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Nano-hardness of Electron Beam Irradiated Polyamide 11

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Abstract. Cross-linking is a process in which polymer chains are associated through chemical bonds. Radiation, which penetrated through specimens and reacted with the cross-linking agent, gradually formed cross-linking (3D net), first in the surface layer and then in the total volume, which resulted in considerable changes in specimen behaviour. In this study there was found that ionizing beta radiation increased the nano-mechanical properties of polyamide 11 (PA11). The measurement results indicated that ionizing beta radiation (66kGy, 132kGy and 198kGy) was a very effective tool for improvement of indentation hardness, indentation modulus, indentation creep and deformation works of studied polymers. The best results were achieved by irradiation at doses of 132 kGy (increase about 40%) by which the highest nano-mechanical properties of PA11 were achieved.

1 Introduction

Polyamides are one of the most commonly used polymers. Due to their very high strength and durability polyamides are commonly used in textiles, carpets and floor coverings or automotive. Probably more familiar name designation is nylon. Polyamide 11 (PA11) is a semi-crystalline thermoplastic material with very high toughness, good chemical stability and impact resistance. PA11 is also a good electrical insulator and as other polyamide insulating properties will not be affected due to moisture. It is also resistant to corrosion. PA11 has many features and enhancements in terms of plasticization of improved varieties. Polyamide 11 is thanks to its very good mechanical properties, which can be even improved as shown in the results, suitable for applications with great demand on the stiffness and resistance of surface layers for instance friction parts used in automotive industry [1-3].

Polyamides are polymers whose repeating units are characterized by the amide group. Through radiation cross-linking, thermoplastic polyamides are turned into plastics which behave like elastomers over a wide temperature range. Cross-linking makes the originally thermoplastic product able to withstand considerably higher temperatures of up to 350 °C. The dimensional stability under thermal stress is also improved. Radiation cross-linked polyamide can often replace thermosetting plastics or high-performance plastics such as PPS, PEI, LCP, etc. One application that has proved most useful over the years is radiation cross-linked components for the electrical industry, e.g. switch components, and the automotive industry, for instance components for the engine compartment [1-3].

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Electron beams (β-rays) generated by accelerators are monoenergetic and the absorbed dose is greatest just below the surface of the irradiated material and falls rapidly at greater depths in the material (Fig. 1). The energy range of electron beams used in radiation processing is from 0.15 to 10 MeV. Compared with gamma irradiation, electron accelerators have advantages of higher power and directional beams. The time of irradiation by β-rays is in seconds. The limited penetrating power of electron beams means that they are mainly used for irradiating relatively thin objects like wires and cable insulation [1-4].

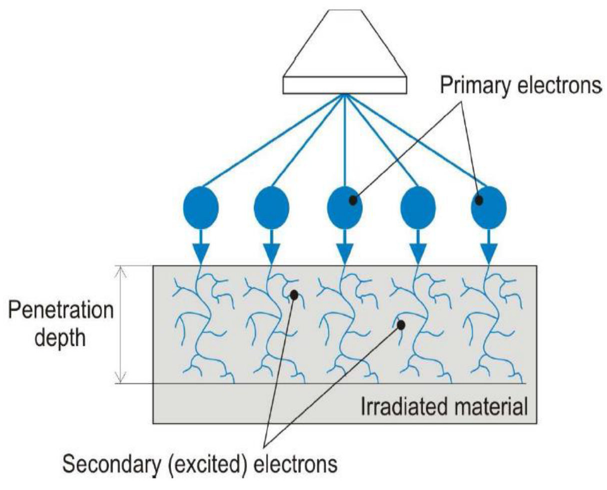

Figure 1. Radiation crosslinking by electrons rays

In general, copolymers cross-link more readily than polyamide. Common PA11, when exposed to the effect of the radiation cross-linking, degrades and its mechanical properties deteriorate. Mechanical properties of polyamides are modified by irradiation, as seen by reduced tensile strength (50% loss when irradiated in air, 16% under vacuum). Aromatic polyamides retain strength better than aliphatic polyamides. Using cross-linking agent TAIC (triallyl isocyanurate) produces a cross-linking reaction inside the PA11 structure. The utility properties of PA11 improve when the non-crystalline part of PA11 is cross-linked [1-4].

