Technical Physics Letters, 2025, Vol. 51, No. 12

# Nonwovens (webs) copoly(urethane-imides) appreted by electrically conductive polypyrrole

© A.L. Didenko, M.A. Shishov, A.M. Kamalov, I.Yu. Sapurina, A.E. Bursian, N.N. Saprykina, A.S. Ivanova, V.E. Kraft, G.V. Vaganov, V.E. Yudin, V.M. Svetlichny, V.V. Kudryavtsev

NRC „Kurchatov Institute“–PNPI–IMC, St. Petersburg, Russia
E-mail: vanilin72@yandex.ru

*Received May 5, 2025*
*Revised June 24, 2025*
*Accepted June 24, 2025*

Nonwoven permeable mats made of nanofibers were obtained by electrospinning on the basis of prepolymers of copoly(urethane-imides). The electrical conductivity of the initial matrix ($10^{-10}-10^{-12}$ S/cm), after dressing with polypyrrol, increased by 10 orders of magnitude and reached $1.5 \pm 0.5$ S/cm. The material has ohmic volt-ampere characteristics and high electrical stability in the range of $\pm 1.0$ V in the presence of a constant electrical potential, as well as under conditions of long-term „cycling“ of the potential. Composites have prospects for use as medical devices, as well as membranes with electrically controlled properties.

**Keywords:** copoly(urethane-imide), electrospinning, polypyrrole.

DOI: 10.61011/TPL.2025.12.62804.8012

Copoly(urethane-imides) (CPUIs) are derivatives of high-strength heat-resistant rigid-chain polyimides and flexible-chain polyurethanes. The molecular structure of CPUIs is dictated by the general formula of $[A-(B)_k]_n$ [1], where $A$ is a rigid aromatic imide block framed by urethane groups and $B$ is a flexible block of aliphatic polyester found in polyurethane. This structure of macromolecules gives rise to phase separation of domains formed by rigid and flexible blocks and ensures that CPUIs take on the unique properties of highly heat-resistant and high-strength elastomers [2–6]. The possibility of producing porous nonwoven mats with controlled thickness and density from copoly(urethane-imide) by electrospinning was demonstrated in [7,8]. Nonwoven permeable mats consisting of nanofibers were obtained based on CPUI prepolymers. In order to impart electrically conductive properties to the material, the nonwoven CPUI matrix was then dressed with an electrically conductive form of polypyrrole (PPy) by heterophase synthesis of PPy on the surface of nanofibers [9]. It should be noted that PPy supports both electronic and ionic conductivity types.

The aim of this study is to obtain an electrically conductive flexible nonwoven CPUI–PPy mat, examine the structure and mechanical properties of the composite and compare it with the original CPUI, and determine the characteristics of electrical conductivity of CPUI–PPy (including its electrical stability).

The following monomers were used in the synthesis of CPUI: pyromellitic anhydride (> 99 %, CAS: 89-32-7), 4,4′-diaminodiphenyl ester (> 98 %, CAS: 101-80-4, Tokyo Chemical Industry), polycaprolactone diol with molecular weight $M_n = 2000$ (> 98 %, CAS: 101-80-4), and 2,4-toluene diisocyanate (> 99.5 %, CAS 584-84-9, Aldrich). The synthesis methods detailed in [10–15] were used.

The structural formula of CPUI in imidized form is shown in Fig. 1.

Electrospinning of prepolymers from solutions of copoly(urethane-amide acids) with characteristic viscosity $[\eta] = 1.1 \cdot 10^2\,\mathrm{cm}^3 \cdot \mathrm{g}^{-1}$ was carried out using a Nanon-01A setup (MECC Co., Japan) at a voltage of 25–30 kV. Samples of nonwoven mats were 300 × 210 mm in size and had a thickness of $\sim 100\,\mu$m.

The CPUI matrix was dressed with an electrically conductive form of PPy by heterophase polymerization of pyrrole under the influence of $FeCl_3$ acting as an oxidizing agent and in the presence of a doping agent (para-toluenesulfonic acid). The reaction proceeded at 0 °C for 20 h in a water-alcohol solution containing the CPUI matrix. When the synthesis process was competed, the matrix, which had acquired a black PPy color, was rinsed with an acidified aqueous solution and dried in air.

