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Influence of electron beam irradiated on the surface properties of polyamide measured by micro-indentation test

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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. This paper studies the effect of different doses of ionizing beta radiation on the micro-mechanical properties of commercially available polyamide. The measured results indicate, that electron beam irradiation is very effective tool for improvement of surface properties of PA6. The micro-mechanical properties after irradiated surface treatment was increased up to 24 % compared to non-irradiated surface.

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 is a semi-crystalline thermoplastic material with very high toughness, good chemical stability and impact resistance. Polyamide 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. Polyamide has many features and enhancements in terms of plasticization of improved varieties. Polyamide 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].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) (Figure 1) and gamma rays (γ-rays) (Figure 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. [3]

In general, copolymers cross-link more readily than polyamide. Common polyamide 6, 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 PA6 structure. The utility properties of PA6 improve when the non-crystalline part of PA6 is cross-linked [1-4].

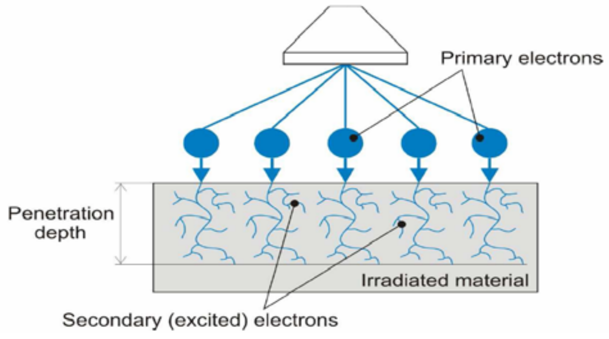

Fig. 1. Radiation crosslinking by electrons rays.

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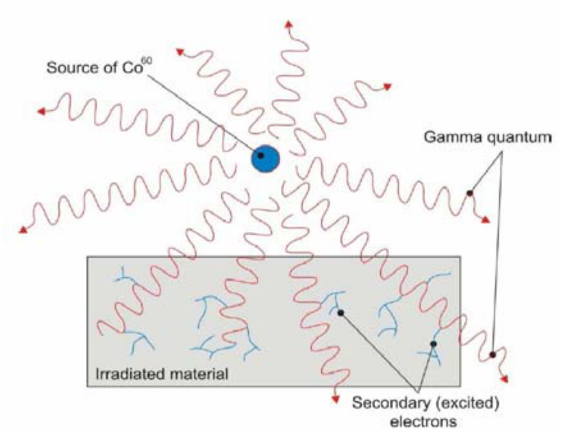

Fig. 2. Radiation crosslinking by Gamma rays.

The thermoplastics which are used for production of various types of products have very different properties. Standard polymers which are easy obtainable with favorable price conditions belong to the main class. The disadvantage of standard polymers is limited both by mechanical and thermal properties (Figure 3). The group of standard polymers is the most considerable one and its share in the production of all polymers is as high as 90% [1] [4].

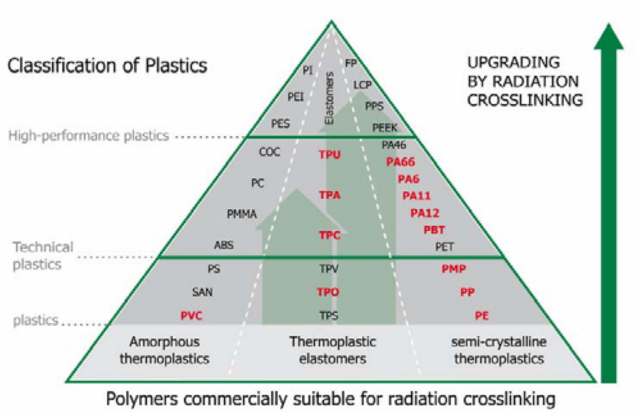

Fig. 3. Upgrading properties by radiation cross-linking.

The aim of this paper is to study the effect of ionizing radiation with different doses, on micro-mechanical properties of PA6 and compare these results with those of non-irradiated samples. These tested polymers find a broad application in many branches of industry and in daily life as well.

2 Experimental

2.1 Material

For this experiment Polyamide Duramid 9TH269 M800/13, PTS Plastics Technology Service, Germany, was used. The material already contained a special cross-linking agent TAIC (5 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 245–265 °C, mold temperature 80 °C, injection pressure 90 MPa, injection rate 50 mm/s. It was used normalized specimen measuring 80x10x4 mm.

2.3 Irradiation

The prepared specimens were irradiated with doses of 0, 33, 66 and 99 kGy at BGS Beta-Gamma Service GmbH & Co. KG, Germany.