The aim of this paper is to study the effect of ionizing radiation with different doses, on nano-mechanical properties of polyamide 11 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 (polyamide 11).

2 Experimental

2.1 Material

For this experiment Polyamide 11 PA11 V-PTS-Creamid-11-AMN 0 TLD, that were supplied by PTS Plastics Technology Service, Germany was used. The material already contained the special cross-linking agent TAIC - triallyl isocyanurate (6 volume %), which should enable subsequent cross-linking by ionizing β – radiation.

2.2 Sample preparation

The samples were made using the injection molding technology on the injection molding machine Arburg Allrounder 470H. Processing temperature 240–260 °C, mold temperature 60 °C, injection pressure 90 MPa, injection rate 50 mm/s. It was used normalized specimen measuring 80x10x4 mm.

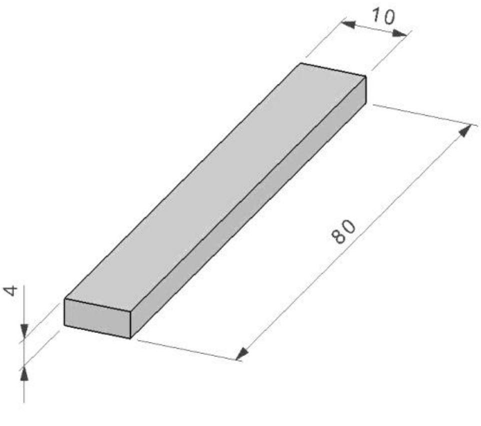

Figure 2. Dimension of sample

2.3 Irradiation

The prepared specimens were irradiated with doses of 0, 66, 132 and 198 kGy at BGS Beta-Gamma Service GmbH & Co. KG, Germany.

2.4 Nano-indentation

Nano-indentation test were performed using a Nano-indentation tester (NHT), CSM Instruments (Switzerland) according to the CSN EN ISO 14577. The tip is made of diamond having the shape of a cube corner (Vickers). In the present study, the maximum load used was 50 mN and loading rate (and unloading rate) was 100 mN/min. A holding time was 90 s at the indentation and 21600 s at the creep.

Figure 3. Nano-indentation tester

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 (ν) according to [4-6]:

$$H_{IT} = \frac{F_{\max}}{A_p} \tag{1}$$

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

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

3 Results and discussion

Radiation cross-linking creates changes in the polyamide 11 structure by creating 3D net. Beta radiation gradually penetrates more deeply into the PA11 structure through the surface layer. The surface layer undergoes changes which have a considerable influence on the nano-mechanical properties of PA11.

The Fig. 4 and Fig. 5 shows a very important correlation between the force and the depth of the indentation. The correlations provide very valuable information on the behavior of tested material and the modified surface layer. The correlation between the force and the depth of the indentation in PA11 also proved very interesting. It demonstrated the influence of radiation on the change of nano-mechanical properties in the surface layer of specimens. The non-irradiated material showed low hardness as well as increasing impression of the indenter in the surface layer. On the contrary, the irradiated PA11 showed considerably smaller depth of the impression of the indenter which can signify greater resistance of this layer to wear.