The morphology of materials was examined with a Supra-55 VP (Carl Zeiss, Germany) scanning electron microscope (SEM). The mechanical properties were determined using an Instron 5940 (Switzerland) universal tensile testing machine in the uniaxial tension mode at a rate of 10 mm/min. Samples had the form of 2-mm-wide strips with a working section length of 25 mm.

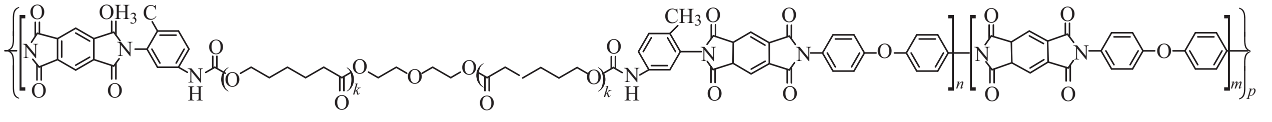

**Figure 1.** Structural formula of CPUI in imidized form ($n = 1$, $m = 10$).

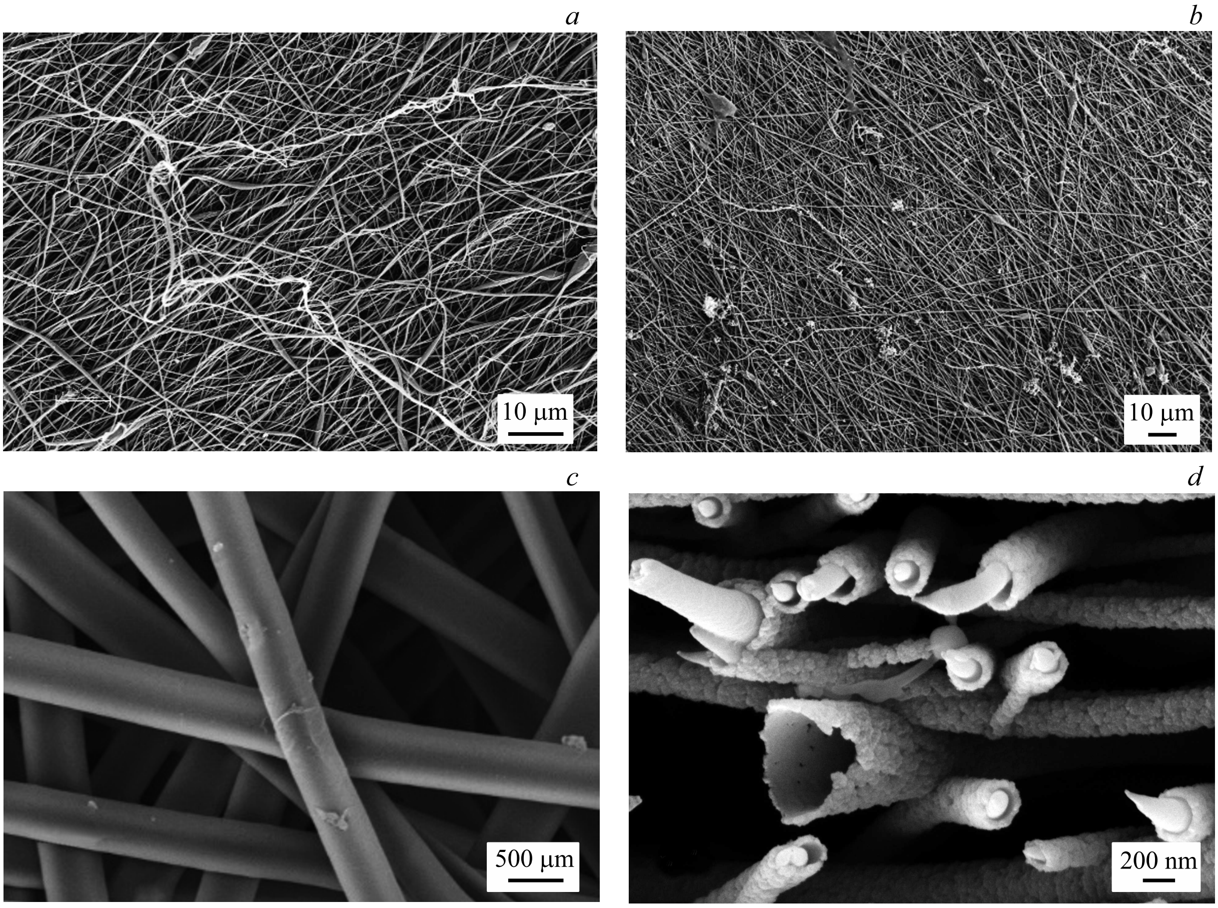

**Figure 2.** SEM images of electrospun CPUI (*a*, *c*) and CPUI–PPy (*b*, *d*) mats at different magnifications. Panel *d* illustrates the cleavage of a CPUI–PPy mat.

