X-ray investigations of proton irradiation induced structure development in polyester fibers

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Abstract. The role of proton irradiation on the structural changes in partially crystalline poly (ethylene terephthalate) (PET) fibres has been investigated using a wide-angle X-ray scattering (WAXS). Experimental data about the influence of the exposure dose and the irradiation conditions in the processes of destruction and crosslinking in the irradiated objects have been obtained. The structural changes and the packing density of the macromolecular chain segments of the poly (ethylene terephthalate) filaments irradiated with different doses have been analyzed. A mechanism of the structural reorganization initiated by the irradiation has been supposed on the basis of the changes in the geometry of the intensity distribution of the X-ray diffraction patterns of the studied objects.

1. Introduction

Poly(ethylene terephthalate) (PET) is a representative of the linear polyesters crystallizable thermoplastic polymers. PET is characterized by relatively high glass transition temperature, high thermal stability and low crystallization rate. Moreover, the widespread use of PET is due to its ability to crystallize in conditions of deformation under temperatures and mechanical stresses applied during various treatments. PET can easily turn into uni- and biaxial oriented state with different qualitative properties. Due to the above-mentioned, PET is a widely used in many technological and industrial areas such as composite materials for the aerospace and space satellite industry, but mainly for the production of thin films and fibers.

The properties of PET filaments are highly dependent on the super molecular structure of the polymer in the oriented state. This, in turn, depends on the type of polymer, the initial isotropic super molecular structure, and the conditions of its restructuring in oriented. Ion beam irradiation is widely used in the polymer technology in order to change and improve the chemical and physical properties of the polymer materials in the recent years [1 - 12]. Proton irradiation of flexible-chain polymers, including PET is quite common in the practice [6 - 9].

Considering the wide application of PET it is interesting and very important from a technological and scientific point of view to study the influence of proton irradiation on the structure and properties of PET filaments.

In the present work is studied the influence of proton irradiation with low power and different exposure durations on the structure and properties of undrawn partially crystalline uniaxially oriented

PET. X-ray diffraction method was used for determination of the of object's ability for reorganization of the super molecular structure.

2. Experimental

2.1. Materials

The initial characteristics of the investigated PET fibres were as follows:

speed of fibrillate 4110 *m/min;*
number of single filaments in the complex thread 32;
diameter of a single fibre 11,0 μm;
degree of crystallinity α = 36,9 %;
birefringence $\Delta n.10^3$ = 5,82.

The studied samples are produced on industrial spinning installation Furnet (France). The presented parameters indicate that the investigated PET fibers are produced at a relatively high spinning speed, possess significant preliminary orientation and respectively degree of crystallinity.

2.2. Methods

2.2.1. Irradiation of the PET samples with protons. PET filaments have been fixed on flat plates with central holes (diameter of 1 *cm*) in the form of a layer with a thickness consistent with the range of the used for the irradiation proton beam. Plates with the samples were mounted on the outside wall of a circular holder (figure 1). The sample holder is placed in a chamber in which is achieved a high vacuum (figure 2). During the measurement the holder is rotated thereby are irradiated all positions of the holder loaded with samples. Samples were irradiated with protons using the accelerator facilities AN 2000 at the National Laboratories of Legnaro, INFN, Italy. Proton beams with energy of 2 *MeV* obtained by Van de Graaff accelerator have been used to irradiate the polymers' samples. The proton beam passed through a beam diffuser was collimated to a diameter of 4 *mm*. The collimated beam gone through the samples was collected for measuring of the total beam charge.

With purpose to prevent the samples from excessive heating the beam current was kept small enough with value of 5 *nA*. For each sample the total beam charge was measured and the number of protons irradiated the sample was calculated.

Figure 1. The circular holder and attached to it plates with the PET filaments.

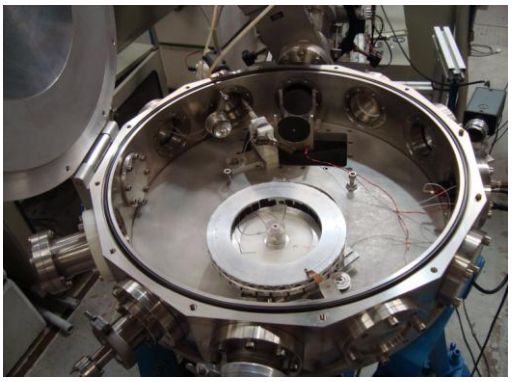

Figure 2. Vacuum camera together with the measuring circular holder.

