EFFECT OF HIGH BETA IRRADIATION ON MECHANICAL PROPERTIES OF SURFACE LAYER OF INJECTION MOULDED LOW DENSITY POLYETHYLENE (LDPE)

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The influence of high doses of beta radiation on the changes in the structure and selected properties (mechanical and thermal) polymers were proved. Using high doses of beta radiation for low density polyethylene (LDPE) and its influence on the changes of mechanical properties of surface layer has not been studied in detail so far. The specimens of low density polyethylene (LDPE) were made by injection moulding technology and irradiated by high doses of beta radiation (0, 132, 165 and 198 kGy). The changes in the microstructure and micromechanical properties of surface layer were evaluated using FTIR, WAXS and instrumented nanohardness test. The results of the measurements showed considerable increase in mechanical properties (indentation hardness, indentation elastic modulus) when the high doses of beta radiation are used.

KEYWORDS
low density polyethylene (LDPE), cross-linking, nano-hardness, nano-indentation, surface layer

1 INTRODUCTION

Cross-linking is a process in which polymer chains are associated through chemical bonds. Cross-linking is carried out by chemical reactions or radiation and in most cases the process is irreversible. Ionizing radiation includes high-energy electrons (electron beam - β-rays) (Fig. 2). These not only are capable of converting monomeric and oligomeric liquids into solids, but also can produce major changes in properties of solid polymers.

The engineering polymers are a very important group of polymers which offer much better properties in comparison to those of standard polymers. Both mechanical and thermal properties are much better than in case of standard polymers. The production of these types of polymers takes less than 1 % of all polymers (Fig. 1).

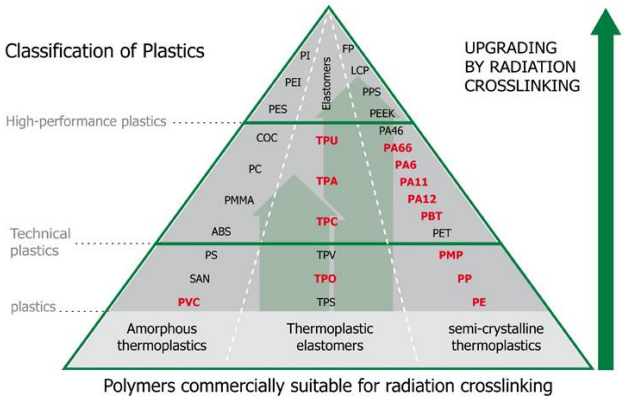

Figure 1. Upgrading by radiation cross-linking of PBT

Low-density polyethylene (LDPE) is a commodity polymer used extensively in extrusion operations such as coating, blown film, blow molding, and foaming. Extrusion of LDPE foams by direct gas injection or the so-called physical foaming can be separated in to five distinctive steps, i.e. melting of the solid LDPE pellets, injection and mixing of the liquid gas in the molten LDPE, cooling and shaping of the melt into the expansion condition, foaming of the melt by the expanding gas and finally cooling of the foam. Although viscosity and melting/crystallization behavior plays an important role in each or most of these process steps, the gas expansion is the crucial step in the foam process. In order to obtain a good foam quality (regular fine cell size and high closed cell content), the gas laden melt needs to be cooled down to a temperature close to the crystallization temperature of the semi-crystalline polyolefin to increase the melt viscosity and reduce the time needed for the transition from melt to solid phase. In practice, this means for semi-crystalline LDPE that the temperature of the melt at the die exit is always a few degree centigrade above the crystallization temperature.

The interaction of polymers with energetic ion or atom beams is of theoretical and practical interest. The related physical and chemical changes induced with high yields may lead to large modifications in the various characteristics of polymers. These include electrical and optical properties, surface wettability, adhesive bonding, biocompatibility, surface hardness and wear resistance, etc. In particular, there are several studies on the various effects induced in polyethylene (PE) by ion beams.

