

Research Article

Synthesis and Properties of Electroconductive Polymeric Composite Material Based on Polypyrrole

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A technique is proposed for obtaining electroconductive, mechanically strong, and elastic composite material based on polypyrrole and hydrophilized polyethylene. The relationship is established between the process parameters and properties of the composite material such as electroconductivity and mechanical strength. Several methods are considered in the view of increasing electroconductivity of the material. Physical and mechanical properties of the composite material are investigated.

1. Introduction

Polypyrrole (PPy) is a typical electroconductive polymer from the class of the unique materials which combine metallic and semiconductor properties with such polymeric characteristics as flexibility, strength, and elasticity. The most essential advantage of such polymers is processability and fine control of their properties by the methods of organic synthesis [1].

Polypyrrole is obtained in the form of black powder by monomer oxidation [2]. By far it is the most extensively studied conducting polymer since a pyrrole monomer is an easily oxidized, water-soluble, commercially available material that possesses environmental stability, good redox properties and high electrical conductivity [3]. Materials based on PPy can be used as different display members, antistatic coatings, and coatings to protect against oxidation and corrosion [4]. However, some factors currently limiting the applications of PPy include its poor mechanical strength and thus low processibility [5]. Single-component materials on the basis of PPy are characterized by extremely low mechanical properties and fragility.

There are some reports pertaining to the preparation of conductive polymer composites with inorganic materials such as fly ash [6] and Ag [7]. However, such composites do not exhibit sufficient mechanical properties. This drawback

can be eliminated if PPy is combined with an elastic substrate matrix that imparts mechanical strength to the composite material. Different flexible-chain polymers such as polyethylene (PE), polypropylene, polyvinylidene fluoride can be used as substrate materials [8–10]. Still, low adhesion of PPy to substrates significantly complicates preparation of composite materials, and this problem still remains unsolved.

In this work it is proposed to use hydrophilized polyethylene for increasing phase interaction of the substrates with PPy. This approach provides high presorption of pyrrole on the surface of the substrate. As a result of polymerization, a conductive PPy coating is formed, which makes tight bonds with hydrophilized polyethylene. In this way two problems are solved in this work. First, a flexible composite material is obtained on the basis of fragile PPy, and second, a phase interaction between the components of the composite material is increased.

The objective of this work is to develop a method for obtaining electroconductive, mechanically strong, and elastic polymeric composite material based on PPy and PE and to study the properties of the obtained material.

2. Experiment

A polyethylene (PE) film was modified with ionic polymers by radiation graft polymerization of acrylic acid onto PE

film preliminary exposed to γ -radiation in the air. The film thickness was 20 μm . The grafting degree of polyacrylic acid (PAA) was determined gravimetrically as a mass difference of the film of PE before and after grafting divided by the mass of the initial PE film. The degree of polyacrylic acid (PAA) grafting was 120–150%. The conditions and parameters of PE modification were described in detail in the previous work [11].

Pyrrole (Pyrrole, extra pure, 99%, Inc. Acros Organics) was predistilled under reduced pressure.

Oxidative polymerization of pyrrole was carried out in the aqueous solution in the presence of PE film hydrophilized with grafted PAA by the following procedure. Preliminary weighed hydrophilized PE film was immersed into the aqueous solution of pyrrole with a concentration of 0.3 or 0.9 mol/dm³ for one day. Then some aqueous solution of the oxidizing agent was added dropwise at 2–7°C under continuous stirring for 1 h. Iron chloride (III) or ammonium persulfate were used as oxidizers. The concentration varied from 0.2 to 4.5 mol/dm³ and from 0.1 to 2 mol/dm³ for iron chloride (III) and ammonium persulfate, respectively. After polymerization of pyrrole the film was washed in water and ethyl alcohol, dried in the air to constant weight. The content of PPy in the composite (Δm , %) was determined gravimetrically.

