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Electrical Properties of Polyesters

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Abstract

Polyesters occupy an important place in the group of polymers as engineering materials to be used in electrotechnology and electronics. These polymers are characterized by excellent electro-insulating properties, showing mechanical strength, thermal resistance, and easiness in processing at the same time. The chapter presents the behavior analysis of the following polyesters in electric field: poly(ethylene terephthalate), poly(lactic acid), and polycarbonate. The effect of polymer microstructure on electric properties is presented, including its susceptibility to polarization that makes it possible to use polyesters as electrets materials. The second trend of the study presents the possibilities of transforming the electro-insulating properties of polyester fabrics to conductive properties with the use of modern processing methods such as PVD, CVD, and digital print. The functionalization of polyester fabrics extends their application range, for example, in e-textiles and reduces the fabric susceptibility to static electricity, increasing the safety of use.

Keywords: polyesters, electrical conductivity, polarization, electrets, static electricity

1. Introduction

Polyesters constitute an important group of polymers widely used in many branches of economy, such as electrical, electronic, building, clothing and packaging industries, and medicine. These polymers are characterized by excellent electro-insulating properties, mechanical strength, thermal resistance, and susceptibility to multiple processing. A common feature of polyesters is the presence of ester group in the main chain structure. This group imparts a polar character to polyesters. Aromatic groups in the repeatable units of polyester chain impart to the polymers an increased physical resistance, such as thermal (increased melting point and glass transition temperature) and mechanical resistance (increased mechanical

parameters such as elasticity and strength). The content of aromatic structures in polyesters is different and has been used for the internal classification of these polymers into aliphatic, aliphatic-aromatic, and aromatic polyesters. Aliphatic polyesters contain no aromatic structures, for example, poly(ethylene adipate). This group includes biodegradable polyesters, such as poly(lactic acid) (PLA) (**Figure 1B**), polyesters of butyric acid (PHB), and poly(butylene succinates) (PBS) widely used in medicine and technology. Aliphatic-aromatic polyesters contain both the aliphatic and aromatic structures (e.g., poly(ethylene terephthalate), polycarbonates) (**Figure 1C, D**). These polyesters show very good thermo-mechanical, impact, tribological, and optical properties, as well as resistance to atmospheric and functional conditions, which qualify them for mass production and versatile use. Finally, polyesters with “purely” aromatic structures—polyarylates (poly(4-hydroxybenzoate), poly(bishfenol-A-terephthalate), liquid crystal polyester) that show excellent thermal and dimensional stability, impact resistance, fire resistance, and nonlinear optical properties (NLO) [1]. Aromatic polyesters are used in the production of membranes, films coatings for electronic and electrical industries, optical waveguides and devices doubling the frequency of electromagnetic waves [1].

The chapter presents the behavior analysis of the following polyesters in DC electric field: aliphatic-aromatic polyesters with the example of poly(ethylene terephthalate) (PET) and polycarbonate (PC) and aliphatic polyester with the example of poly(lactic acid).

The processes of nonstationary current flow in polyesters and possible mechanisms that generate the nonstationary states are presented. Using the example of PET film tests, the ionic character of current conduction is shown. It is the effect of air humidity in the environment where a product is used that is connected with the ionic character of current conductance. There observed a well-known effect of deteriorating the PET film electro-insulating properties with increasing the content of water vapor in air [2]. In this study, it has been shown that this effect additionally depends on the form of product, and it is particularly intensified in fibrous structures, where the conduction is increased by about 1000 times. The effect of the physico-chemical state and coarseness of surface on the level of static electricity charge is shown. The processes of static electricity of polyesters, electricity conditioning, and hypotheses explaining these processes with a particular consideration of the static electricity of polyester-metal contact are discussed. The polyesters are important precursors for making electrets. The various techniques of electrets making and the issues of the electric charge relaxation that are of

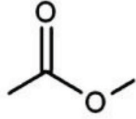
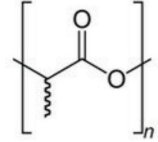
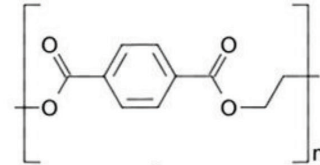
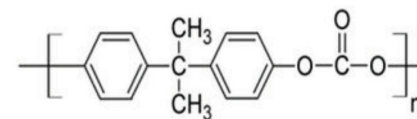
 <p>a)</p>	 <p>b)</p>	 <p>c)</p>	 <p>d)</p>
Ester group	Aliphatic polyester Polylactide (PLA)	Aliphatic-aromatic polyester, Poly(ethylene terephthalate (PET)	Aliphatic-aromatic polyester Polycarbonate (PC)

Figure 1. Structures of chemical groups in polyesters.

great importance for the electrets stability are presented. Information about the development trends of polyester and new fields of application are also included.

2. Electrical conductance of polyesters in a DC field

Polyesters are real dielectrics with a low electric conductance, polarizability in electric field, and a strong susceptibility to static electricity. Electric properties are determined by the presence of connected charges and trace quantities of free electric charges that are generated by defects, impurities, technological additives, or injected from electrodes or environment (e.g., low-temperature plasma). During the interaction of DC field, free charges undergo migration and connected charges are polarized. Migration and polarization processes occur in parallel, shaping a characteristic, nonstationary image of the polymer electric conductance.

The current that flows in a real polymeric dielectric under DC field is transient in nature and called absorption current. The density of absorption current decreases in time to reach a steady-state value called conductance current. The transient (absorption) current " $j(t)$ " is presented as a sum of the steady-state conduction current " j_c ," the transient current (displacement current) " $j_p(t)$," and diffusion current " j_d ":

$$j(t) = j_c + j_d + j_p(t) \quad (1)$$

In many polymers, the decreasing transient polarization current is in a direct relation with the function of polarization decay $P(t)$. The polarization decay occurs according to the dependence:

$$P(t) = P_o \cdot \exp\left(-\frac{t}{\tau_p}\right) \quad (2)$$

where: t —time and τ_p —macroscopic relaxation time of electrical polarization. The decrease in current in dielectric polymer can be approximated by Curie function:

$$j = A \cdot t^{-n} \quad (3)$$

where: A —coefficient of proportionality dependent on temperature, n —power coefficient dependent on relaxation processes, $n < 1$ for times $t > \tau$, while $n > 1$ for $t < \tau$. With the use of the above approximation to transient conduction processes in PET, the following values of power coefficient are obtained: $n = 0.75$ [3], $n = 0.33$ [4], and $n = 0.79$ [5]. The transient character of current indicates a complicated behavior of electric charges in dielectric polymers. The values of conductance current are lower by one to several orders compared to the initial absorption current and the time of reaching a steady-state value is from several minutes to dozen hours depending on polymer. To metrologically characterize a polymer, it is indispensable to determine the isochronal absorption current (i.e., current at constant times).