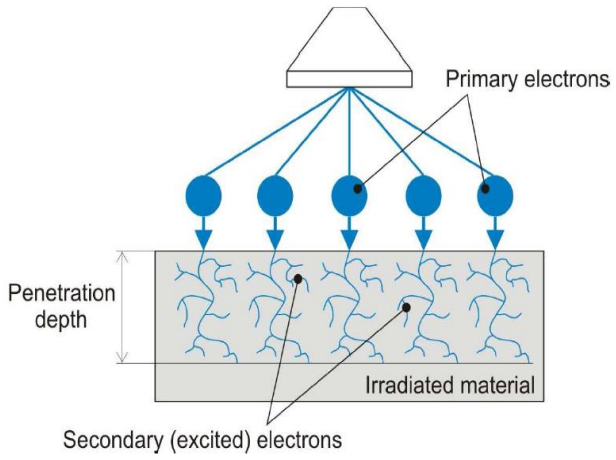

Figure 2. Design of Electron rays

The aim of this paper is to study the effect of ionizing radiation with different doses, on nano-mechanical properties of surface layer of low-density polyethylene (LDPE) and compare these results with those of non-irradiated samples. Experimental

1.1 Material and methods

For this experiment low density polyethylene (DOW LDPE 780E) (unfilled, LDPE) was used. Irradiation was carried out in the company BGS Beta Gamma Service GmbH & Co, KG, Saal an der Donau, Germany with the electron rays, electron energy 10 MeV, doses minimum of 0, 132, 165 and 198 kGy on air by the ambient temperature (Fig. 3).

The samples were made using the injection moulding technology on the injection moulding machine Arburg Allrounder 420C. Processing temperature range 210–240 °C, mold temperature 50 °C, injection pressure 80 MPa, injection rate 50 mm/s

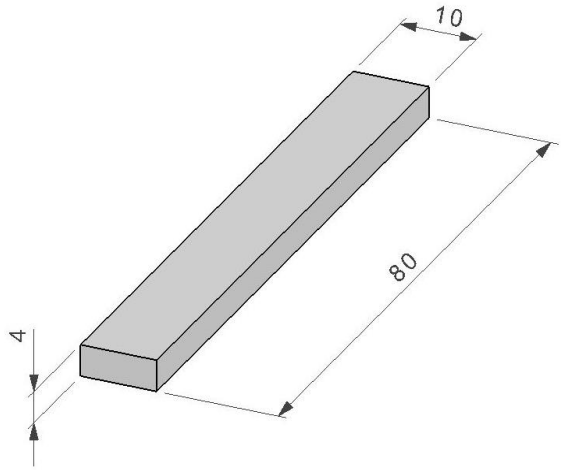

Figure 3. Dimension of sample

1.2 Nano-indentation test

Nano-indentation test were done using a Nano-indentation tester (NHT) (Fig. 5), CSM Instruments (Switzerland) according to the CSN EN ISO 14577. Load and unload speed was 20 mN/min. After a holding time of 90 s at maximum load 10 mN the specimens were unloaded. The specimens were glued on metallic sample holders (Fig. 3).

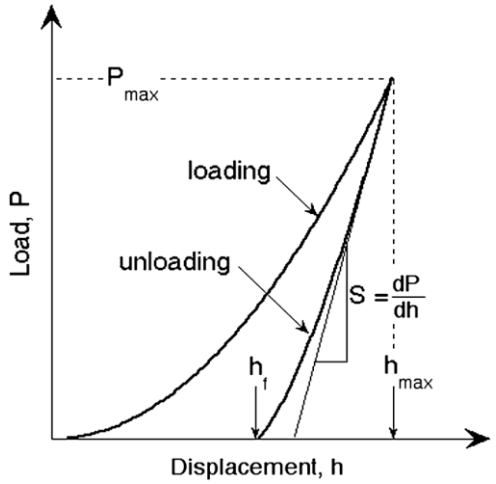

Figure 4. Schematic illustration of indentation curve

$$H_{IT} = \frac{F_{\max}}{A_p} \quad (1)$$

$$E_{IT} = E^* \cdot (1 - \nu_s^2) \quad (2)$$

The indentation hardness (H_{IT}) was calculated as maximum load (F_{max}) to the projected area of the hardness impression (A_p) and the indentation modulus (E_{IT}) is calculated from the Plane Strain modulus (E*) using an estimated sample Poisson's ratio (Fig. 4).