Repeated polymerization of pyrrole was carried out to increase PPy content in the composite. Prepared composite material PE-PAA-PPy was immersed into the aqueous solution of pyrrole with a concentration of 0.3 or 0.9 mol/dm³. Then a solution of the iron chloride (III) was added dropwise at 2–7°C under continuous stirring for 1 h. After polymerization of pyrrole the film was washed in water and ethyl alcohol, dried in the air to constant weight.

Electronic conductivity was measured by a four-probe method at the upper limit of electric current $8.2 \cdot 10^{-2}$ A. A distance between tungsten carbide probes in in-line position was (1.30 ± 0.01) mm. A mean value of six-point measurements on two sides of the composite material was taken as a measurement result.

The structure of the composite material was studied by the IR spectroscopy using a Fourier spectrometer FS-1202.

Distribution of carbon, oxygen, and chlorine throughout the thickness of the composite material was studied by scanning electron microscopy and tip scanning X-ray microanalysis using a scanning electron microscope JS-U3 “Jeol” with the energy-dispersive X-ray attachment Win EDS “Getac”.

Surface morphology of the composite material was studied by transmission microscopy at the Research Institute of Physico-Chemical Medicine.

Ionic conductivity of the samples was calculated from the values of the absolute resistance, which were measured with an AC bridge (0–39.9) mA at the operating frequency (1 ± 0.0001) MHz. The samples preswollen in the electrolyte were placed in a cell to measure the electrical resistance of the material, and the cell was immersed into 0.1 M–1 M acid (HCl, H₃PO₄) solutions.

The absolute resistance of the material (R_x , Ohm \cdot cm²) was calculated by the formula:

$$R_x = (R_{\text{el.s.}} - R_{\text{el.}}) \cdot S, \quad (1)$$

where $R_{\text{el.s.}}$ is the electrical resistance of the electrolyte with a sample, Ohm; $R_{\text{el.}}$ is the electrical resistance of the electrolyte, Ohm; S is the area of the material equal to the working area of the platinum electrodes (2.7 cm²).

A reverse value of the absolute resistance, S/cm², was taken for ionic conductivity of the sample.

A temperature of thermal transitions of the samples was determined by the DSC method using a differential scanning calorimeter PT/10 “Linseis”. The measurements were made at a heating rate of 5°C/min from room temperature up to 250°C. The midpoint of the baseline change was used as the glass transition temperature and the T_m was defined as onset temperature.

Mechanical properties of the composite material were determined using a mechanical testing machine “Zwick” at a speed of 5 mm/min.

3. Results and Discussion

3.1. Synthesis and Structure of the Composite Material. Polypyrrole can be obtained by chemical or electrochemical synthesis [12–16]. Chemical polymerization makes it possible to form PPy coatings on the objects of different geometry (microspheres, solid, and porous films, etc.) present in the reaction volume.

The synthesis of composite PE-PAA-PPy consisted of two stages: postradiation graft polymerization of acrylic acid onto PE film, and polymerization of pyrrole in the bulk and on the surface of PE film modified with PAA. The synthesis of composite material based on PPy and PE film hydrophilized with grafted PAA is shown in Figure 1.

A composite material obtained in such a way consists of PPy, PE, and PAA, where the first component is responsible for electronic conductivity, the second one for mechanical strength and elasticity, and the third one provides both adhesion of PPy to the substrate and ionic conductivity. Thus PAA is a coupling agent that increases phase interaction between PPy and PE.

The composition of the prepared material was studied by the IR spectroscopy. The IR spectra of the polyethylene matrix, polypyrrole polymer, and composite material based on PE and PPy are shown in Figure 2.

As shown in Figure 2, the absorption bands at 3417 cm⁻¹ and 1638 cm⁻¹, which correspond to the stretching vibrations of N–H and C=C_(aromat.) bonds of the pyrrole ring, respectively, can be used as characteristic bands for the analysis of PPy, and the absorption band at 1716 cm⁻¹ corresponding to the stretching vibrations of C=O groups in the PAA can be considered a characteristic band for the analysis of the matrix. Therefore, the IR spectroscopy qualitatively confirms that a composite material thus obtained is based on PE and PPy.