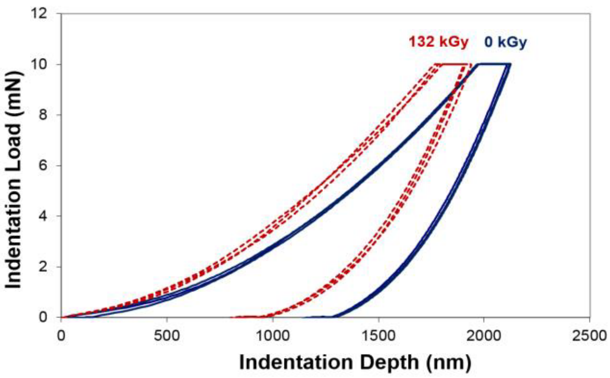

Figure 4. Indentation characteristic of irradiated PA11

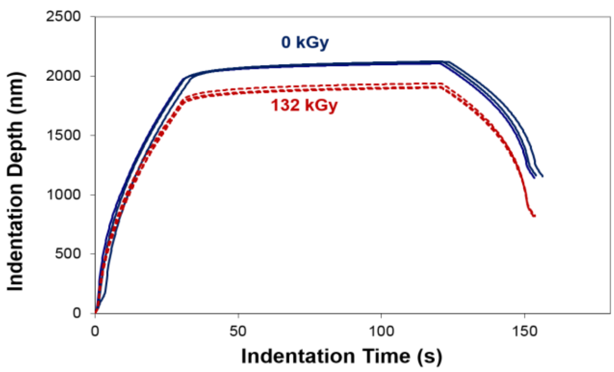

Figure 5. Indentation characteristic of irradiated PA11

The greatest values of nano-hardness test were obtained for PA11 irradiated with dose of 132 kGy as is apparent in Table 1.

Table 1. Summary of measured values

Irradiation doses	0kGy	66kGy	132kGy	198kGy
H_{IT} [MPa]	110,0	132,4	**153,5**	134,1
HV_{IT} [Vickers]	10,4	12,1	**14,6**	12,9
E_{IT} [GPa]	1,8	2,0	**2,1**	2,0
C_{IT} [%]	7,4	7,8	**7,5**	7,2
W_{el} [pJ]	2984,8	2887,7	**3266,7**	3039,6
W_{pl} [pJ]	5350,2	5224,2	**4490,4**	4974,4

Nano-indentation test of PA11 modified by beta radiation showed that the highest values of indentation hardness and Vickers hardness were found for PA11 modified by the radiation dose of 132 kGy (H_{IT} = 153.5 MPa, HV_{IT} = 14.6 Vickers). The smallest value of indentation hardness a Vickers hardness was found for non-irradiated PA11 (H_{IT} = 110.0 MPa, HV_{IT} = 10.4 Vickers). The increase of indentation hardness value for PA11 irradiated by the dose of 132 kGy was by 40% (Fig. 6, Fig. 7) in comparison with the non-irradiated PA11.

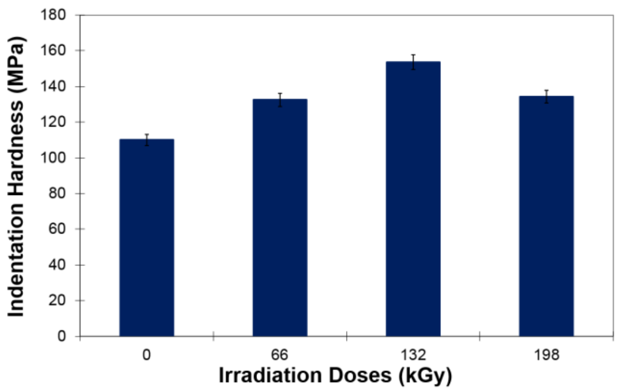

Figure 6. Indentation hardness (H_{IT})

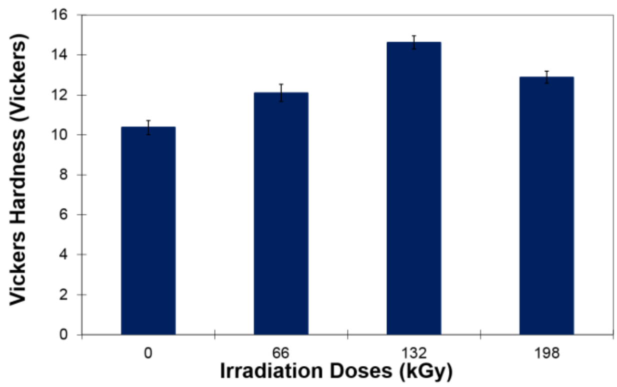

Figure 7. Vickers hardness (HV_{IT})

Similar behaviour was found for indentation modulus E_{IT} according to Oliver and Pharr method (see Fig. 8), which also increases with increasing irradiated doses. Values of stiffness showed the highest value 2.1 GPa at 132 kGy radiation dose, while the lowest stiffness value 1.8 GPa was found in non-irradiated PA11. This represents increase in indentation modulus by 17%.

