Ultra-nano Indentation Test of Crosslinked PBT Irradiated by Beta Rays

M. Ovsik, M. Stanek, A. Dockal and M. Manas, V. Senkerik

***Abstract*—** This article deals with the use of Ultra-nano indentation Tester UNHT^3 for the measurement of (ultra nano) mechanical properties. The effect of electron beam (EB) radiation on Polybutylene terephthalate (PBT) was investigated. To clarify whether crosslinking could take place without or only with the presence of a crosslinking agent, special attention was paid to the incorporation of this agent into tested polymer. In this study we have investigated the effect of crosslinking agent, and instantaneously electron beam radiation-induced crosslinking in the presence of Triallyl cyanurate on various mechanical properties of PBT. The results show that the influence of radiation has improved the observed properties in the surface layer. The increase in ultra-nano properties was around 26% over the basic material. Engineering plastics like Poly (butylene terephthalate) due to their desirable properties have various industrial applications.

***Keywords*—**PBT, crosslinked, beta rays, ultra-nano indentation, hardness.

I. Introduction

POLYBUTYLENE Terephthalate (PBT) is a semi-crystalline engineering thermoplastic material. It has similar properties and composition to polyethylene terephthalate (PET). It is a member of polyester family of polymers. PBT is produced by polycondensation of terephthalic acid or dimethyl terephthalate with 1,4–butanediol using special catalysts (Figure 1). [1] [2]

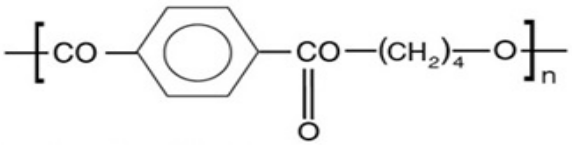

Fig. 1. Molecular Structure of Polybutylene Terephthalate. [1]

Polybutylene terephthalate has gained commercial interest due to its wide range of applications ranging from automotive, electrical and electronics, medical and many more. Properties of PBT: [3-5]

- It delivers excellent short-term mechanical properties, such as high strength, toughness and stiffness as well as good practical impact.
- It provides good creep resistance, dimensional stability and low moisture absorption characteristics.
- It gives good durability under thermal stress and harsh chemical environments, particularly in automotive underhood applications.

E-beam crosslinking is a powerful tool used to improve the properties of a wide range of polymers in the creation of value-added specialty products. The crosslinking of polymers through electron-beam processing changes a thermoplastic material into a thermoset. [6][7] When polymers are crosslinked, the molecular movement is severely impeded, making the polymer stable against heat. Crosslinking is the interconnection of adjacent long molecules with networks of bonds induced by chemical treatment or electron-beam treatment. This locking together of molecules is the origin of all of the benefits of crosslinking, including the improvement of the following properties: [8]

- Thermal: resistance to temperature, aging, low-temperature impact, etc.
- Mechanical: tensile strength, modulus, abrasion resistance, pressure rating, creep resistance, etc.
- Chemical: stress crack resistance, etc.
- Other: heat shrink memory properties, positive temperature coefficient, etc.

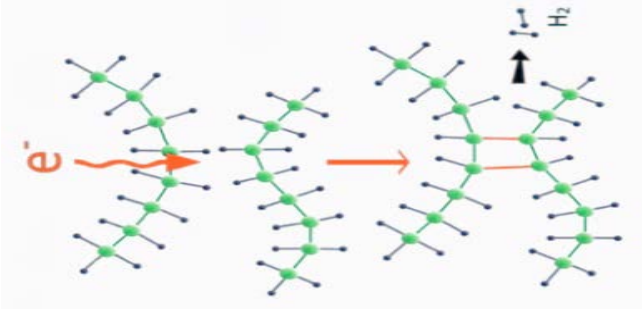

Fig. 2. Crosslinking process. [8]

Cross-linking is a process in which polymer chains are associated through chemical bonds. Cross-linking is carried

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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. 1). These not only are capable of converting monomeric and oligomeric liquids into solids, but also can produce major changes in properties of solid polymers [6, 7].

Common PBT, when exposed to the effect of the radiation cross-linking, degrades and its mechanical properties deteriorate. Using cross-linking agent TAIC (triallyl isocyanurate) produces a cross-linking reaction inside the PBT structure. The utility properties of PBT improve when the noncrystalline part of PBT is cross-linked [8].