Test results indicate that the transient character of current depends on the factors connected with the object tested (chemical structure and the presence of polar groups, physical microstructure, thermal and electric history of a sample) and test conditions (field intensity, temperature and relative humidity of the medium, and electrode material and the presence of residual charge in the material tested).

Das-Gupta in his studies [7–9] has presented several mechanisms explaining the transient current flow in polymers. His intention was to indicate a method of identifying the mechanism type. The identification consists in performing a series of tests for the given polymer: relationship between electric field and the isochronal current transient, temperature dependence, effect of electrode material, thickness dependence, and time dependence of transient current. Then, the test results are analyzed with respect to the probability of the given mechanism. Das-Gupta characterizes the features of five mechanisms potentially generating transient current flows:

1. Electrode polarization: isochronal current proportional to field, a strong effect of the electrode material by blocking the flow, the process is thermally activated, power coefficient: initially $n = 0.5$ followed by $n > 1$.
2. Orientation of dipoles uniformly arranged through the polymer volume: isochronal current proportional to field, the process is thermally activated, electrode materials and thickness sample independent of isochronal current at DC field, power coefficient $0 \leq n \leq 2$.
3. Charge injection forming trapped space charge: isochronal current is controlled by injection method (electronic, corona discharge, and glow discharge methods), the thickness sample independent of isochronal current at DC field, dependence electrode material related to injection method, thermally activated process related to injection method, power coefficient $0 \leq n \leq 1$.
4. Charge tunneling from electrodes to empty traps: (isochronal current proportional to field, thickness sample inversely proportional dependent of isochronal current at DC field, the process is thermally independent, strongly dependence electrode material, power coefficient $0 \leq n \leq 2$
5. Hopping of charge carriers from one localized state to another: isochronal current proportional to field, the process is thermally activated, thickness sample and electrode materials independent of isochronal current at DC field, power coefficient $0 \leq n \leq 2$.

The starting point of recognizing the conductance process is the determination of charge carrier nature (electrons, ions). The assessment of carrier types is carried out by direct testing through comparing the charge transferred with the mass of substance released on electrodes in contact with the polymer (mass spectrometry and neutron activation analysis). Indirect methods include: tests of voltage-current and current-temperature characteristics [5, 10, 11], dielectric tests [12], tests of photo-electric and electro-chemical effects as well as tests of the dependence of polymer conductance on pressure [13]. The image of the pure polymer conductance significantly differs from that of polymer containing ionogen compounds (e.g., stabilizers, catalyst residues, impurities, other additives, and products of chemical decomposition). Compounds of this type (e.g., water) easily dissociate in volume or on the polymer surface imparting an ionic character to conductance.

In studies carried out on a pure PET, their authors present divided views: Amborski [10], Saito [13] declare themselves in favor of the ionic conductivity mechanism in PET. Based on testing the electro-chemical effect with the use of thermally stimulated currents (TSC), Sawa [14] concludes that electronic conduction occurs at temperatures to T_g and ionic conductance at temperatures above T_g . The concept of ionic conductance in polymers is based on the assumption of the presence of molecules capable of dissociating in the polymer structure and various structural effects that determine the available internal volume of polymer and are responsible for the diffusion processes and ion transport in the polymer volume. The migration of free ions consists in specific, hopping change in ion positions [15] Charge motion is given by the carrier hopping over the potential barrier. It takes place from one to the other position, in which the ion achieves the minimal value of potential energy. The mobility of free ions is limited by the value of potential barrier W_B , which should be defeated by the ion during migration. The electric field reduces the barrier by the value " Δ ":

$$\Delta = \frac{1}{2} e \cdot a \cdot E \quad (4)$$

where: E is DC field intensity, e —electron charge, and a —hopping dislocation path of ion. Based on the calculations of the probability of change in ion position in the polymer during migration and the rate of ion dislocation from one to the other position [15], the current density of conduction under the conditions of the DC action can be given as follows:

$$j = z \cdot e \cdot n \cdot \left(a \cdot v \cdot \exp \left[-\frac{W_B}{kT} \right] \cdot 2 \cdot \sinh \left[\frac{z \cdot e \cdot E \cdot a}{2kT} \right] \right) = G \cdot \sinh(H \cdot E) \quad (5)$$

where: z —number of elementary charges, e —electron charge, n —density of dissociated molecules, a —path of the charge hopping dislocation, k —Boltzmann constant, W_B —barrier of the charge potential energy, E —DC field intensity, T —temperature, G and H —constants in the generalized form of Eq. (5).

2.1. Electrical conductivity of poly(ethylene terephthalate) films

Poly(ethylene terephthalate) is a commonly used polymer in electrical engineering and electronics, where its electro-insulating properties are successfully used. In this study, commercial PET films, Estrofol type, containing indispensable additives, such as catalysts and stabilizers: manganese acetate (0.035% by wt.), calcium acetate (0.052% by wt.), antimony trioxide (0.040% by wt.), and phosphorus compounds (0.035% by wt.) were tested. Three variants of PET film with different supermolecular structures were tested: oriented films technologically drawn in a single-axis direction in a ratio of 2×, 3.5×, and 4×.

Al electrodes with a protective ring were evaporated on the purified film surface. The kinetics of absorption/desorption (depolarization) currents were examined for 20 min with the use of the measurement system described in paper [16]. **Figure 2** shows the kinetics of the volume absorption current in PET film (**Table 1**, draw ratio 4.0×) measured for 10 min. After this time, DC field was turned out and with earthed electrodes, the depolarization current (desorption current) was recorded for 10 min.

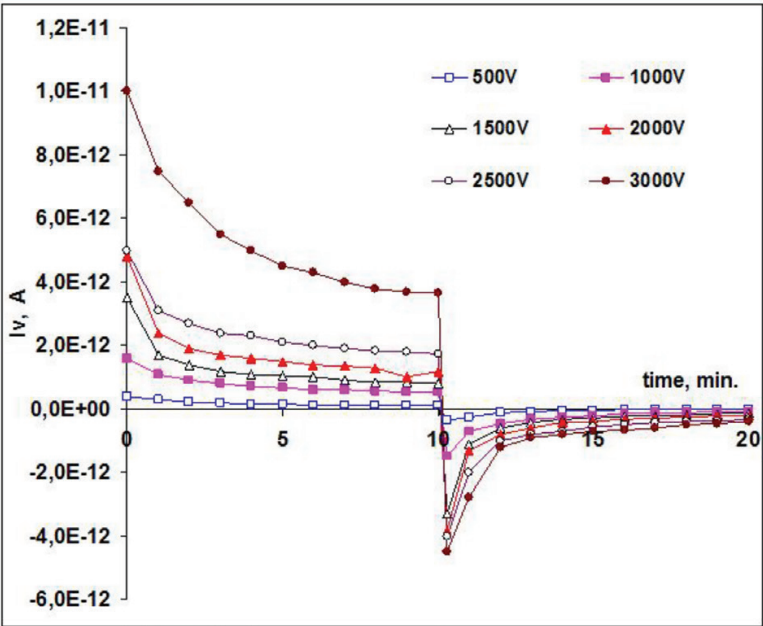


Figure 2. Decay of the transient (A) and depolarization (D) currents $I_v = f(t)$ in a PET film ($R = 4.0\times$) under a DC field (Al electrodes, $t = 23^\circ\text{C}$, $\text{RH} = 25\%$).

