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Production of polyimide nonwoven fabric with low dielectric permittivity

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Abstract. This work is devoted to the production of nonwoven polyimide material by electroforming from aqueous solutions of polyamide acid salts based on pyromellitic dianhydride (PMDA) and 4,4′-oxydiphenylenediamine (ODA). The dielectric and mechanical properties of the nonwoven material were determined over a wide frequency and temperature range. The dielectric permittivity of the material at 20 °C and a frequency of 1 Hz was 1.5.

Keywords: electroforming, polyimide, nonwoven material, relative permittivity, elastic modulus

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Получение полиимидного нетканого материала с низкой диэлектрической проницаемостью

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Аннотация. Данная работа посвящена получению нетканого полиимидного материала методом электроформования из водных растворов солей полиамидокислоты на основе пиромеллитового диангидрида (ПМ) и 4,4′-диаминдифенилового эфира (ДАДФЭ). Были определены диэлектрические и механические свойства нетканого материала в широком интервале частот и температур. Диэлектрическая проницаемость материала при температуре 20 °С и частоте 1 Гц составила 1.5.

Ключевые слова: электроформование, полиимид, нетканый материал, диэлектрическая проницаемость, модуль упругости

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Introduction

In modern integrated circuits, materials with low dielectric constant ε are needed to reduce resistive capacitance delay and minimize crosstalk. Flexible printed circuit boards (FPCs) are widely used in complex electronic products because of their outstanding characteristics such as light weight, size and flexibility. Polyimide is most commonly used for flexible printed circuit boards as an insulating dielectric layer between metals because of its high mechanical and heat resistance properties [1]. However, polyimide films have a relatively high dielectric permittivity (3–3.5), which does not meet the requirements for the design of modern integrated circuits. Thus, the creation of composites based on polyimides with low dielectric permittivity has become one of the actual problems in the field of high-frequency and high-speed signal transmission.

Recently, the technology of electroforming nanofibers from polymer solutions, in particular polyimides, has been increasingly developed. Thus, composite materials with unique properties are produced. High values of specific surface (porosity of the material) enable their application in power engineering and medicine: porous electrodes, interelectrode separators, filters and sensors [2,3].

In this research we study a nonwoven polyimide (PI) material obtained by electroforming (EF) from aqueous solutions of triethylammonium salt of poly (amic acid) (SPAA) based on pyromellite dihydride (PMDA) and 4,4′-diamindiphenyl ether (ODA) [4,5].

The aim of the work is to obtain and study the dielectric and mechanical properties of polyimide nonwoven materials obtained by electroforming.

Materials and Methods

The synthesis of PAA salts (SPAA) was performed at Laboratory № 1 (Synthesis of High-Temperature Resistant Polymers) of the Institute of Macromolecular Compounds Russian Academy

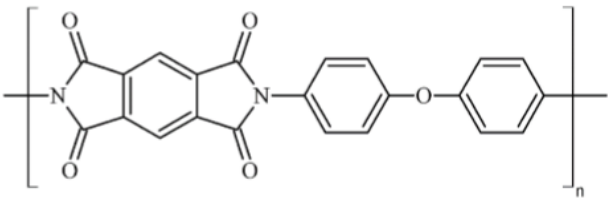

Fig. 1. Chemical formula of polyimide PMDA–ODA

of Sciences (IMC RAS); the detailed synthesis process is described in our previous work [4].

The process of electroforming is significantly affected by the parameters presented in Table 1.

Table 1

Parameters of electroforming of nonwoven material

Process parameters (experiment)	Optimal values according to literature data [1]
$\gamma = 10^{-2}$ S/m	$\gamma = 10^{-6}$–10^{-2} S/m
$\sigma = 0.031$ N/m	$\sigma < 0.05$ N/m
$U = 20.5$ kV	$U = 20 – 30$ kV

Here γ is the specific volumetric conductivity. Low conductivity leads to slowing down of the EF process, due to fast relaxation of the free charge under the influence of an external electric field. High specific conductivity contributes to reduction of fiber diameters due to greater tensile force in the electric field.

The surface tension coefficient of the solution σ is one of the determining parameters of the electroforming process, because in the initial stage of the electroforming process, the deformation of the solution drop together with the formation of the primary jet leads to an increase in the surface area.

Viscosity affects the EF process and determines the fiber thickness. When using low viscosity solutions, the formation of defects such as droplets is inevitable, which deteriorates the properties of the obtained material. However, with excessive viscosity of the solution, energy losses for overcoming internal friction of the solution at its exit from the nozzle increase.

There are also other parameters: the geometry of the process in the unit, the rate of delivery of the solution, and so on. The optimum selection of all of the above properties of the spinning solution and the process parameters is a research task for each individual case. The study of this process is still ongoing.

