Nano-indentation test of PA12 after radiation cross-linking

Martin Ovsik, David Manas, Miroslav Manas, Michal Stanek, Petr Kratky, and Vojtech Senkerik

***Abstract*—**This article describes the effect of radiation cross-linking on the nano-mechanical properties of polyamide 12. Cross-linking is a process in which polymer chains are associated through chemical bonds. These nano-mechanical properties were measured by the DSI (Depth Sensing Indentation) method on samples which were non-irradiated and irradiated by different doses of the β - radiation. The best results were achieved by the irradiation with doses of 132 kGy. The nano-mechanical properties (nano-hardness, elastic modulus, deformation work, creep) after irradiation was increased up to 67 % compared to untreated material.

***Keywords*—**Polyamide 12, cross-linking, Depth sensing indentation, nano-indentation hardness, nano-indentation modulus.

I. 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 12 (PA12) is a semi-crystalline thermoplastic material with very high toughness, good chemical stability and impact resistance. PA12 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. PA12 has many features and enhancements in terms of plasticization of improved varieties. Polyamide 12 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. The chemical formula of PA12 is shown in Fig. 1. In comparison with PA6 and PA66 has PA12 lower melting point and density, with very high moisture regain [1].

Polyamides are polymers whose repeating units are characterized by the amide group. Through radiation crosslinking, thermoplastic polyamides are turned into plastics which behave like elastomers over a wide temperature range. Crosslinking 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 crosslinked polyamide can often replace thermosetting plastics or high-performance plastics such as PPS, PEI, LCP, etc. [2], [3], [4].

Table 1 The main differences between beta and gamma rays

Main difference	gamma rays	electron rays
penetration capacity	high	depends on the energy of the accelerated electron
required dose	several hours	seconds

Crosslinking is a process in which polymer chains are associated through chemical bonds. Crosslinking is carried out by chemical reactions or radiation and in most cases the process is irreversible. Ionizing radiation includes high-energy electrons (electron beam), γ-rays, and x-rays (Table 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 [1], [5], [6].

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 [4], [7], [8], [9].

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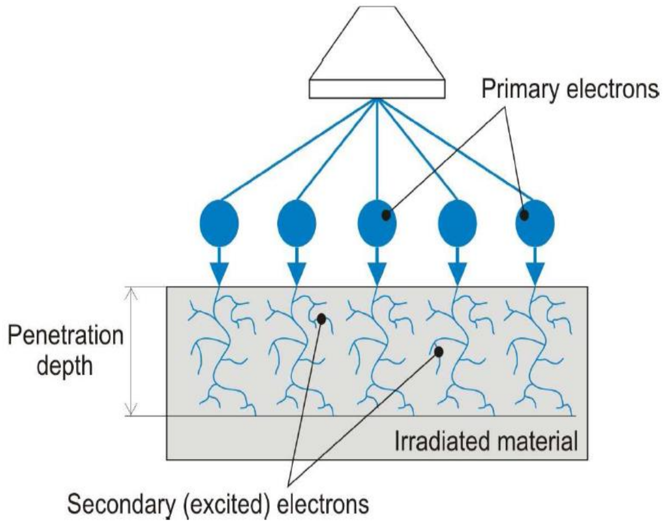

Fig. 1 Radiation crosslinking by electrons rays

Gamma radiation has a high penetration capability at relatively low dose intensity as shown. The most used source of gamma rays (Fig. 2) is cobalt-60 (Co60). The energy of emitted gamma rays is about 1.3 MeV. Conversely the electron accelerators, source of gamma rays cannot be turned off. Therefore the rays are sheltered, in most cases by water tank. Time of irradiation depends on dose intensity and reaches up to several hours. The gamma radiation is mainly used for radiation sterilization [1], [2], [10].

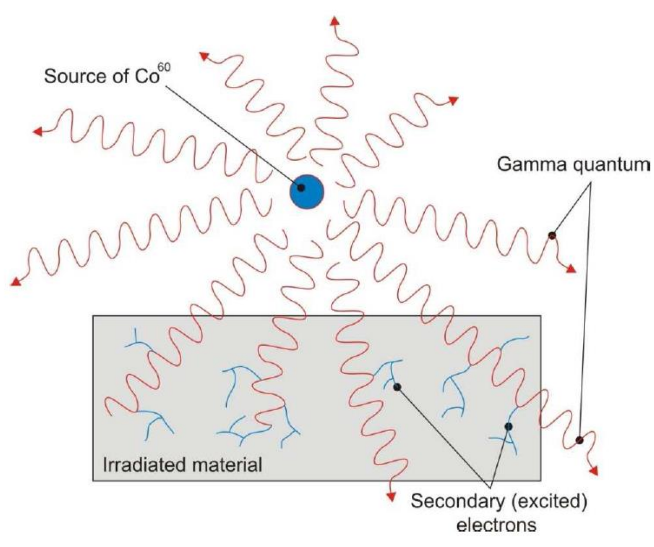

Fig. 2 Radiation crosslinking by gamma rays

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 (fig. 3) [11], [12].

