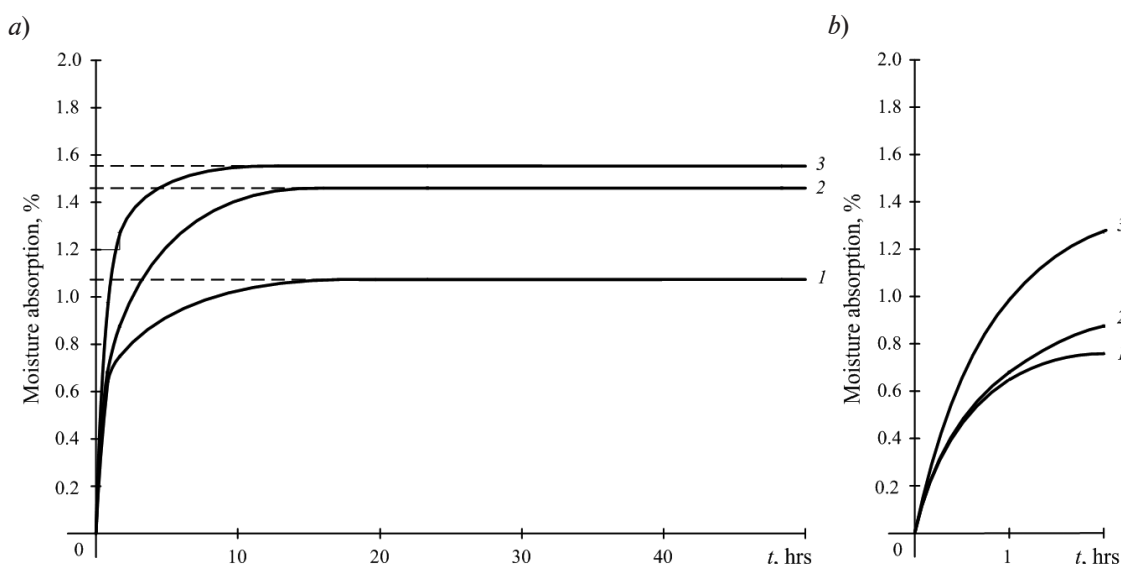

Fig. 2. Moisture absorption dependences of R-BAPB polyimide films with different degrees of crystallinity (DoC) versus the hydration time in the ranges $(0 - 50)$ h (*a*) and $(0 - 2)$ h (*b*); DoC, %: 0 (*1* is the amorphous sample), 20 (*2*) and 40 (*3*)

Table 1

Maximum hygroscopicity values of R-BAPB polyimide samples with different degrees of crystallinity

Degree of crystallinity, %	0 (amorphous)	20	40
Maximum hygroscopicity, %	1.07	1.46	1.55

The humid environment was generated in a desiccator with an aqueous solution of copper sulfate.

Results and discussion

Hygroscopicity study. The curves obtained for the increase in the mass of films with different degrees of crystallinity depending on the hydration time are shown in Fig. 2. Evidently, hygroscopicity of polyimide films increases with increasing degree of crystallinity of the material. The maximum hydration levels of the samples are given in Table 1.

The maximum hygroscopicity values obtained were lower than for the samples of industrial PM polyimide, whose hygroscopicity is 2.3 − 3.0% [9].

Polyimide films absorb moisture within 10 − 18 h; samples with a higher degree of crystallinity reach the hydrated state faster and adsorb more moisture than amorphous samples. The increase in hygroscopicity can be explained by a larger interface between the crystalline and amorphous phases of the material. An additional free volume evolves in the region of this interface. Fig. 3 shows micrographs of the film surface for an amorphous sample and a polyimide sample with a degree of crystallinity of 40% (at two magnifications). It can be seen from the photographs that as the degree of crystallinity of polyimide increases, its structure loosens and the degree of heterogeneity of the material increases, which is accompanied by a growing amount of micropores.