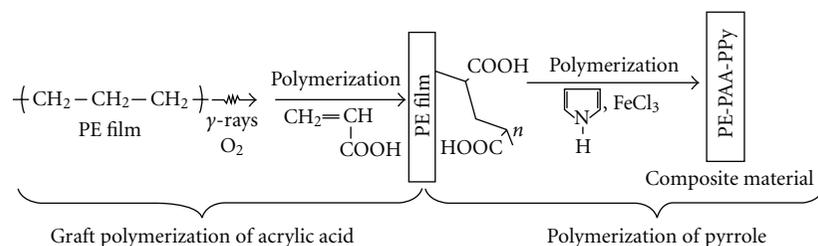


FIGURE 1: Schematic presentation of composite material synthesis based on PE film and PPy.

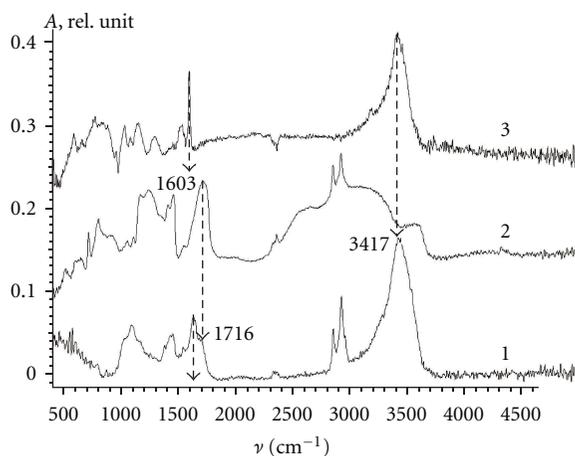


FIGURE 2: IR spectra of the composite material based on PE matrix and PPy (1), polyethylene matrix (2), and polymer PPy (3).

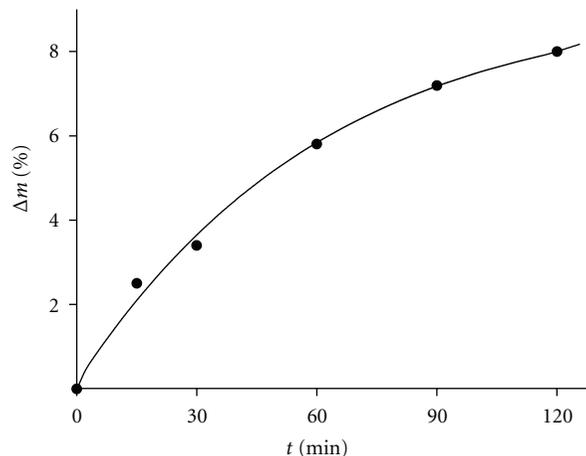


FIGURE 3: The kinetics of pyrrole polymerization on the polyethylene matrix. Oxidizer—2 M FeCl₃; polymerization temperature—5°C.

The kinetics of pyrrole polymerization onto PAA-modified polyethylene substrate was investigated. The polymerization was carried out in the presence of 2 M iron chloride (III). The dependence of PPy content in the composite material on polymerization time is shown in Figure 3.

As shown in Figure 3, PPy content increases at a constant rate; after one hour of polymerization its rate decreases essentially. Such a character of polymerization is probably connected with the formation of the dense PPy layer on the matrix surface, which prevents further diffusion of the oxidant (iron ions (III)) into the matrix and, consequently, causes termination of pyrrole polymerization.

To study the penetration of PPy into the bulk of PE matrix, a distribution profile was obtained for the characteristic emission of the elements (C, O, and Cl) in the cross-section of composite material (Figure 4). It is seen that distribution of carbon and oxygen in the bulk of the matrix is constant (Figure 4, graphs 1 and 2), and chlorine, a dopant directly bonded with PPy, is concentrated mainly on the film surface (Figure 4, graph 3). The content of chlorine in the bulk of the film is about 2.5 times less than on the surface, but its concentration in the matrix bulk is constant. This suggests that polymerization of pyrrole occurs not only on the surface of the matrix but also in the bulk.