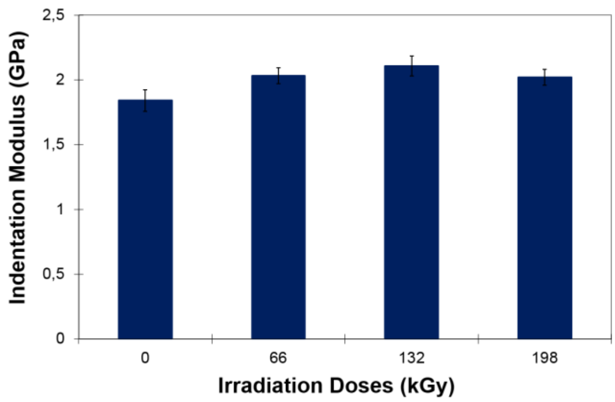

Figure 8. Indentation modulus (E_{IT})

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Very important values were found for indentation creep (C_{IT}). The lowest value of indentation creep was measured at radiation dose of 198 kGy (C_{IT} = 7.2%). The highest indentation creep value measured at non-irradiated PA11 (C_{IT} = 7.8%). Decrease in creep values was 9% for irradiated PA11 compared to the non-irradiated one as is seen at Fig. 9.

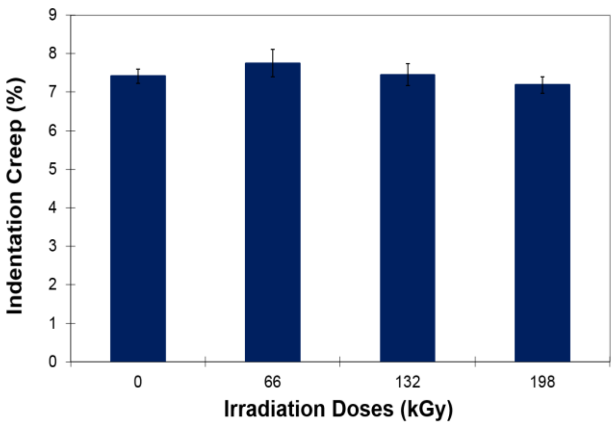

Figure 9. Indentation creep (C_{IT})

Interesting results were found for elastic and plastic part of deformation work. The highest value of elastic and plastic deformation work was measured for non-irradiated PA11. The lowest value at both deformation work was found when the highest value of radiation dose of 132 kGy was applied (Fig. 10).

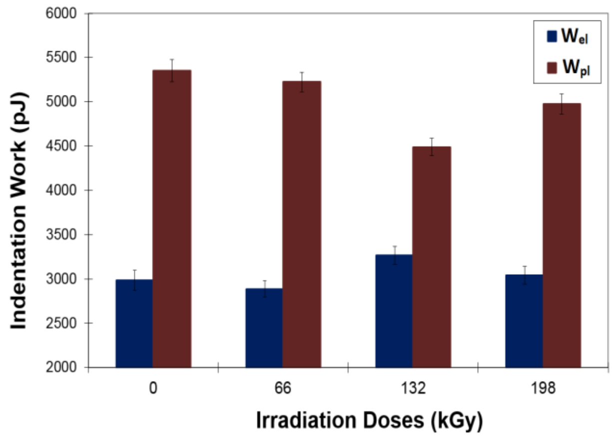

Figure 10. Elastic and plastic part of deformation work

Higher radiation dose does not influence significantly the nano-mechanical properties. 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-mechanical properties decreases which can be caused by radiation induced degradation of the material.

4 Conclusion

This research paper investigates influence of modified polymer material (beta radiation) on the nano-indentation test. The surface layer of PA11 is modified by β – radiation with doses of 66, 132 and 198 kGy.

Radiation, which penetrated through specimens and reacted with the cross-linking agent, 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.

The nano-mechanical properties of surface layer of PA11 modified by beta radiation improved significantly. The nano-hardness values increased by about 40% (132 kGy). Stiffness of surface layer increased significantly by 17% (132kGy) as a result of radiation. Also different depths of indentation in the surface layer of tested specimen were significantly different. The highest values of nano-mechanical properties were reached at radiation dose of 132 kGy. It also proved the fact that higher doses of radiation do not have very positive effects on the nano-mechanical properties, on the contrary due to degradation processes the properties deteriorate.

Acknowledgment

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