

# Mechanical properties of surface layer of unfilled polypropylene

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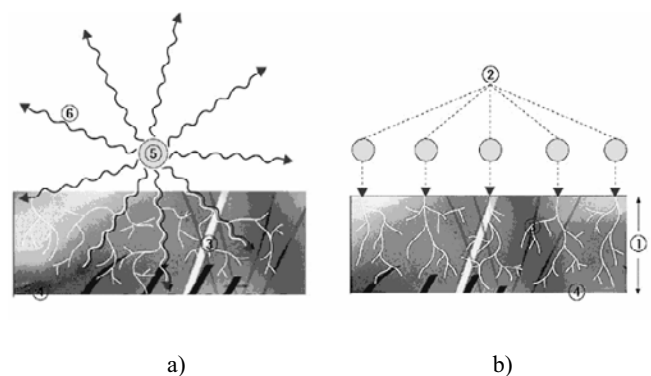
**Abstract.** Using high doses of beta radiation for unfilled polypropylene (PP) and its influence on the changes of micromechanical properties of surface layer has not been studied in detail so far. The testing samples polypropylene (PP) were made by injection moulding technology and irradiated by high doses of beta radiation (0, 15 and 33 kGy). The changes in the microstructure and micromechanical properties of surface layer were evaluated using WAXS and instrumented ultra nano-hardness test. The results of the measurements showed considerable increase in micromechanical properties (indentation hardness, indentation elastic modulus) when low doses of beta radiation are used.

## 1 Introduction

Polypropylene is a versatile, low cost, chemically stable and lightweight polymer, which offers attractive mechanical, electrical and thermal properties due to its relative higher degree of crystallinity. This is used in many applications such as radiation-sterilized medical and pharmaceutical components, food packaging materials and cosmetics [5]. A literature survey [6–11] indicates that effects of 14.89 MeV electron irradiation on polyethylene and polystyrene in the dose range of 57.6–576 KGy showed a greater red shift in absorption edge of polyethylene as compared to polystyrene [6]. Whereas, the enhancement in the thermal properties, dielectric constant, dielectric loss and crystallinity of 2 MeV and 1.5 MeV electron irradiated polypropylene has also shown considerable modifications [7,8]. However, more investigations are needed as far as the radiation energy, mode of energy deposition and energy densities are concerned. In particular, the effects of highenergy pulsed electron irradiation on mechanical Properties such as surface hardness and surface roughness of polypropylene needs more attention. Out of several types of radiations that can be used for radiation processing, high-energy electrons are of particular interest, especially for polymers, due to their high dose rates and consequently high-energy deposition in lesser time intervals. This not only achieves high process rates, but also allows crosslinking, as oxidation effects are relatively weak at the high dose rates. Moreover, electron beam irradiation also offers facility of easy control, maintenance of steady dose rate without any depletion and homogeneous energy deposition [2,6,12].

The principle of the radiation process is the ability of the high energy radiation to produce reactive cations, anions and free radicals in the material. The industrial

application of the radiation process (Figure 1) on polymer and composites includes polymerization, crosslinking and degradation. The radiation process involves mainly the use of either electron beam from electron accelerators or gamma radiation from Cobalt – 60 sources.



**Fig. 1.** Design of Gamma rays (a) and Electron rays (b).  
a) 3 – secondary electrons, 4 – irradiated material, 5 – encapsulated Co – 60 radiation source, 6 – Gamma rays  
b) 1 – penetration depth of electron, 2 – primary electron, 3 – secondary electron, 4 – irradiated material

The aim of this paper is to study the effect of ionizing radiation with different doses, on ultra nano-hardness of surface layer of polypropylene (PP) and compare these results with those of non-irradiated samples. The study is carried out due to the ever-growing employment of this type of polymer polypropylene (PP) [3-10].

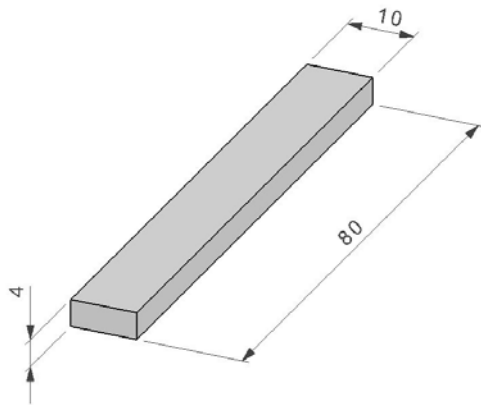
## 2 Experimental

### 2.1 Material and methods

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For this experiment PTS-Crealeen EP-2300L1-M800; PTS Plastics Technologie Service, Germany (unfilled, iPP+TAIC, MFR—230 °C /2,16 kg—6 g/10 min) was used. The material already contained a special cross-linking agent TAIC—triallylisocyanurate (6 volume %), which should enable subsequent cross-linking by ionizing  $\beta$ -radiation. Irradiation was carried out in the company BGS Beta Gamma Service GmbH & Co, KG, Germany with the electron rays, electron energy 10 MeV, doses minimum of 0, 15 and 33 kGy on air the ambient temperature.