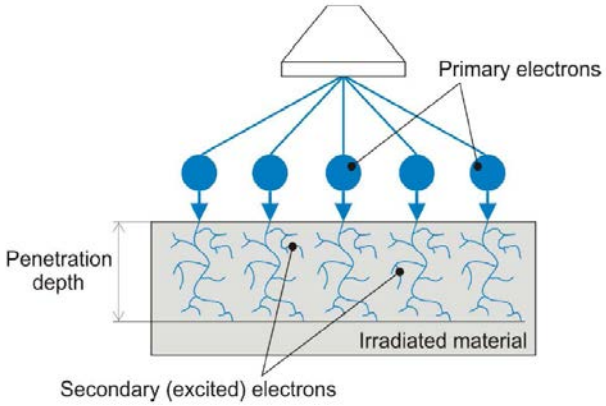

Fig. 3. Radiation crosslinking by electrons rays [9].

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 [9, 10].

The present work deals with the influence of ultra-nano indentation properties of irradiated crosslinked PBT. The aim of this paper is to study the effect of ionizing radiation with beta irradiation, on mechanical properties of surface layer of polybutylene terephthalate (PBT) and compare these results with those of non-irradiated samples.

II. Experimental

A. Material

For this experiment Polybutylene terephthalate (PBT) V-PTS-CREATECB3HZC * M800/25 nature (PTS Plastics Technologie Service, Germany) was used. The material already contained the special crosslinking agent TAIC - triallyl isocyanurate (6 volume %), which should enable subsequent crosslinking by ionizing β – radiation.

B. Sample preparation

The samples were made using injection molding technology on an Arburg Allrounder 470H injection molding machine (Loßburg, Germany). The normalized specimens, with dimensions of (80 x 10 x 4) mm, were used (Figure 4). The process parameters were set according to the manufacturer's recommendations; see Table 1.

Table 1 Process parameters.

Parameters	Unit	PBT
Injection Pressure	MPa	70
Cooling Time	s	20
Mould Temperature	°C	60
Zone 1	°C	250
Zone 2	°C	260
Zone 3	°C	270
Zone 4	°C	280

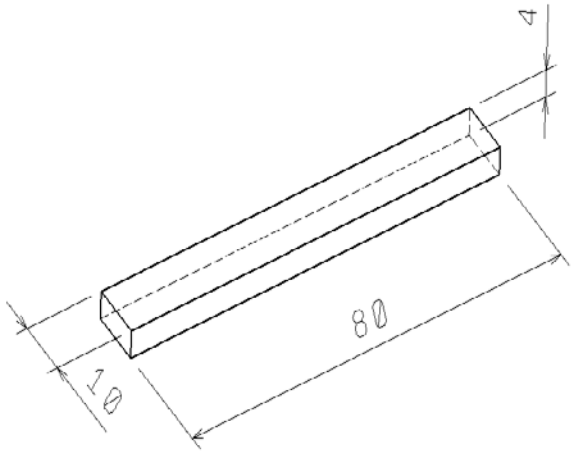

Fig. 4 Dimension of sample.

C. Irradiation process

The crosslinking causes the connection of polymeric chains to each other, most often using covalent bonds to form the spatial network. Test bodies were irradiated under industrial conditions on a commercially available irradiation device in a broader range of radiation doses (0, 33, 66 and 99 kGy) compared to the doses corresponding to the experience in the practice.

All samples were irradiated with electron (beta) rays (accelerated electrons - A Rhodotron R E-beam accelerator, electron energy 10 MeV) in the firm BGS Beta Gamma Service GmbH & Co, Saal am Danau – Germany.

D. Ultra-nano indentation test

Ultra-nano indentation tests were performed using a special technics ultra-nano indentation tester UNHT^3 (Figure 5), made by Anton Paar (Graz, Austria), according to the CSN EN ISO 14577 standard. The measurement was carried out using the depth sensing indentation (DSI) method. This method enables one to measure the force acting on the indentor, as well as the displacement of the indentor´s tip. The tip is made of diamond and its shape is that of a cube corner (Vickers).

The measurement parameters are shown in Table 2. In Table 3 the Ultra Nanoindentation Tester - UNHT³ is technically specified.

Table 2. Measurement parameters.

Parameters	Unit	Value
Maximum Load	uN	500
Load/Unload Speed	uN/min	1000
Holding Time	s	90

Table 3. Technically specified.