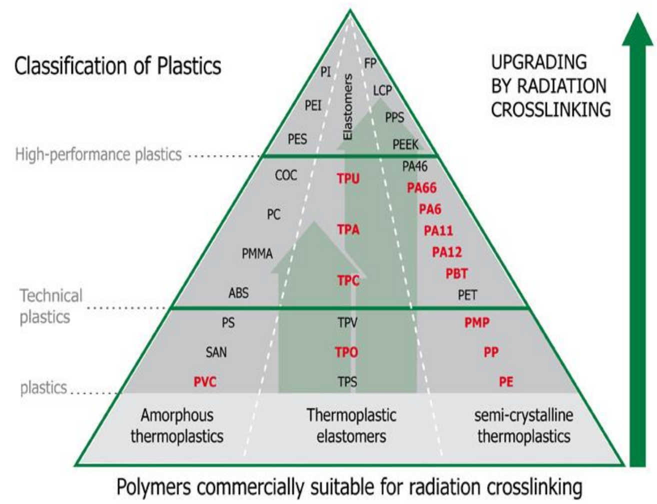

Fig. 3 Hardness HIT of PA12 vs. irradiation doses

Common PA12, 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 PA12 structure. The utility properties of PA12 improve when the noncrystalline part of PA12 is cross-linked.

The aim of this paper is to study the effect of ionizing radiation with different doses, on nano-mechanical properties of polyamide 12 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.

II. Experimental

A. Material and irradiation

For this experiment polyamide 12 V-PTS-Creamid-12-AMN 0 TLD, that were supplied by PTS Plastics Technology Service, Germany (unfilled, PA12+TAIC) 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. The prepared specimens were irradiated with doses of 0, 66, 132 and 198 kGy at BGS Beta-Gamma Service GmbH & Co. KG, Germany.

B. Injection moulding

The samples (fig. 4) were made using the injection molding technology on the injection moulding machine Arburg Allrounder 420C. Processing temperature 220–250 °C, mold temperature 60 °C, injection pressure 80 MPa, injection rate 50 mm/s.

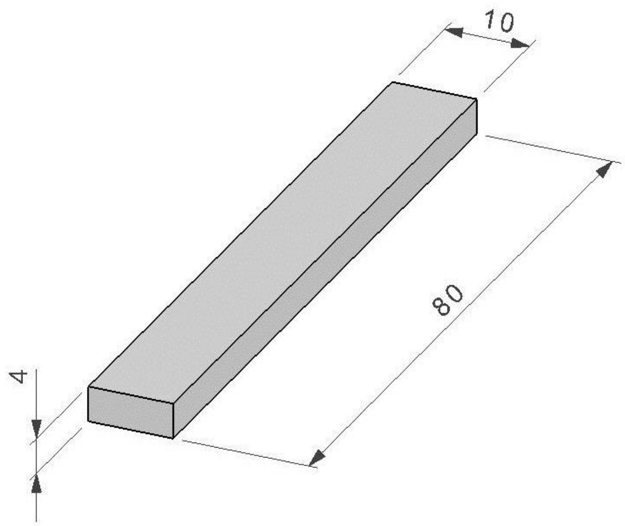

Fig. 4 Dimension of sample

C. Nano-indentation test

Nano-indentation (nano-hardness) tests were done using a Nano-indentation tester (NHT), CSM Instruments (Switzerland) according to the CSN EN ISO 14577. Load and unload speed was 20 mN/min and 500 mN/min. After a holding time of 90 s at maximum load 10 mN and 250 mN the specimens were unloaded (Fig. 5).

Fig. 5 Nano-hardness tests

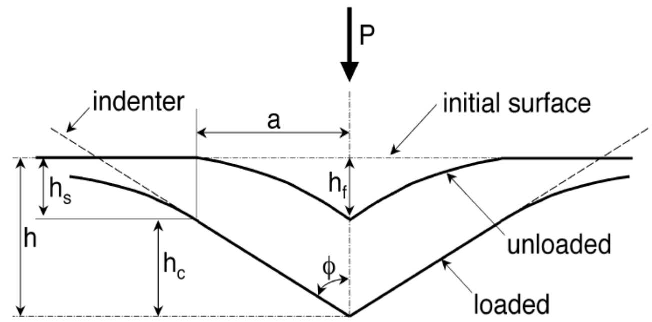

Fig. 6 Schematic illustration of unloading process

The indentation hardness (H_{IT}) was calculated as maximum load (F_{max}) to the projected area of the hardness impression (A_p): (Fig. 6, 7) [7], [13], [14], [15]

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

The indentation modulus (E_{IT}) is calculated from the Plane Strain modulus (E*) using an estimated sample Poisson's ratio (ν) according to: [8], [16], [17]

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

Determination of indentation hardness C_{IT}: [18], [19]

$$C_{IT} = \frac{h_2 - h_1}{h_1} \cdot 100 \tag{3}$$

Where h_1 is the indentation depth at time t_1 of reaching the test force (which is kept constant), h_2 is the indentation depth at time t_2 of holding the constant test force [5], [12], [20].