2.4 Micro-indentation

Micro-indentation test were performed using a Micro-indentation tester (Micro Combi Tester) (Figure 4), 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 0.5 N and loading rate (and unloading rate) was 1 N/min. A holding time was 90 s at the indentation and 21600 s at the creep.

Fig. 4. Micro-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 (Figure 5) [2-4]:

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

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

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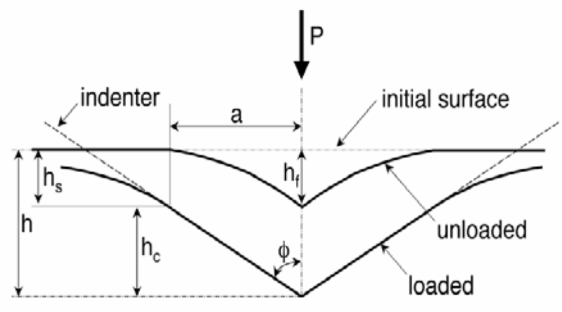

Fig. 5. Schematic illustration of unloading process.

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

3 Results and discussion

Gel content showed the highest values at radiation dose of 99 kGy at which it reached 60.0% degree of cross-linking (Figure 6).

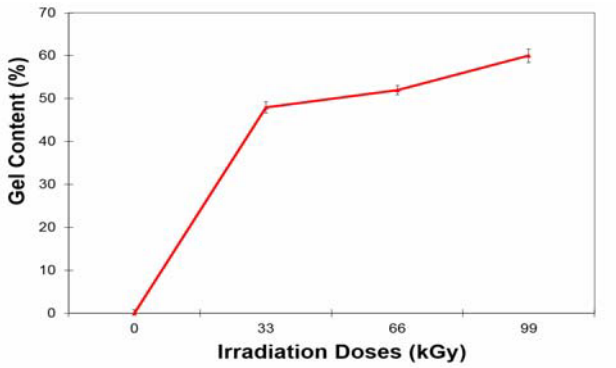

Fig. 6. Gel content of PA6.

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.

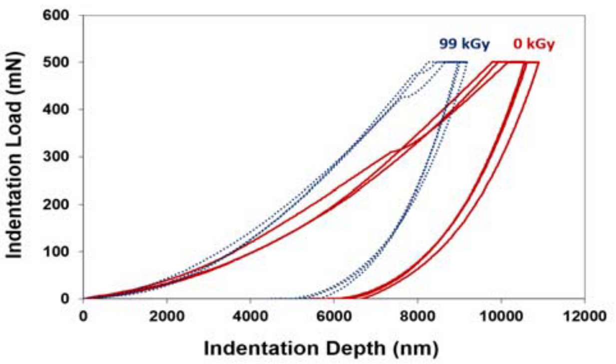

Fig. 7. Indentation characteristic of irradiated PA6.

Micro-indentation characteristics determined by DSI method are depicted in Figure 7 and Figure 8. They characterize course of loading force in dependence on indentor penetration depth, which gives an idea about course of instantaneous values of observed micro-mechanical properties.

It demonstrated the influence of radiation on the change of micro-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 PA6 showed considerably smaller depth of the impression of the indenter which can signify greater resistance of this layer to wear (Figure 7 and Figure 8).

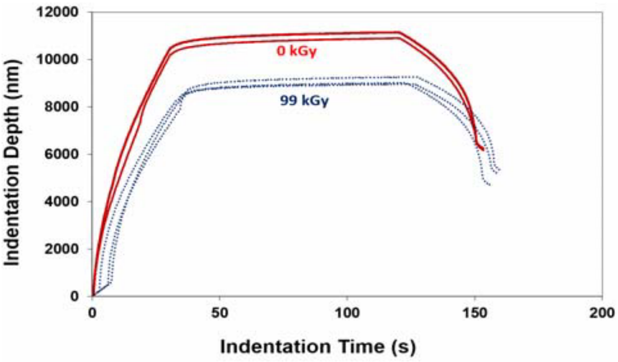

Fig. 8. Indentation characteristic of irradiated PA6.

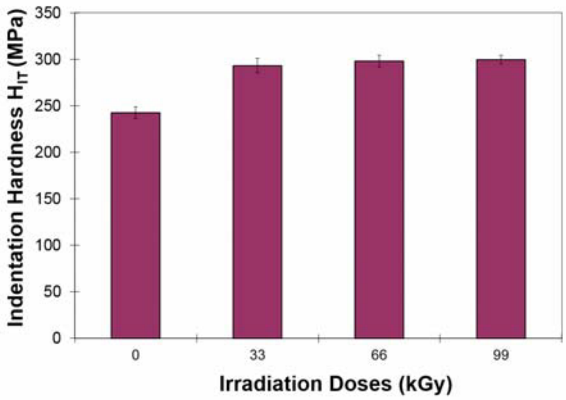

Fig. 9. Indentation hardness (H_{IT}).