The samples (Figure 2) were made using the injection molding technology on the injection moulding machine Arburg Allrounder 420C. Processing temperature 245–295 °C, mold temperature 85 °C, injection pressure 80 MPa, injection rate 45 mm/s. [7-17]



**Fig. 2.** Dimension of sample.

## 2.2 Ultra nano-hardness test

Nano-indentation test was done using a Ultra Nanoindentation Tester (UNHT) (Fig. 5), CSM Instruments (Switzerland) according to the CSN EN ISO 14577. Load and unload speed was 1000  $\mu$ N/min. After a holding time of 90 s at maximum load 500  $\mu$ N the specimens were unloaded. The specimens were glued on metallic sample holders (Fig. 2). [7-17]

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



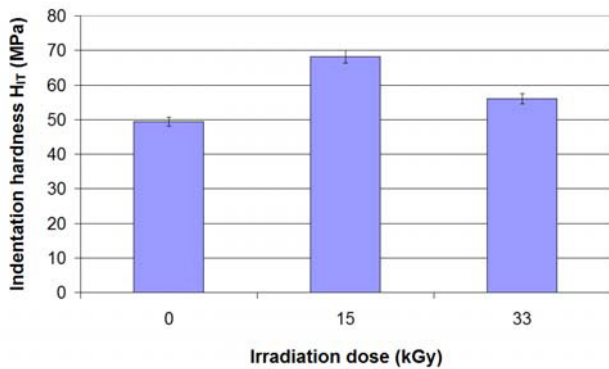
**Fig. 3.** Ultra nano-indentation tester.

## 2.3 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  $\text{CuK}\alpha$  radiation was Ni-filtered. The scans ( $4.5^\circ 2\Theta/\text{min}$ ) in the reflection mode were taken in the range  $5\text{--}30^\circ 2\Theta$ . The sample crystallinity (X) was calculated from the ratio of the crystal diffraction peaks and the total scattering areas. Crystall size  $L_{100}$  of  $\alpha$  most intensive peak at 100 was calculated using Scherrer equation. As a standard "perfect" crystal terephthalic acid with the peak at  $2\Theta = 17.4^\circ$  and the half maximum breadth  $0.3^\circ 2\Theta$  was chosen [7-17].

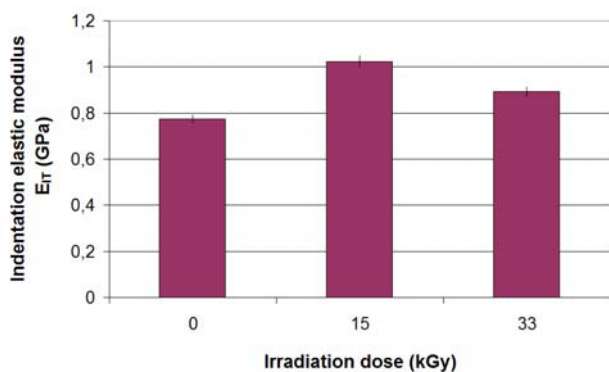
## 3 Results and discussion

The development of micromechanical properties of irradiated polypropylene (PP) was characterized by the instrumented test of ultra nanohardness (indentation hardness  $H_{IT}$ ), as can be seen in Figure 4. The highest values of indentation hardness (68 MPa) were found on polypropylene (PP) irradiated with radiation dose of 15 kGy radiation dose, while the lower value of indentation hardness (56 MPa) was measured at 33 kGy radiation dose. The lowest values (49 MPa) of indentation hardness were found on non-irradiated polypropylene (PP). The increase of microhardness at 15 kGy radiation dose was by 38 % compared to the non-irradiated polypropylene (PP).



**Fig. 4.** Indentation hardness  $H_{IT}$  vs. irradiation doses.

Similar development was recorded for microstiffness of specimens represented by the elastic modulus of indentation ( $E_{IT}$ ) illustrated in Figure 5. The results of measurements show clearly that the highest values of microstiffness were measured on the polypropylene (PP) (1.02 GPa) irradiated with radiation dose of 15 kGy, while the lower values were reached in polypropylene (PP) irradiated by 33 kGy dose (0.82 GPa). The lowest values (0.77 MPa) of microstiffness were found on non-irradiated polypropylene (PP). A significant increase of microstiffness (32 %) was recorded at the radiation dose of 15 kGy compared to the non-irradiated polypropylene (PP).



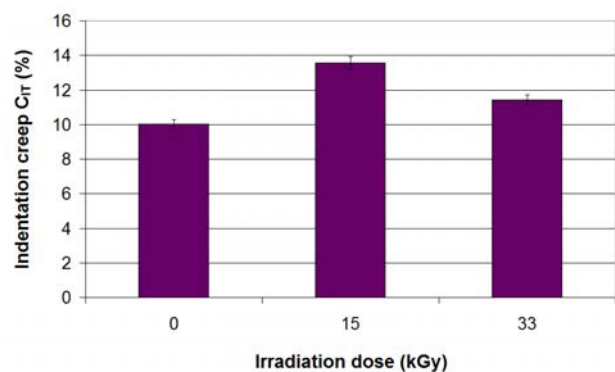
**Fig. 5.** Indentation elastic modulus  $E_{IT}$  vs. irradiation doses.

