EFFECT OF LOW BETA IRRADIATION DOSE ON MECHANICAL PROPERTIES OF SURFACE LAYER OF INJECTION MOULDED POLYAMIDE 11 (PA 11)

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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 polyamide 11 (PA 11) and its influence on the changes of mechanical properties of surface layer has not been studied in detail so far. The specimens of polyamide 11 (PA 11) were made by injection moulding technology and irradiated by low doses of beta radiation (0, 33, 66 and 99 kGy). The changes in the microstructure and micromechanical properties of surface layer were evaluated using FTIR, WAXS and instrumented microhardness 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

Polyamide 11 (PA 11), cross-linking, micro-hardness, micro-mechanical properties, surface layer

1 INTRODUCTION

The engineering polymers are a very important group of polymers which offer much better properties in comparison to those of standard polymers [Woods 1974, Barlow 1979]. Both mechanical and thermal properties are much better than in case of standard polymers [Pharr 1998, Drobny 2003]. The production of these types of polymers takes less than 1 % of all polymers (Fig. 1).

Cross-linking is a process in which polymer chains are associated through chemical bonds [Oliver 2004, Zamfirova 2010]. 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.

Polyamide 11 (PA 11) is a bio-based crystallizable polymer which is produced from castor oil and is gaining an increasing importance due to its potential to replace petroleum-based polymers [Ragan 2012]. It is used for many high-performance engineering applications due to its balanced property profile including relatively high thermal stability, excellent chemical resistance, and reasonable mechanical characteristics.

As a rule, holding for all crystallizable polymers the properties of PA 11 depend on the semicrystalline morphology which can be adjusted in wide ranges regarding the structure, fraction, shape, and spatial arrangement of crystals [Behalek 2013, Ovsik 2012-2015].

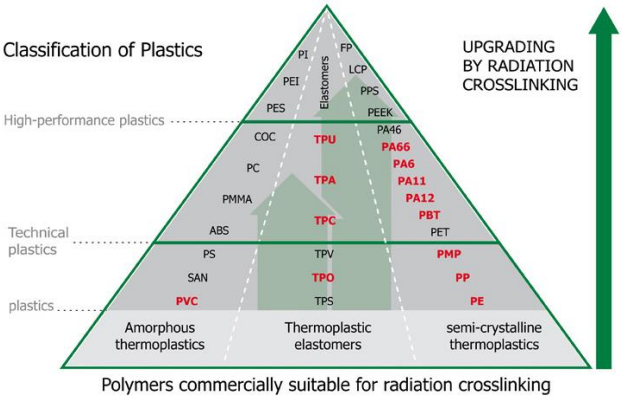

Figure 1. Upgrading by radiation cross-linking of PBT

Major tools to control such structural parameters are the variation of the condition of melt crystallization or the addition of nucleating agents, promoting the crystallization process [Dobransky 2015]. Though typically added to tailor properties according to composite rules in this work, the effect of the presence of two different types of nanofillers on the crystallization kinetics and the semicrystalline morphology of PA 11 is evaluated [Manas 2015].

Regarding the crystallization behavior of the unmodified PA 11, it is known that, depending on the crystallization conditions, different crystal structures may form. Slow cooling of the melt leads to formation of triclinic δ-crystals which convert reversibly to α-crystals at the Brill transition temperature of about 100 °C. The equilibrium melting temperature of the α-structure is between 203 and 220 °C and the bulk enthalpy of fusion is between 189 and 244 J g^{-1}. These crystals, which form at low supercooling of the melt, are of lamellar shape and are organized within spherulites. Rapid cooling of the melt at rates between 100 and 500 K s^{-1} suppresses δ/α-crystal formation at low supercooling and leads to development of a pseudohexagonal δ'-phase of nodular shape at temperatures lower than 80 °C even faster cooling prevents all ordering and causes complete vitrification of the melt at the glass transition temperature T_g of around 40 °C. Recent analysis of the rate of isothermal crystallization revealed maxima at about 105 and 70 °C, with the bimodal dependence of the crystallization rate on temperature related to the occurrence of different nucleation mechanisms; this view is supported by an analysis of the nucleation density of samples crystallized at different supercooling.