Figure 5. Nano-indentation tester

1.3 Gel Content

Gel test is done to find the content of non-filtered phase – gel of the given material according to standard CSN EN 579. The portion of 1g (of material radiated by high radiation doses) weighed with a precision of three decimal places was mixed with 100-250 ml of solvent. Xylol was used for LDPE because it dissolves the amorphous part of LDPE, the crosslinking part does not dissolve. The mixture was extracted for 6 hours. Then solutes were separated by distillation. After removing the residual Xylol the crosslinked extract was rinsed by distilled water. The rinsed extract was dried for 6 - 8 hours in vacuum at 100°C. The dried and cooled residue was weighed again with precision to three decimal places and compared to the original weight of the portion. The result is stated in percentage as the degree of crosslinking.

$$G_i = \frac{m_3 - m_1}{m_2 - m_1} \cdot 100 \quad (3)$$

Where,
G_i is the degree of crosslinking of each specimen expressed in percentage
m_1 is the weight of the cage and lid in milligrams
m_2 is the total of weights of the original specimen, cage and lid in milligrams
m_3 is the total of the weights of the residue of specimen, cage and lid in milligrams.
The result of G_i is rounded to the nearest whole number

1.4 *Wide-angle X-ray scattering*

Wide-angle X-ray diffraction patterns were obtained using a PANalytical X´Pert PRO X-ray diffraction system (Netherlands). The CuKα radiation was Ni-filtered. The scans (4.5 ° 2 Θ/min) in the reflection mode were taken in the range 5–30 ° 2 Θ. The sample crystallinity (X) was calculated from the ratio of the crystal diffraction peaks and the total scattering areas.
Crystall size L110 of α most intensive peak at 110 was calculated using Scherrer equation. As a standard "perfect" crystal terephthalic acid with the peak at 2 Θ = 17.4 ° and the half maximum breadth 0.3 ° 2 α was chosen.

1.5 *Fourier transformed infrared spectroscopy (FTIR)*

Infrared spectra were measured by ATR technology using single reflection ATR (GladiATR, PIKE Technologies), which was equipped with diamond crystal of refractive index of 2.4 and impact angle 45°). Spectra were measured by FTIR spectrometer Nicolet 6700 FTIR (Thermo Nicolet Instruments Co., Madison, USA) blown with dry air. Spectra were measured at the definition of 2 cm-1 using 64 scans. Pure ATR diamond crystal was used for the background and ATR correction was used for the adjustment of spectra. Manipulation with spectra was done using OMNIC Software 8.2. Each specimen was measured 2 times on each side.

2 RESULTS AND DISCUSSION

The development of micromechanical properties of irradiated low density polyethylene (LDPE) was characterized by the instrumented test of nanohardness, as can be seen in Fig. 6. The highest values (41.86 MPa) of indentation hardness (H_{IT}) were found at 132 kGy radiation dose. Lower value of indentation hardness (31.57 MPa) was measured on non-irradiated low density polyethylene (LDPE). The increase of indentation hardness at 132 kGy radiation dose was by 32 % compared to the non-irradiated low density polyethylene (LDPE). The lowest values of indentation hardness was found for low density polyethylene (LDPE) modified by the radiation dose of 198 kGy (30.1 MPa).

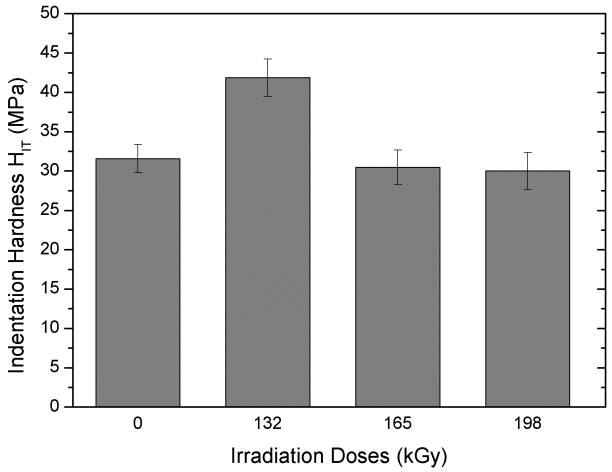

Figure 6. Indentation hardness H_{IT} of LDPE vs. irradiation doses.