2.2.2. Wide-angle X-ray scattering. Due to the precise geometric and structural sensitivity of X-ray diffraction methods, the angular deviation of the diffraction reflections gives perfect information about

the packing density of the structural elements on the atomic-molecular level. Knowing very well the crystallography of PET, the alteration in the geometry of the intensity distribution of the diffracted X-ray radiation can adequately visualize the repacking of the macromolecular chain segments in the volume of the crystal polymer phase, the transient zones of the crystallites and its mesophases. Furthermore, the changes in the intensity ratios, profile characteristics and angular deviation of the diffraction reflections provide information concerning to the crystalline phase perfection.

The structure of the non-irradiated fibers was studied by wide- angle X-ray scattering (WAXS) using a diffractometer HZG 4 (Freiberger Präzisionsmechanik, Germany) and Ni-filtered Cu K_α radiation with a wavelength of 1,5418 *Å*. Equatorial scattering was monitored in transmission mode.

Structure of the irradiated fibers was studied by wide-angle X-ray scattering Diffractometer URD - 6 (under license of SIEMES) of the company "Freiberger Präzisionsmechanik" (Freiburg im Breisgau, Baden-Württemberg, Germany). Used is β-filtered with Ni-filter Cu K_α radiation with the same wavelength as mentioned above.

3. Results and discussion

The main effects of proton irradiation of polymer objects, in particular PET fibers might be destructive and crosslinking effects as the crosslinking effects are secondary after ionization and radicalization. The intensity distribution of the diffracted X-ray radiation of the non-irradiated PET fibers is present on the figure 3. The diffraction patterns obtained after the proton irradiation of the studied objects for 20 *s* (5.10^{12} *p/cm*^{2}), 40 *s* (10^{13} *p/cm*^{2}) and 2040 *s* (5.10^{14} *p/cm*^{2}) are shown on figure 4. The comparison between the intensity distribution of the source structure of PET fibers (figure 3) and the proton irradiated for 20 *s* (figure 4) shows partially crystalline structure formed during the fibre formation process.

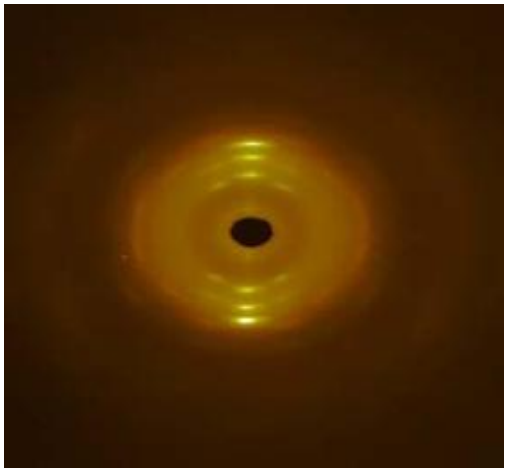

Figure 3. WAXS of non-irradiated PET fibbers.

The observed impact of the irradiation on the geometry of the intensity distribution of the diffracted X-ray radiation in the objects diffraction patterns consists of angular deviation of intensity changes in the range 10 $^0 2\theta$ - 30 $^0 2\theta$. In the diffraction patterns obtained after irradiation for 40 *s* and 2040 *s* (figure 4) can be formulated the following basic changes.

Main trend in the observed diffraction pattern of the PET fibers exposed for 40 *s* is the displacement of the diffraction peaks to the smaller diffraction angles. Observed effect is due to the increase in the distances as well between the folds as well as between the planes of the folding in the crystalline phase of the polymer.

The widening between the folds is larger, which can be a result from reasons as follows:

- the folds stretching, twisting of segments and distancing of the stretched during the fibrillate chains added contribution to increasing of the degree of crystallinity [13];
- improvement of the stacking of the macromolecular chain segments in the transition zones;
- formation of crystals with stretched chains.

