

## Electret and dielectric properties of electrospun nonwoven polyimides

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Electrospun polyimide nonwovens based on the polyamide acid salt of pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA) with different molar masses were obtained. Their dielectric and electret properties have been studied. It has been established that these materials have a low dielectric constant ( $\epsilon' = 1.55\text{--}1.91$ ). Charge relaxation of nonwoven polyimides was studied using the method of thermally stimulated depolarization currents. The activation energies of relaxation processes  $W = 0.81\text{--}0.90$  eV were calculated using computer simulation.

**Keywords:** polyimide, electrospun, dielectric constant, electret, computer simulation.

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Electret nonwoven membranes are used to produce air filtration devices that provide a high particle collection efficiency without excessive pressure differences in the filter material [1]. These properties make electret devices suitable for air purification applications (heating, ventilation, and air conditioning systems) [2]. There is a possibility for oil and alcohol aerosols in cleaning systems to interact with the electret filter material at both low and high ambient temperatures. Therefore, the polymer material must remain resistant to aggressive media within a wide temperature range. Such polymer materials include nonwoven materials based on polyimide, which offer an increased thermal stability (up to 500°C), fine mechanical characteristics (a strength of 30 MPa), and electret properties (capacity for charge accumulation and retention) [3].

The aim of the present study is to examine the dielectric and electret properties of electrospun nonwoven polyimide (PI) materials based on polyamide acid salts as functions of their molar mass.

Nonwoven polyimide materials based on pyromellitic dianhydride and 4,4'-oxydianiline (PMDA–ODA) were produced by electrospinning using a NANON-01 system (Mecc Co., Japan). Triethylamine salt of polyamide acid (SPAA) was used in the preparation of solutions. The polyelectrolyte structure ensures solubility of SPAA in water. This offers an opportunity to form more hydrolytically stable aqueous solutions and reduce the imidization temperature compared to a polyamide acid due to the catalytic effect. Salts were synthesized according to the procedure detailed in [4] at an ODA:PMDA ratio of 1:1, 0.98:1, and 0.97:1 and the molar mass of PMDA–ODA varying from 49,300 to 13 400 g/mol. The determination of molar mass was discussed in detail in our study [5]. The density of the obtained nonwoven materials was estimated by the pico-

metric method at  $\rho_{1:1} = 0.29$  g/cm<sup>3</sup>,  $\rho_{0.98:1} = 0.36$  g/cm<sup>3</sup>,  $\rho_{0.97:1} = 0.42$  g/cm<sup>3</sup>.

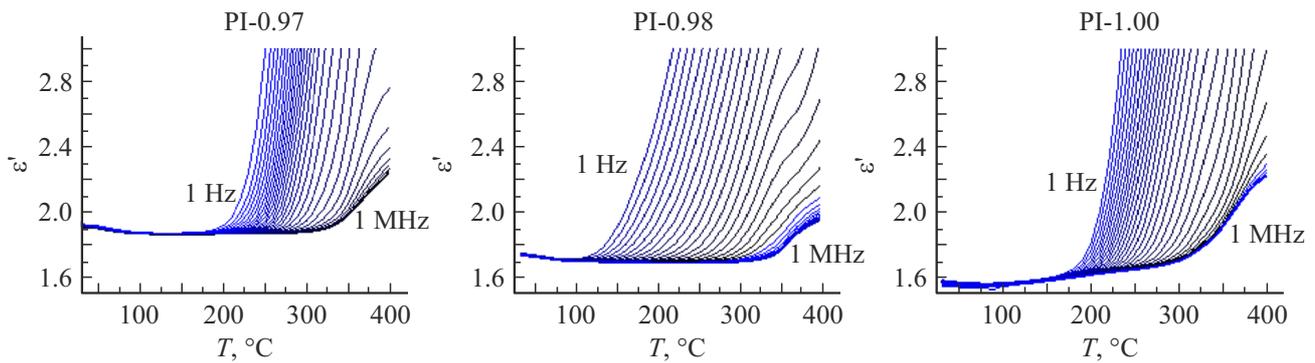
Permittivity  $\epsilon'$  of the samples of nonwoven PI materials with an ODA:PMDA ratio of 1:1 (PI-1.00), 0.98:1 (PI-0.98), and 0.97:1 (PI-0.97) was measured with a Concept-81 broadband dielectric spectrometer (Novocontrol, Germany) with an ALPHA-ANB high-resolution automatic frequency analyzer. The measurements were carried at frequencies of 1 Hz–1 MHz and temperatures of 30–400°C.

