

Influence of Ar and He implantation on surface morphology of polymers

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Surface morphology of irradiated isotactic polypropylene (iPP) and high density polyethylene (HDPE) was studied using scanning electron microscope (SEM) technique. The main objective of the work is to get an insight into surface changes induced by ion irradiation in order to better understand the mechanisms of surface modification of polymers. The results obtained revealed several mechanisms that may occur in irradiated polymers; among them decomposition and irradiation-induced crystallization are the most pronounced.

1. Introduction

Polymers are materials enjoying a wide range of industrial applications. Polymer materials have many advantageous properties, such as low weight, moldability, corrosion resistance and low manufacturing cost. Polymers are used for manufacturing of mechanical, optical or electronic elements. The ever expanding use of polymers revealed the inherent limitation of polymers – low hardness of these materials. In fact for numerous applications it is sufficient to improve the surface hardness only. Optical lenses made of polymers can serve as a typical example. Several techniques were tested to improve the surface properties of polymers: conventional wet chemistry approach [1], physical vapour deposition techniques [2], [3], photon source [4], electron beam technique [5]. Recently, it has been found that ion implantation may constitute an interesting alternative to these classical technologies. Ion implantation used for modification of kapton, teflon, tefzel or mylar [6] resulted in significant modification of their electrical [7], optical [8] or mechanical [6], [9], [10] properties. The improvement of the adhesion of thin polymer layers to B⁺, N⁺ or Ar⁺ ion implanted substrates has been observed as well [6], [11].

Taking into account that ion implantation is generally the last treatment applied to the very surface of the object, it is important to assess to what extent this process may alter the surface morphology of irradiated polymers. The effect of surface topology modification was only mentioned in few articles [6], [12], it is thus important to study this problem in detail. Complete description of the changes induced by ion implantation in surface morphology is also essential for the correct interpretation of the results of micromechanical measurements.

The article presents the analysis of the changes in surface topography induced by ion implantation in two types of polymers: HDPE and iPP. The role of ion mass and of ion dose on surface morphology was studied using SEM technique.

2. Experimental

Two polymers were used in the study: iPP and HDPE. The basic physical properties of these materials are listed in Tab. 1 [13]. Samples of iPP and HDPE in form of flat, 3 mm thick samples were synthesized in Institute of Polymers, Technical University of Łódź, Poland. Ion implantation processes were performed in the Institute of Electronic Materials Technology, Warsaw, Poland.

The samples of iPP and HDPE polymers were irradiated with 150 keV Ar⁺ or 100 keV He⁺ ions. The detailed description of irradiation fluencies is listed in Tab. 2. The Ar and He ions were chosen because of the differences in their interaction with the solids. Argon ions lose their energy mainly due to elastic collisions with target nuclei, hence the irradiation with Ar ions leads mainly to degradation of polymer

Table 1. Physical properties of the polymers studied.

Polymer	Density [g/cm ³]	Degree of crystallinity [vol %]	Melting temp. [°C]	Molecular weight <i>M_w</i>
iPP	0.910	39.7	163	232
HDPE	0.971	70.1	133	94

Table 2. Details of ion implantation processes.

Polymer	Fluences of Ar ions [at./cm ²]	Fluences of Ar ions [at./cm ²]
iPP	1×10 ¹⁴	3×10 ¹⁴
	3×10 ¹⁴	1×10 ¹⁵
	1×10 ¹⁵	3×10 ¹⁵
	3×10 ¹⁵	1×10 ¹⁶
	1×10 ¹⁶	3×10 ¹⁶
HDPE	1×10 ¹⁴	3×10 ¹⁴
	3×10 ¹⁴	1×10 ¹⁵
	1×10 ¹⁵	3×10 ¹⁵
	3×10 ¹⁵	1×10 ¹⁶
	1×10 ¹⁶	3×10 ¹⁶

caused by the scission of polymer chains. Conversely, helium ions interact with the solid almost exclusively via inelastic collisions with target electrons. The irradiation with He ions leads thus to cross-linking of polymers chains. The latter process is, of course, limited to materials in which such cross-linking is possible.

Ion implantation processes were carried out using Balzers MPB 202 RP implanter. In order to avoid significant target heating the beam current density was kept below $0.1 \mu\text{A}/\text{cm}^2$. The surface microtopography was assessed with OPTON DSM 950 scanning electron microscope. Once again, the accelerating voltage and electron current were limited (5 keV and $20 \mu\text{A}$, respectively) to avoid target heating.