The development of micro-mechanical properties of irradiated polyamide was characterized by the instrumented test of micro-indentation hardness (H_{IT}), as can be seen in Fig. 9. The highest values (300 MPa) of micro-indentation hardness were found at 99 kGy radiation dose, while the lowest value of micro-indentation hardness (242 MPa) was measured on non-irradiated polyamide 6. The increase of micro-indentation hardness at 99 kGy radiation dose was by 24% compared to the non-irradiated PA6. Similar development was recorded for micro-stiffness of specimens represented by the elastic modulus of indentation (E_{IT}) illustrated in Fig. 10. The results of measurements show clearly that the lowest values of micro-indentation modulus were measured on the non-irradiated PA6 (5.0 GPa), while the highest values were reached in PA 6 irradiated by 99 kGy dose (6.2 GPa). A significant increase of micro-indentation modulus (24%) was recorded at the radiation dose of 99 kGy compared to the non-irradiated PA6.

Fig. 10. Indentation Modulus (E_{IT}).

Very important values were found for indentation creep (C_{IT}). The lowest value of indentation creep was measured at radiation dose of 99 kGy (C_{IT} = 12.2%). The highest indentation creep value measured at non-irradiated PA6 (C_{IT} = 14.3%). Decrease in creep values was 17% for irradiated PA6 compared to the non-irradiated one as is seen at Figure 13.

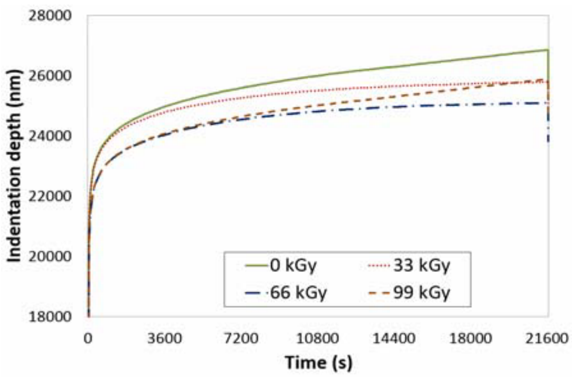

Fig. 12. Indentation creep (C_{IT}).

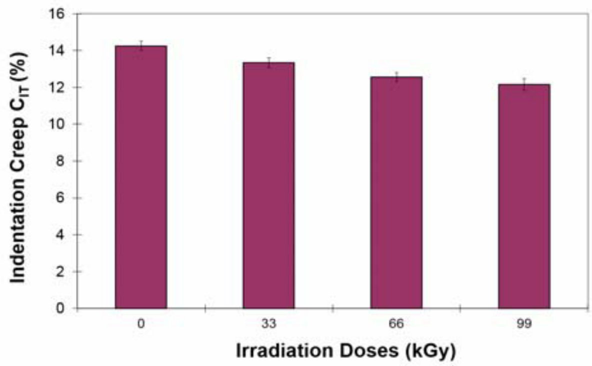

Fig. 13. Indentation creep (C_{IT}).

Radiation cross-linking creates changes in the PA6 structure by creating 3D net. Beta radiation gradually penetrates more deeply into the PA6 structure through the surface layer. The surface layer undergoes changes which have a considerable influence on the micro-mechanical properties of PA6.

Higher radiation dose does not influence significantly the micro-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 micro-hardness results that when the highest radiation doses are used, micro-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 micro-indentation test. The surface layer of PA6 is modified by β – radiation with doses of 33, 66 and 99 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 behaviour.

The micro-mechanical properties of surface layer of PA6 modified by beta radiation improved significantly. The indentation hardness an indentation modulus values increased by about 24% (99 kGy) as a result of radiation. Also different depths of indentation in the surface layer of tested specimen were significantly different. The highest values of micro-mechanical properties were reached at radiation dose of 99 kGy. It also proved the fact that higher doses of radiation do not have very positive effects on the micro-mechanical properties, on the contrary due to degradation processes the properties deteriorate.

Improvement of micro-mechanical properties of radiated PA6 has a great significance also for industry. The modified PA6 shifts to the group of materials which have considerably better properties. Its micro-mechanical properties make PA6 ideal for a wide application in the areas where higher resistance to wear, creep are required. Commonly manufactured PA6 can hardly fulfil these criteria.

Acknowledgment

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