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Structural investigations of amines treated polyester thin films by FTIR-ATR spectroscopy

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The poly(ethylene terephthalate) thin films were exposed to vapour of ethylenediamine for treatment times of 10, 15, 17, 20 and 30 min in order to modify the structure of their surface. The presence of amine and amide groups make possible the further derivatization of modified poly(ethylene terephthalate) films due to ability of these units to react with isocyanates, expoxides, esters, phosphorus trichloride. The experimental Fourier Transform Infrared Attenuated Total Reflexion (FTIR-ATR) spectra provided information related to the changes in the chemical structure of poly(ethylene terephthalate) after each step of treatment. The FTIR ATR analysis was performed in a wide range of wavenumber 400–3000 cm^{-1} paying particular attention to typical CH_2, C=O, amide I, amide II and ester vibrations.

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1. Introduction

During the past four decades thin films of organic and anorganic materials have been a subject of intensive investigations for both academic and industrial research [1]. The functionalization of the polymers and especially the surface modification of the polymer films are in the attention of many researchers and have been in great demand over the last years due to the potential of this type of transformation to generate diversity of materials and properties. The structural modifications can appear in defined domains of the polymer surface as a consequence of the scission or formation of physical or chemical bonds. The surface functionalization of the polymer supports is essential in order to target them to specific areas and allow them to selectively interact with (bio)molecules. The ability to control the chemical and structural properties of surfaces is very important for advancements in selective and environmental friendly catalysis, biomedicine, coatings, electronics, chemical sensing, and many other applications. The research in this field provides very important information for fundamental studies in chemistry and biochemistry fields [2-5].

For more than 70 years researchers and engineers have been focusing their attention on poly(ethylene terephthalate) (PET) because of its chemical, physical and mechanical properties as well as its successful industrial applications in fibres, wire, cable insulators, sheets, plastics, packaging, flexible substrate, magnetic media, photographic films, etc [6-8]. Biaxially-oriented polyethylene terephthalate (boPET, Mylar) film is used for its high tensile strength, chemical and dimensional stability, transparency, gas and aroma barrier properties and electrical insulation. An important consequence of the molecular orientation is that it induces the formation of many crystallites that grow rapidly and remain smaller than the wavelength of visible light and as a result PET film has excellent clarity, despite its semicrystalline structure [9]. Commercial biaxially oriented laminate PET film containing a certain percent of isophthalic acid comonomer to reduce crystallinity [10]. A considerable amount of research has been concerning with the physico-chemical treatment of poly(ethylene terephthalate) in order to overcome its disadvantages. The versatility of the PET for the covalent surface derivatization is based on the reactions with OH and COOH end groups and with ester bond included into poly(ethylene terephthalate) chains that allow modification of their structure and are favourable for the preparation of new materials. Reactions of semicrystalline poly(ethylene terephthalate) film with ester-selective reagents to perform reagent-induced functionality at surface of polymer can be carried out at the film-solution interface or in reagent vapour-film system. The modification reactions involve chain cleavage and can lead to significant sample degradation and therefore the modification reaction conditions must be optimized to maximize conversion and minimize degradation. It should be possible to restrict the chemical modification of polyester to the surface of the polymer film by choosing the proper experimental conditions, namely exposure time, reagents, temperature [11].

The reaction of the ester bond included into polyesters chains with amines is one of the various attempts tested in order to obtain materials which may be tailored to the demanding requirements of the specific applications. It is expected that the amide groups included by modification of structure of PET surface should generate potential sites for the creation of physical bonds of hydrogen or van der Waals type and should improve the wettability of polymer. The further derivatization of thus modified PET could be based on amine and amide ability to react with isocyanates, expoxides and other compounds and makes possible the use of PET for special purposes. Nitrogen containing poly(ethylene terephthalate) is a potential substrate for attachment of proteins and other biologically active molecules such as enzymes, insulin, L-cysteine. In

addition the studies related to modification of PET surface in the presence of amines are important due to the fact that the amines are among environmental pollutants in the atmosphere. After aminolysis the polymer has two additional electronegative nitrogen atoms (NH and NH_2) on the surface, which would increase the polarity of the surface. It is expected that the treatment of PET film with amine results in an increase in the surface basicity [12-14].