Other important material parameters obtained during the micro-hardness test were elastic and plastic deformation work. The mechanical work  $W_{total}$  induced by the indentation is only partly consumed as plastic deformation work  $W_{plast}$ . During the removal of the test force the remaining part is set free as work of the elastic reverse deformation  $W_{elast}$ .

Very important values were found for indentation creep. For materials which creeps as polymers, a basic calculation of that creep can be measure during a pause at the maximum force. The creep is the relative change of the indentation depth when the test force is kept constant measured by instrumented test of microhardness showed (Figure 6) that the lowest creep values were measured on non-irradiated polypropylene (PP) (10 %), while the highest creep value was found in polypropylene (PP) irradiated by 15 kGy dose (13 %). The creep increased by

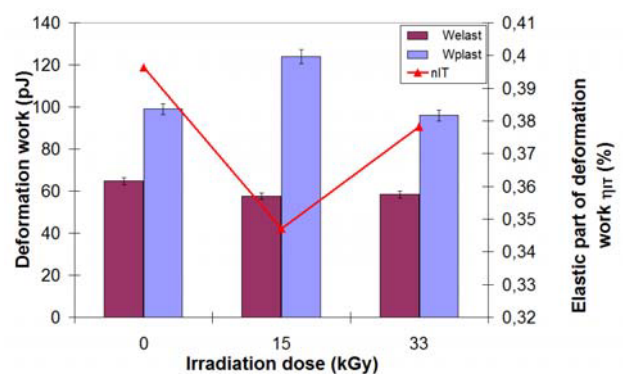
35 % as a result of radiation, which represents a considerable decrease of surface layer resistance.

When applying  $\beta$ -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 45-67 %). Cross-linking occurs in the remaining noncrystalline part which has a significant influence on the mechanical properties of the surface layer. The greatest size (Table 1) of crystalline phase was found in the case at the radiation dose of 15 kGy (67 %). The smaller size of crystalline phase was found in the case at the radiation dose of 33 kGy (54 %). On the contrary the smallest size of crystalline phase was measured at non-irradiated (45 %). Its influence on the mechanical behavior is insignificant.



**Fig. 6.** Indentation creep  $C_{IT}$  vs. irradiation doses.

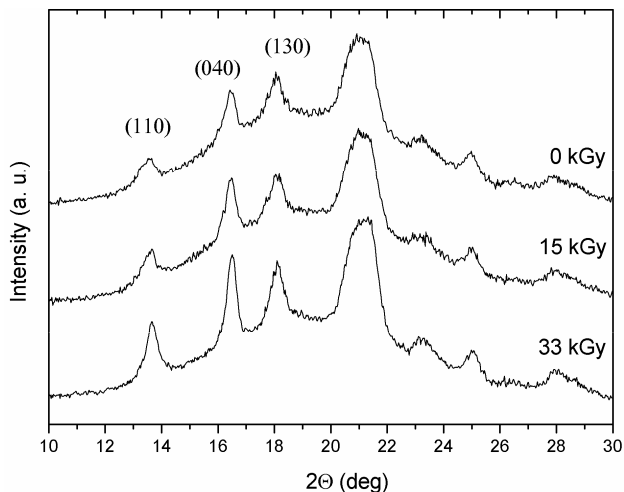
The highest values of elastic deformation work were obtained for non-irradiated polypropylene (PP). The highest values of plastic deformation work were obtained for polypropylene (PP) irradiated with radiation dose of 15 kGy. The lowest values of  $W_{el}$ , were obtained for polypropylene (PP) irradiated with dose of 15 kGy. Radiation of specimens caused lower values of plastic deformation work which is in Figure 7.



**Fig. 7.** Deformation work vs. irradiation dose.

Higher radiation dose does not influence significantly the micro-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 micro-hardness results reveals that when the highest radiation doses are used, micro-hardness decreases which can be caused by radiation induced degradation of the material.



**Fig. 8.** X-ray diffraction non-irradiated and irradiated PBT.

The figure 8 shows typical X-ray diffraction spectrum of the non-irradiated and irradiated polypropylene (PP). There is an apparent presence of  $\alpha$ -phase in the non-irradiated specimen. The greatest grow of  $\alpha$ -phase is seen at the radiation dose of 15 kGy (Figure 8).

**Table 1.** X-ray diffraction of non-irradiated and irradiated PP.

Sample	X X-ray, %,±1%
0 kGy	45
15 kGy	67
33 kGy	54

## 4 Conclusion

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 polypropylene (PP). Polypropylene (PP) was modified by beta irradiation at doses of 0, 15 and 33 kGy. The changes of micromechanical properties were found at the radiation dose of 15 kGy for indentation hardness which decreased by 38% compared to the non-irradiated polypropylene (PP). Improvement of mechanical properties in micro and macro scale of radiated polypropylene (PP) has a great significance also for industry. The modified polypropylene (PP) shifts to the group of materials which have considerably better properties. Its micromechanical properties make polypropylene (PP) ideal for a wide application in the areas where higher resistance to wear, scratch are required.

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