An increased content of PPy on the surface is confirmed by the transmission microscopy studies (Figure 5). Thus,

it can be concluded that during polymerization PPy precipitates from the reaction volume on the surface of the composite material in the form of fine granules. Surface-adsorbed PPy does not pill off during mechanical actions such as polishing and flexing.

Formation of PPy inside PAA-modified PE matrix can be explained based on Gierke's cluster-channel model [17]. According to this model, the swelling of ion-exchange membrane (PE with grafted PAA chains) in the solution of pyrrole results in the formation of the ion clusters interconnected by narrow channels (Figure 6). Due to such a cluster lattice penetrating the entire matrix, pyrrole diffuses into the bulk of PE film and polymerizes on the surface and in the bulk of the substrate when an oxidizing agent is added.

3.2. Electronic Conductivity of Composite Material. Electronic conductivity of the composite material depends mainly on the content of PPy. In its turn, the content of PPy is affected by such conditions and parameters of PPy polymerization as the temperature, time of polymerization and concentration of the oxidizing agent.

The content of PPy (Figure 7, curve 1) and electronic conductivity of the composite material (Figure 7, curve 2) were investigated depending on iron chloride (III) concentration. The curves of PPy content and composite material conductivity are symbate, and represent extremes with a

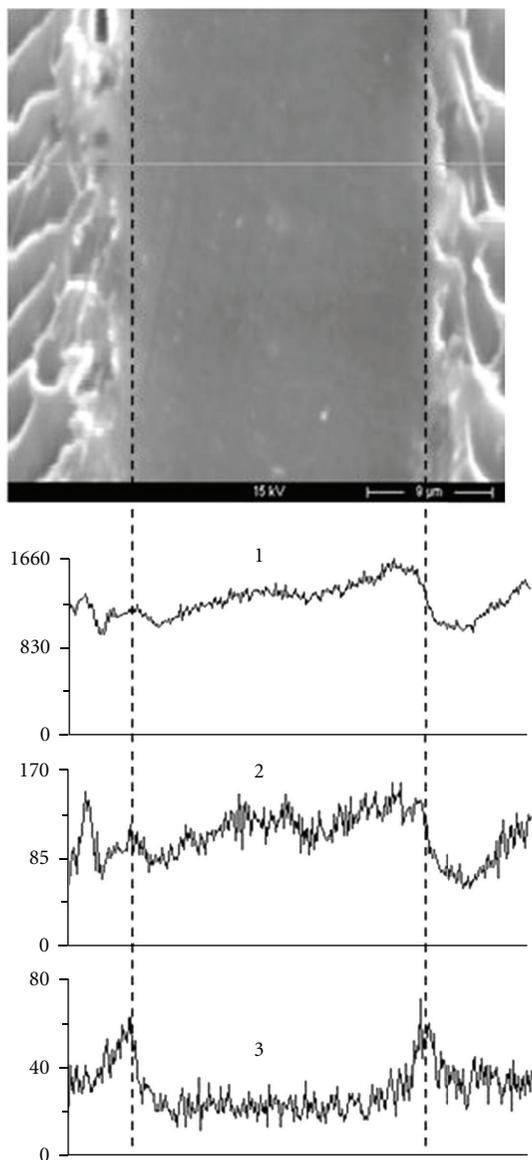


FIGURE 4: Distribution of carbon (1), oxygen (2), and chlorine (3) through the thickness of the composite material.

maximum at the concentration of iron chloride 3 mol/dm^3 . The content of PPy reaches 6.8%, and conductivity— $(1.72 \pm 0.09) \text{ S/cm}$. An extreme character of the obtained dependence is related to changing the length of conjugated PPy chains. These dependencies are in good agreement with the data obtained in paper [13].

The dependencies of PPy content (Figure 8, curve 1) and conductivity (Figure 8, curve 2) of the composite material on the concentration of ammonium persulfate have a similar shape. The content of PPy in the composite reaches 6%, and the electronic conductivity is $(0.179 \pm 0.018) \text{ S/cm}$ at the concentration of ammonium persulfate 0.1 mol/dm^3 .