It is known that FT-IR spectroscopy is one of the most established methods for the characterization of amide group and provides information regarding the crystalline phase of the samples. Also, vibrational spectroscopy, namely FT-IR is sensitive to conformational isomers of aliphatic segments from polyester chains. Moreover, Fourier Transform Infrared Attenuated Total Reflexion spectroscopy (FTIR-ATR) provides information about surface structure of polymers and structural variations in the surface region [15-18].

In this work we wish to present our data related to structural characterization by FTIR-ATR spectroscopy of aminated surfaces of poly(ethylene terephthalate) film. The incorporation of amide groups into the chains of PET was carried out by exposure of the polyester films to amine in the vapour state. Ethylenediamine was used to introduce N atoms to the surface of a biaxially oriented PET film. The amination at the surface was monitored for several different reaction times.

2. Experimental

Material

The biaxially drawn PET film (commercial), with thickness of 30 μm was used after ultrasonic cleaning with toluene, acetone and tridistilled water. Then the samples were dried at 40 ^oC and stored in a closed vessel. Ethylenediamine (m.p. 8.5°C, b.p. 117°C, vapour pressure:1.4 kPa, pK_b 3.92), used as aminolysis reagent was supplied from Fluka.

Treatment procedure

The PET film samples (approximately 10 mm×50 mm) were submitted to ethylenediamine vapour at a temperature of 80 ^oC. A laboratory installation was used in order to perform the experiments. After exposure, the aminated samples were rinsed with copious amounts of tridistilled water to remove excess ethylenediamine reagent. Samples were then dried and stored in a desiccator over phosphoric oxide.

Measurements

The exposed samples were taken out at different time intervals, and the measurement of the absorption spectra was carried out. The modification in the PET surface structure was examined by FTIR-ATR spectroscopy in the range 600-4000 cm^{-1}. The spectra were recorded on a BRUKER VERTEX70 spectrometer at a resolution of 2 cm^{-1} at incidence angle of 45^o. The signal-to noise ratio was improved by coadding 100 scans per spectrum.

3. Results and discussion

The changes in the chemical structure of the polyester were evidenced by FTIR ATR spectroscopy analysis which can be considered a valuable method for the characterization of polymer surface and amide groups. The amide group (CO-NH) is a complex vibrational unit in IR range and involves stretching and bending vibrations. Also, it is well known that the absorption bands in infrared spectroscopy are structure- and orientation-sensitive.

Surface functionalization was performed by interaction between amine in vapour state and ester groups and involves the chemical scission of ester linkages in the main chains of polymer by the nucleophilic attack of the nitrogen on the carbonium center of the carbonyl ester. Ethylenediamine, a multifunctional amine which are known to have a lower reactivity was chosen as reagent. After each scission both amide group and primary amine functionality are generated. The process seems to be dependent on chain mobility and permeability of polymer film.

Fig. 1 shows the progress of the aminolysis evidenced in the experimental IR spectra in the 600-4000 wavenumber range. Starting from the background spectrum the following spectra were recorded after different reaction time intervals up to the 30 min (10, 15, 17, 20 and 30 min).

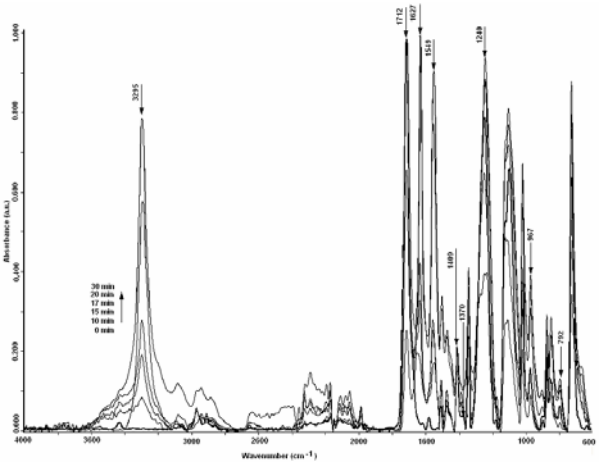

*Fig. 1. FTIR-ATR spectra of PET (**solid line**) and aminated PET film samples (fine line).*

There are clear changes observed in the spectrum of PET as a result of treatment with amine at 80 ^oC. Absorbance of bands in the infrared spectra of PET change and, at the same time a number of new bands in other part of the spectrum begin to emerge and grow during exposure to amine vapour. The changes in the infrared spectrum consist of change in the shape, number, position and intensity of the bands and are observed in the regions containing: CH, CH_2, C=O, COO and NH bands.