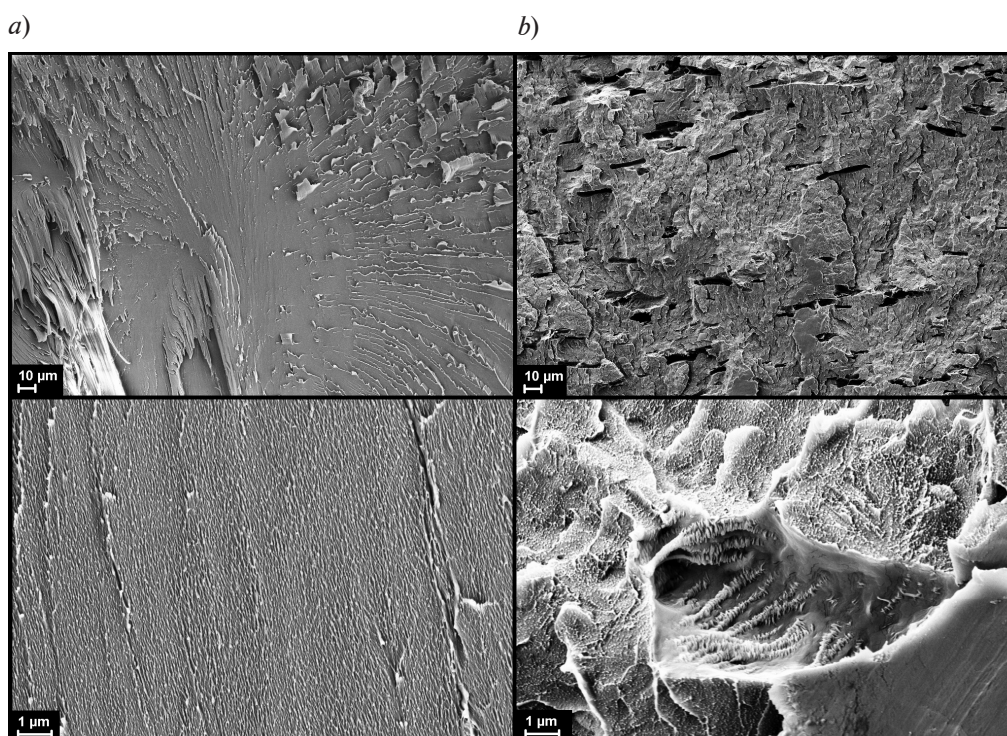a)   b)

Fig. 3. Micrographs of the surface of R-BAPB polyimide films with different degrees of crystallinity: *a* is the amorphous sample, *b* is the sample with DoC = 40%; images with different magnifications are shown

Charge relaxation studies. Fig. 4 shows the TSDC spectra of the hydrated and non-hydrated polyimide films with different degrees of crystallinity. Comparing these spectra for two series of films indicates that hydration changes the behavior of the curve and leads to a shift in the temperature of the current maxima.