Film symbol	Draw ratio	Thickness, μm	Density kg/m^3	Crystallinity degree*, %	Herman's coefficient of orientation, f_o
A	2.0x	79	1344	7.4	0.12
B	3.5x	57	1352	14.5	0.44
C	4.0x	54	1358	19.8	0.58

* determined by the densitometric technique.

Table 1. Characteristics of PTE films.

Current-voltage characteristics were determined on the basis of the absorption current corrected by the desorption component according to the procedure of Badiana [17]. The characteristics $j = f(E)$ shown in **Figure 3** indicate linear behavior of the films and a shift into nonlinear state at an intensity of $3.5 \times 10^7 \text{ V/m}$. Based on the nonlinear range of field intensity that in the case of samples B and C is developed within a high range of the intensity of field E , the analysis of the ionic conductance of the films was carried out.

The experimental current-voltage characteristics of samples B and C were approximated with the Eq. (5). The approximation consisted in directing the function: $j = G \cdot \sinh H \cdot E$ to a linear form, that is, to develop it into Taylor series according to the procedure given in monograph [18], taking into account only the linear elements of this solution. In calculations based on the minimization procedure, the following parameter values were obtained:

- for PET ($R = 3.5\times$) $G = 7.20 \times 10^{-13} \text{ m/V}$, $H = 2.4 \times 10^{-8} \text{ m}^2/\text{A}$, $a = 1.24 \text{ nm}$
- for PET ($R = 4.0\times$) $G = 7.41 \times 10^{-13} \text{ m/V}$, $H = 2.4 \times 10^{-8} \text{ m}^2/\text{A}$, $a = 1.24 \text{ nm}$

a —path of the hopping shift of charge between successive equilibrium positions.

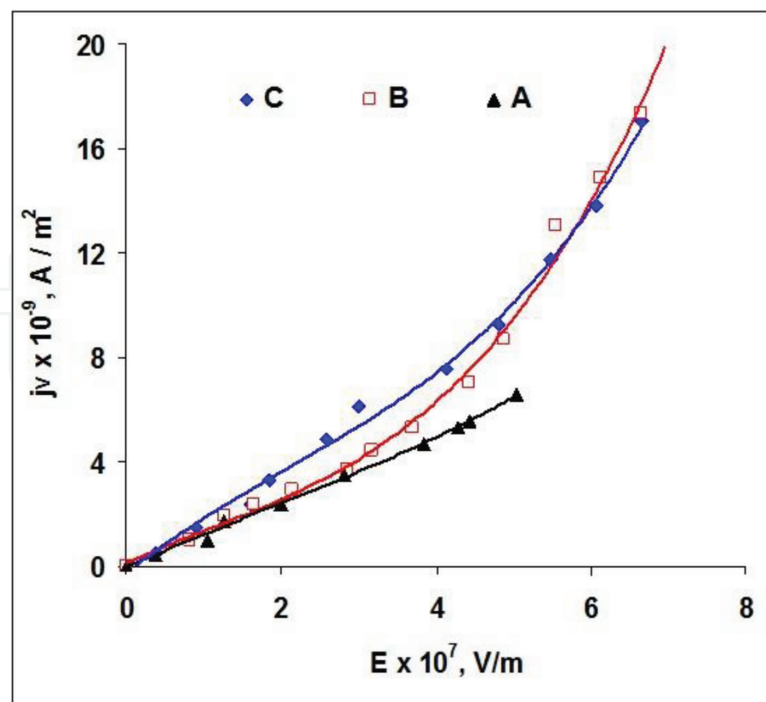


Figure 3. Characteristics of PET films. Films denotation according to **Table 1**.

Parameter “H” characterizes the migration of the charge carriers in the process of conduction. With an assumption of one carrier type (e.g., proton, $z = 1$), the path of protons in the PET tested amounts to 1.24 nm and is the same for the film stretched 3.5 and 4.0 times. The value calculated is probable if we consider the distances between PET macromolecules. The investigations of PET films by the method of wide-angle diffraction [19] prove that the phenyl ring planes of macromolecules in the crystalline areas are oriented in parallel to the film plane. The distance between the phenyl ring planes perpendicular to the film plane (i.e., toward field E)—thus toward the motion of charge carriers according to the calculation [19], it amounts to 0.32 nm. If the migration of charge carriers occurs in the noncrystalline areas of polymer, where the intermolecular distances are higher than 0.32 nm, the value of the charge hopping shift is real. **Figure 4** shows the comparison of theoretical and experimental $j = f(E)$ characteristics of PET films.

The conformity of current-voltage courses allows one to think that in the PET films tested, the conduction of charges is of ionic character. The resistivity of PET films calculated for the proportional range of characteristics $I = f(U)$ is for $R = 2.0 \times \lg \rho_v = 15.400 \pm 0.157$, for $R = 3.5 \times \lg \rho_v = 15.500 \pm 0.128$, and for $R_x = 4.0 \lg \rho_v = 15.277 \pm 0.177$. It seems that the structural differences in the films tested do not influence the DC conductance in a statistically significant way.

Urbaniak-Domagala has presented in her study [16] the tests results of DC conductance in polylactide film. The tests were carried out with the use of Al and Au rigid electrodes within the range of DC field from 8.3 to 33.3 MV/m. In DC field, polylactide behaves as PET, showing a low conductance, a transient in nature current flow, dependence of current density on the electrode material $j_{\text{PET-Al-PET}} > j_{\text{PET-Au-PET}}$ and a low energy of the conduction activation energy (0.4–0.7) eV that increases in the area of glass transition (0.9–1.1) eV.