When reaction time increased from 0 to 15 min an upshift of the zero line of the spectra was observed, while after 20 min a progressive downshift takes place. This behaviour could be explained by the increase of the

heterogeneity of the system until the first 15 min of treatment that determines an increase of the scattered radiation. Over 20 min the degradation of film is advanced and the homogeneity of the system increases. This leads to a decrease of the scattered radiation. During aminolysis there seems to be a critical point, at 15 min when many of absorption bands become to decrease and change their shape.

Spectrum of PET has the characteristic absorption peaks at 1712 cm^{-1} (C=O bonds), 1410, 1018, and 872 cm^{-1} (vibration of aromatic ring), 1340 and 1177 cm^{-1} (bending vibration of -CH_2 groups), 1244 and 964 cm^{-1} (stretching vibration of C-O bonds), 1124 and 1100 cm^{-1} (stretching vibration of C-O bonds due to amorphous and crystalline structure of PET respectively).

The band at 1410 cm^{-1} resulting from phenylene ring vibrations (C-H bend coupled with ring C-C stretch) has usually been considered to be insensitive to orientation and conformation and is a reference band [17].

Surface analyses by FTIR-ATR, revealed the presence of nitrogen-containing functional groups C-N both in the amide and amine at the surface of the chemical modified PET film which are assigned to absorption band at 1177 cm^{-1}. The other type of N bonding, namely C=N due to the tautomerism of the amide functionality may be present at the surface of the film as a result of the aminolysis.

The -O-CH_2-CH_2-O- moieties from molecular chain structure of PET, show *gauche* (relaxed) and *trans* (extended) conformers through the internal rotation of the C-C bond. The PET sample being a commercial product it is plausible to assume that in the crystalline regions of the sample –O-CH_2-CH_2-O- moiety adopts a *trans* conformation, whereas in the amorphous regions it predominantly adopts the *gauche* conformation [7]. Consequently, the *trans* form can be present both in the crystalline and in the amorphous phase, the exact proportions depending on the treatment of the polymer. The chain segments in the *trans* conformation could be also viewed as forming an ordered amorphous phase and can be oriented [19]. In FTIR-ATR spectra the bands positioned at 1470, 1340, 970, and 847 cm^{-1} arise from vibrations of the *trans*-ethylene glycol conformer while the bands located at 1455, 1370, 1040, and 898 cm^{-1} are due to vibrations of the *gauche* conformer.

The two bands at 1340 cm^{-1} and 1370 cm^{-1} assigned to the CH_2 wagging mode (γ_w) in *trans* and *gauche* conformers, respectively.

The fraction of *trans* conformer (*T*) of the film was calculated, taking in account the intensities of the two bands at 1340 cm^{-1} (A_{1340}) and 1370 cm^{-1} (A_{1370}), respectively assigned to *trans* and *gauche* conformers, by the following equation [20]:

$$T = \frac{A_{1340}}{A_{1340} + 6.6 \times A_{1370}} \quad (1)$$

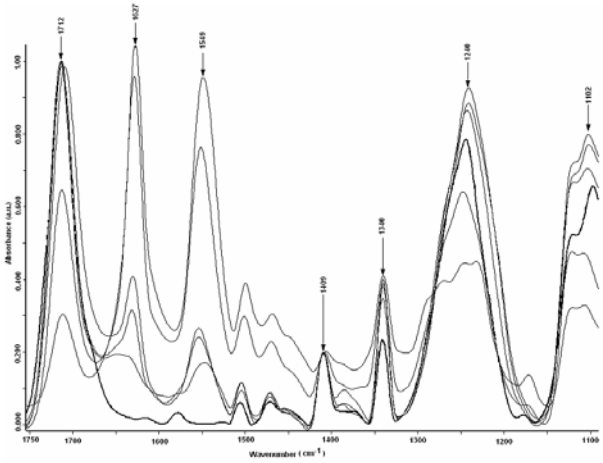

Fig. 2. 1100-1750 cm^{-1} region of the FTIR-ATR spectra of PET film treated with amine vapour at 80°C (1409 cm^{-1} ref.).

