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EFFECT OF CHEMICAL TREATMENT OF POLY(ETHYLENE TEREPHTHALATE) SURFACES ON MECHANICAL AND WATER-SORPTION PROPERTIES

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A suitable method to functionalize the surface of polyethylene terephthalate (PET) consists in the chemical treatment with different amines such as triethylenetetramine (TETA), or tetraethylenepentamine (TEPA).

The paper describes the influence of PET surface amination on the mechanical and water-sorption properties. Superficial chemical treatment involves micro-structural changes such as molecular rearrangements in the amorphous and crystalline region respectively, which in turn, are reflected in mechanical properties. The abilities of these materials to resist loads and deformation and also, to absorb energy were affected by the amination of the surfaces. Additionally, the presence of amine groups on the PET surface increases the water sorption capacity.

The activation of PET surface using amines leads to producing of new binding sites for collagen immobilization and thus, improves the biocompatibility of this material.

Keywords: Poly(ethylene terephthalate), mechanical properties, water sorption capacity, surface functionalization

1. Introduction

Various strategies of surface alteration have been developed over the time, because the biological response to materials and devices is largely controlled by materials surface chemistry and structure. The surface modification can be carried out by physical or chemical changes, using different techniques such as immobilization of biological molecules, irradiation of surfaces followed by grafting [1], etc.

Many methods have been developed to control the surface functionality such plasma, corona discharge, radio frequency (rf) discharge, ion beam

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irradiation, different surface modification techniques giving specific surface functionality on the polymer surface.

Poly(ethylene terephthalate) (PET) is one of the most versatile polymers used as films in many biomedical application due to its excellent mechanical properties and moderate biocompatibility [2,3,4]. PET is efficacious for these applications due to its chemical, physical and mechanical properties [5]. The methods used to increase the hydrophilicity of the PET surface and/or to introduce specific functional groups on them are: controlled chemical breaking of ester bonds [6,7,8,9,10], surface grafting polymerization [11,12,13] and plasma treatment [14,15,16,17,18].

PET belongs to oriented semicrystalline polymers containing both crystalline and amorphous fractions [19].

The aim of this work was to increase hydrophilicity of PET surfaces using chemical modification with two amines triethylenetetramine (TETA) and tetraethylenepentamine (TEPA), as it is notorious that PET has a pronounced hydrophobic character. The activation of PET surface using these amines would create new binding sites in order to immobilize further proteins such as collagen.

The results presented in this study also demonstrate that aminolysis of polymer surfaces may be used as a functionalization method for the adsorption of proteins. The surface properties induced the protein adsorption behavior. Changing the chemical functional groups present on the surface affects several surface properties, which may all influence the protein adsorption process.

The influence of PET surface amination on the mechanical and water-sorption properties was investigated in this study. The major differences were found in the carbonyl region assigned to the formation of amides and hydroxyl groups.

So, we have compared the mechanical properties (Young modulus, elongation at break and elastic resilience) before and after surface reaction of PET with these two aminolysis reagents. The functionalized films with TETA and TEPA show a higher ability for water adsorption than the original films, due to the increase of hydrophilic content on the film surfaces.

2. Characterization of chemically functionalized PET surface

Biaxially oriented PET film samples (5 x 5 cm^2), produced by S. C. TEROM of Iasi-Romania, were used as previously was reported [20]. Thus, the PET surfaces were aminolyzed using a sandwich model, in dark, at 90° C for different times (10 and 20 min), in an oven. This procedure allows the functionalization only on one side of the PET films. For this test two types of amines were used: triethylenetetramine (TETA) and tetraethylenepentamine (TEPA). After chemical treatment, the samples were rinsed with ethanol and tridistilled water, and ultrasonically cleaning to remove the reagent excess. The treated samples were denominated as following: PET-TETA 10 and PET-TETA 20 for the PET films treated 10, respectively 20 min with TETA; PET-TEPA 10 and PET-TEPA 20 for the PET films treated 10, respectively 20 min with TEPA.

The FTIR-ATR spectra of the unmodified and modified PET samples are shown in Fig. 1.