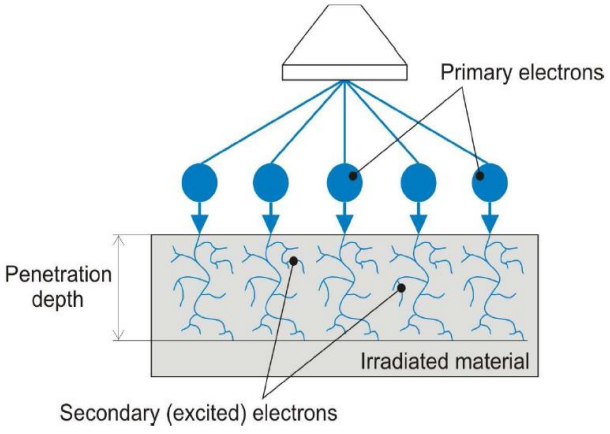

Figure 2. Design of Electron rays

The aim of this paper is to study the effect of ionizing radiation with low doses beta irradiation, on mechanical properties of surface layer of polyamide 11 (PA 11) and compare these results with those of non-irradiated samples.

2 EXPERIMENTAL

2.1 Material and methods

For this experiment polyamide 11 V-PTS-CREAMID-11T*M600/13 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, 33, 66 and 99 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.

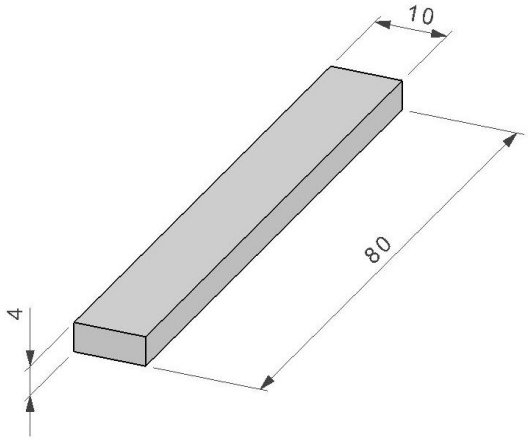

Figure 3. Dimensions of sample

2.2 Micro-indentation test

Micro-indentation test were done using a Micro-indentation tester (NHT) (Fig. 5), CSM Instruments (Switzerland) according to the CSN EN ISO 14577. Load and unload speed was 1 mN/min. After a holding time of 90 s at maximum load 0.5 N the specimens were unloaded. The specimens were glued on metallic sample holders (Fig. 3).

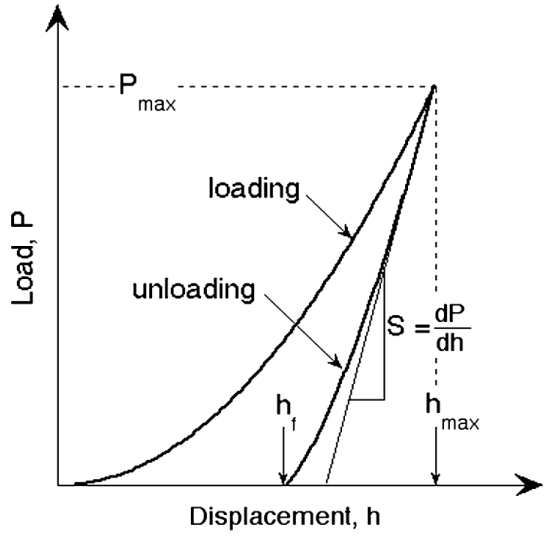

Figure 4. Schematic illustration of indentation curve

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

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

The indentation hardness (H_{IT}) was calculated as a 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

2.3 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 PA 11 because it dissolves the amorphous part of PA 11, 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

2.4 *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.

2.5 *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.

3 RESULTS AND DISCUSSION

The development of micromechanical properties of irradiated polyamide 11 (PA 11) was characterized by the instrumented test of microhardness, as can be seen in Fig. 6. The highest values (127.9 MPa) of indentation hardness (H_{IT}) were found at 33 kGy radiation dose. The lowest value of indentation hardness (123.5 MPa) was measured on non-irradiated polyamide 11 (PA 11). The increase of indentation hardness at 33 kGy radiation dose was by 3.5 % compared to the non-irradiated polyamide 11 (PA 11).