Parameters	Unit	Value
Force	mN	0.01 - 100
Resolution	nN	3
Depth	um	100
Resolution	nm	0.003
International standards		ISO 14577, ASTM E2546

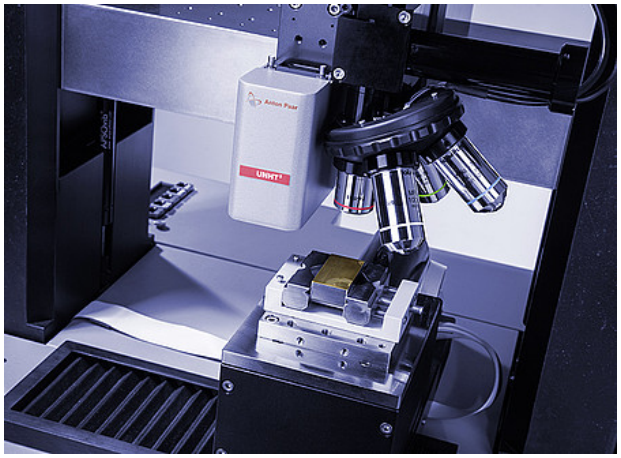

Fig. 5. Ultra-nano indentation Tester UNHT³

The indentation hardness (H_{IT}) was calculated as maximum load (F_{max}) to the projected area of the hardness impression (Ap) and the indentation modulus (E_{IT}) is calculated from the Plane Strain modulus (E*) using an estimated sample Poisson's ratio (ν) according to [11-17]:

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

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

Elastic and plastic part of the indentation work (figure 5):

$$\eta_{IT} = \frac{W_{elast}}{W_{total}} \cdot 100 \quad (3)$$

$$W_{total} = W_{elast} + W_{plast} \quad (4)$$

Plastic part W_{plast} / W_{total} follows as 100% - ηIT

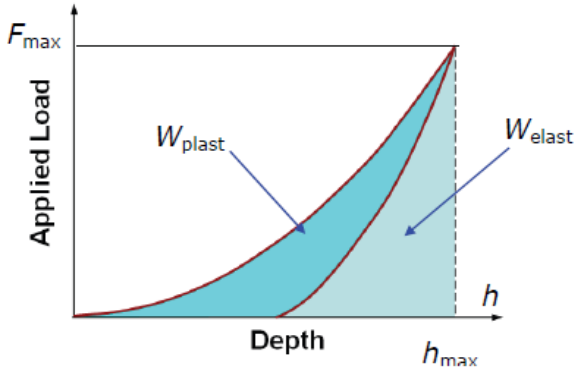

Fig. 6. Indentation work

Measurement of all above mentioned properties was performed 10 times to ensure statistical correctness.

E. 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.

F. 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.

III. Results and Discussion

In Figures 7 and 8, indentation characteristics which are the basic measurement output are shown. From these dependencies the mechanical properties characterizing the surface of the test material are calculated. The test surface depth is 600 nm as shown in Figures 7 and 8.

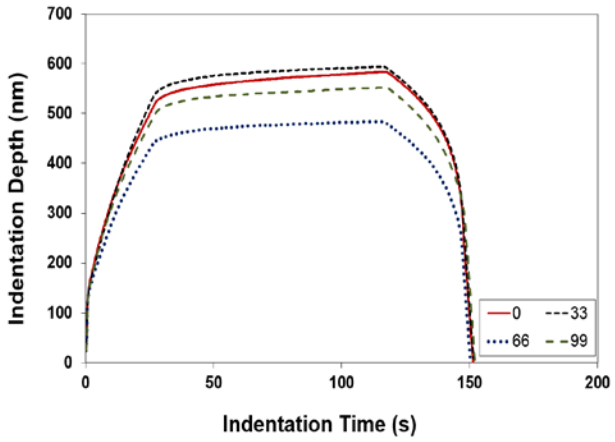

Fig. 7. Indentation characteristic

Figure 6 shows the dependence of the indentation depth on the indentation time. From this dependence, it is possible to determine creep properties of the tested material. Figure 8 shows the dependence of the indentation load on the indentation depth. Mechanical properties such as hardness, modulus, deformation work, etc. were calculated from this dependence, etc. Thanks to these indentation curves, it is possible to assess the behaviour of the material and its surface properties.