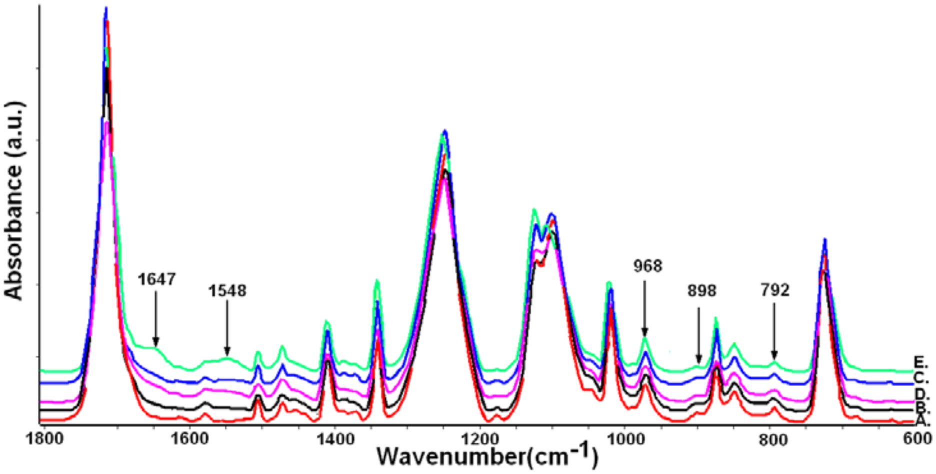

Fig. 1. FTIR-ATR spectra of the original and modified PET films between 1800-600 cm^{-1}: A. PET; B. PET-TEPA-10; C. PET-TEPA-20; D. PET-TET-10; E. PET-TETA-20.

All the samples were characterized through infrared spectroscopy, a valuable method for the analysis of polymer functional groups. The spectra were acquired using a Bruker Vertex 70 FTIR spectrometer equipped with a Specac Golden Gate ATR accessory. The spectra were recorded in the range 4000-600 cm^{-1}, with a resolution of 2 cm^{-1}, and the signal-to noise ratio was improved by co-adding 64 scans per spectrum. Subsequent manipulation was carried out with Opus 6.5 software. For all treated PET samples, it has been demonstrated that functional groups containing nitrogen were present onto PET films surface [20].

Thus, from these spectra it is observed the appearance of some new peaks at 1647 cm^{-1} assigned to amide I, and at 1548 cm^{-1} assigned to amide II. Likewise, the intensities of the 849, 1386 and 1471 cm^{-1} peaks associated with trans isomer increase and gauche isomer peaks at 898, 1340 and 1456 cm^{-1} decrease (Table 1).

The aminolysis rate depends on the polymer morphology, crystallinity values, relative humidity and temperature. The process of aminolysis involves changes in density due to the scission of chains in the amorphous regions resulting in short chains with a sufficient mobility, which can further crystallize. The crystallinity changes of the modified PET films analyzed in the present work used the 793 cm^{-1} band intensity as internal standard for measuring the content of the trans and gauche conformation isomers (Table 1). The determination of conformer content units by infrared spectroscopy use the 968 cm^{-1} band intensity of the trans isomer (O–CH_2 stretching vibration) and the 898 cm^{-1} band intensity of the gauche isomer (glycol segment). The used reference band was from 793 cm^{-1} (CH aromatic deformation mode) [21].

Table 1

Contents of the trans and gauche conformation isomers of the original and modified PET films

Sample	I_{968}/I_{793}	I_{898}/I_{793}
PET	2.17	0.74
PET - TETA 10	2.19	0.61
PET - TETA 20	2.5	0.59
PET - TEPA 10	2.23	0.63
PET - TEPA 20	2.67	0.57

3. Mechanical properties of the functionalized PET surface

Physico-mechanical analysis demonstrates the extent of the super molecular modifications of polymers obtained as a function of their structural changes. In this context, stress–strain measurements were performed at room temperature on dumbbell-shaped samples (1 mm thickness), on an Instron Single Column Systems tensile testing machine (model 3345) equipped with a 1 kN load cell and activated grips, which prevented slippage of the sample before break, operated according to SR EN ISO 527:1996. The used cross-head speed was 10 mm/min and the gauge length 40.0 mm. Stress-strain graphs reveal that there are two ranges in the diagrams, representing different behaviors of these materials. The elastic range includes the region where the specimen regains its original dimensions upon removal of the load. Beyond this domain, there is the plastic range where permanent deformations take place. Sometimes, the initial elastic range is a straight line and the stress-strain relation is expressed by Hooke's Law, can be evaluated using equation (1):

$$E = S/\varepsilon \quad \text{or} \quad F/A = E\,\Delta L/L \tag{1}$$

where E – modulus of elasticity or Young's modulus; S – stress; ε - strain; F – the applied force; A – the cross-sectional area of the material; ΔL - the change in length that results after the stress is applied and L - the original length of the material [22].

From the stress-strain diagram some mechanical properties such as strength, deformation and energy properties of the material can be obtained. These represent the abilities of materials to resist loads, to withstand deformation, and to absorb energy, respectively.