It was found experimentally that the most suitable for EF is 12 wt.% SPAA in an alcohol-water solvent with an ethyl alcohol content of 70% and 30% water.

The EF can be performed on different grounded electrodes: on the flat electrode and on the rotating collector drum (Fig. 2) The EF process was performed in the NANON-01 Ver. 1.33 MECC Co. 2010. Electroforming was done on a grounded rotating drum.

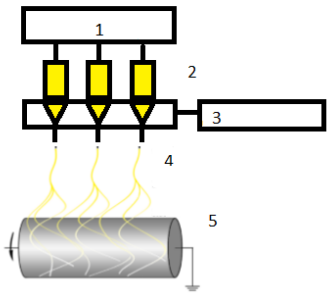

Fig. 2. Schematic diagram of the installation for electroforming: feed rate control *1*; solution *2*; high voltage source *3*; nozzles *4*; grounded rotating collector drum *5*

The microstructure of the nonwoven samples was studied by scanning electron microscopy (SEM). In this work, a Supra 55VP-32-49 microscope (Carl Zeiss, Germany) was used in the secondary electron detection mode. Before placing the samples inside the microscope chamber, a thin conductive layer of platinum was sprayed on their surface using an Eiko-IB3 unit. The diameter of the fibers was determined from microphotographs using the ImageJ software product.

The temperature dependences of the dynamic modulus of elasticity (*E'*), and the tangent of the angle of mechanical loss (tgδ) were measured to estimate the temperatures of relaxation transitions of nonwoven polyimide materials. The measurements were performed on a Dynamic Mechanical Analysis (DMA) DMA 242 C (NETZSCH, Germany) at a frequency of 1 Hz, the strain amplitude of the films was 0.1%, and the temperature rise rate was 5 °C/min.

Dielectric spectra were obtained on a broadband dielectric spectrometer Concept-21 (Novocontrol Technologies GmbH) with an automatic frequency analyzer of high resolution ALPHA-ANB. Temperature-frequency dependences of dielectric permittivity ε and dielectric loss angle tgδ were obtained in the frequency range of 1 Hz–15 kHz and temperatures 20–400 °C.

Results and Discussion

Fibers oriented along the axis of rotation were investigated using SEM (Fig. 3.). The thickness of the fibers averaged 500 nm, which corresponds to the industrial criterion, according to which the thickness of the fibers is taken less than 500 nm [1]. This is due to the effect of thickness on consumer properties - hydrophobicity, tribological properties, mechanical strength and others [1]. With a decrease in fiber diameter, the mechanical properties of the material, such as tensile strength, tensile strength, elastic modulus, increase.

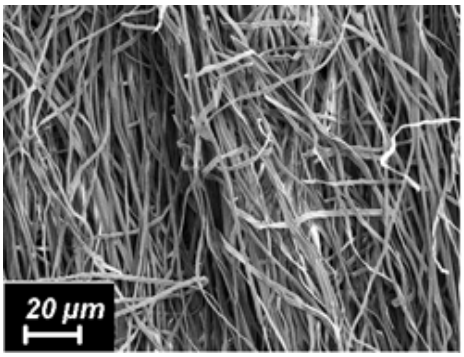

Fig. 3. Microphotograph of polyimide nonwoven material obtained from the rotating drum

The obtained PAA nonwovens were subjected to imidization in a thermostat according to the following regime: heating from 25 °C to 250 °C for 2 hours with isothermal exposure at 250 °C for 1 hour [6]. The thickness of the obtained nonwoven material after heat treatment was 24 μm.

The dielectric and DMA dependences of polar polymers are convenient to consider together because of the relationship between the maximums of their relaxation transitions: α, β, and γ. This is due to the coincidence of their losses associated with dipole-group and dipole-segmental relaxations. The low-temperature γ-transition depends on the method of polymer preparation, on the thermal background, and on the degree of moisture penetration into the polyimide [7]. The low-temperature γ peak is observed around −50 °C on the tgδ (T) dependence, the medium-temperature β-transition has a local relaxation character and is determined by the unfreezing of dipole groups, the maximum is in the region of 50 °C. The high-temperature α-transition (383 °C) is related to the unfreezing of the segmental mobility of the polymer.