At 30°C, relative permittivity  $\epsilon'$  of nonwoven polyimide PMDA–ODA decreases with an increase in molar mass from 1.91 to 1.55 (Fig. 1). The obtained permittivity values are consistent with literature data for nonwoven PI materials [6]. The permittivity of the nonwoven material may be adjusted by varying the molar mass of polyimide.

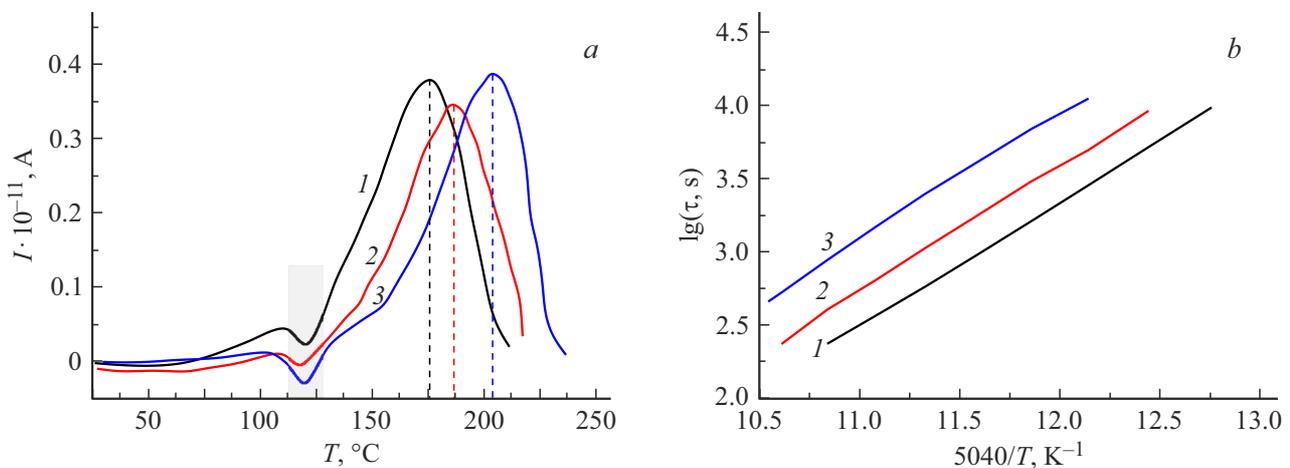
The electret effect in a dielectric may be induced in different ways (e.g., by polarizing the dielectric in an electric field or by introducing charged particles from a gas discharge into the dielectric). In most cases, polymers with high permittivity  $\epsilon'$  are polarized more strongly in an electric field, providing a high initial charge.

Nonwoven PI samples were pre-charged in a corona discharge under normal conditions for 1 min at a potential of –6 kV between a needle and a grounded electrode. A grid mounted between the needle and the sample surface ensured uniform distribution of the charge and helped control it. A negative potential of –500 V was applied to the grid. The key characteristic of electrets is potential difference  $U_E$  related to surface charge density  $\sigma$ . It was measured by the electrostatic induction method [3].

The charge relaxation processes were examined using the method of thermally stimulated depolarization (TSD) currents in the open circuit mode under sample heating at a constant rate of 2°C/min. A Keithley 6487 picoammeter/voltage source was used for current measurements. The spectra of TSD currents of nonwoven materials with differ-



**Figure 1.** Dependences of the permittivity of nonwoven PI materials with different molar masses (PI-0.97, PI-0.98, and PI-1.00) on temperature within the frequency range from 1 Hz to 1 MHz.