The value of percent of *trans* conformer was about 37.5±2.5% that evidenced a greater degree of structural order at the surface of PET. This result implies that de degree of crystallinity of polymer film is greater too. The percent of conformer can be estimated also taking in consideration the intensities of bands positioned at 973 and 898 cm^{-1}. In this case the *trans* conformer fraction of about 0.35±2 was found.

Figure 2 shows the FTIR spectra in 1100-1750 cm^{-1} range of the PET film at different times during treatment with amine vapour at 80 °C.

It can be clearly seen from Figure 2 that as the reaction time increases, the absorbance of 1340 cm^{-1} band grows, while the band at 1370 cm^{-1} changes considerably. Until 15 min of exposure to amine vapour the maximum of the *gauche* CH_2 wagging band (1370 cm^{-1}) shifts to the high-wavenumber region and become visible as shoulder at band positioned at 1386 cm^{-1}, corresponding to crystalline phase. At a treatment times beyond 20 min two distinct bands, one at 1370 cm^{-1} and other at 1386 cm^{-1} appear. On further treatment, as time of exposure increase at 30 min these bands significantly decrease in intensity and they can hardly be observed. The absorbance changes of the 1340 cm^{-1}, 1370 cm^{-1} and 1386 cm^{-1} bands indicate the occurrence of reorientation of the PET chains and increasing of crystallinity mainly due to recrystallization of the amorphous region promoted by mobility of chains.

The bands at 1475 cm^{-1} and 1453 cm^{-1} associated with CH_2 bending vibration of *trans* and *gauche*-glycol conformer, respectively increases and decreases, respectively during the experiments. The *trans* CH_2 rocking band at 848 cm^{-1} increases in the first 15 min of treatment and then decreases.

The vibrational bands associated with the methylene groups next to the CO groups (at about 978 and 1054 cm^{-1}) and those associated with the methylene groups next to the NH groups (1230 and 1320 cm^{-1}) from ethylenediamine are residue are overlapped with other bands from polyester.

The changes in 600-1000 cm^{-1} regions of ATR experimental spectra of PET film treated with ethylenediamine are presented in Figure 3.

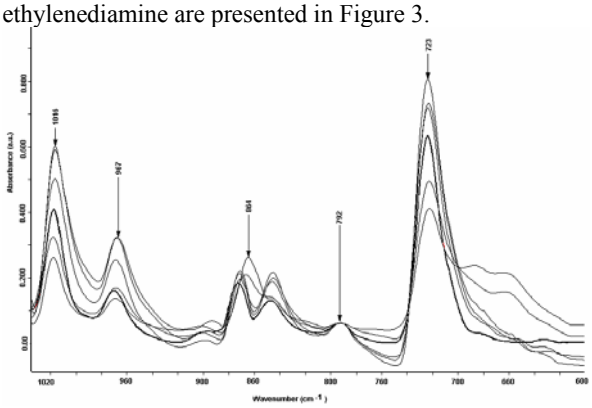

Fig. 3. The FTIR-ATR spectra in the 600-1000 cm^{-1} region of PET film normalized to the band at 792 cm^{-1}

The CO component of chain structure of PET samples was also affected by the amine treatment. The 970 cm^{-1} band that corresponds to the asymmetric C-O stretching vibration of the *trans* unit in the ethylene glycol linkage is very sensitive to the development of order in PET. Its intensity increases for treatment time up to 15 min and then a decrease of this vibration was observed. At the same time the band intensity at 898 cm^{-1} (*gauche*) did not decrease appreciably. The polymer film after being treated at 80 ^{o}C for a time period of 30 min became brittle due to advanced degradation process both in the amorphous and crystalline regions.