Due to the different densities of the crystals with stretched chains and crystals with folded chains could be formed crystallites or a micelle structure with a lower physical density of the crystal, respectively, distances between the chains. Furthermore, the angular deviations can be a result of widening and multiple splitting of peaks, which in turn may be due to the morphology of the crystalline phase formed in different sizes and dispersion, type, quality and perfection.

The trend observed in the diffraction pattern of the PET fibers irradiated with 5.10^{14} p/cm^2 (figure 4) is the offset of the diffraction peaks towards larger diffraction angles. In this diffraction spectra (lasting 2040 *s* exposure) sufficiently precise information indicating the possibility of realization of recrystallizations processes resulting from the relaxation after the segmental destruction occurred.

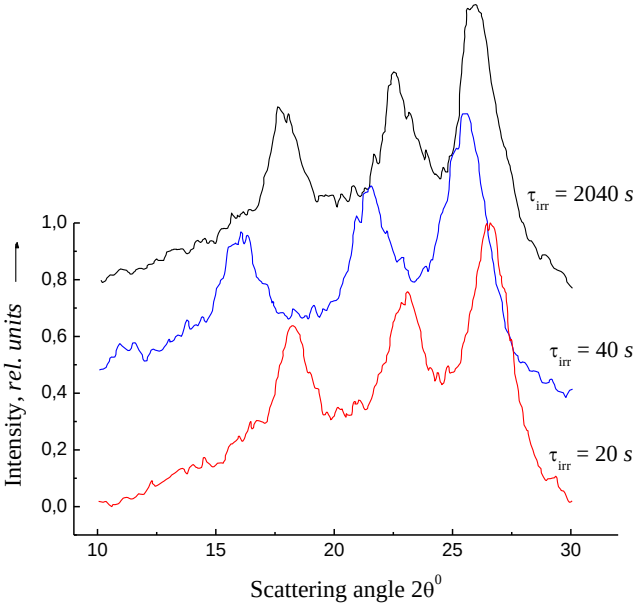

Figure 4. WAXS diffraction patterns of PET fibers irradiated with protons for 20, 40 and 2040 *s*. The curves are shifted vertically for clarity.

Interesting is that the proton irradiation during 2040 *s* returned to middle position and narrowed somewhat, again in an intermediate position the distances between the peaks. Observed effects are evidence of completely increasing of the studied between planar distances in the elementary crystal cell. On one hand such an extension of the cell (decreasing of the polymer mass density) can be associated with the logical improving the arrangement of the segments in the cell. Moreover, the displacement of the small angular diffraction peaks is larger than the shift of the peaks formed at larger angles. On the other hand, the third longest exposure causes a slight positional shift of the multiple peaks back to the right to the larger angles, as well as bringing them closer to each other.

This is the opposite effect to the observed at exposures 20 *s* and 40 *s*, but to a lesser extent. The complex summary variation in the position of the diffraction peaks may be interpreted as steps of the improvement of the polymer crystalline phase. In the starting structure of this type of samples having a sufficiently large preliminary orientation exist the so called frozen micro stresses.

It can be assumed that the destruction over a certain level of the blocking and supporting the tension segments, fixing the momentary raw structures, does not improve the structural perfection but leads to distortion of the achieved order. The clarification of such ambiguities requires further planning of multi factorial extended experiment that also includes other analytical methods, as is the purpose of our future work.

4. Conclusions

On the basis of the experiments of proton irradiation of the studied polymer objects and subsequent analyzes can be made conclusions about the relationship between the radiation rate and the changes of the fibers super molecular structure organization as follows:

The low energy proton irradiation with low power and beam current of 5 *nA* during relatively short exposition to irradiation, (respectively the absorbed dose) can cause noticeable structuring effect in the studied PET fibers.

Through examination of the angular deviations, changes in the intensity ratios and the profile of specific diffraction reflections of PET are defined the changes in the segmental packing in the amorphous and crystalline phase of the polymer.

The complex summary variation in the position of the diffraction peaks may be interpreted as steps of the improvement of the polymer crystalline phase.

It is supposed that the major modifying and structuring effects of the proton irradiation are ionization, radicalization, destructions, recombination and cross linking.

The complete clarification of the existing ambiguities requires further planning of multi factorial extended experiment that also includes other analytical methods, as is the purpose of our future work.

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