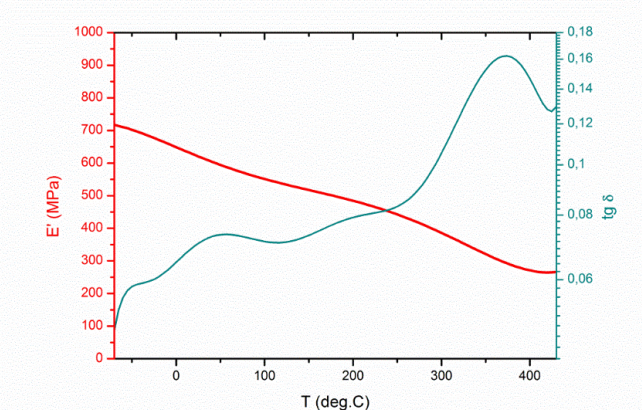

Fig. 4. Temperature dependence of Young's modulus E' and tgδ of mechanical losses at a frequency of $f = 1$ Hz

Fig. 4 shows the temperature dependence of E' and tg δ. The modulus of elasticity E' has values of the order of 600 MPa at 25 °C. The modulus of elasticity on the temperature dependence has three relaxation regions, the first (in the region of −50 °C), the second (in the region of 50 °C) reflects the non-cooperative movement of the diamine fragment in the structure of the PMDA-ODA polyimide under consideration, and the third (in the region of 350 °C) is associated with the defrosting of the polymer segmental mobility. The curve tgδ(T) of nonwoven polyimide PMDA-ODA is characterized by distinct maximum at 383 °C that corresponds to glass transition temperature T_g of polyimide. According to the literature [8] the glass transition temperature of PMDA-ODA film lies in the range from 360−410 °C depending on the research method.

The dielectric properties of the nonwoven PI are shown in Fig. 5. As can be seen from the dependence ε′(T) the dielectric permittivity at frequency $f = 1$ Hz is $\varepsilon' = 1.5$. On the temperature dependence tgδ(T) three relaxation regions can be distinguished, the first β-transition is due to

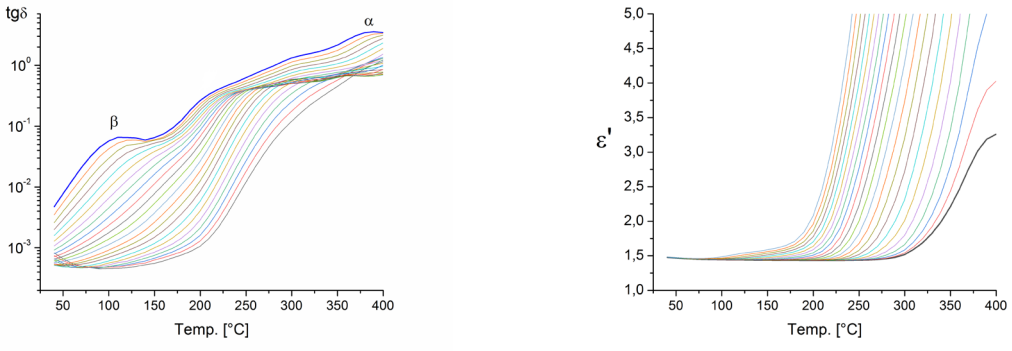

Fig. 5. Temperature dependence of tg δ and ε′ in frequency range
f = 1Hz–15kHz (growth of frequency from left to right)

local mobility in the dianhydride part of the macromolecule, rotation of the para-phenylene links in the diamine part or local motions in both parts of the macromolecule simultaneously. The high-temperature α-transition is associated with the transition from a glassy to a highly elastic state and is defined by T_g.

Dielectric spectroscopy and DMA results identify the β and α relaxation processes in the glassy and highly elastic states of PI PMDA-ODA respectively.

Fig. 6 presents a comparison of the dielectric permittivity of the film and nonwoven material of the same chemical structure PMDA-ODA. The graph illustrates a significant difference ε′, so the nonwoven material has ε′ = 1.5, and the film has ε′ = 3.5. Thus, it is possible to justify the use of materials obtained by the electroforming process in modern integrated circuits, which have requirements for low dielectric permittivity.

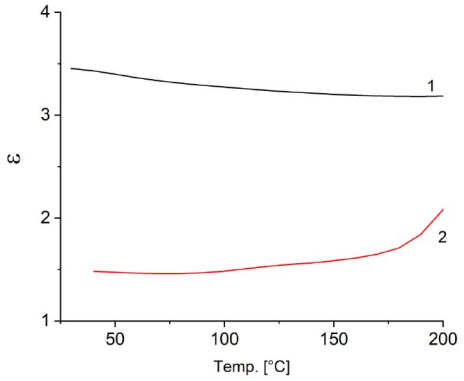

Fig. 6. Comparison of dielectric permittivity of film (1)
and nonwoven material (2) at 1Hz electric field frequency

Conclusion

A nonwoven polyimide material PMDA-ODA with low dielectric permittivity ε′ = 1.5 and low loss tgδ was obtained, which will significantly expand the use of polyimide in modern integrated circuits.

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