Examination of the ester bands at 1244 cm^{-1} and 1124 cm^{-1} from Figure 2 indicate also that the degree of crystallinity of the samples undergoing aminolysis continues to increase with time. This is shown by the increase in intensity and slight shifting to lower frequencies of the band at 1244 cm^{-1} for the first 15 min of reaction due to contribution of amide III band. Then the absorbance decreases and after a treatment time of 30 min the shape of band changes and is shifted to 1269 cm^{-1} due to C-O bonds stretching of crystalline PET and to degradation of the polymer film. The intensity of the band at about 1124 cm^{-1} also increases because is overlapped with the absorption associated with amide group.

The chain scission of the PET is reflected in the FTIR ATR spectra (see Figure 2) by decreasing of IR band corresponding to the carbonyl ester group at ca. 1712 cm^{-1} as a function of treatment time with amine vapour. At the same time a new strong absorption at about 1630 cm^{-1} assigned to the amide I band, which has a main contribution of the stretching vibration, $\nu_{C=O}$ occurred. This position of the amide I band is red shifted during aminolysis as expected for an environment with hydrogen bonding. The amide II band, mainly decided by NH bending vibration (δ_{NH}) appears at about 1548 cm^{-1}. From the ATR-FTIR studies it was found that normalized peak intensity for amide I and amide II bands increased significantly during treatment of PET with amine. The amide I intensity as well as amide II intensity after 20 min exposure increase more four times, compared to that the intensity of these bands from the spectrum of the PET film treated for 10 min. The position of amide I and amide II bands reveal that hydrogen bonding involving amide C=O is present. This result suggests that the carbon chains in the amine molecule is orienting toward the film surface [12].

Fig. 4 present the 2400-4000 cm^{-1} region of the spectra of the PET samples treated with ethylenediamine for different reaction times.

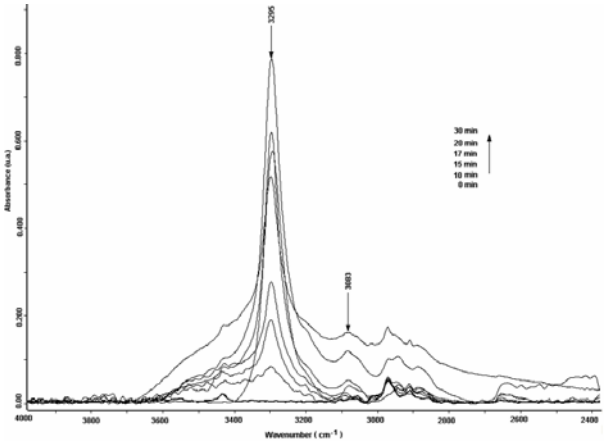

Fig. 4. Changes of intensity of the FTIR-ATR bands in the OH, CH and NH regions of PET film untreated and treated for 10, 15, 17, 20, 30 min

The shape and intensities of the bands at 2970 and 2920 cm^{-1}, assigned to stretching vibrations of CH_2 group (the former for antisymmetric and the latter for the symmetric mode) change also during exposure to amine vapour (see Figure 4). The 3336 cm^{-1} band (combination of the carbonyl stretch with the phenyl deformation) and the overtone of the carbonyl stretching vibration (3434 cm^{-1}) both behave as the 1340 cm^{-1} band. These results are in agreement with these reports by Oultache et al. [21]. With increasing time of exposure the bands associated with NH stretch vibrations appear at 3293, 3200, and 3080 cm^{-1}. The last two bands are attributed to amide I and amide II overtones.

4. Conclusions

The spectral changes observed in the FTIR-ATR spectra of aminated PET film seems to be due to the combined effects of molecular orientation, conformational changes, initial degradation restricted to the amorphous regions, the chain scission of tie segments between crystallites and reaction of ester group with ethylenediamine. Both amine and temperature could contribute to variation in the structure of polymer film. Modification in chemical structure and increased mobility of the main chain in the polymer lead to generation of amide, amine and OH groups and apparent increasing in

the crystallinity, respectively. During aminolysis conformational disorder occurs in the methylene sequences. Consequently, one can summarize that the exposure to amine vapour favoured crystallization, formation of amide group and degradation of PET simultaneously. The presence of amine groups in the structure of treated PET film is favourable for further derivatization of polymer with biomolecules.

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