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EFFECT OF PROTON IRRADIATION ON THE STRUCTURE DEVELOPMENT OF POLYETHYLENE TEREPHTHALATE FIBERS

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Abstract: *The influence of proton irradiation on the structural changes in partially crystalline poly(ethylene terephthalate) (PET) filaments has been investigated using a wide-angle X-ray scattering (WAXS). Experimental data about the role 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 polyethylene 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 intensive distribution of the X-ray diffraction patterns of the objects.*

Key words*: poly (ethylene terephthalate), fibers, proton irradiation, WAXS, structure development mechanism.*

1. Introduction

Poly (ethylene terephthalate) (PET) is a crystallizable thermoplastic polymer widely used in many technological and industrial areas in the form of fibers, films, construction details, etc. The applications of PET are based on its relatively high glass transition temperature and low crystallization rate. Moreover, PET can easily turn into uni- and biaxial oriented state with different qualitative properties.

Furthermore, the widespread use of PET is due to its ability to crystallize in terms of deformation at temperatures and mechanical stresses applied during the various treatments.

It is very important from technological economic and scientific point of view to investigate the role of proton irradiation on the structure and properties of undrawn amorphous uniaxially oriented PET [1-4].

The ionizing radiations are widely used in the polymer technology, operation and investigations [1-3, 5, 6].

With the present experiment, we aim to investigate the influence of the proton irradiation on the structural reorganization of undrawn partially crystalline PET fibers.

2. Materials

The initial characteristics of the studied PET fibers were as follows:
speed of fibrillate 2280 *m/min;*
number of single fibers in the complex filament 32;
diameter of a single fiber 14.5 μm;
degree of crystallinity α = 23,7 %;
birefringence $\Delta n.10^3$ = 5,12.

The filaments are produced from industrial installation of the company "Furnie" (France).

3. Methods

3.1. Irradiation of the PET samples with protons

Fibres of poly (ethylene terephthalate) have been placed in a flat surface very close each other thus forming a layer with a thickness inferior with respect to the range of the protons used for the irradiation. 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* delivered by Van de Graaff accelerator have been used to irradiate the polymers' samples. The proton beam passed through a beam diffuser and was collimated to a diameter of 6 *mm*. The collimated beam passed through the samples and was collected for measuring the total beam charge. The beam current was kept as low as 5 *nA* to prevent the sample heating. For each sample the total beam charge was measured and the number of protons irradiated the sample was calculated.

3.2. Wide-angle X-ray scattering

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 $\AA$. Equatorial scattering was monitored in transmission mode.

The 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 $^{K_\alpha}$ radiation with a wavelength of λ = 1.5418$\mathring{A}$.

4. Results and Discuss

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 [7], 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 intensity distribution of the diffracted X-ray radiation in the diffraction patterns of the non-Irradiated (Fig. 1) and proton irradiated for 20*s* fibers (Fig. 2) shows a structure similar to the PET amorphous state like its super cooled melt.

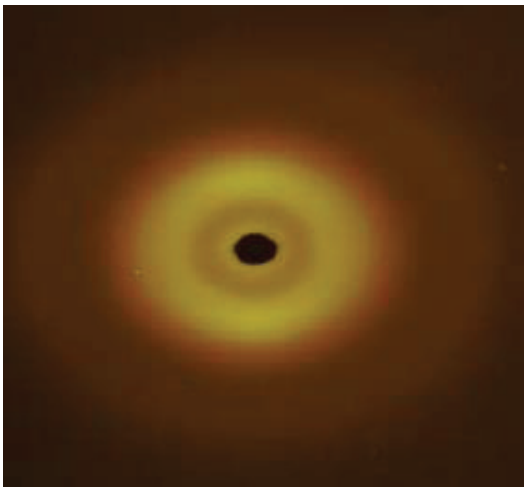

Fig.1.WAXS of non-irradiated PET fibers.

The average distance between the macromolecular chain segments (MMCS) in the volume of the polymer can be assumed about 4,35 $\mathring{A}$. The additional proton irradiation of this type of PET fibers with the same power of irradiation, but with different continuation leads to noticeable changes in the geometry of the intensity distribution of the diffracted X-ray in the interval from 10^0 2θ to 30^0 2θ. After 20 *s* proton irradiation sample S1 shows visible deviation from close to the Gaussian of the profile of the distances between MMCS distribution.