3. Results and discussion

3.1. Isotactic polypropylene

Figure 1 presents the surface of an untreated iPP sample. One can note the presence of scratches and of characteristic bubbles having 10–20 μm in diameter. Ion implantation with Ar ions leads to continuous smoothing of the surface, clearly seen as progressive disappearance of scratches (Fig. 2). Figure 3 shows details of the polymer surface after irradiation up to 1×10^{14} or 1×10^{16} at/cm^2 (Fig. 3a and b, respectively). The lowest irradiation dose caused the formation of radially organized

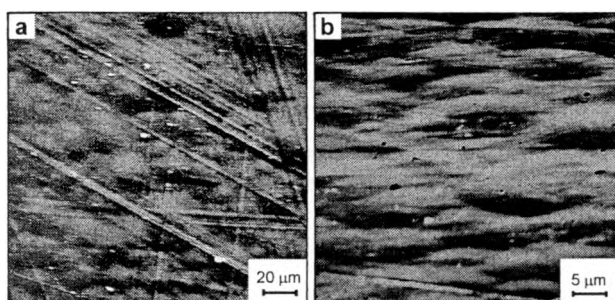


Fig. 1. SEM micrographs of the surface of untreated iPP polymer.

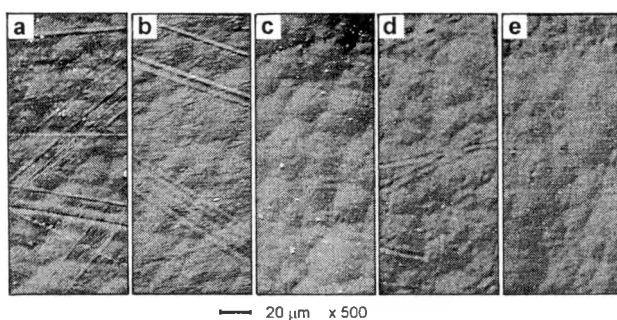


Fig. 2. SEM micrographs of Ar-implanted iPP polymer: 1×10^{14} at/cm^2 (a), 3×10^{14} at/cm^2 (b), 1×10^{15} at/cm^2 (c), 3×10^{15} at/cm^2 (d) and 1×10^{16} at/cm^2 (e).

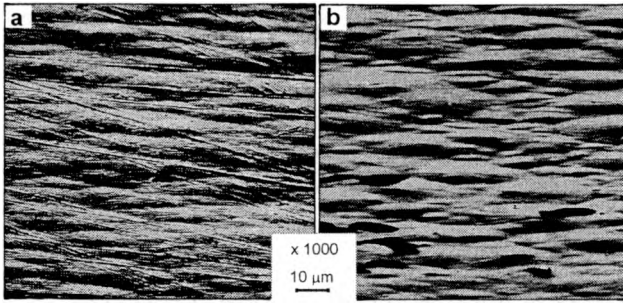


Fig. 3. SEM micrographs of Ar-implanted iPP polymer: 1×10^{14} at./cm² (a) and 1×10^{16} at./cm² (b).

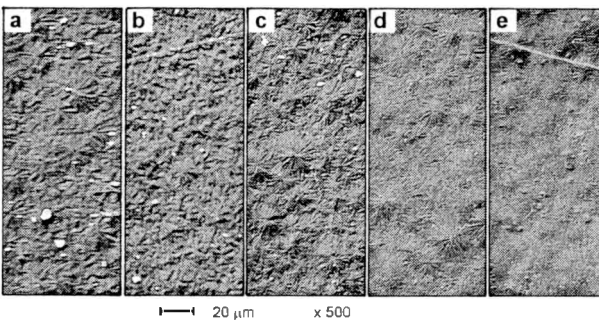


Fig. 4. SEM micrographs of He-implanted iPP polymer: 3×10^{14} at./cm² (a), 1×10^{15} at./cm² (b), 3×10^{15} at./cm² (c), 1×10^{16} at./cm² (d) and 3×10^{16} at./cm² (e).

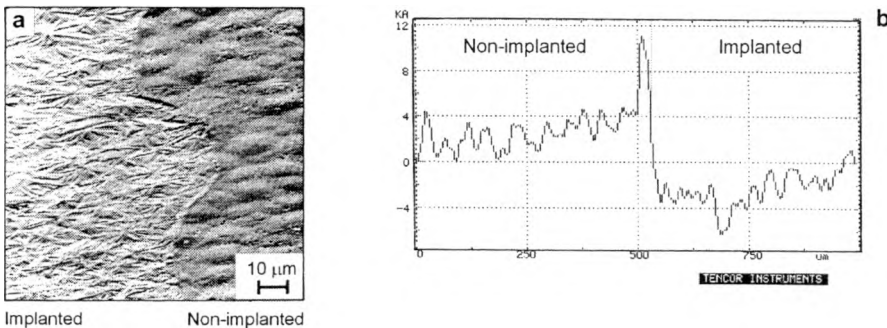


Fig. 5. SEM micrographs of untreated and He-implanted iPP polymer (a) and profilometric scan through the border between He-implanted and untreated areas of the iPP polymer (b).

