Nano-Hardness of PA12 after Cross-linking Due to Beta Radiation

M. Ovsik, D. Manas, M. Manas, M. Stanek, M. Bednarik, P. Kratky and A. Mizera

Abstract**—** This article deals with the influence of different doses of β - radiation on nano-mechanical properties of Polyamide 12. 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 aim of the article is to find out the influence of the radiation on the nano-hardness of the modified PA12.

Keywords**—** polyamide 12, irradiation, crosslinking, β – radiation, Depth sensing indentation, nano-hardness.

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] - [2].

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$$- [NH - (CH_2)_{11} - CO]_n -$$

Fig. 1 Chemical formula of polyamide 12

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. 2) [6] [7].

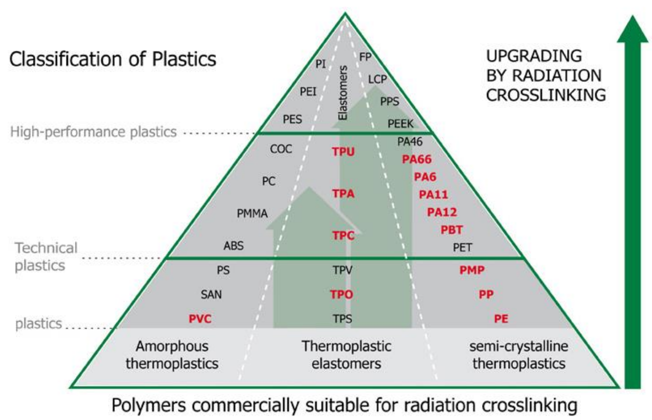

Fig. 2 Hardness HIT of PA12 vs. irradiation doses

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. [8] [15].

High-energy radiation is a well-known technique for modification of polymers. Polymers become electronically excited or ionized after absorption of energy. The excited molecules are able to enter into chemical reactions leading to chemically reactive products that initiate the crosslinking reaction. The electron beam technology improves productivity, speeds up production, lowers cost and makes news and often better products. At the same time, it uses less energy, drastically reduces polluting emission and eliminates flammable and polluting solvents. This technology is widely used. The cross-linking among the polymer molecules improves their thermal, electrical and mechanical properties thereby enabling its application in different fields where the improvements of these properties are required. A heterogeneous cross-linking formation in the hydrocarbon polymers by gamma and electron beam irradiation has been extensively investigated. During the last few decades, the industrial employment of the ionizing radiation has been growing for cross-linking thermoplastic, with excellent results in several sectors [1] [2] [5] [16] - [22].

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. These not only are capable of converting monomeric and oligomeric liquids into solids, but also can produce major changes in properties of solid polymers [8] [23].

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. 3). 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] [24].

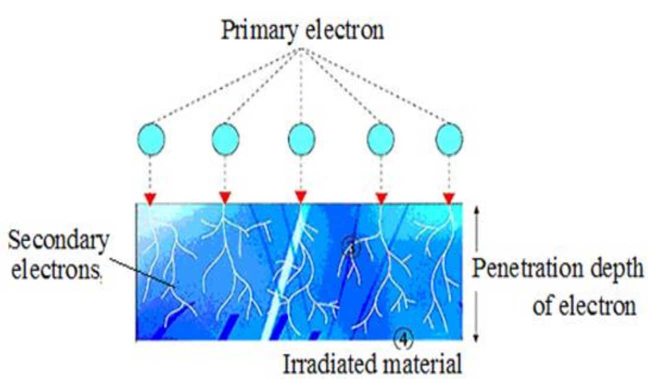

Fig. 3 Scheme of radiation crosslinking by electrons rays

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 [2] [6] [9] [25] - [30].