Similar development was recorded for microstiffness of specimens represented by the elastic modulus of indentation (E_{IT}) illustrated in Fig. 7. The results of measurements show clearly that the lowest values of microstiffness were measured low density polyethylene **(**LDPE) irradiated by 198 kGy dose (0.24 GPa), while the highest values were reached in low density polyethylene **(**LDPE) irradiated by 132 kGy dose (0.31 GPa). Lower value of indentation elastic modulus (0.26 GPa) was measured on non-irradiated low density polyethylene **(**LDPE). A significant increase of microstiffness (16 %) was recorded at the radiation dose of 132 kGy compared to the non-irradiated low density polyethylene (LDPE).

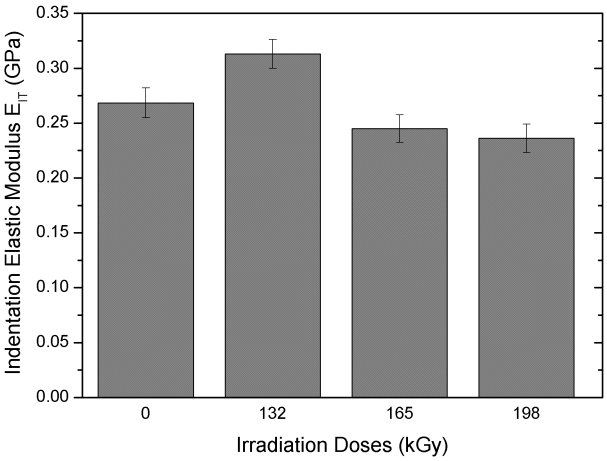

Figure 7. Indentation elastic modulus E_{IT} of LDPE vs. irradiation doses.

Table 1. Gel content of LDPE vs. irradiation doses

Irradiation doses	**0kGy**	**132kGy**	**165kGy**	**198kGy**
Gel content (%)	0	55	58	65

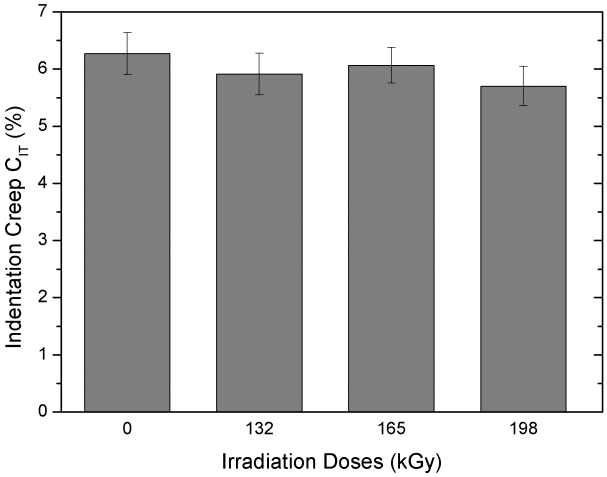

Figure 8. Indentation creep C_{IT} of LDPE vs. irradiation doses.

Plastic (W_{plast}) and elastic (W_{elast}) deformation measured during nanohardness test also showed (Fig. 9) that the lowest values of plastic deformation work were measured at the radiation dose of 132 kGy, while the highest values of plastic deformation work were found in non-irradiated low density polyethylene. This was also confirmed (Fig. 9) by the results of measurements of reverse relaxation coefficient (η_{IT}).