The surface resistance of electrospun materials modified with PPy was measured in accordance with the AATCC 76-2005 (GOST 10589–87) test procedure using a clamping electrode consisting of two plane-parallel platinum strips 10 mm in length secured at a distance of 10 mm from each other. The device was positioned on the studied sample and pressed with a force of 10 N. The surface resistance was calculated as $R = R_s l/w$, where $R$ is the resistance expressed in $[\Omega/\text{sq}]$, $R_s$ is the resistance expressed in $[\Omega]$, $l$ is the electrode length, and $w$ is the interelectrode distance [9].

The through resistance was measured by placing flat round stainless steel electrodes with a diameter of 0.8 cm on both sides of the sample. In the process of measurement, these electrodes were clamped with a spring dynamometer with a controlled force of 10 N.

The resistance was calculated as $R = \frac{\rho l}{S}$, where $R$ is the resistance expressed in $[\Omega]$, $\rho$ is the sought-for resistivity expressed in $[\Omega/\text{mm}]$, $S$ is the area of sample–electrode contact expressed in $[\text{mm}^2]$, and $l$ is the interelectrode distance expressed in [mm]. The sample thickness was measured with a micrometer (MKTs-25 Etalon) with a division value of 0.001 mm [16].

The electrical resistance of PPy obtained under the same experimental conditions was determined by the four-point probe method using PPy powders pressed into tablets. To compare the characteristics of powdered and electrospun materials, their Ω/sq parameters were converted into electrical conductivity units [S/cm]. Measurements were carried out using a Keithley 2010 voltmeter-ammeter and a Keithley 237 current source at room temperature and humidity [17,18].

The electrochemical characteristics of the CPUI–PPy composite were studied using an ELINS P-30J potentiostat/galvanostat in a Teflon cell with plane-parallel platinum electrodes [17,18].

The morphology of electrospun CPUI and CPUI–PPy samples is shown in Fig. 2. It is evident (Fig. 2,*a*,*b*) that these CPUI and CPUI–PPy samples are uniform mats consisting of extended fibers of a submicrometer diameter. Fibers are laid in uniform layers mostly parallel to each other; the interfiber spaces are on the order of 1 $\mu$m both in CPUI and in CPUI–PPy. Widely spaced light „islands“ are visible on the surface of the CPUI–PPy mat (Fig. 2,*b*). These islands correspond to PPy residue that is not fixed on the surface of fibers. High-magnification images (Figs. 2,*c*,*d*) allow one to examine individual

Stress-strain properties of CPUI and CPUI–PPy

| Sample | Tensile strength, MPa | Modulus of elasticity, MPa | Breaking strain, % |
|---|---|---|---|
| CPUI | $24 \pm 3$ | $240 \pm 20$ | $50 \pm 10$ |
| CPUI–PPy | $15 \pm 2$ | $260 \pm 10$ | $13 \pm 2$ |

fibers. In the case of CPUI (Fig. 2, *c*), the fibers are smooth; in CPUI–PPy (Fig. 2, *d*), the surface of fibers is rough and covered with a shell of densely packed PPy particles 30–40 nm in diameter. The imaged cleavage of a CPUI–PPy mat (Fig. 2, *d*) reveals that each CPUI fiber has a continuous PPy shell. The shell thickness is determined by the size of PPy nanoparticles; in the examined case, this thickness is 30–40 nm. Thus, the CPUI–PPy composite has a fiber-in-shell structure with extended CPUI fibers of a submicrometer diameter encapsulated in PPy, which takes the form of a monolayer of closely packed spherical nanoparticles.

The mechanical characteristics of CPUI and CPUI–PPy are presented in the table.

It is evident that PPy dressing has a negative effect on the strength characteristics and elasticity of the CPUI mat. The mechanical properties of nonwovens are set by their specific application and may be improved significantly by applying such techniques as additional orientation, thermo-pressing, and calendering of fibers.