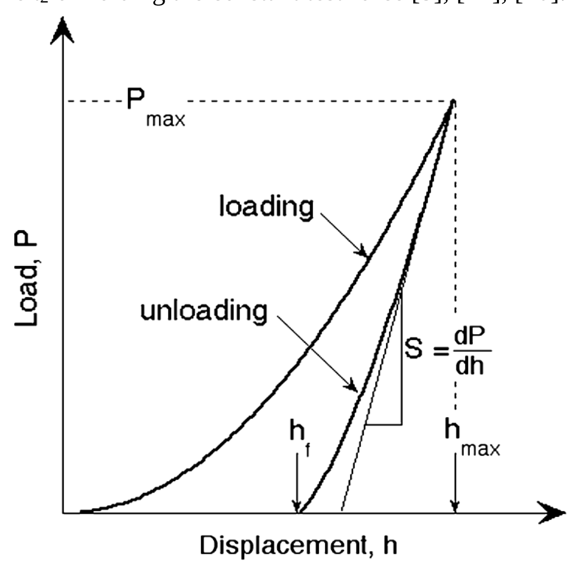

Fig. 7 Schematic illustration of indentation curve

Indentation work (Fig. 8):

$$\eta_{IT} = \frac{W_{elast}}{W_{total}} \cdot 100 \quad \text{with} \quad W_{total} = W_{elast} + W_{plast} \tag{4}$$

Plastic part W_{plast} / W_{total} follows as 100% - η_{IT} (5)

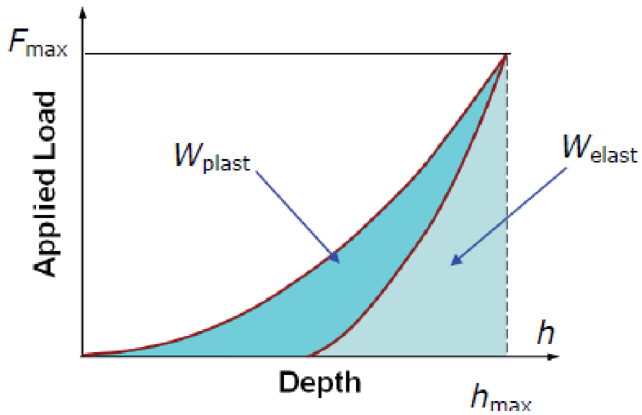

Fig. 8 Indentation work η_{IT}

III. Results and Discussion

A. Indentation load - 10 mN

The values measured during the nano-hardness test showed that the lowest values of indentation hardness and Vickers hardness were found for the non-irradiated PA12. On the contrary, the highest values of indentation hardness and Vickers hardness were obtained for PA12 irradiated by a dose of 132 kGy (by 61% higher in comparison with the non-irradiated PA12), as can be seen at Fig. 9.

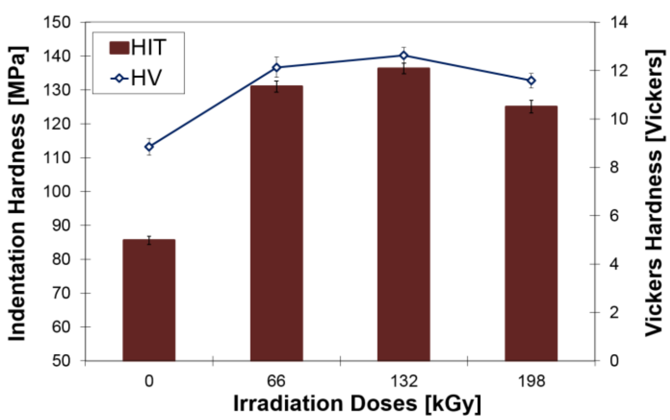

Fig. 9 Hardness H_{IT} of PA12 vs. irradiation doses

According to the results of measurements of nano-hardness, it was found that the highest values of indentation modulus of elasticity were achieved at the PA12 irradiated with dose of 132 kGy (by 21% higher than compared with non-irradiated PA12). On the contrary, the lowest values of the indentation modulus of elasticity were found for non-irradiated PA12, as is seen at Fig. 10.

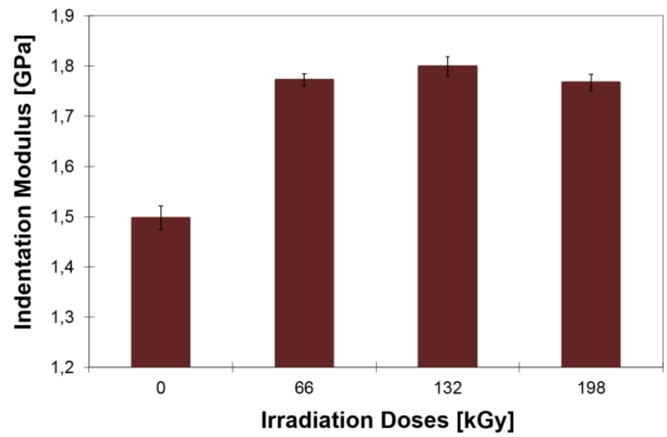

Fig. 10 Elastic modulus E_{IT} of PA12 vs. irradiation doses

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

Other important material parameters obtained during the nano-hardness test were elastic (W_{el}) and plastic deformation work (W_{pl}). The lowest values of plastic and elastic deformation work were obtained for non-irradiated PA12. The greatest values of both elastic and plastic deformation work were obtained for PA12 irradiated with dose of 198 kGy. Radiation of specimens caused lower values of elastic as well as plastic deformation work which is apparent in Fig. 11.