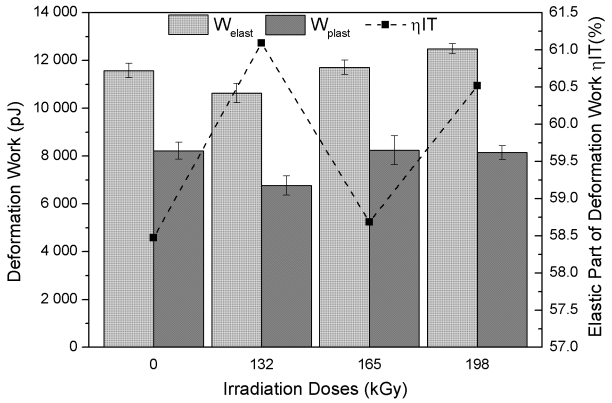

Figure 9. Deformation work of LDPE vs. irradiation doses.

Material deformation in time under constant stress (indentation creep) measured by instrumented test of nanohardness showed (Fig. 8) that the highest creep values were measured on non-irradiated low density polyethylene (6.27 %), while the lowest creep value was found in low density polyethylene irradiated by 198 kGy dose (5.7 %). The creep dropped by 10 % as a result of radiation, which represents a considerable increase of surface layer resistance.

Radiation, which penetrated through specimens, gradually formed cross-linking (3D net), first in the surface layer and then in the total volume, which resulted in considerable changes in specimen behavior. 3D net together with crystalline phase caused changes mainly in the surface layer, which led to a significant increase of indentation hardness and microstiffness of surface layer. This caused higher resistance of surface layer to wear, scratch, etc. Also, the creep values decreased as a result of changes made after the specimens were subjected to beta radiation.

Gel content showed the highest values at radiation dose of 198 kGy at which it reached 65 % degree of cross-linking, while the lowest value of degree of cross-linking was measured on non-irradiated (Table 1).

The figure 10 and show typical X-ray diffraction spectrum of the non-irradiated and irradiated low density polyethylene (LDPE). There is an apparent presence of α-phase in the non-irradiated specimen. The greatest grow of α-phase is seen at the radiation dose of 132 kGy (Fig. 10).

When applying β-radiation the structure of low density polyethylene undergoes loss and then a grow of the crystalline phase (Fig. 12). It can be assumed that the size of individual crystals will correspond with the loss of crystalline phase (crystalline value X calculated lay in the range 34.21-36.65 %). The greatest size of crystalline phase was found in the case at the radiation dose of 132 kGy (36.65 %). The lowest size of crystalline phase was found in the case at non-irradiated (34.21 %). Its influence on the mechanical behavior is insignificant. Cross-linking occurs in the remaining noncrystalline part which has a significant influence on the mechanical properties of the surface layer. Its influence on the mechanical behavior is insignificant.

The infra-red spectroscopy, IR, is the versatile method to follow chemical modifications in a polymeric material. Studies carried through by some researchers presented the formation of carbonyl groups.

The results of the infrared spectroscopy showed changes of relative representation of hydroxyl and carbonyl groups in relation to the radiation dose (Fig. 11). For evaluation hydroxyl groups we used an area of the strip integrated in the area of 3680-3126 cm^{-1}, (Each specimen was measured twice on both sides). For evaluation carbonyl groups we used an area of the strip integrated in the area of 1816-1500 cm^{-1}, (Each specimen was measured twice on both sides). When the specimen is irradiated, it leads to oxidation on C-H bonds and formation of oxygenic functional groups.

The smallest values of relative change of representation of hydroxyl and carbonyl groups were found at radiation dose of 0 kGy. At these doses the best values of mechanical properties of surface layer of the tested low density polyethylene (LDPE) were measured. The greatest change was found at radiation dose of 165 kGy (At this dose the poorer values of mechanical properties of surface layer of the tested low density polyethylene were measured). These changes of the structure correspond with the changes of mechanical properties of modified low density polyethylene (LDPE) beta radiation.