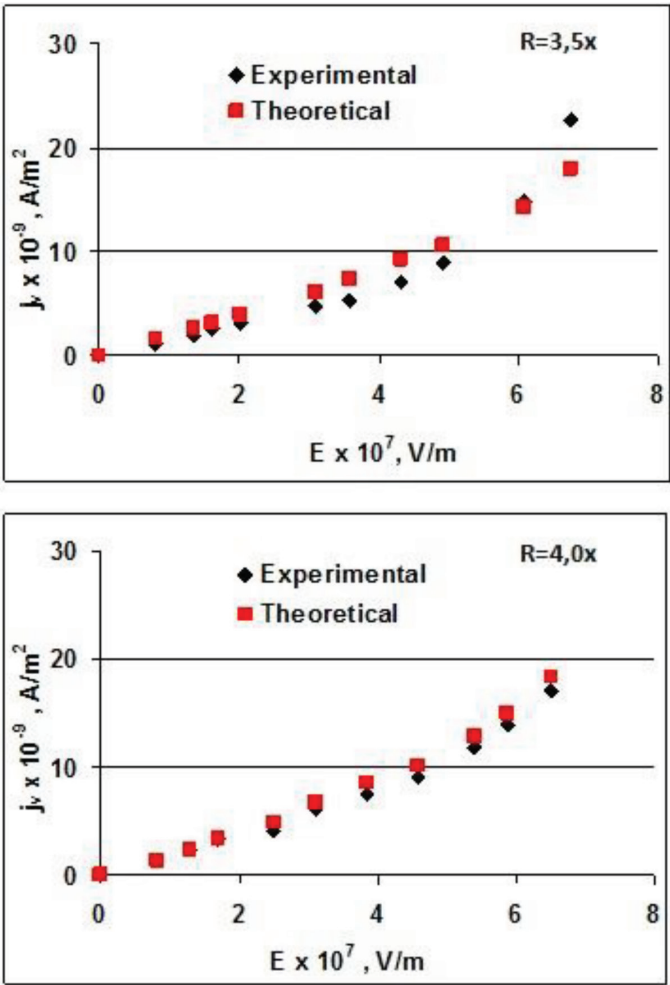


Figure 4. Comparison of theoretical and experimental density current - DC field intensity characteristics of PET films.

2.2. Effect of the medium relative humidity (RH) on the electric conductance of PET products in DC field

There are many examples of end products (films woven and knitted fabrics, nonwovens) designed for protective applications, such as electro-insulating barriers and protective clothing that are used under variable environmental conditions. Environmental factors bring about polymer aging [2]. Qualitative and quantitative tests of the polyester product aging have shown a significant effect of water vapor in air as an ionogenic factor that is permanently present during operational use, while the content of water vapor is variable as the relative humidity in the medium. The interaction of water vapor is dependent not only on the polymer absorption properties, but also on the product structure. This effect is particularly distinct in textile fabrics, where the fabric structure has a hierarchic character determined by complex systems of fibers with micrometric thickness, forming a yarn and the yarn threads form a higher structure such as thread repeat. The textile fabric structure intensifies absorption processes due to capillary processes that do not occur in monolithic products such as films or foils.

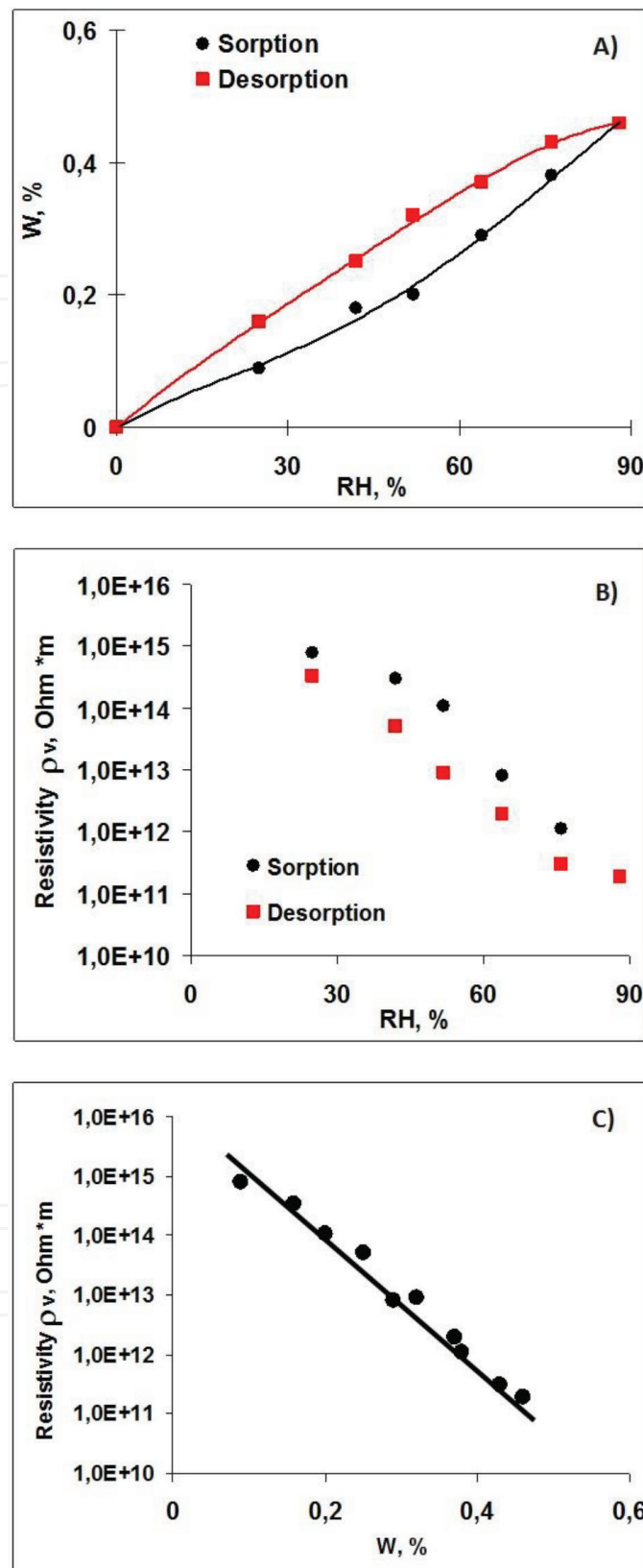


Figure 5. Effect of relative humidity (RH) of air in an isothermal medium on the volume resistivity " ρ_v " of PET woven fabric: (A) absolute humidity of woven fabric " W " = $f(RH)$, (B) ρ_v = $f(RH)$, (C) $\log \rho_v$ = $f(W)$.

The importance of the problem of the air humidity effect in environment on the processes of current flow in a product in DC field was presented using an example of woven fabric made of 100% PET fibers. In order to do that, the isochronal current absorption and current depolarization in the woven fabric for 10 min were examined using an electrostatic field intensity of $E = 1 \text{ kV/mm}$. The fabric was first purified and its surface weight was 100.0 g/m^2 and thickness of 0.2 mm . They used rigid electrodes with a diameter 50 mm and a constant unit load according to EN 1149-2:1999 + Ap1:2001, in a standard screened measurement system [16]. Before the tests, the woven fabrics were preheated to constant weight " m_s " considered as dry mass. Then, isothermal environment conditions were established ($t = 23^\circ\text{C}$) under which the air relative humidity was changed from 25 to 88% followed by return to the initial humidity 25%. For each variant of RH in the range of 25–88%, the samples were air conditioned for 24 h and then tested under these conditions. The tests were carried out in an air conditioning chamber Feutron. In parallel to the absorption and depolarization currents, the mass of moist fabric " m_w " was determined and then the absolute humidity of fabrics " W " was calculated from the dependence:

$$W = \left(\frac{m_w - m_s}{m_s} \right) \cdot 100\% \quad (6)$$

Figure 5 presents the effect of relative humidity (RH) of air in the isothermal medium on the volume resistivity " ρ_v " of PET woven fabric in the process of sorption followed by desorption.