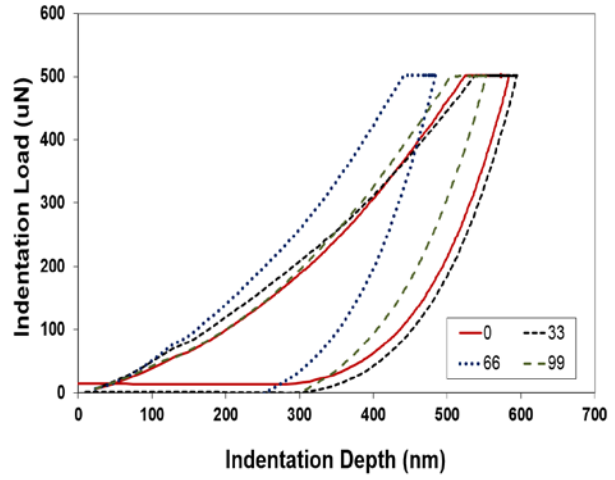

Fig. 8. Indentation characteristic

The measured values of the ultra-nano indentation test were obtained for PBT irradiated with beta rays as shown in Table 4.

Table 4. Ultra-nano indentation values

Parameters	Unit	0 kGy	33kGy	66kGy	99kGy
H_{IT}	MPa	116,89	130,49	137,25	141,13
HV_{IT}	Vickers	10,83	12,08	12,71	13,07
E_{IT}	GPa	1,93	1,99	1,99	2,18
Wel	pJ	39,62	39,31	39,97	34,53
Wpl	pJ	68,41	63,32	59,79	54,46
C_{IT}	%	11.87	9.93	9.86	9.14

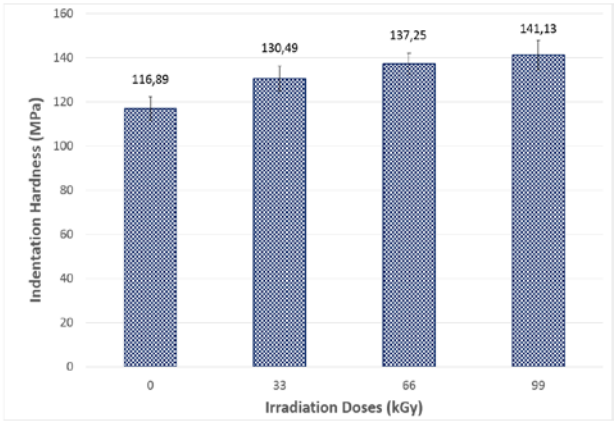

Fig. 9. Indentation hardness vs. Irradiation doses

From the results of the ultra-nano indentation test it is clear that irradiation has a positive effect on the indentation hardness of the surface layer of the tested PBT. The non-irradiated material exhibited an indentation hardness of approximately 117 MPa, while the highest hardness value was measured for PBT irradiated at the dose of 99 kGy, where the indentation hardness was 141 MPa. This performance improvement was up to 21%, bringing PBT to the area of materials with better properties (Figure 9).

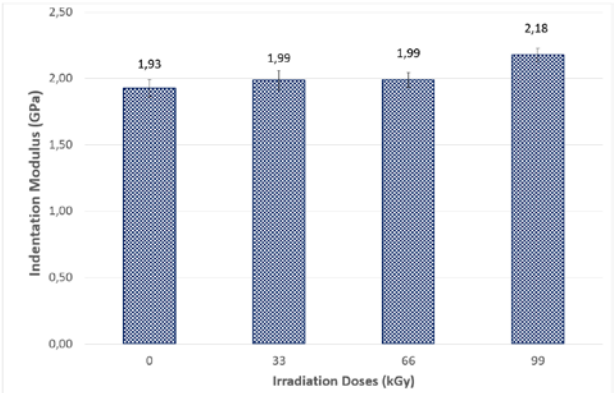

Fig. 10. Indentation modulus vs. Irradiation doses

An important feature for assessing the mechanical properties of the surface of the component is the stiffness of the surface

layer, which is characterized by the indentation modulus, as can be seen at Figure 10. This modulus corresponds to the modulus of elasticity obtained from the tensile test. Again, the base material showed the value of the indentation modulus 1.9 GPa. The highest improvement in the properties was due to irradiation of the tested PBT at a dose of 99 kGy, where the indentation modulus was 2.2 GPa. The increase of the indentation modulus was 13%.

Similar results were obtained at Vickers hardness. The smallest Vickers hardness value was again fount out at non-irradiated material (11 Vickers). With the increasing radiation dose, the properties have gradually improved. The best values were measured at a dose of 99 kGy (13 Vickers). The increase in vickers hardness at a radiation dose of 99 kGy was 21%.