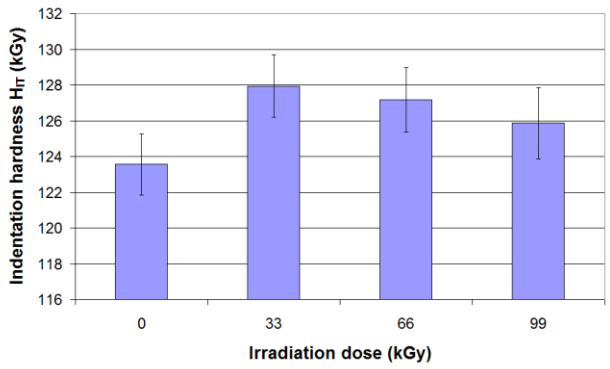

Figure 6. Indentation hardness H_{IT} of PA 11 vs. irradiation doses.

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 on non-irradiated polyamide 11 (PA 11) (1.83 GPa), while the highest values were reached in polyamide 11 **(**PA 11) irradiated by 33 kGy dose (1.86 GPa). The Lowest value of indentation elastic modulus (1.83 GPa) was measured on non-irradiated polyamide 11 (PA 11). A significant increase of microstiffness (1.5 %) was recorded at the radiation dose of 33 kGy compared to thnon-irradiated polyamide 11 (PA 11).

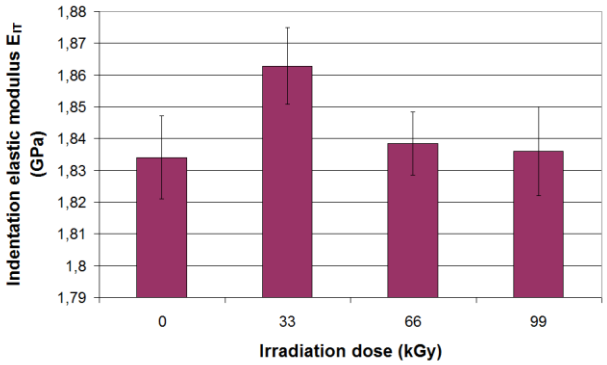

Figure 7. Indentation elastic modulus E_{IT} of PA 11 vs. irradiation doses

Irradiation doses	0kGy	33kGy	66kGy	99kGy
Gel content (%)	0	33	87	76

Table 1. Gel content of PA 11 vs. irradiation doses

Sample LDPE	$X_{X\text{-}ray}$, %, ±1%
0 kGy	35
33 kGy	38
66 kGy	40
99 KGy	37

Table 2. X-ray diffraction of non-irradiated and irradiated PA 11

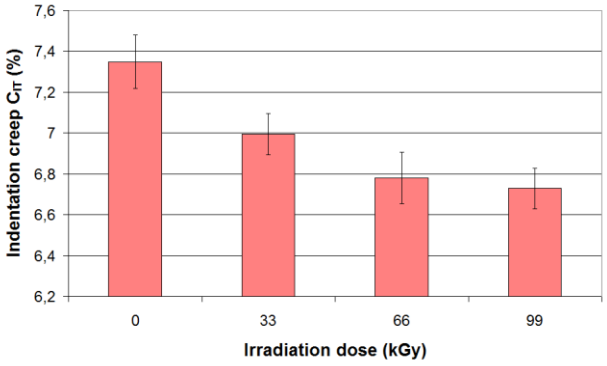

Figure 8. Indentation creep CIT of PA 11 vs. irradiation doses

Material deformation in time under constant stress (indentation creep) measured by instrumented test of microhardness showed (Fig. 8) that the highest creep values were measured on non-irradiated polyamide 11 (7.34 %), while the lowest creep value was found in polyamide 11 irradiated by 99 kGy dose (6.72 %). The creep dropped by 5 % as a result of radiation, which represents a considerable increase of surface layer resistance.

Plastic (W_{plast}) and elastic (W_{elast}) deformation measured during microhardness test also showed (Fig. 9) that the lowest values of plastic deformation work were measured at the radiation dose of 99 kGy, while the highest values of plastic deformation work were found in non-irradiated polyamide 11. This was also confirmed (Fig. 9) by the results of measurements of reverse relaxation coefficient (η_{IT}).