Figure 5A shows that with increasing RH from 25 to 88%, the volume resistivity of PET woven fabric is decreased by about 1000 times. Changes in resistivity are nonlinear and conditioned by the modifying interaction of the molecules of water absorbed from air and physico-chemically and physically added to the fabric as shown by the sigmoidal character of the sorption and desorption isotherms (**Figure 5B**). Moreover, it is observed that the humidity and resistivity " ρ_v " depend on the way of reaching the physical equilibrium of sample by wetting or drying, which results in the hysteresis of humidity of fabrics and hysteresis of volume resistivity. The occurrence of hysteresis parameters proves how important is the definition of the fabric pre-conditioning and its acclimatization for tests.

The absolute humidity of woven fabric is an important factor influencing the processes of charge conductance and depolarization. For the PET woven fabric tested in the electrostatic field $E = 1 \text{ kV/mm}$, the volume resistivity " ρ_v " of the fabric as a function of humidity " W " (**Figure 5C**) satisfy the generalized dependence:

$$\log \rho_v = -aW + b \quad (7)$$

where: W —absolute humidity of fiber, $a = -10.559$, $b = 16.150$ (**Figure 5C**), which is consistent with the results of Morton and Hearle [20]. Based on the above dependence, one can estimate the volume resistivity of PET woven fabrics in the state of humidity $W = 0\%$ at a level of $\log \rho_v = 16,150$ with correlation coefficient $R^2 = 0.98$.

3. Static electricity of polyesters

Polyesters form a group of polymers with a high susceptibility to static electricity and a long lifetime of charges generated on surface and in volume. This feature results from a low

number of free charges and a low electric conductance. On account of a high Debye radius, a charge can be formed in both the polymer top layer and volume [21]. The mechanism of static electricity of polymers is complex since the electric loading state attained constitutes a resultant effect of three partial processes: charge generation, charge storage on polymer surface, and in its volume and charge decay by relaxation and transport. Each of these partial processes proceeds differently in the case of so-called contact electricity, triboelectric, induction, injection in corona and glow discharges, γ -irradiated, laser-irradiated, and UV-irradiated electricity [22, 23]. It is the contact electricity that has been best known, particularly in polymer-metal systems, on account of the possible specification of molecular and energetic parameters for metals. Already in studies [24, 25], attempts have been undertaken to model contact electricity with the assumption that in the polymer counter-surface contact, the charge carriers are transferred from one surface to the other contacting surface, while the direction of charge transfer depends on parameters such as: work charge exit from contacting surfaces, surface temperature, and initial concentration of charge carriers.

The next question to be solved is the assessment of the carrier nature responsible for electricity. Many authors believe that electricity depends on the injection of electrons from/to the polymer surface [26, 27]. The mechanism of contact electricity with the polymer-metal system is considered when we use the notions of band structure of a solid body (insulator or semiconductor) to describe the polymer energetic structure. For polymers, the occurrence of a wide band of forbidden positions and a specified work of electron exit are assumed. A characteristic feature is the occurrence of discrete donor and acceptor energetic states in the band of forbidden energies. These states are localized at the edges of conduction and valence bands. The succession of the presence of discrete states is the broadening of band edges. According to Fuhrmann [28], Fabish [25], and Mizutani [29], these states can trap the charge carriers and take part in contact electricity.

Energetic states localized in the polymer top layer are energetically different as a result from the presence of impurities, free radicals, absorbed molecules, products of polymer oxidation, ends and branches of macromolecules, and structural defects. The nature of localized energetic states is also modified by the polymer physical microstructure, mainly by the content of crystalline phase, shape, and perfectness of crystallite and interphase structures: crystallite-amorphous zone. The use of the notion of trapping states is convenient for the description of the processes of charge displacement and accumulation in polymeric dielectrics. The filling of traps with various charges leads to a permanent presence of charges in polymer.

An open issue is the investigation method of the distribution of the charge generated in polymers. The knowledge of charge distribution is indispensable for the identification of electric conductance processes, strength of polymeric dielectrics, and their aging as well as the mechanisms of polarization in polymeric electrets. The classic methods of investigating the distribution of charges and electric relaxation of polymers include the methods thermally stimulated currents (TSC) and thermally stimulated depolarization currents (TSDC) [30]. The drawback of TSC and TSDC methods is their destructive character in relation to the sample tested. Apart from the thermally stimulated method, they developed acoustic methods suitable for a direct use in testing polymeric insulations under voltage, measurements of the distributions of electric fields [31, 32], and tracing the development of polarization in polymers under high field voltage. Three types of acoustic methods using different techniques of acoustic wave

generation are now under improvement: laser induced pressure pulse (LIPP) [32], pressure wave propagation (PWP) [33], and electrically stimulated acoustic wave (ESAW) [34–36]. The analysis of signals from polymers affected by impulsing allows one to diagnose the space distribution of charge in polymers. According to the opinion of Motyl [37], the use of two measurement methods, for example, PWP and ESAW increases the reliability of results and extent the range of diagnosis. In PWP method, the deformation wave causes local changes in free and polarization charges in time, which is a source of the signal observed. In ESAW method, the applied voltage impulse to sample generates a signal from the whole charge and the homogeneously distributed dipoles are not detected.

3.1. Contact electricity in the PET film-metal system

Hennecke et al. [24] have proposed an analog model of polymer electricity consisting in contacting with metals in the interrupting way repeated until the charge is established. The qualitative interpretation is based on the concept of the band polymer model, where the occurrence of the energetic levels of forbidden bands and heights of barrier between these levels in polymer were taken into account. The static electricity of polymers with the repetition of contacts has been also analyzed by Fuhrmann [28], Fabish and Duke [25], Lowell [26] and Mizutani et al. [29]. Fabish and Duke have observed a reversible change in the sign of charge transferred on polymer from metals after successive contacts. These authors explain this phenomenon with the presence of charges in the form of molecular ions in the polymer top layer. These ions form local energetic states.

Mizutani et al. [29] have determined the properties of the metal-polymer contact by means of the photo-injection of electrons from metal (Cu, Al) to PET, indicating the existence of energetic states on the surface of PET. These researchers also assessed the density of surface states amounting to $1.7 \times 10^{14} \text{ (cm}^{-3} \text{ eV}^{-1}\text{)}$ and confirmed a strong dependence of the contact energetic barrier on atmospheric conditions, including the presence of adsorbed oxygen molecules on the PET surface. Oxygen molecules, on account of a high affinity of electrons, can form surface states and act as electron traps. According to the opinion of Brennan et al. [38], during single and multiple contacts of polymer with counter-surface a charge is created whose range is limited to a depth of maximum 3 nm.