The studies were made to increase the electronic conductivity of the composite material due to increasing monomer concentration in the reaction mixture and repolymerization

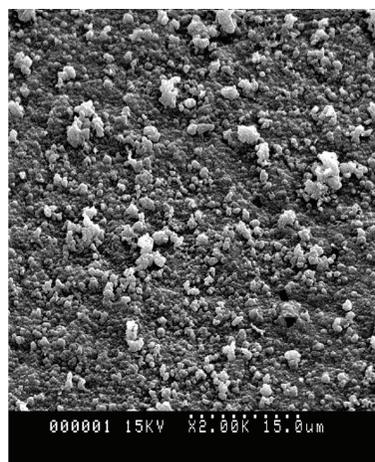


FIGURE 5: Surface micrograph of the composite material based on PE and PPy.

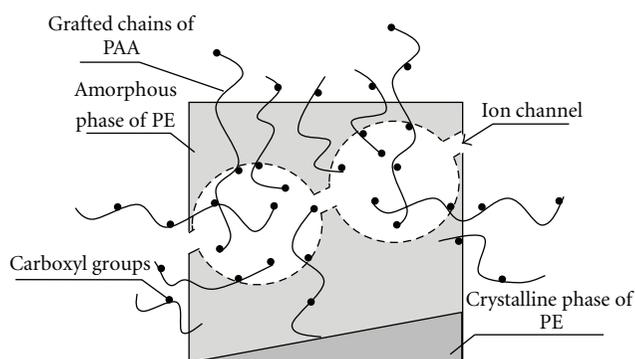


FIGURE 6: Schematic structure of the swollen composite substrate according to Gierke's cluster-channel model.

of pyrrole in the obtained composite material. It was established that increasing of pyrrole concentration in the reaction mixture from 0.3 to 0.9 mol/dm^3 did not result in a significant improvement of electronic conductivity (1.62 S/cm and 1.66 S/cm). Under repolymerization of pyrrole the electronic conductivity increased more than three times: 1.66 S/cm and 5.43 S/cm for single and double polymerization, respectively.

3.3. Ionic Conductivity of Composite Material. A composite material contains polyethylene modified with PAA, which exhibits ion exchange properties due to the presence of carboxyl groups. Polypyrrole can also participate in the process of ion exchange due to availability of proton-adding nitrogen atoms in the pyrrole ring. To determine the effect of PPy on the ionic conductivity of the composite material, the proton conductivity was studied and compared with the values of the initial PE-PAA matrix.

The ionic conductivity was investigated depending on the concentration of FeCl_3 used for composite material synthesis (Figure 9). Hydrochloric and phosphoric acids of various concentrations were used as electrolytes.

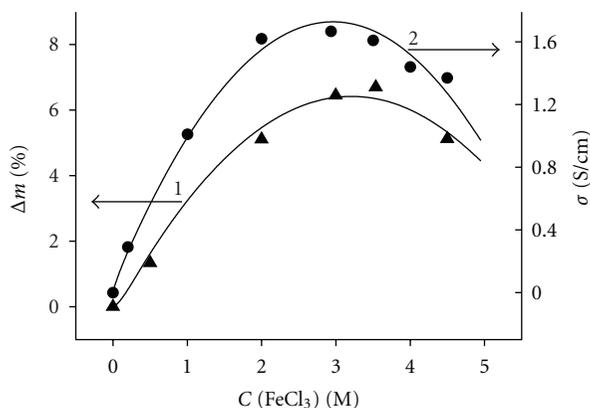


FIGURE 7: Dependence of PPy content (1) and electronic conductivity of the composite material (2) on the concentration of FeCl₃.