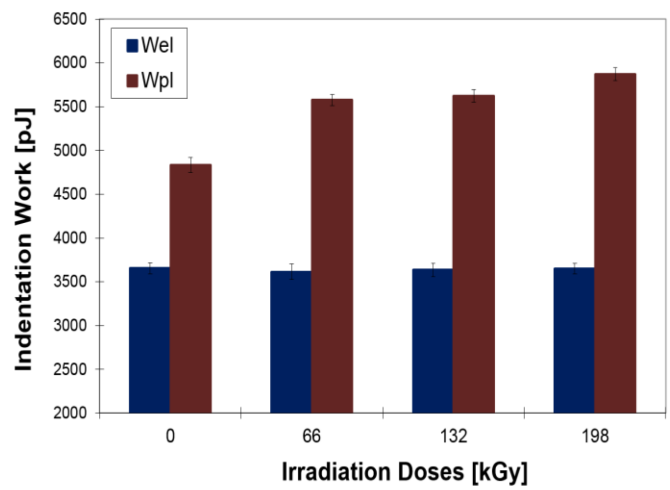

Fig. 11 Deformation work vs. irradiation dose

According to the results of measurements of nano-hardness, it was found that the lowest values of indentation creep were achieved at the PA12 irradiated with dose of 132 kGy (by 34% lower than compared with non-irradiated PA12). On the contrary, the highest values of the indentation creep were found for non-irradiated PA12 as is seen on Fig. 12.

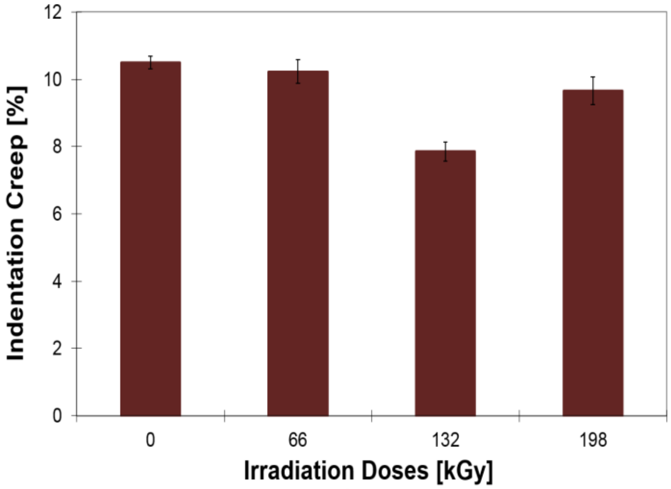

Fig. 12 Creep of PA12 vs. irradiation doses

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.

It demonstrated the influence of radiation on the change of 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 PA12 showed considerably smaller depth of the impression of the indenter which can signify greater resistance of this layer to wear (Fig. 13, 14).

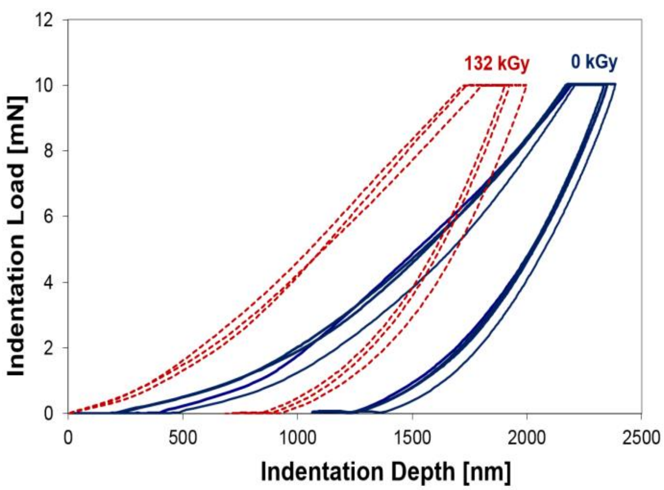

Fig. 13 Indentation depth vs. time

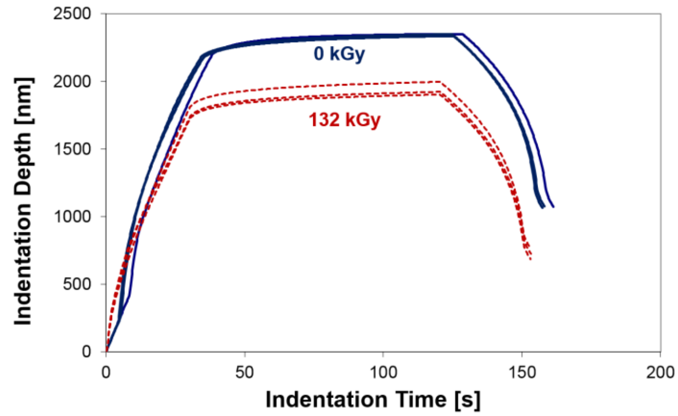

Fig. 14 Force vs. Indentation depth

B. *Indentation load - 250 mN*

The values measured during the nano-hardness test showed that the lowest values of indentation hardness and Vickers hardness were found for the non-irradiated PA12. On the contrary, the highest values of indentation hardness and Vickers hardness were obtained for PA12 irradiated by a dose of 198 kGy (by 57% higher in comparison with the non-irradiated PA12), as can be seen at Fig. 15.