Lowell [26, 27] proposes a mechanism of charge transfer from metal to polymer (PET and PTFE). In the case of a single contact of polymer and metals (Al, Pt, and Hg), Lowell has found that the charge density does not depend on the type of metal. He puts forward a thesis that during a single contact, the tunneling of electrons occur from metal to traps in the polymer top layer, but the system does not reach thermodynamic equilibrium. The difference in electrostatic potentials created in the charge layer is inadequate to increase the energy of trap levels up to the Fermi energy of the metal. Only with a multiple contact, the charge is transferred to a higher depth. Then, it is possible to reach the equilibrium state. Lowell predicts the achievement of equilibrium charge density that will be linearly dependent on the metal work-function.

3.1.1. Contact electricity in the PET film-Al, PET film-Au systems

In this study, the susceptibility of PET film to static electricity in contact with metals (Al and Au) was investigated. Two pairs of cylindrical electrodes made of brass with a diameter of

50 mm and a height of 30 mm were used. Au and Al metals were evaporated onto the polished cylinder surface in the glow discharge aided with Argon. The coatings obtained were characterized by a high stability of the joint with the substrate, which made it possible to purify the surfaces before the tests of contact electricity. The PET films purified and devoid from charges were located between earthed electrodes in the following systems: Au-PET-Au and Al-PET-Al for 60s and then the electrodes were taken off in a frictionless way. The measurements of the sample surface charge were carried out in a contactless way by means of the probe of field intensity meter in the system described in paper [16]. During repeated contacts, the surface charge increased up to the saturation state that was obtained with the number of contacts of at least 100. The contact electricity was performed for PET film samples described in **Table 1**. The test results obtained are listed in **Table 2**.

3.1.2. Contact electricity of activated PET surface films

In this study, we also attempted to answer the question how the activation of PET surface influences its susceptibility to electricity. To that end, the films were subjected to an activating plasma treatment. The process was realized in a low-temperature plasma, in glow discharge RF under reduced pressure air with the use reactor system described in paper [39]. The test results were supplemented with the examinations of the sample volume and surface resistivity in DC field with the use of rigid Al electrodes.

In **Table 2** are listed the test results of volume and surface resistivity in contact with Al electrode, surface density of the charge were generated in contact with Au and Al metals. The resistivity was calculated on the basis of absorption and depolarization currents according to proceeding Badian [17]. The polarization component of the PET film surface free energy before and after the plasma treatment is also shown.

Based on the tests of the surface and volume resistance of untreated films (**Table 2**), one can think that the structural changes expressed by the crystallinity degree ranging from 7.4 to

Draw ratio	Treatment time, min.	$\lg \rho_s$	$\lg \rho_v$	$\sigma \times 10^{-11}$ C/cm ² , PET-Au	$\sigma \times 10^{-11}$ C/cm ² , PET-Al	$\gamma_p \times 10^{-3}$, N/m
R=2	0	15.776 ± 0.188	15.400 ± 0.157	-5.1 ± 3.0	-6.7 ± 3.0	10.5
	3	15.652 ± 0.148	15.075 ± 0.128	-3.3 ± 2.0	-4.2 ± 2.1	28.2
	10	15.615 ± 0.168	15.143 ± 0.209	-3.4 ± 2.0	-4.8 ± 1.5	32.2
	30	15.601 ± 0.211	15.114 ± 0.133	-0.7 ± 0.5	-2.7 ± 1.3	32.0
R=3,5	0	15.700 ± 0.043	15.500 ± 0.128	-6.6 ± 3.2	-8.8 ± 1.2	11.8
	3	15.553 ± 0.215	15.292 ± 0.165	-3.9 ± 1.3	-5.2 ± 1.3	30.4
	10	15.538 ± 0.204	15.281 ± 0.094	-2.4 ± 1.9	-4.0 ± 2.0	30.4
	30	15.580 ± 0.208	15.283 ± 0.232	-0.9 ± 0.5	-2.2 ± 1.0	32.8
R=4,0	0	16.306 ± 0.398	15.277 ± 0.177	-5.2 ± 4.0	-8.6 ± 3.5	11.1
	3	15.957 ± 0.080	15.095 ± 0.135	-3.0 ± 1.9	-3.6 ± 1.8	29.9
	10	15.932 ± 0.118	15.085 ± 0.143	-3.0 ± 2.0	-4.4 ± 2.7	33.5
	30	15.750 ± 0.190	14.952 ± 0.230	-0.9 ± 0.5	-2.0 ± 0.7	33.5

Table 2. Results of testing the surface properties of untreated and air plasma-treated PET films (power 100 W, flow 100sccm, pressure 20mTr).

19.8% and the Herman's coefficient of orientation from 0.12 to 0.58 do not influence, in a statistically significant way, the DC conduction in the top layer and volume of the films. Also, no significant effect of changes in physical structure on the level of charge generated in contact with Al and Au metals was found. On the other hand, a significant effect of the metal type on the charge value is observed. The density of charge generated on the PET film surfaces in contact with aluminum is higher than that in contact with gold. Let us assume Lewell hypothesis [26] that the value of static charge depends on the difference in the exit works of materials in contact. According to Davies [40], the values of the exit work of the material tested are arranged in the following sequence PET > Au > Al. This relation of exit works justifies the negative sign of charge generated on the PET surface in contact with metals, as well as the higher charge density in contact with aluminum compared to that in contact with gold.

The processes of static electricity of polymers are typical surface processes. The physicochemical and physical states of surface are of importance for the course of contact electricity processes. In this study, the physicochemical and physical properties of the PET film top layer were modified by air plasma treatment. The physicochemical properties of PET films were assessed by measuring the contact angle with water and methylene iodide and the free energy calculated according to procedure of Owens and Wendt [41]. In **Table 2** are listed the values of the polar component of the surface energy of films treated with plasma. The dispersion component was unchanged and therefore it was omitted. The plasma treatment was carried