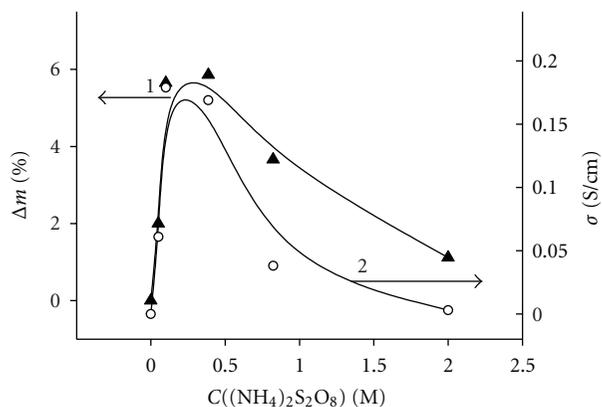


FIGURE 8: Dependence of PPy content (1) and electronic conductivity of the composite material (2) on the concentration of ammonium persulfate.

As shown in Figure 9, the ionic conductivity increases linearly with increasing concentration of the hydrochloric and phosphoric acids, and in case of hydrochloric acid the conductivity increases much faster. The value of the ionic conductivity does not depend on the concentration of the oxidant.

Thus, polypyrrole formed in the bulk PAA chains does not affect the proton conductivity, which only depends on the ion exchange properties of PAA-modified polyethylene substrate.

3.4. Physical and Mechanical Properties of Composite Material.

A differential scanning calorimetry was used in the temperature range 30–200°C to make a thermal analysis of the PAA-modified polyethylene matrix-substrate (Figure 10, curve 1), PE-PAA-PPy composite (Figure 10, curve 2), mechanical mixture of PE-PAA and PPy (Figure 10, curve 3), and pure PPy (Figure 10, curve 4). A phase transition temperature of the samples was evaluated from the thermograms (Table 1). In the case of PE-PAA graft copolymer a thermogram is characterized by two thermal transitions, where the first one (67.5°C) corresponds to the glass transition temperature of

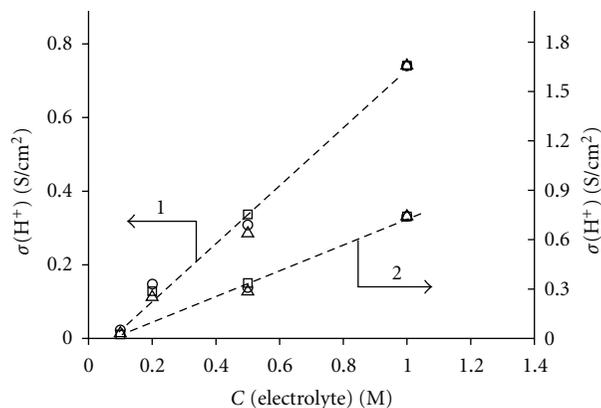


FIGURE 9: Dependence of the proton conductivity on electrolyte concentration (1) HCl; (2) H₃PO₄. Concentration of FeCl₃, mol/L: (o) 0; (□) 0.2; (Δ) 2.

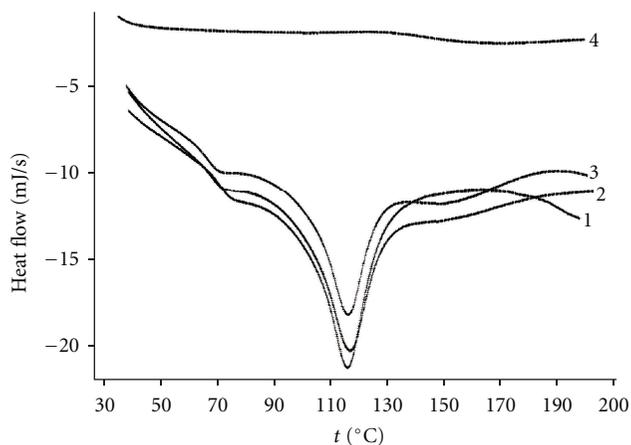


FIGURE 10: Temperature curves of the substrate (1), composite material (3), mechanical mixture of PE-PAA + PPy (2), and PPy (4).

PAA, and the second transition at 101.4°C—to the melting point of PE. Thus, a matrix substrate consists of two PE and PAA phases. It is known that a glass transition temperature of the homopolymer PAA is 106°C, though in [18] it was specified equal to 75°C. For our sample of PAA-modified polyethylene substrate a glass transition temperature of PAA was 67.5°C. A shift of PAA glass transition temperature to the lower range is probably caused by decreasing interaction between the segments of PAA chains which are formed in the amorphous PE phase interlacing with incompatible (hydrophobic) PE chains.