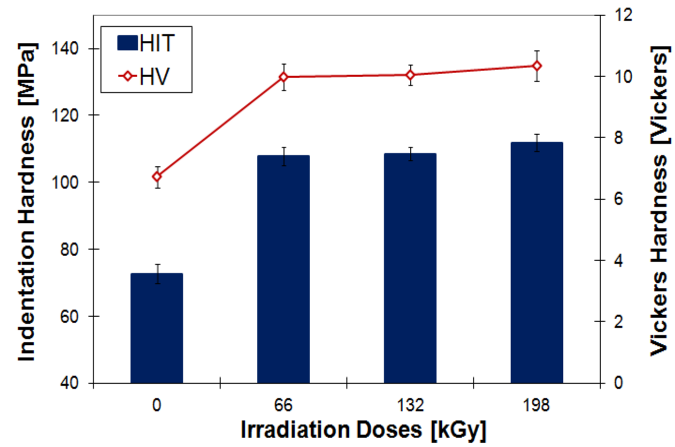

Fig. 15 Hardness H_{IT} of PA12 vs. irradiation doses

In the case of indentation modulus the highest value was found for PA12 irradiated by the radiation dose of 132 kGy. The smallest value of indentation modulus was found for non-irradiated PA12. The increase of the value of PA12 irradiated by the radiation dose of 132 kGy was by 67% in comparison to the non-irradiated PA12, as is seen at Fig. 16.

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

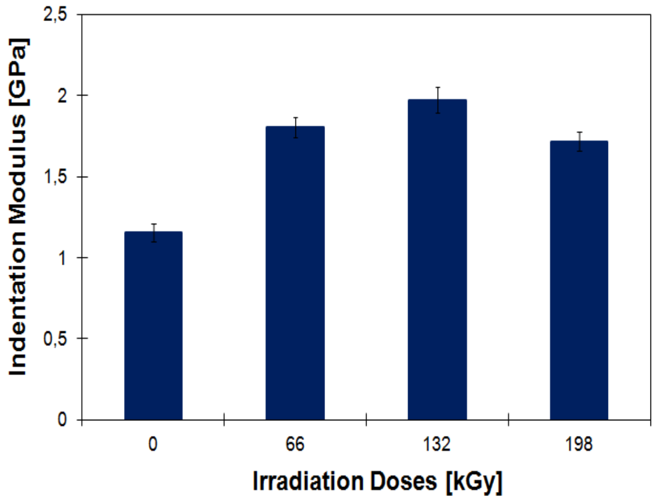

Fig. 16 Elastic modulus E_{IT} of PA12 vs. irradiation doses

Interesting results were found for elastic deformation work and plastic part of deformation work. The highest value of elastic deformation work (W_{el}) and plastic deformation work (W_{pl}) was measured for non-irradiated PA12. The lowest value at both deformation work was found when the highest value of radiation dose of 198 kGy was applied (Fig. 17).

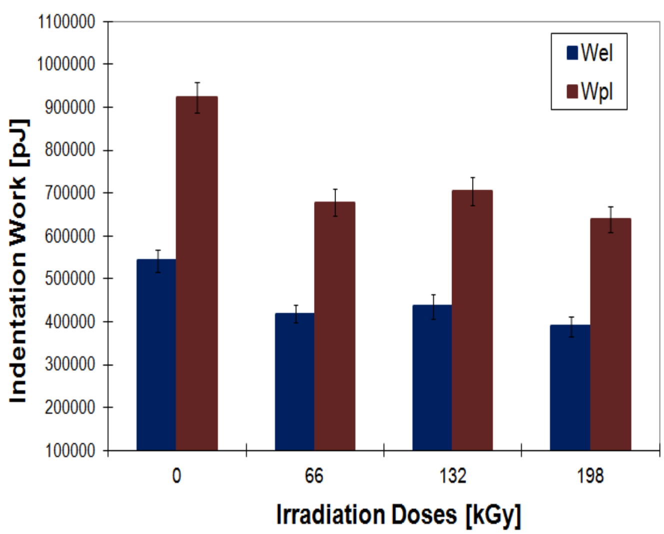

Fig. 17 Deformation work vs. irradiation dose

According to the results of measurements of nano-hardness, it was found that the lowest values of indentation creep were achieved at the PA12 irradiated with dose of 66 kGy (by 66% lower than compared with non-irradiated PA12). On the contrary, the highest values of the indentation creep were found for non-irradiated PA12 as is seen on Fig. 18.