It is known that polyimides and polyurethanes have high electrical resistance [19–21]. Its value for CPUI mats is $10^{10}-10^{12}$ S/cm. The electrical resistance of the CPUI–PPy matrix was measured in accordance with the AATCC 76-2005 procedure in units of $\Omega$/sq. The surface resistance is $65 \pm 6\,\Omega$/sq, and the through resistance is $80 \pm 10\,\Omega$/mm at a sample thickness of $0.105 \pm 0.008$ mm. Converting these data into S/cm units, we obtain 1.5 S/cm. Thus, the electrical conductivity of CPUI–PPy is ten orders of magnitude higher than that of CPUI and is close to the conductivity of PPy itself ($\sim 10$ S/cm) [22].

Figure 3 presents data on the electrical stability of CPUI–PPy examined with constant or variable potentials of ±1 V applied to the sample. The samples were tested both in their dry state and in an aqueous electrolyte solution (0.9 % NaCl). When a constant voltage of +1 or −1 V is applied to CPUI–PPy (at an interelectrode distance of 1 cm), the sample carries a stable current of $18 \pm 0.8$ mA (Fig. 3, *a*). When the sample is wetted with electrolyte, a small initial increase in current to 20 mA (due to „switching on“ of ionic conductivity) is seen, but then the current starts decreasing slowly, indicating the formation of a double electric layer that screens and reduces the electrode potential. The results are reproducible.

When a cyclic sawtooth potential within the range of ±1 V is applied to CPUI–PPy (Fig. 3, *b*), a synchronized variation of currents in the sample is observed. The peak values of currents do not decrease, which is indicative of stability of the material. The current amplitudes in the wetted sample (line *2*) are 2 mA higher than in the dry one, which is also attributable to the presence of an ionic conductivity component.

It should be noted in conclusion that the combination of a porous permeable structure with fine mechanical properties and electrical conductivity opens up prospects for application of CPUI–PPy in sensorics and biomedicine. The obtained materials may be used to advance technological expertise in flexible electronics.

## Funding

This study was carried out under the state assignment (research topic „Polymer and Composite Materials for Advanced Technologies,“ registration number 1023031700040-5-1.4.4).

## Conflict of interest

The authors declare that they have no conflict of interest.

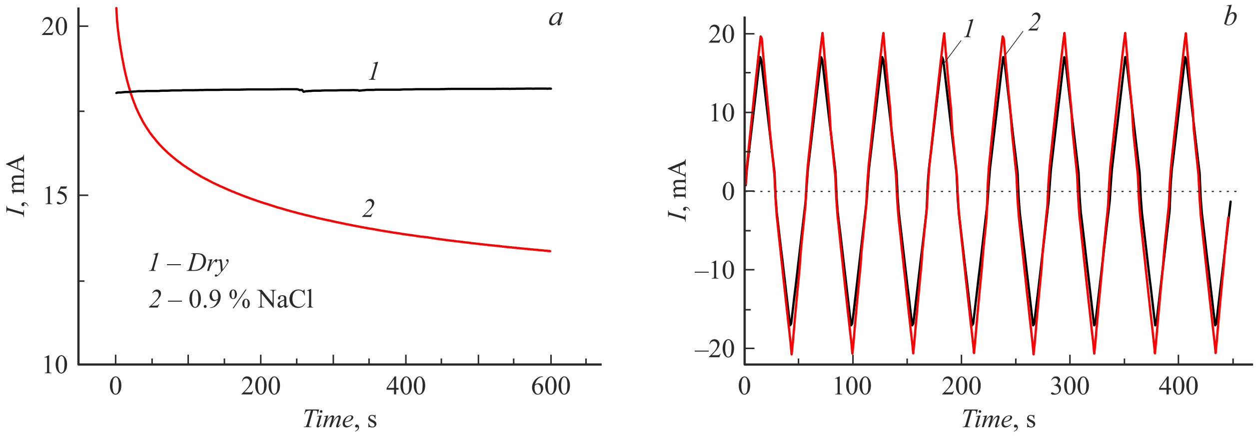

**Figure 3.** Currents flowing through CPUI–PPy when a constant potential of +1 V (*a*) and a cyclic sawtooth potential with an amplitude of ±1 V and its sign changing every 28 s (*b*) are applied to the sample. *1* — Dry sample; *2* — sample in electrolyte.

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*Translated by D.Safin*