The obtained TSDC spectra, appearing to be curves with one or two peaks, have a complex character. As the degree of crystallinity of the material increases, the low-temperature peak grows. This maximum most likely due to the release of the charge from additional traps formed at the interface between the amorphous
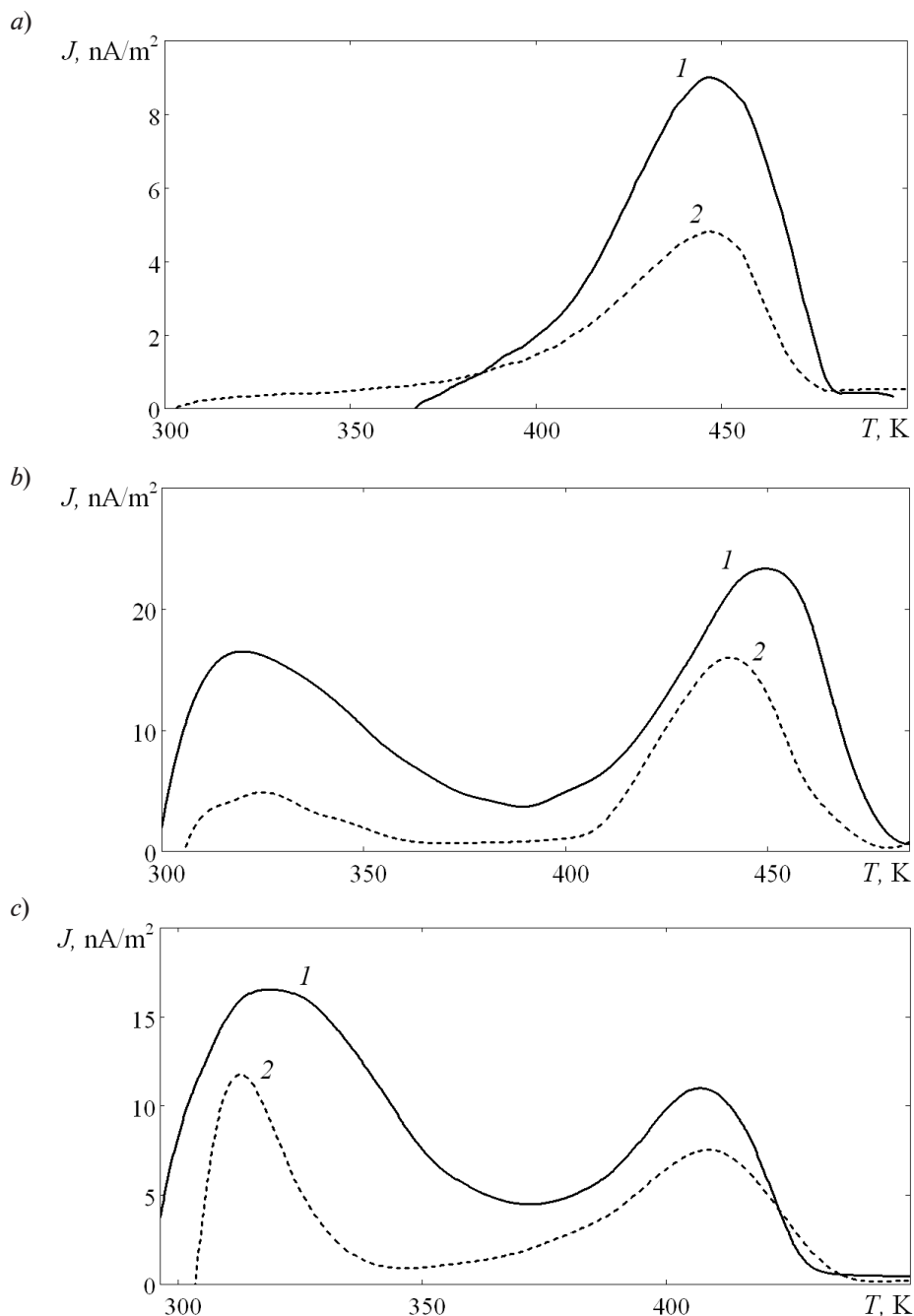
a)

b)

c)

Fig. 4. TSDC spectra of the heated (*1*) and hydrated (*2*) polyimide film samples with different degrees of crystallinity, %: 0 (*a*), 20 (*b*), 40 (*c*)

and crystalline phases.

As established in [10], the high-temperature maximum is due to intrinsic conductivity of the R-BAPB polyimide for all polyimide films (with the degrees of crystallinity of 0, 20, and 40%).