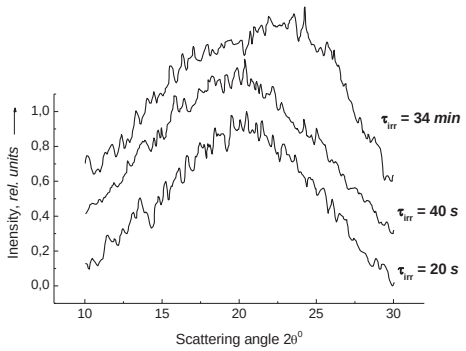

Fig. 2.WAXS curves of PET fibers irradiated with protons for 20 seconds, 40 seconds, and 34 minutes.

It may be noted probable formation of nematic mesophase with average statistical distance between MMCS about 4,08 *Å*. This may be due to destructive processes, facilitating repackaging of MMCS and change of the statistical average distance between them from 4,15 *Å* to 4,08 *Å*. It may be noted slight increase in the intensity at angles around 13^0 *2θ* and 29^0 *2θ*.

The possible occurrence of preliminary orderliness preceding the future formation of crystalline phase in the presence of diffraction reflection 01-3 about 29^0 *2θ* with increasing of the time of proton irradiation of objects probably emphasizes the nematic nature of the mesophase that is forming in the fibers.

Similar suggestion may explain the preservation of the enhancement of the intensity at an angle of about 13^0 2θ around which there is no probability for formation of diffraction reflection. The exposure which is twice higher (Fig. 2, τ = 40 *s*) confirms the above suggestions and shows further intensity increases at angles about 16^0 *2θ* and 25^0 *2θ*. Eventually, these might be positions for diffraction reflections 01-1 and 100. It is observed general displacement of the increase of the intensity enhancement to the left towards the smaller angles (to the larger interplanar distances).

The additional exposure, about 50 times longer, (Fig. 2, τ = 34 *min*) confirms the discussed possible trends due to the alternative influence of the destructive and crosslinking processes as a result of the irradiation.

The trends from curve 2 (Fig. 2, τ = 40*s*) are confirmed, but with significantly greater intensity increase in the angular interval from 21^0 *2θ* to 27^0 *2θ*. These are the peaks from the group: -111, 1-10, 011, 1-12, 100, 1-11 as well as intensity increase in the places of reflections 110 and 100. This suggests a certain improvement of the smectic nature of the mesophases with formation of transient structure towards perfection of the known crystal structure of PET.

5. Conclusions

On the basis of the experiments and analyzes can be made some preliminary conclusions and recommendations as follows:

The low energy proton irradiation with low power within the range of 10^{12}-10^{15} $p/cm^2.s$ during comparatively short exposition to irradiation, (respectively the absorbed dose) can cause noticeable structuring effect in the studied PET fibers.

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

The complete clarification of the studied effects requires profound and extensive investigation of the quality, density, and the segmental packing in the amorphous and crystalline phase of the polymer and similar experiments are coming.

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References

[1] N. L. Singh; Nilam Shah; C. F. Desai; K. P. Singh; S. K. Arora, Radiation Effects and Defects in Solids, Vol. 159, 8, 9, 475 – 482, 2004;

[2] B. Mallick, T. Patel, R.C. Behera, S. N. Sarangi, S.N. Sahu, R. K. Choudhury, Microstrain Section B: Beam Interactions with Materials and Atoms, 248, 2, 305 – 310, 2006;

[3] S. P Tripathy, R. Mishra, K. K. Dwivedi, D.T. Khating, S. Ghosh, D. Fink, Radiation Effects and Defects in Solids, 157, 4, 1, 1-11 2002;

[4] Totev Hr. The value of the securities (Bonds and shares), Journal science education innovation, 1, 144-152, 2013;

[5] Z. Lounis-Mokrani, A. Badreddine, D. Mebhah, D. Imatoukene, M. Fromm, M. Allab, Radiation Measurements, 43, 41-47, 2008;

[6] G. Szenes, K. Havancsák, V. Skuratov, P. Hanák, L. Zsoldos, T. Ungár, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 166-167, 2, 933-937, 2000;

[7] Kilian et. Al, Koll. Zeitschrift, 172 (2), 166, 1960.