**Figure 2.** TSD currents (a) and temperature dependences of relaxation time (b) of nonwoven PI materials. 1 — PI-1.00, 2 — PI-0.98, and 3 — PI-0.97.

ent molar masses are shown in Fig. 2, a. It can be seen that the TSD current maxima shift toward higher temperatures as the molar mass decreases from 49 300 g/mol (PI-1.00) to 13 400 g/mol (PI-0.97). This corresponds to a more stable electret state induced by an increase in percentage content of PI in the nonwoven fabric ( $\rho_{0.97:1} = 0.42 \text{ g/cm}^3$ ) and higher permittivity  $\epsilon'$ . In general, the TSD spectra maxima may be established by various relaxation processes. Since polyimide is a polar polymer [6], dipole-group polarization (heterocharge) may be induced even in the process of charging in a corona discharge in the field of the space charge accumulated in the dielectric. The negative direction of the maximum current at 120°C in the TSD spectra may be attributed to the heterocharge relaxation. As the molar mass decreases, this peak shifts to the low-temperature region, which is consistent with the data of dielectric spectroscopy and dynamic mechanical analysis [5]. The high-temperature peak at 175–210°C is associated with relaxation of the trapped homocharge. The PI-0.97 sample with a density of 0.42 g/cm<sup>3</sup> has more stable electret characteristics.

Main calculated parameters of the TSD current spectra

Calculated maxima	$J_m \cdot 10^{-8}, \text{ A/m}^2$	$T_m, \text{ K}$	$W, \text{ eV}$
$J_{1:1}$	1.89	442	0.81
$J_{0.98:1}$	1.70	454	0.85
$J_{0.97:1}$	1.92	470	0.90

Temperature dependence of relaxation times  $\tau(T)$  was calculated from the experimental spectra of TSD currents:

$$\tau(T) = \frac{Q(T)}{I(T)} = \frac{1}{\beta J_{\text{TSD}}} \int_{T_0}^{\infty} J_{\text{TSD}} dT, \quad (1)$$

where  $Q$  is the total accumulated charge in the electret,  $I$  is the measured current,  $J_{\text{TSD}}$  is the current density,  $\beta$  is the heating rate, and  $T_0$  is the initial temperature.

Dependences  $\lg \tau = f(5040/T)$  for samples with different molar masses are shown in Fig. 2, b. The values of  $\tau$  within the entire studied temperature range may be

determined by analyzing the maximum TSD current. This provides an opportunity to assess quantitatively the charge stability based on  $\tau$ . With a reduction in molar mass, the charge relaxation time increases by a factor of approximately 3 throughout the entire examined temperature range. A theoretical analysis of the TSD current spectra was performed via computer modeling in order to determine activation energies  $W$  of relaxation processes. The maximum of the TSD current spectra was fitted to the experimentally measured one by varying the following three parameters:  $J_m$ ,  $T_m$ ,  $W$ . TSD current density  $J_{\text{TSD}}$  may be written as [7]

$$J_{\text{TSD}} = \frac{d\sigma}{dt} = J_m \exp \left[ \frac{W}{k} \left( \frac{1}{T_m} - \frac{1}{T} \right) \right] \times \exp \left\langle - \frac{W}{k T_m^2} \int_{T_m}^T \exp \left[ \frac{W}{k} \left( \frac{1}{T_m} - \frac{1}{T'} \right) \right] dT' \right\rangle, \quad (2)$$

where  $T'$  is the current temperature and  $k$  is the Boltzmann factor.

The calculation was performed for the high-temperature peak only. The modeling parameters are listed in the table.

Thus, electrospun nonwoven polyimide materials based on the polyamide acid salt of PMDA–ODA were synthesized. It was established that these materials have low permittivity  $\varepsilon' = 1.55–1.91$ . The value of  $\varepsilon'$  decreases with increasing molar mass (Fig. 1). It was demonstrated that the nonwoven PI material has fine electret characteristics. A reduction in molar mass leads to a 3-fold increase in charge relaxation time within the entire studied temperature range (Fig. 2, *b*), enhancing the efficiency of application of nonwoven polyimide materials as electret filter devices. The activation energy of the relaxation high-temperature peak increases from 0.81 to 0.90 eV as the PMDA–ODA molar mass varies from 49 300 g/mol (PI-1.00) to 13 400 g/mol (PI-0.97), respectively (Fig. 2, *a*).

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## Conflict of interest

The authors declare that they have no conflict of interest.

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