It can be seen from the experimental curves in Fig. 4 (dashed lines) that sample hydration leads to reduction in the area under the TSDC curve, i.e., a decrease in the charge accumulated in the sample. The most significant change in the spectrum is observed in the low-temperature region. A possible explanation for this is that the moisture absorbed in the sample creates new traps, localized mainly in the near-surface regions. It is known that sorbed water can exist in polymers in three states: free, moderately and strongly bound. Each of these states affects the charge accumulation and relaxation processes in different ways. Free water in the polymer increases its conductivity, while the water in the moderately and strongly bound states forms new trapping levels resulting from hydrolysis-induced breakdown of cyclic imides. Both negatively charged hydrogen vacancies evolving in benzene rings and COOH groups as a result of hydration can act as such trapping levels. Positively charged NH^+ groups, which are also formed due to breakdown of cyclic imides in the polymer can act as trapping levels as well

[5, 11 − 15].

Analysis of TSD currents. The obtained TSDC spectra of the dried and hydrated samples were analyzed by "fitting" based on the model of superposition of elementary Debye peaks $\sum_{1,2,3}^{n} J_n$ governed by first-order kinetics. In this case, the TSD current density J_{TSD} of each peak is described by the expression

$$J_{TSD} = J_m \exp\left[\frac{W}{k}\left(\frac{1}{T_m} - \frac{1}{T}\right)\right] \times$$

$$\times \exp\left\langle -\frac{W}{kT_m^2}\int_{T_m}^{T}\exp\left[\frac{W}{k}\left(\frac{1}{T_m} - \frac{1}{T'}\right)\right]dT'\right\rangle,$$

where the peak current density J_m is calculated as

$$J_m = \frac{\varepsilon\varepsilon_0\varepsilon_{lay}U_{e0}}{(\varepsilon h_{lay} + \varepsilon_{lay}h)\tau_m} \times$$

$$\times \exp\left\{-\frac{W}{kT_m^2}\int_{T_0}^{T_m}\exp\left[\frac{W}{k}\left(\frac{1}{T_m} - \frac{1}{T'}\right)\right]dT'\right\}.$$

Here ε_{lay} and h_{lay} are the dielectric permittivity and the thickness of the insulating layer; k is Boltzmann constant; T_0 and T' are the initial and the final temperatures, respectively; T_m is the temperature in the current density peak J_m;
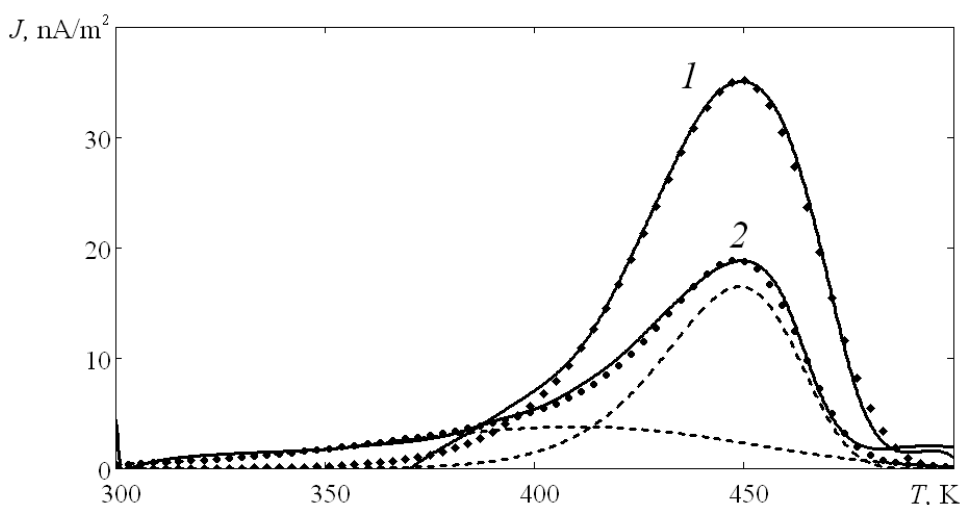

Fig. 5. Experimentally measured (solid lines) and calculated (dotted lines) TSDC spectra for the non-hydrated (*1*) and hydrated (*2*) amorphous polyimide films.
The dashed line for spectrum *2* is the result of decomposition into elementary components
(see Table 2, data for the second sample)

ε and h are the dielectric permittivity and the thickness of the sample film; U_{e0} is the initial value of the potential difference in the electret; τ_m is the relaxation time at peak temperature, and ε_0 is the dielectric constant.