Elastic strength represents the transition from the elastic to the plastic range where permanent deformation takes place. For the materials with linear stress-strain relations in the elastic range, the elastic resistance of them to deformation is expressed by the elasticity modulus. This modulus is associated with all inter-and intra-molecular elastic forces from the polymer matrix which are opposing deformation. The larger the Young's modulus, the more stress is required to stretch the material to the same extent. Physically, this means that the elastic modulus is a measure of the mechanical energy density of the system.

Another material property is resilience, which represents its ability to absorb energy or internal work in the elastic range. This property is quantified by the modulus of elastic resilience (U) and is equal to the internal work done in stressing a unit volume of the material to the elastic, according to equation (2):

$$U = {Sp^2}/{2E} \tag{2}$$

The effect of the short time treatment of the PET surface with amines, involves micro-structural changes such as molecular rearrangement in their amorphous and crystalline region, which is subsequently reflected in their mechanical properties, including elastic and plastic deformation as well as thermal stress.

The stress-strain curves of samples used in this study are presented in Fig. 2 and Fig. 3. The presence of amino groups on PET surface (TETA and TEPA) produces a different impact on mechanical properties.

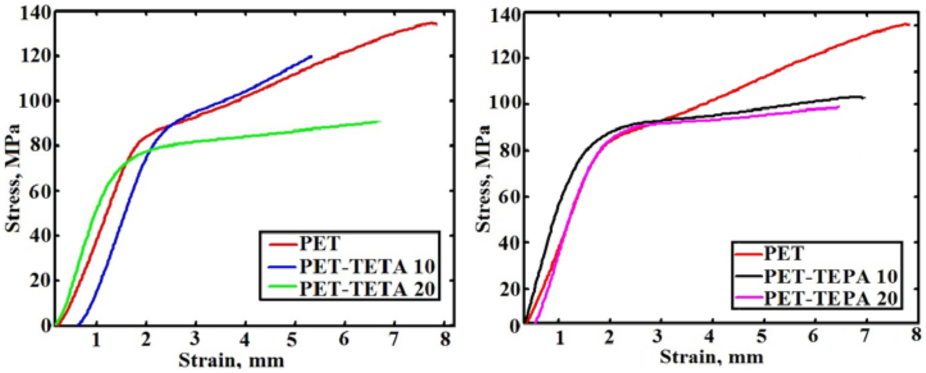

Fig. 2. Stress-strain curves for the aminated PET surfaces

For a moderate time of aminolysis, in several cases, the treatment time did not have a statistically significant effect. However, at a first glance of the stress-strain curves it may be noticed that the aminated samples behave differently than control sample. Thus, PET-TETA 20 and PET-TEPA 10 respectively, are more elastic than another, phenomenon noticed both in the stress-strain curves (Fig. 2 and Fig. 3) and also in the elongation at break values (Table 2).

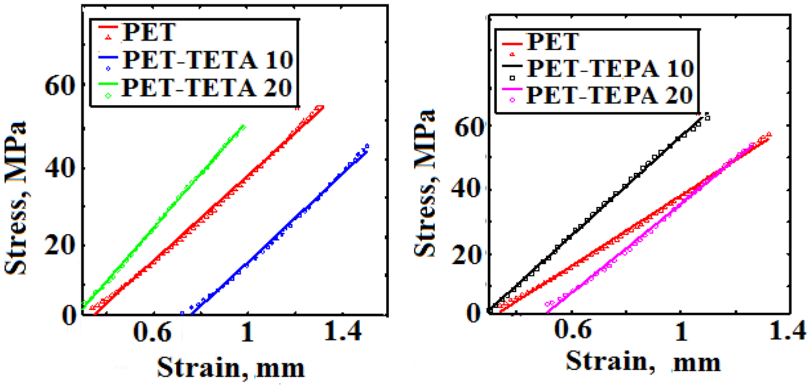

Fig. 3. Stress-strain curves in the elastic range for the aminated PET surfaces

Thereby, the elongation at break decreases with the increasing of reaction time. For all the functionalized PET surfaces, the Young modulus in the elastic range has a higher value than for the blank sample, but the evolution, as a process, is specific for each sample (Table 2).

Table 2

Tensile properties of PET samples

Sample	Young's modulus[a], (MPa)	Elastic resilience, (MPa)	Elongation at break, (mm)
PET	55.04	28.43	7.88
PET-TETA 10	56.69	17.41	7.14
PET-TETA 20	69.53	18.60	6.73
PET-TEPA 10	77.27	26.68	7.03
PET-TEPA 20	69.43	20.69	6.73

[a] calculated in the elastic range

Thus, for all samples, the elastic modulus increases with the reaction time. A higher modulus shows that the polymer is more structured, more rigid and has more physical and chemical cross-linking.