structures within the bubbles. These structures disappear at higher fluences. The effects of irradiation with He ions are shown in Figs. 4 and 5. The formation of radially organized structures is clearly visible, especially at 3×10^{15} at./cm². At highest irradiation fluences the surface becomes smoother, as it was the case of Ar irradiation. Figure 5a shows the border between implanted and unimplanted areas of the sample. Two conclusions can be drawn from this figure. First, the formation of radially

organized structures, that were identified as spherulites, is due to irradiation with ions, not to temperature rise caused by an irradiation process. Second, the density and distribution of irradiation-induced spherulites corresponds to the density of bubbles, already present in unimplanted material. Apparently ion irradiation causes shrinking of the surface, which in turn is related to transformation of bubbles into crystalline spherulites. The shrinking of surface layer is evidenced in Fig. 5b, showing the profilometric scan through the border shown in Fig. 5a. The irradiated area is located about 500 nm below the surface of unimplanted part of the sample.

Another characteristic feature observed on irradiated samples, not seen on SEM images, is the continuous color transformation. The unimplanted samples are milky white; this color changes to yellow at intermediate irradiation fluences and finally becomes black at highest doses. The color changes can be explained by the degradation of polymer leading to the carbon enriched surface layer.

3.2. HDPE polymer

The surface of untreated HDPE polymer is smooth and uniform (Fig. 6). Even at high magnification only small imperfections, having the dimensions below $1\ \mu\text{m}$, are seen. The effects of ion irradiation are less pronounced than in case of the iPP polymer. One can note slight smoothening of the surface (Fig. 7a), especially for the highest doses of Ar ions. Similar features can be observed after irradiation with He ions (Fig. 7b).

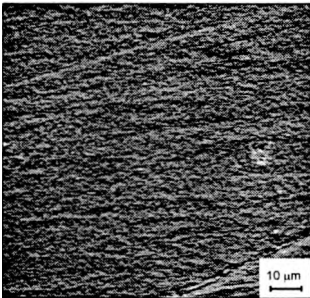


Fig. 6. SEM micrographs of untreated HDPE polymer.

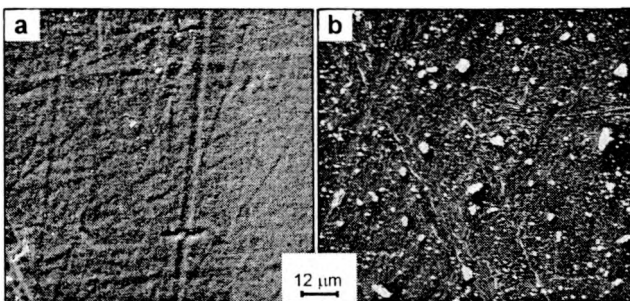


Fig. 7. SEM micrographs of Ar-implanted (1×10^{16} at./ cm^2) (a) and He-implanted (3×10^{16} at./ cm^2) (b) HDPE polymer.

Profilometric measurements performed in the vicinity of the border between irradiated and unirradiated parts of the samples did not reveal the formation of step, similar to that observed for iPP polymer.

4. Conclusions

Previous studies revealed various effects occurring in irradiated polymers. Such mechanisms as: cross-linking, branching, scission of polymer chains leading to decomposition have been identified [6], [10], [12]. Formation of step on the surface of irradiated iPP polymer can likely be explained by densification and/or decomposition of material [6], [10]. Decomposition due to chain scission is a general characteristic of irradiated polymers, observed in all materials implanted with sufficiently high irradiation fluences. A specific sign of decomposition is a change of polymer color from white or transparent first to yellow, then brown and finally black. The color changes are caused by surface layer enrichment with carbon atoms. During polymer decomposition hydrogen and oxygen atoms are easily released from the surface, the remaining structure contains thus more carbon. Decomposition is several times faster when the material is irradiated with argon than helium. This is clearly due to the fact that heavy ions transmit their energy directly to target atom nuclei, causing atomic displacements. Conversely, light ions losing the energy in inelastic collisions favor cross-linking of polymer chains. A new effect observed in this study is the possibility of ion-induced crystallization of polymers [14]. The latter effect is likely related to irradiation and not to temperature rise. Despite the fact that the temperature of crystallization for iPP material is rather low, about 100 °C [15], such temperature rise is unlikely when taking into account the power density at sample surface. Moreover, the effect is strictly limited to the irradiated part of sample surface and depends on the ion mass. It is interesting to note that crystallization is more efficient in the case of light ion irradiation, hence it seems to be related to ionization processes. Finally, the last observation from the study is the apparent smoothing of polymer surface, especially pronounced for iPP polymer. The latter effect can also be of interest for practical applications.

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