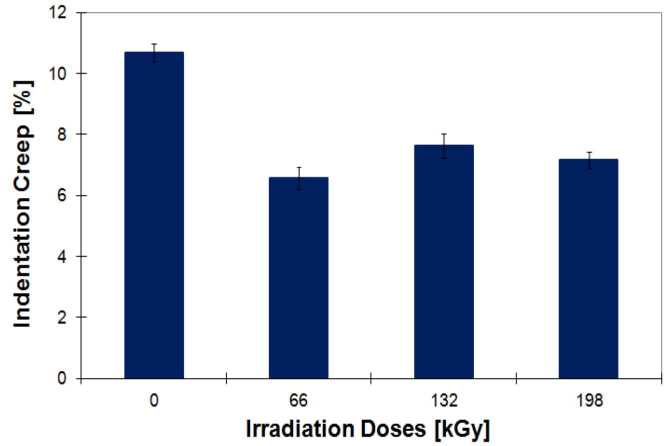

Fig. 18 Creep of PA12 vs. irradiation doses

There is also a very important correlation between the force and the depth of the indentation (Fig. 19, Fig. 20). The correlations provide very valuable information on the behavior of tested material and the modified surface layer

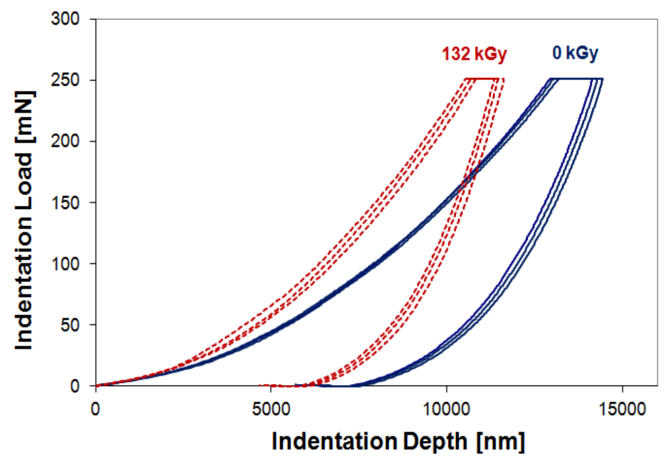

Fig. 19 Indentation depth vs. time

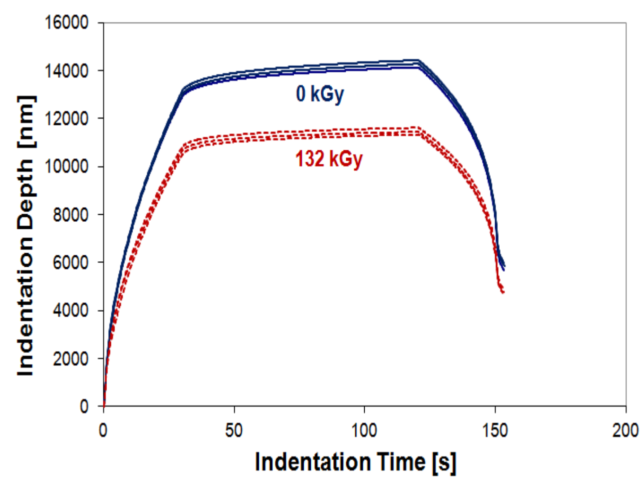

Fig. 20 Force vs. Indentation depth

The correlation between the force and the depth of the indentation in PA12 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 PA12 showed considerably smaller depth of the impression of the indenter which can signify greater resistance of this layer to wear.

C. Indentation load - 10 mN and 250 mN

The load applied for nano-hardness test was 10 mN and 250 mN. We observed the effect of the load on the resulting properties of the surface layer of PA12 modified by beta radiation. The measurement results show that at all loads applied the highest value of nano-hardness was found when the radiation dose was 132 kGy. When higher radiation doses are applied, nano-hardness values decline, showing constant values. At higher loads there is a slight but not significant nano-hardness values. They range within statistical discrepancy. The increase in nano-hardness values at 250 mN load is caused by deeper penetration of the indentor, thus reaching semicrystalline structure of PA12. The increase in nano-hardness of the surface layer at the dose of 132 kGy compared to the non-irradiated specimen was found to be around 61% at the indentation load 10mN (Fig. 21).

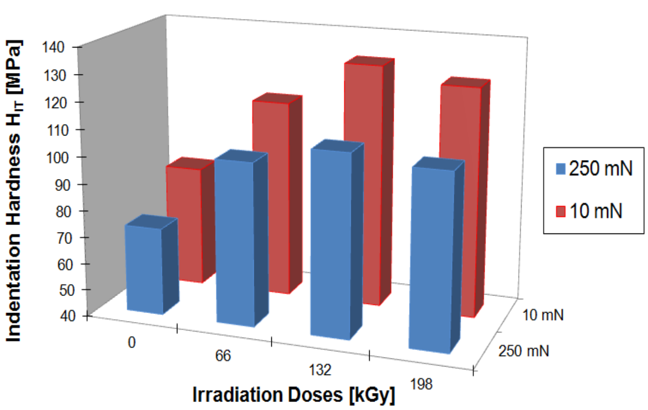

Fig. 21 Indentation hardness H_{IT} of PA12 vs. irradiation doses

When observing the changes of stiffness of the surface layer measured by nano-hardness test it was proved that the maximum value of stiffness was found at radiation dose of 132 and 198 kGy, when applying all three loads (10 mN, 250 mN). The non-irradiated specimen showed the lowest value. At higher radiation dose, increase in the stiffness of the surface layer is not uniform. In general it can be said that stiffness of the surface layer increased by 67% in the tested specimen (132 kGy and 198 kGy) compared to the non-irradiated specimen (Fig. 22).