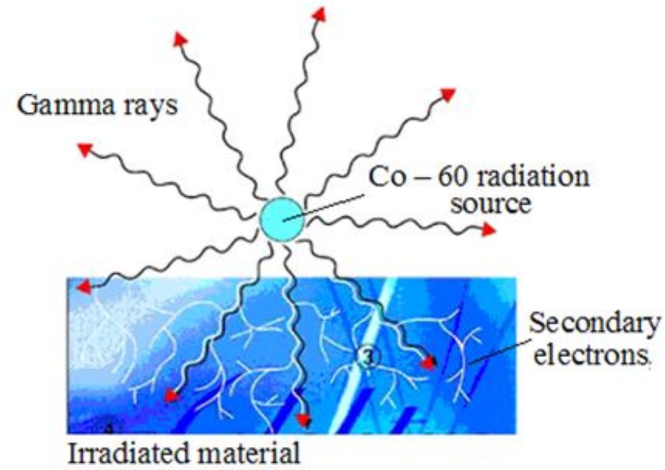

Fig. 4 Scheme of radiation crosslinking by gamma rays

High-energy radiation involves loss of two hydrogen atoms from adjoining chains and consequent bonding between the two carbon-centered free radical sites, leading to inter or intra chain bonding, as can be seen in Fig. 5. To reduce the dose required for crosslinking, crosslinking agents are used.

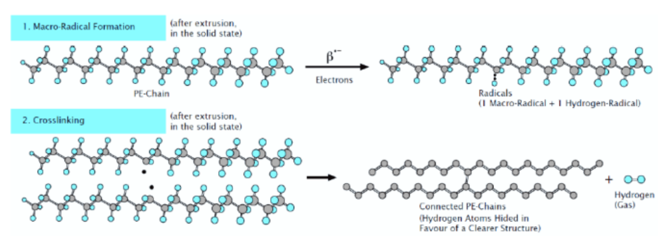

Fig. 5 Mechanism of radiation crosslinking

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 [31].

This paper discusses the influence of radiation doses on the nano-hardness of beta irradiated cross-linked polyamide 12.

II. EXPERIMENTAL

A. *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, 33, 66 and 99 kGy at BGS Beta-Gamma Service GmbH & Co. KG, Germany.

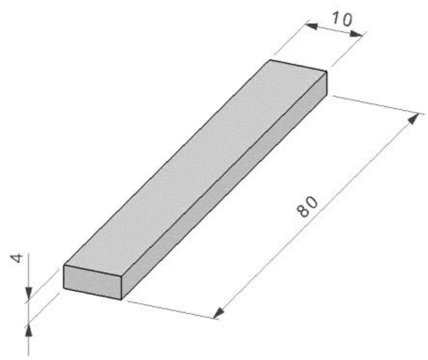

Fig. 6 Dimension of sample

B. Injection molding

The samples were made using the injection molding technology on the injection moulding machine Arburg Allrounder 420C (Fig. 6). Processing temperature 220–250 °C, mold temperature 60 °C, injection pressure 80 MPa, injection rate 50 mm/s.

C. Instrumented nanohardness tests

Instrumented nano-hardness tests were done using a Nano-indentation tester (NHT), CSM Instruments (Switzerland) according to the CSN EN ISO 6507-1. Load and unload speed was 20 mN/min, 100 mN/min and 500 mN/min. After a holding time of 90 s at maximum load 10 mN, 50 mN and 250 mN the specimens were unloaded (Fig. 7).

Fig. 7 Nano-indentation tester

The indentation hardness H_{IT} was calculated as maximum load to the projected area of the hardness impression according to [6] [13] [31] - [35]:

$$H_{IT} = \frac{F_{max}}{A_p} \quad \text{with} \quad h_c = h_{max} - \varepsilon \frac{F_{max}}{S} \tag{1}$$

where h_{max} is the indentation depth at F_{max}, h_c is contact depth. In this study the Oliver and Pharr method was used calculate the initial stiffness (S), contact depth (h_c). The specimens were glued on metallic sample holders (Fig. 8).