One of the possible interpretations and mechanisms responsible for this phenomenon can be the following. When the applied stress increase, the forces impeding deformation are increasing due to the rearrangement of the macromolecules after aminolysis process. This is due to the crosslinking effect, resulting in the formation of rigid-segments. This behavior is most likely due to the steric requirements involved during the orientation and attachment of the amine to the carbonyl ester group in the aminolysis reaction. Thus, the aminolysis acts as a plasticization of PET surfaces. On the other hand, when the liquid and polymer have similar solubility parameters, the solvent-polymer interactions become significant. The solubility parameter of PET has been recorded as 10.7 while the value for pure TETA is 10.76 [23]. The interactions cause the increase of molecular segments mobility by lowering the intermolecular bonding forces. When these interactions become strong enough, the polymeric chains may be mobile to rearrange into lower thermodynamic energy, a crystalline conformation. Since the solubility parameter for TETA and PET are quite similar, it is expected to provide sufficient plasticizing of the polymer.

4. Humidity absorption study

Another goal of this study was to establish the water vapor sorption behavior and physical stability of the aminated PET samples using the IGAsorp system (a fully automated gravimetric analyzer supplied by Hiden Analytical, Warrington - UK). The IGAsorp is a standard sorption equipment, which has a sensitive microbalance (resolution 1μg and capacity 200 mg), which continuously records the weight of the sample together with the temperature and relative humidity (RH) around the sample. The vapors pressure was increased in 10% humidity steps, every having a pre-established equilibrium time between 10-15 minutes. The drying of the samples before sorption measurements was carried out at 37 ^{o}C in flowing nitrogen (250 mL/min) until the weight of the sample was in equilibrium at RH<1%.

The material properties can change as a function of humidity and temperature, and the interactions of water molecules with the surfaces are of high importance. These interactions include physical adsorption, chemical bonding and hydroxylation. Water sorption can also induce bulk changes such as hydration and amorphous phase transitions [24].

The sorption/desorption isotherms of the PET samples are presented in Fig. 4.

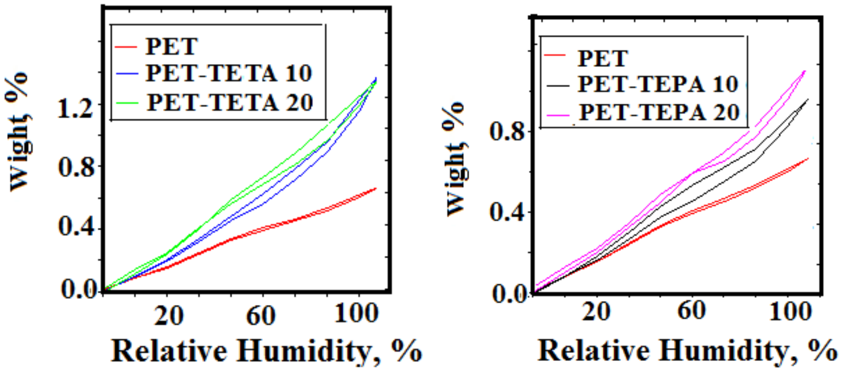

Fig. 4. Sorption-desorption isotherms of the PET samples

From these figures it may be noticed that the increase in reaction time leads to an increase of water sorption capacity caused by the modification of the surface. The new materials become more heterogeneous and rough. The moisture sorption/desorption isotherms are similar with type V, according to IUPAC classification, isotherms characteristic for hydrophobic materials with weak water-sorption interactions [25]. The impact in the moisture comes from their rapid absorption and desorption of moisture for all treated samples as compared with untreated PET surface exposed to the same equilibrium moisture conditions.

As expected, the presence of amine and amide groups on the PET surface increases the water sorption capacity of the samples, this fact improving the biocompatibility of the materials.

5. Conclusions

Chemical modifications of PET films using aminolysis is a reliable functionalization method of polyester surfaces. This procedure has an important role on PET films surfaces, introducing new functional groups. Infrared spectroscopy has revealed that reaction of „aminolysis" induce scission of polymer chains and increase the hydrophilicity due to the increase of hydroxyl, amine and amides groups on the PET film surface.

Infrared spectroscopy was also used for measuring of the crystallization degree and the content of the trans and gauche conformation isomers in the original and modified PET films. For all treated samples, the total content of the trans and gauche conformation isomers are modified. The films functionalized by TETA and TEPA show a higher ability for water adsorption than the original films, due to the increase of hydrophilic content on the film surfaces. Young's modulus of the modified PET films and the stress before breakage increases with increasing content of the trans isomers on surface treated PET films, effect of aminolysis reaction.

The amount of water absorbed at a given temperature is dependent of the modification of polymeric surfaces and is of outstanding importance aiming to develop materials that could maximise the materials performance in specific applications.

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