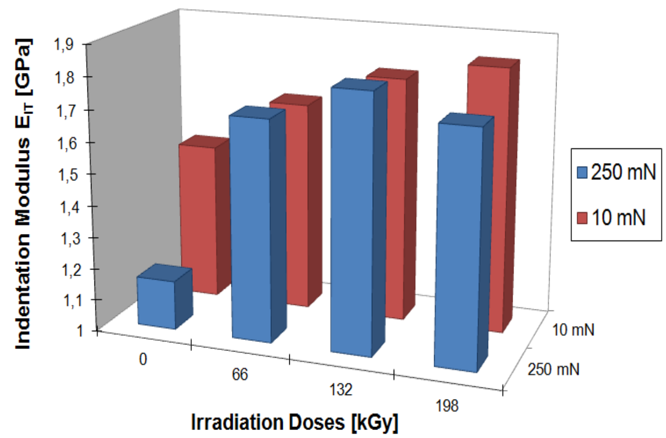

Fig. 22 Elastic modulus E_{IT} of PA12 vs. irradiation doses

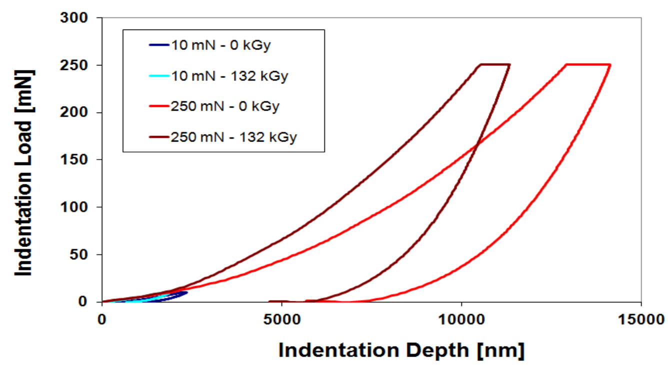

Fig. 23 Indentation load vs. Indentation depth

The figure 23 and 24 shows a very important correlation between the force and the depth of the indentation. It demonstrated the influence of radiation on the change of mechanical properties in the surface layer of specimens. The non-irradiated material showed low hardness as well as increasing impression of the indentor in the surface layer. On the contrary, the irradiated PA12 showed considerably smaller depth of the impression of the indentor which can signify greater resistance of this layer to wear.

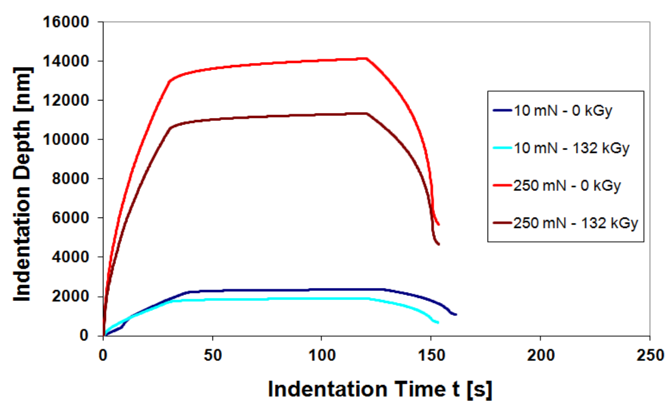

Fig. 24 Indentation depth vs. Indentation time

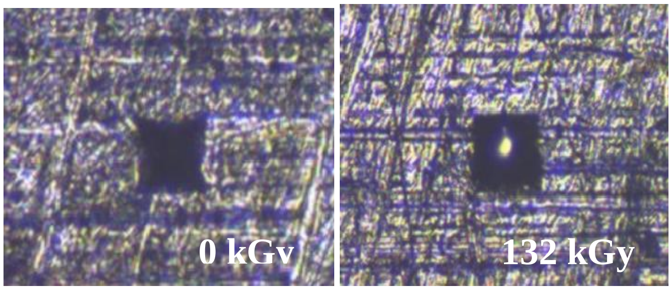

Fig. 25 Vickers indentation produced on PA12

The figure 25 shows the difference in the indentation of non-irradiated PA12 and PA12 irradiated at doses of 132 kGy.

IV. Conclusion

The article is the assessment of nano-mechanical properties (nano-hardness) of the surface layer of modified polyamide 12. The surface layer of the polymer material such as polyamide 12 is modified by β – radiation with doses of 66, 132 and 198 kGy.

Irradiation of Polyamide 12 with a β -radiation influences the nano-mechanical properties in the following way:

• Radiation of specimens caused improvement values of indentation hardness and indentation modulus.

• Higher radiation dose does not influence the indentation hardness and indentation modulus significantly, on the contrary due to degradation processes the properties deteriorate.

• Values of indentation hardness and indentation modulus correspond to the deformation works.

The properties of surface layer of PA12 modified by beta radiation improved significantly. The nano-hardness values increased by about 61%. Stiffness of surface layer increased significantly by 67% as a result of radiation. The creep values decreased by 66% on average for irradiated PA12. Changes of behavior in the surface layer were confirmed by final values of elastic and plastic deformation work whose values decreased in correlation with the increasing radiation dose. 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 mechanical properties, on the contrary due to degradation processes the properties deteriorate.