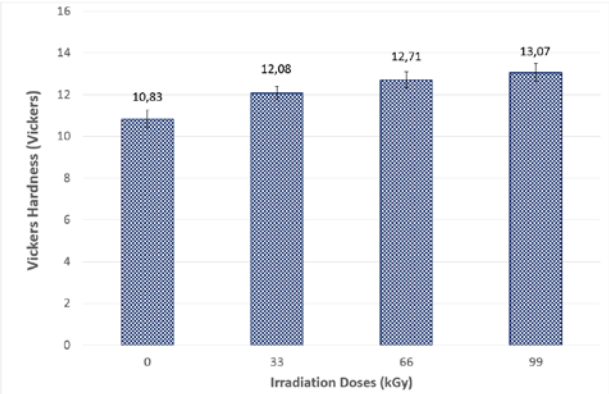

Fig. 11. Indentation Vickers hardness

To assess the properties of the surface layer is an important parameter of the deformation work, which describes the elastic and plastic part of the material (Figure 12.). The non-irradiated material showed a value of 68 pJ of plastic work and the elastic part of the work was 40 pJ. With the dose of radiation there was a decrease in both components of the deformation work. The plastic work was 54 pJ and the elastic work was 35 pJ. The difference in the decrease of both works was 26%.

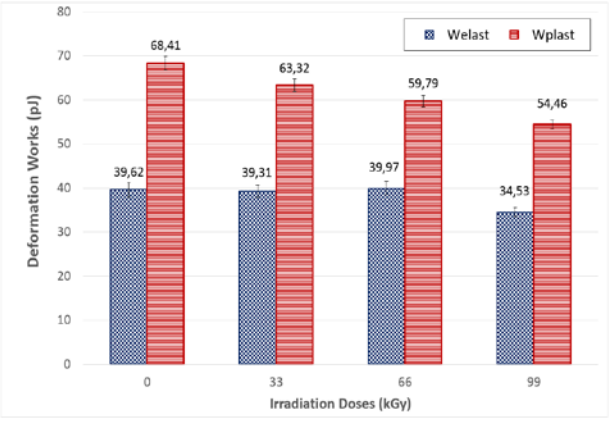

Fig. 12. Indentation works vs. Irradiation doses

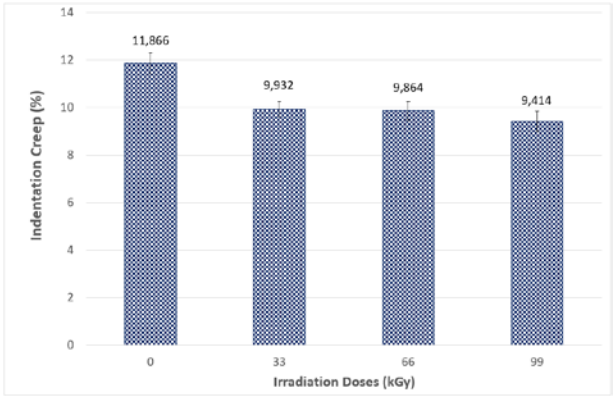

Fig. 13. Indentation creep vs. Irradiation doses

Indentation creep is very important property for description of polymer behavior. If the change of impression depth during constant stress is measured a relative depth impression can be calculated (this value represents material fluidity – creep).

Worst value (11,9 %) of creep was measured in polymer that was not irradiated. With increasing value of radiation an improvement in creep value could be observed in the tested material. Results of testing clearly show that best creep value (9,4 %) was measured in material irradiated by 99 kGy of radiation. When comparing unaltered material and material exposed to 99 kGy of radiation, an improvement to material fluidity during constant stress was up to 27 %.

Table 5. X-ray diffraction of PBT

Irradiation doses (kGy)	$X_{X\text{-ray}}$, %, ±1%
0	31
33	29
66	33
99	31

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 stiffness 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.

The Figure 14 shows typical X-ray diffraction spectrum of the non-irradiated and irradiated polybutylene terephthalate. 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 99 kGy (Fig. 12).

When applying β-radiation the structure of polypropylene undergoes loss and then a grow of the crystalline phase. 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 29-33 %). Cross-linking occurs in the remaining noncrystalline part which has a significant influence on the mechanical properties of the surface layer. The greatest size of crystalline phase was found in the case at the radiation dose of 66 kGy (33 %). The lowest size of crystalline phase was found in the case at the radiation dose of 99 kGy (31 %). On the contrary the smaller size of crystalline phase was measured at non-irradiated (31 %). 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 carbonyl groups in relation to the radiation dose (Fig. 13).

When the specimen is irradiated, it leads to oxidation on C-H bonds and formation of oxygenic functional groups.