A shift of PAA glass transition temperature to the lower range was even more noticeable for the composite material. It is highly probable that this shift is also caused by decreasing interaction between PAA chains due to formation of a new PPy phase in the volume of amorphous PAA. Polypyrrole exhibiting high thermal stability [2] does not affect a melting temperature of the substrate and, as shown above (Figures 4 and 6), forms a separate conducting phase in the ion clusters of the amorphous phase of the substrate. Formation

TABLE 1: Thermal transition temperatures of the substrate, composite material and mechanical mixture of PE-PAA and PPy.

Parameter	Substrate PE-PAA	Mechanical mixture PE-PAA and PPy	Composite PE-PAA-PPy
Glass transition temperature, °C	67.5	65.1	63.2
Melting temperature, °C	101.4	101.4	102.6

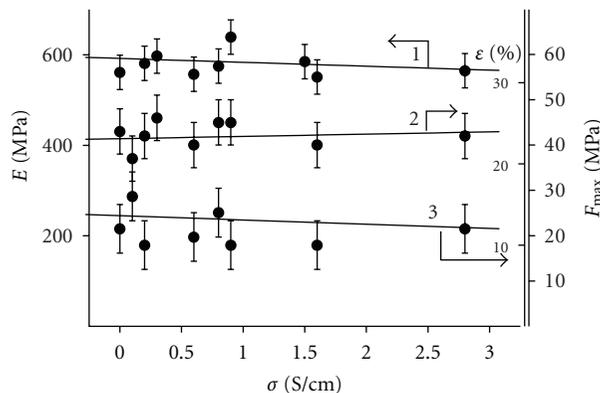


FIGURE 11: Conductivity dependence of the mechanical characteristics of composite material (1) Young's modulus, (2) maximum load-at-break, (3) elongation-at-break.

of a separate phase of PPy in the matrix-substrate and its influence on the mobility of PAA chains was confirmed by a thermal analysis of the mechanical mixture of PE-PAA and PPy. The sample obtained by mechanical mixing of two materials (PAA-modified polyethylene substrate and PPy), where PPy does not penetrate into the bulk of the substrate, has nearly the same temperatures of thermal transitions as the original substrate.

Application areas depend on the mechanical properties of composite materials. The films of conductive polymers are highly fragile and have extremely low elasticity. Furthermore, if conductive polymers are incorporated into other materials (substrates) as fillers, the mechanical properties of the substrates are usually reduced. Therefore, mechanical properties are a decisive criterion for identifying possible areas of composite material application.

Mechanical strength (Young's modulus, maximum load-at-break) and flexibility (relative elongation-at-break) of the composite samples were tested depending on the electronic conductivity (Figure 11).

As shown in Figure 11, average values of Young's modulus, maximum load-at-break and elongation-at-break obtained by the least square method are (591 ± 38) MPa, (43 ± 2) MPa and (11 ± 1) %, respectively.

A shape of the stress-strain curves obtained for the composite materials is the same as for PE matrix, that is, a composite "inherits" the nature of elastic component deformation, which determines its mechanical properties. Such behaviour of the composite material during the tests can indicate that PPy polymerization proceeds in the bulk of PE matrix and results in the formation of the spatially continuous phase of the rigid-chain polymer in a flexible substrate.

The mechanical tests did not show any signs of PPy peeling even at the composite break, that is, all the composite samples are characterized by high adhesion of the conductive component to the substrate.

4. Conclusions

Thus, in this work a technique is proposed for obtaining three-component composite materials on the basis of PE substrate modified with grafted PAA and PPy. It is shown that the composite materials exhibit good mechanical properties due to the presence of PE film tightly bonded with PPy through PAA. The materials thus obtained combine electronic and ionic conductivity with high mechanical strength. The ways of increasing electronic conductivity are determined.

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