The relaxation time is described by the expression

$$\tau = \tau_m \exp\left(\frac{W}{kT} - \frac{W}{kT_m}\right).$$

The calculations are based on the characteristic values of the peak current density J_m and the peak temperature T_m, which are determined from the experimental TSDC data; the value of the activation energy W varies in this case.

Table 2 lists the results of calculations using the above-described simulation method. An example of decomposition of the TSDC spectra into elementary peaks is shown in Fig. 5 for amorphous samples.

As a result of processing the experimental data by mathematical modeling methods, the number of elementary Debye peaks in the TSDC spectra increases. It is established that hydration of polyimide films induces additional relaxation mechanisms, which is accompanied by new elementary current density peaks appearing on the experimental spectra.

Conclusion

Based on the results of the study, the following conclusions can be drawn:

regardless of the degree of crystallinity, the R-BAPB polyimide is less hygroscopic than the industrially used PM polyimide (1.55% for R-BAPB versus 2.30% for PM). Therefore, it is expedient to use this material under high humidity and temperature;

Table 2

Main parameters of the experimental TSDC spectra decomposed into elementary peaks for R-BAPB polyimide films

Film		Peak position T_m, K	Activation energy W, eV
DoC,%	H_2O		
0	−	449	0.83
0	+	449	1.05
		410	0.30
20	−	448	0.93
		367	0.58
		337	0.52
		314	0.50
20	+	441	1.10
		367	0.58
		339	0.75
		321	0.70
40	−	407	1.00
		362	0.65
		333	0.61
		313	0.58
40	+	409	0.90
		348	0.50
		320	0.80
		312	1.20

Notes. The zero degree of crystallinity (DoC) corresponds to an amorphous film; a plus in the H_2O column indicates that the film was hydrated

the hygroscopicity of the films increases from 1.07 to 1.55% as the degree of crystallinity of the R-BAPB polyimide increases from 0 to 40%, leading to a decrease in the charge relaxation time. This is likely due to a change in the structure of the film, with a large number of micropores evolving and the free volume of the polymer increasing;

the TSDC spectra become more complex with increasing degree of crystallinity of the samples: low-temperature peaks emerge and grow, indicating that the charge relaxation region shifts towards low temperatures and the electret properties of the material become less stable;

hydration of the material under consideration leads to a change in the charge relaxation mechanisms, accompanied by transformation of the TSDC spectra. For example, the spectrum of an amorphous material gains a shoulder at low temperatures.

To summarize, we have established that moisture affects the charge relaxation process in R-BAPB polyimide films with different degrees of crystallinity, developed at the Institute of Macromolecular Compounds of the Russian Academy of Sciences. We can recommend this material for use under elevated humidity and temperature.

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THE AUTHORS

BORISOVA Margarita E.
Peter the Great St. Petersburg Polytechnic University
29 Politechnicheskaya St., St. Petersburg, 195251, Russian Federation
vladimirl.borisov@gmail.com

KAMALOV Almaz M.
Peter the Great St. Petersburg Polytechnic University
29 Politechnicheskaya St., St. Petersburg, 195251, Russian Federation
1.almaz.kamalov@gmail.com

ORLOV Ivan D.
Peter the Great St. Petersburg Polytechnic University
29 Politechnicheskaya St., St. Petersburg, 195251, Russian Federation
ivaorlov@yandex.ru

SMIRNOVA Valentina E.
Institute of Macromolecular Compounds RAS
31 Bolshoy Ave. V.O., St. Petersburg, 199004, Russian Federation
ves@hq.macro.ru