The results of nano-mechanical properties of surface layer of modified Polyamide 12 show that it can be used in more difficult applications in some industrial fields, in particular where there are high requirements for strength, stiffness and hardness of surface layer which appears to be the most suitable area of application.

References

[1] M. Ovsik, D. Manas, M. Manas, M. Stanek, M. Hribova, K. Kocman, D. Samek, "Irradiated polypropylene studied by microhardness and WAXS" ,*Chemicke listy*, Volume 106, 2012, pp. 507-510.

[2] D. Manas, M. Hribova, M. Manas, M. Ovsik, M. Stanek, "The effect of beta irradiation on morphology and micro hardness of PP thin layers" ,*Thin Solid Films*, Volume 530, 2012, pp. 49-52.

[3] G. Zamfirova, V. Gaydarov, T. Zaharescu, L. G. Silva, "Micro indentation study of electron beam irradiated polyamide samples", *Chemicke Listy*, 104, 2010, pp. 283-286.

[4] M. Ovsik, D. Manas, M. Manas, M. Stanek, M. Bednarik, P. Kratky, A. Mizera, "Micro-indentation hardness of glass fiber-filled PA6 influenced by beta irradiation" *in Proc. 17th WSEAS International Conference on Systems*, 2013, pp. 225-229.

[5] G. M. Pharr, "Measurement of mechanical properties by ultra-low load indentation", *Materials Science and Engineering*. 1998, pp. 151 – 159.

[6] D. Manas, M. Ovsik, M. Manas, M. Stanek, P. Kratky, A. Mizera, M. Bednarikl, "Effect of beta low irradiation doses on the microhardness of PC" *in Proc. 17th WSEAS International Conference on Systems*, 2013, pp. 196-200.

[7] W. C. Oliver, G. M. Pharr, "Measurement of hardness and elastic modulus by instrumented indentation", *Journal of Materials Research*. 2004, Volume 19, no. 1.

[8] A. Bolshakov and G. M. Pharr, "Influences of pile-up on the measurement of mechanical properties by load and depth sensing indentation techniques", *J. Mater. Res*. 13, 1998, pp. 1049-1058.

[9] W. D. Nix and H. Gao, "Indentation size effects in crystalline materials: A law for strain gradient plasticity". *J. Mech. Phys. Solids*. 46, 1998, pp. 411-425.

[10] M. Ovsik, D. Manas, M. Manas, M. Stanek, K. Kyas, M. Bednarik, A. Mizera, "Microhardness of HDPE influenced by beta irradiation", *International Journal of Mathematics and Computers in Simulation*, Volume 6, Issue 6, 2012, pp. 566-574.

[11] M. Ovsik, D. Manas, M. Manas, M. Stanek, M. Bednarik, P. Kratky, "Effect of beta irradiation on microhardness of polyamide 6", *Key Engineering Materials*, Volume 586, 2014, pp 218-221.

[12] M. Manas, D. Manas, M. Stanek, A. Mizera, M. Ovsik, "Modification of polymer properties by irradiation properties of thermoplastic elastomer after radiation cross-linking", *Asian Journal of Chemistry*, Volume 25, Issue 9, 2013, pp. 5124-5128.

[13] Y. H. Lee, U. Baek, Y. I. Kim, S. H. Nahm, "On the measurement of pile-up corrected hardness based on the early Hertzian loading analysis", *Materials Letters*, Volume 61, 2007, pp. 4039-4042.

[14] Z. Wei, Y. Lu,, Y. Meng, L. Zhang. Study on wear, cutting and chipping behaviors of hydrogenated nitrile butadiene rubber reinforced by carbon black and in-situ prepared zinc dimethacrylate, 2012, *Journal of Applied Polymer Science 124 (6*) , pp. 4564-4571.

[15] H. Buckle, In Science of hardness testing and its research applications. edited by J.H. Westbrook and H. Conrad (American society for metals, Metals Park, Ohio, (1971) ch. 33, p. 453-491.

[16] A. Pusz,K. Michalik., Creep damage mechanisms in gas pipes made of high density polyethylene,2009 *Archives of Materials Science and Engineering* 36 (2) , pp. 89-95.

[17] M. Ovsik, D. Manas, M. Manas, M. Stanek, M. Bednarik, P. Kratky, A. Mizera, "Effect of Beta Low Irradiation Doses on the Nano-hardness of PBT", *International Journal of Mechanics*, Volume 7, Issue 3, 2013, p. 310-317.

[18] M. Ovsik, P. Kratky, D. Manas, M. Manas, M. Stanek, M. Bednarik, "Micro-hardness and morphology of LDPE influenced by beta radiation", *Key Engineering Materials*, Volume 606, 2014, pp 253-256.

[19] C. J. Perez, E. M. Valles, M. D. Failla, The effect of post-irradiation annealing on the crosslinking of high-density polyethylene induced by gamma-radiation. *Radiation Physics and Chemistry* 79, 2010, p 710–717.

[20] O. Bilek, D. Samek, O. Suba, Investigation of Surface Roughness while Ball Milling Process. *Key Engineering Materials*, 10., vol. 581, 2013, pp. 335–340.