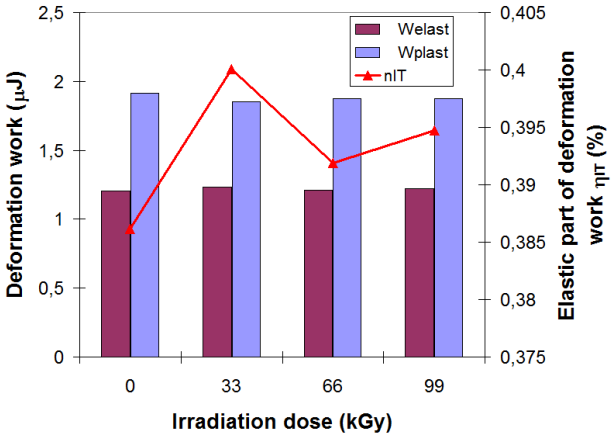

Figure 9. Deformation work of PA 11 vs. irradiation doses

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 87 % 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 polyamide 11 (PA 11). 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 33 kGy (Fig. 10).

When applying β-radiation the structure of polyamide 11 undergoes loss and then a grow of the crystalline phase (Table 2). 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 35-40 %). The greatest size of crystalline phase was found in the case at the radiation dose of 66 kGy (40 %). The lowest size of crystalline phase was found in the case at non-irradiated (35 %). 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 3570-3006 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 1768-1483 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 worse values of mechanical properties of surface layer of the tested polyamide 11 (PA 11) were measured. The greatest change was found at radiation dose of 33 kGy (At this dose the best values of mechanical properties of surface layer of the tested polyamide 11 (PA 11) were measured). These changes of the structure correspond with the changes of mechanical properties of modified polyamide 11 (PA 11) beta radiation.

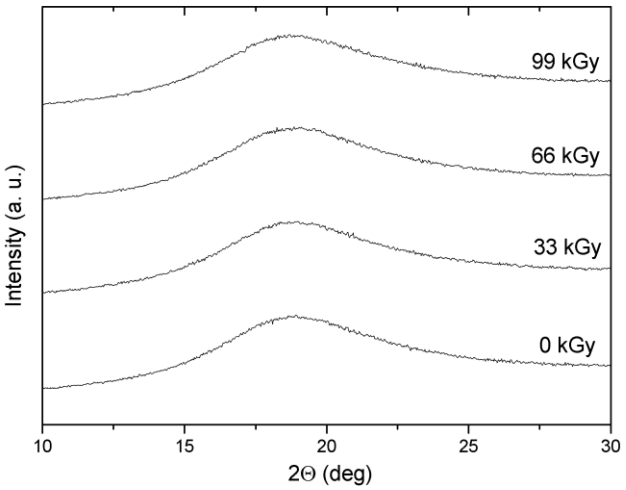

Figure 10. X-ray diffraction of non-irradiated and irradiated PA 11

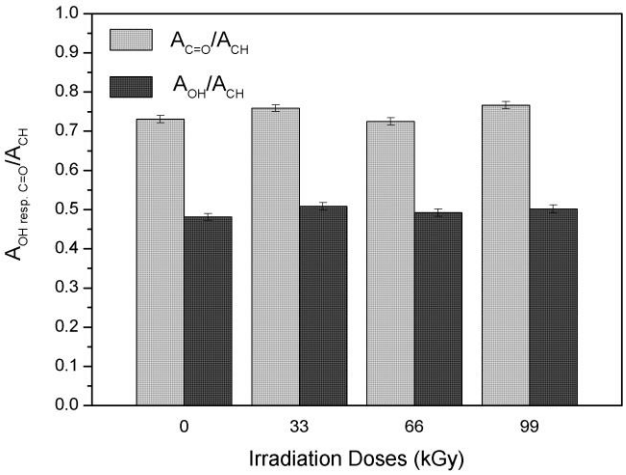

Figure 11. Change in the relative representation of hydroxyl and carbonyl groups of PA 11 in relation to the irradiation doses

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.

4 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 polyamide 11 (PA 11). Polyamide 11 was modified by beta irradiation at doses of 0, 33, 66 and 99 kGy. The changes of micromechanical properties were found at the radiation dose of 33 kGy for indentation hardness and elastic modulus (which increased by 3.5 % and 1.5 %) compared to the non-irradiated polyamide 11. Improvement of mechanical

properties in micro scale of radiated polyamide 11 has a great significance also for industry. The modified polyamide 11 shifts to the group of materials which have considerably better properties. Its micromechanical properties make polyamide 11 ideal for a wide application in the areas where higher resistance to wear, scratch are required.

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