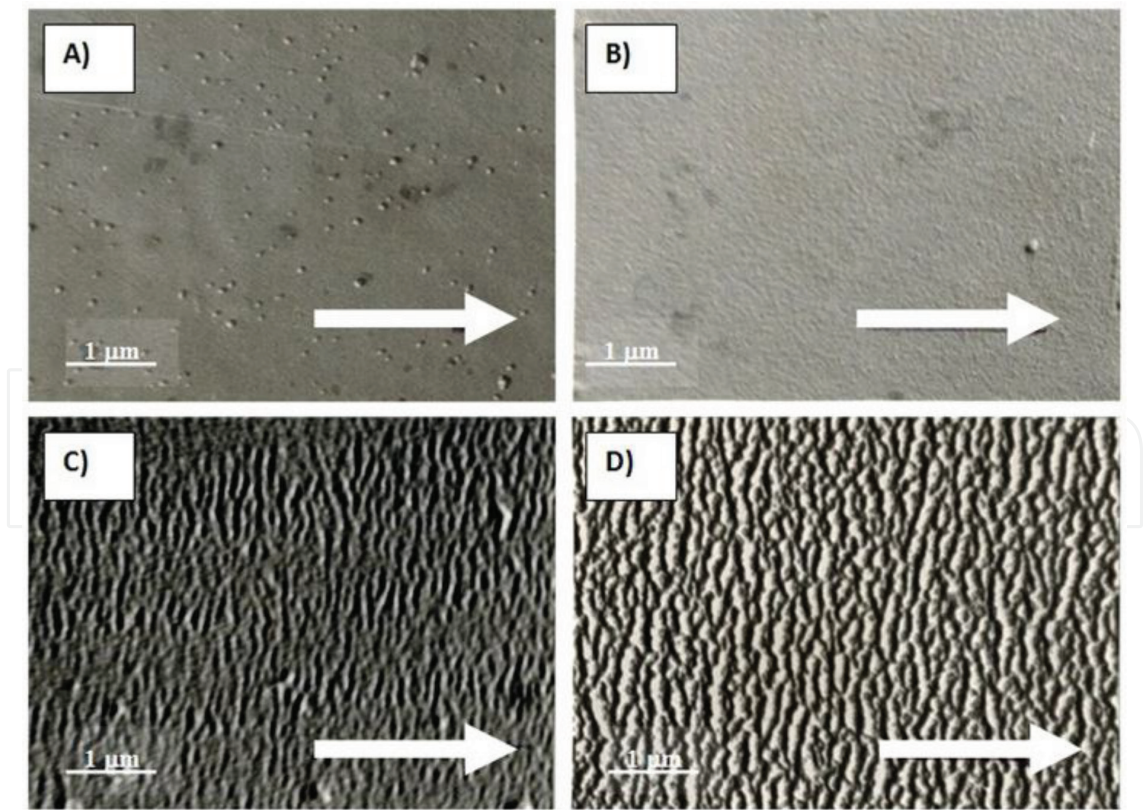


Figure 6. Electron microscopy images of PET film surface, (A) untreated; treated with air plasma (power 100 W, flow 100 sccm, pressure 20 mTr): (B) 1 min, (C) 3 min, (D) 30 min. The arrows show the direction of films orientation.

out for 1–30 min. Already from 1 minute to 3 minutes, the plasma treatment strongly increases the polar component of the top layer of the PET films. The physicochemical changes result in a negligible decrease in the value of surface and volume resistivity of the films. The PET film surfaces modified with plasma in contact with Al and Au metals still show a negative charge, but the surface density of charge in PET films is significantly decreased. The generation of charges is the more weakened, the longer the surface was treated with plasma. These changes can be related to the surface physical state. The plasma interaction causes significant physical changes in the film surface microtopography. **Figure 6** shows the electron microscopic images of the PET film surfaces treated with plasma for 1, 3, and 30 min.

The effect of etching the polymer in its top layer that intensifies with increasing the plasma treatment time is observed. The surface is curved to form groove cavities located crosswise to the direction of stretching the film. The height of microroughness of surface subjected to plasma exposure for 30 min. With the strongest effect of etching can be assessed to about 0.04 μm . The character of surface carving is conditioned by the physical microstructure of PET. Based on the hypothesis of the polymer semi-crystalline structure, they are distinguished into two principal phases: crystalline and amorphous phases. The crystalline phase is characterized by a high energy of molecular cohesion that conditions its particular resistance to destructive factors, such as heat and the forces of interactions with plasma molecules. Considerably less resistant is the amorphous phase, in which the interaction between molecules are statistically incidental, and this phase is etched in the first place. In the image of the etched top layer, the protrusions seem to be formed by the crystalline phase of PET periodically occurring with long period in macro-fibrils. The etching effect generates the coarseness of surface that intensifies with prolonging the plasma action. The surface coarseness determines the real surface of film contact with metals. The coarser the surface, the lower is the charge that was found in measurements.

4. Polyester electrets

Electrets are materials in which a permanent electric charge occurs. The charge in electrets is stable for a longer time and its stability depends on the type of materials and exploitation conditions. It can last for years, while the material is an active source of electric field. The electrets are widely used in dust and gas filters, micro-machines, xerography, electro-acoustic transducers. Many electro-insulating polymers are used as electret precursors, including dipole (PET, PMMA and PS) and nondipole polymers (PTFE, PP and PE). The use of precursors in the form of films allows one to miniaturize the devices based on electrets. The charging state of electret material is obtained in various ways [22, 32, 46] using triboelectric effect (triboelectrets), DC electric field (thermo-electrets), UV and VIS radiations (photo-electrets), β and γ radiation (radio-electrets), glow and corona discharges (corona electrets).

Polyesters are materials with potential use as electret precursors owing to their susceptibility to dipole polarization and good mechanical parameters. Thermoelectrets are made by polymer polarization in DC electric field under conditions above the glass transition temperature and then after charging, they are refrigerated to freeze the state of oriented dipoles. The surface

charge formed is called heterocharge if its sign is opposite to the sign of electrode potential in contact and is connected with ordering the dipole polarization or the separation of already existing free charges. The homocharge has a sign consistent with the electrode potential sign in contact during the electret formation and shows the incorporation of charge carriers from electrode. During the formation of thermo-electret in the external electric field, the relaxation polarization component influences the process of dipole polarization.

Two types of the relaxation mechanisms were found: α - and β -relaxation. The former one occurs at temperatures above the glass transition temperature of PET or at a low field frequency, while β -relaxation appears at lower temperatures below the glass transition temperature of PET or at higher field frequencies. According to the present views, α -relaxation results from the co-operative motion of the kinetic units of macromolecule chain with discrete changes in the energy of orientation positions in the electric field. Groups $\text{—O—CH}_2\text{—CH}_2\text{—O—}$ and p-phenyl bonds are the kinetic units in PET. According to Saito et al. [13], the active kinetic units of polymer contain more than one mer macromolecule. Peruccini et al. [42] present the opinion that α -relaxation is an isotropic process and occurs in amorphous areas.