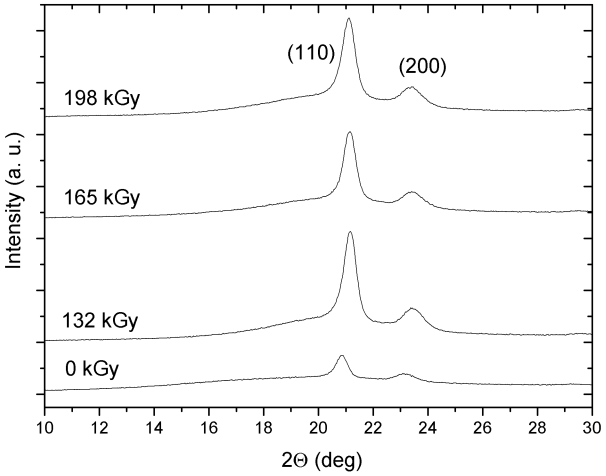

Figure 10. X-ray diffraction of non-irradiated and irradiated LDPE.

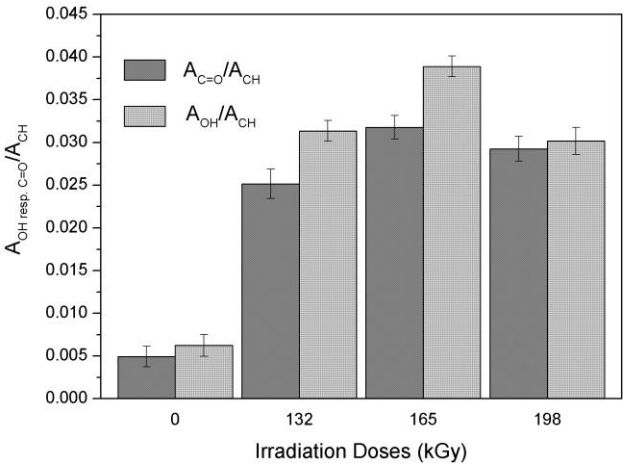

Figure 11. Change in the relative representation of hydroxyl and carbonyl groups of LDPE in relation to the irradiation doses

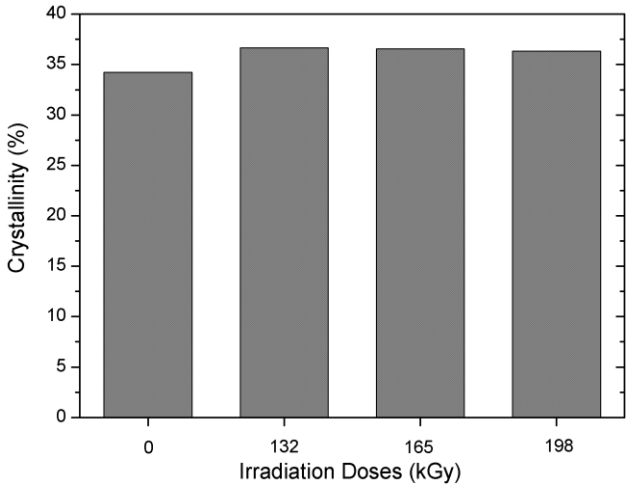

Figure 12. Crystalinity of non-irradiated and irradiated LDPE

Higher radiation dose does not influence significantly the nano-hardness value. An indentation hardness increase of the surface layer is caused by irradiation cross-linking of the tested specimen. A closer look at the nano-hardness results reveals that when the highest radiation doses are used, nano-hardness decreases which can be caused by radiation induced degradation of the material.

3 CONCLUSIONS

The experimental study deals with the effect of modification of the surface layer by irradiation cross-linking on the properties of the surface layer of low density polyethylene (LDPE). Low density polyethylene was modified by beta irradiation at doses of 0, 132, 165, 198 kGy. The changes of micromechanical properties were found at the radiation dose of 132 kGy for indentation hardness and elastic modulus (which increased by 32% and 16%) compared to the non-irradiated low density polyethylene. Improvement of mechanical properties in micro and macro scale of radiated low density polyethylene has a great significance also for industry. The modified low density polyethylene shifts to the group of materials which have considerably better properties. Its micromechanical properties make low density polyethylene ideal for a wide application in the areas where higher resistance to wear, scratch are required.

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