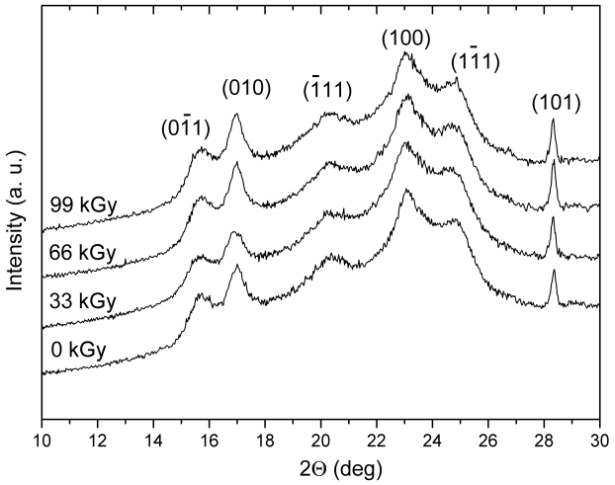

Fig. 14. X-ray diffraction of non-irradiated and irradiated PBT

Differential spectra of PBT specimens in the area of 1850 – 1200 cm^{-1}. Spectra are dominated by bands of valence vibrations of C=O of bonds of carboxyl groups at ~1700 cm^{-1} and C-O at 1265 cm^{-1}. Negative bands of small intensity at 1472 and 1462 cm^{-1} belong to deformation vibrations of aliphatic C-H bonds.

Change in relative abundance of carbonyl groups depending on the radiation dose of PBT. Changes in the content of carbonyl groups were expressed by the ratio between the band area in 1800-1500 cm^{-1} and the band area of valence vibrations of aliphatic C-H bonds in 3000 – 2700 cm^{-1}.

The smallest values of relative change of representation of carbonyl groups were found at radiation dose of 0 kGy. At this dose the worse values of mechanical properties of the tested polybutylene terephthalate (PBT) were measured. The greatest change was found at radiation dose of 99 kGy. These changes of the structure correspond with the changes of mechanical properties of modified polybutylene terephthalate (PBT) beta radiation.

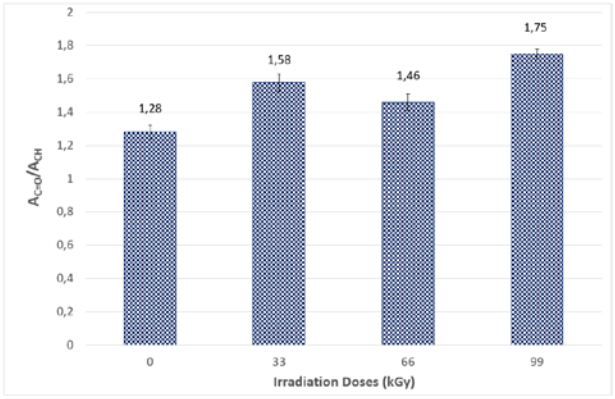

Fig. 15. Change in the relative representation of carbonyl groups of PBT in relation to the irradiation doses

IV. Conclusions

From the above results, it is evident that beta radiation crosslinking has an influence on the micro-mechanical properties of PBT. These polymers were modified using beta radiation of differing radiation doses (33, 66 and 99 kGy).

The micro-mechanical properties (indentation hardness and indentation modulus), were measured using the DSI method for all of the polymers tested. The thermo-mechanical analysis confirmed the influence of radiation doses on the structure of the polymers that were studied. The higher the dose of radiation, the higher the micro-mechanical properties of the studied polymers above the values of micro-mechanical properties of a basic polymer (0 kGy), which was compared with the knowledge gained from the literature. From the measurements, it can be stated that the highest changes were achieved by all materials examined at higher doses of radiation (99 kGy). Indentation hardness was increased by 21 % (figure 9). Indentation modulus rose by 13% (figure 10), hardness by Vickers rose by 21 % (figure 11), both components of deformation work had better values in samples irradiated by 99 kGy of radiation respectively (figure 12). Nevertheless, it is necessary to mention that it is always necessary to thoroughly consider the final radiation dose with respect to the efficiency of the irradiation process. In some cases, it is possible to also choose a lower radiation dose with comparable modification results being reached.

The micro-mechanical properties results were supported by the measurement of the structure, where gel test measurement, wide-angle X-ray diffraction, and Raman spectroscopy tests were performed.

It should also be noted that a higher dose of radiation intensity does not necessarily mean a higher improvement in the desired properties. For a particular application and material it is always necessary to look for a suitable radiation dose intensity.

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