The process of β -relaxation occurs under conditions of a limited mobility of the main chain of macromolecule as a result of the rotation movements of single groups of atoms —(CO—O)— [6, 13, 43] with a stable dipole moment around the axis consistent with the axis of polymer orientation. Because of a considerable intermolecular interaction of the group of atoms, the process of β -relaxation shows an anisotropic nature [6, 13, 44, 45] and occurs in both amorphous and crystalline areas. Time changes leading to the stabilization of electret caused by relaxation processes and also by the effect of environmental conditions are known as aging [46, 47]. The study [16] describes the formation of thermo-electret from the PLA film precursor by isothermal polarization and demonstrates a stabilized density of surface charge and the dependence of charge level on the polarization intensity of filed E_{polar} and charging time. In the case of field intensity $E_{\text{polar}} < 20 \text{ MV/m}$, the heterocharge is observed that is stabilized in the processes of dipole relaxation and volume charge within 30 days. The use of higher field intensities $E_{\text{polar}} > 20 \text{ MV/m}$ results in the transition of homocharge into heterocharge, which can be caused by the process of an additional injection of charge from electrodes or a change in the direction of dipole moment of molecular dipoles [48]. The prolongation of the PLA isothermal charging results in an increased charge density on the surface, which is consistent with the theory of isothermal dipole polarization, according to which the charge density exponentially depends on the charging time and relaxation time.

In the method of electret formation by irradiation with UV, VIS or ionizing β and γ , in the precursor electrons are excited from the basic state and the deep traps to the conduction band. The precursor in that time is in electric field, where a directed transport of charge carriers and trapping in new positions take place. Once the field and irradiation are turned off, the precursor shows a stable heterocharge. Zllangr et al. [23] analyzed the state of energetic traps the PET radio-electret made during the exposure to γ irradiation. The authors quantitatively characterized the average depth of trap level, density and distribution of traps by the technique of thermally stimulated currents (TSC). As precursor they used PET from various stages of production: an amorphous film, oriented in two directions and film crystallized in the process

of heating. The processes of molecular orientation, increasing the content of crystalline phase and irradiation caused an increase in the depth of localized states from 1.36 to 2.15 eV linearly with increasing the molecular orientation, from 1.20 to 1.40 eV with increasing the content of the PET crystalline phase and from 1.30 to 1.70 eV with increasing the dose of γ radiation. In the interpretation of authors [23], the processes of polymer crystallization, orientation of macromolecules and ionizing radiation cause new structural defects: on the crystallites-noncrystalline border, along the border of oriented and nonoriented areas as well as cracked polymer macromolecules due to radiation, confirmed by a decrease in the molecular weight. An increase in defects generates new types of localized energetic levels, an increase in their number, decomposition, and depth. In the study [23] three models of traps are proposed, in relation to three methods of the PET treatment on the basis of quantitative data of TSC.

Currently, a great importance is ascribed to electrets in which a permanent charge is incorporated by the injection from external sources by means of corona or glow discharge [22, 49]. A charge is incorporated into polymer located in the zone of the electrode of glow discharge. Blade electrodes with a high potential generate in space electrons and various types of ions [50, 51] that recombine on the polymer surface, causing chemical changes and the residue diffuses into the polymer top layer and is trapped. During corona discharge, double bonds $C=C$ and carbonyl groups are formed that can constitute additional traps for current carriers. Charges are accumulated near the polymer surface. The relative depth of charge localization related to the film thickness is assessed to 5%. Charging at increased temperature increases the stability of electret, which is exploited in the formation of pneumo-thermal nonwovens. The process effects are closely dependent on the gas composition and air humidity, if it proceeds under atmospheric conditions [52]. The mechanism of a permanent charge in material proceeds as in glow discharge. A decrease in the process pressure makes it possible to perform the synthesis of polymer and the simultaneous charging of the polymer that shows the features of electret [53].

5. Imparting electro-conductive and antistatic properties to polyesters

Polyesters (PET) have found their use as antistatic and electro-conductive materials. An increase in electric conductance of polyesters has been obtained to provide an effective dissipation of electrostatic charges and reduce electrostatic discharges. Owing to that, the use of polyester materials/fabrics has become safe, particularly in areas endangered with explosion and for workers using protective clothing. A high level of polyester conductance can be obtained by making polymeric composites. Composites are made according to two conceptions. The first one consists in combining at least two components, where the polymeric matrix is formed by polyester in which a conducting phase is scattered. The conducting phase can consist of: metal particle, carbon black, carbon fibers or nano-tubes, graphene, metalized fibers, conducting salts, and organic conductors, for example, conjugated polymers. The type of the scattered phase determines the electric conduction of composite. The scattered phase should be used in a quantity not lower than the percolation threshold. The value of

Type polyester substrate	Resistance related to the fabric square, R_{\square} [Ω/cm^2]		
	unmodified	Antistatized, non rubbed	Antistatized, rubbed (according to PN-EN ISO 105-X12)
PLA	$4.4 \pm 1.3 \times 10^{12}$	$2.0 \pm 0.4 \times 10^4$	$6.1 \pm 0.5 \times 10^4$
PET	$1.5 \pm 0.4 \times 10^{13}$	$7.2 \pm 0.3 \times 10^4$	$1.4 \pm 0.3 \times 10^5$
PC	$3.6 \pm 0.8 \times 10^{11}$	$5.1 \pm 0.2 \times 10^4$	$7.5 \pm 0.7 \times 10^4$

Table 3. Test results of different kinds of antistatic polyester films coated with polypyrrole (test conditions $t = 23^{\circ}\text{C}$, $\text{RH} = 25\%$).

percolation threshold depends on the coefficient of the shape of conducting particles, their dimensions and arrangement in the matrix [54–56]. Particularly beneficial is the use of nano-phase scattered in PET and PLA [57–64]. The lower the value of percolation threshold, the more beneficial are the mechanic properties of composite.

The other conception of making composites consists in coating the polyester surface (substrate) with the conducting phase. The examples of conducting phase include: metals condensed on polyester surfaces by the PVD technique [65], conjugated synthetic polymers such as polyaniline and polypyrrole [62–64] deposited by the “in situ” technique or CVD, carbon nano-tube, and graphenes deposited by the printing technique [61, 66–70].

Table 3 presents the results of our own studies obtained for conducting composites such as PET-PPy, PLA-PPy, PC-PPy with polypyrrole coating (PPy) deposited by the CVD method. Surface resistance measurements were carried out according to standard PN-EN ISO 3915. The specific resistance related to the fabric square, expressed as, R_{\square} [Ω/cm^2], was the quantitative parameter of resistance properties. The polypyrrole coating imparts antistatic properties to polyesters. The combination of PPy with PET substrates is stable and resistant to the mechanical wear conditions.

Antistatic polyester composites find many applications as conducting elements of electronic circuits, sensors, semi-transparent, and elastic electrodes in electronic-organic elements, opto-electronic and e-textiles, active layers, and transporting charge carriers in organic electroluminescent diodes and elements of organic solar cells.

6. Conclusions

The presentation of electric properties of polyesters including conventional and biodegradable polymers indicates that these polymers are continually an attractive group of materials. In polyesters, many problems concerning their behavior in electric DC field are still open as a subject of fundamental research. This type of thermoplastic polymers is continually subjected to various chemical and physical transformations, owing to which polyesters offer newer and newer solutions for the market and economy needs.

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