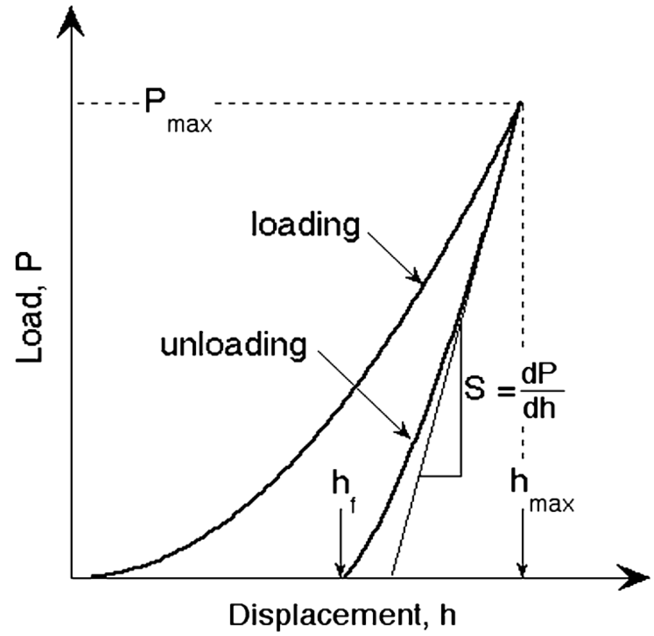

Fig. 8 Schematic illustration of indentation curve

The indentation modulus is calculated from the Plane Strain modulus using an estimated sample Poisson's ratio:

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

The deduced modulus is calculated from the following equation:

$$E_r = \frac{\sqrt{\pi \cdot S}}{2 \cdot \beta \cdot \sqrt{A_p(h_c)}} \tag{3}$$

The Plane Strain Modulus E* is calculated from the following equation:

$$E^* = \frac{1}{\frac{1}{E_r} - \frac{1-\nu_i^2}{E_i}} \tag{4}$$

Where E_i is the Elastic modulus of the indenter, E_r is the Reduced modulus of the indentation contact, ν_i is the Poisson´s ratio of the indenter. [3] [11] [33].

Determination of indentation hardness C_{IT}:

$$C_{IT} = \frac{h_2 - h_1}{h_1} \cdot 100 \tag{5}$$

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 (Fig. 9) [1] [7] [15].

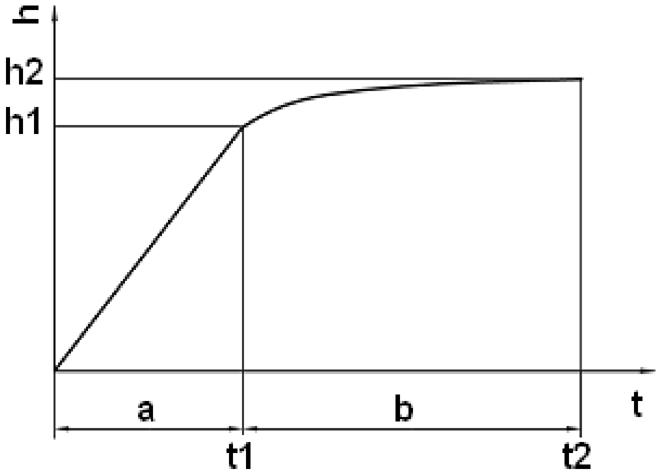

Fig. 9 Expression of indentation creep

Elastic part of the indentation work ηIT (Fig. 10):

$$\eta_{IT} = \frac{W_{elast}}{W_{total}} \cdot 100 \quad \text{with} \quad W_{total} = W_{elast} + W_{plast} \qquad (6)$$

Plastic part W_{plast} / W_{total} follows as 100% - ηIT (7)

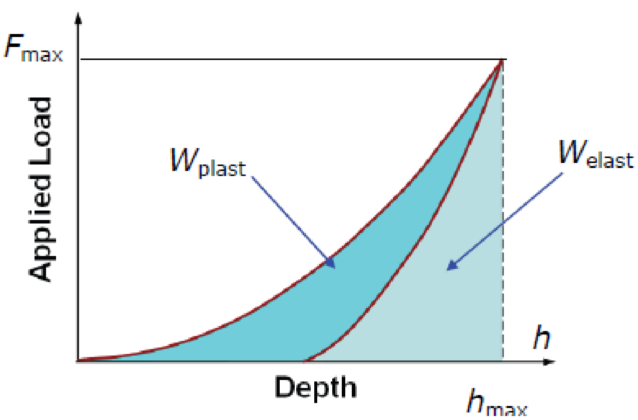

Fig. 10 Indentation work η_{IT}

III. Results and Discussion

The figure 11 and 12 shows a very important correlation between the force and the depth of the indentation. The correlations provide very valuable information on the behaviour of tested material and the modified surface layer.

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 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.

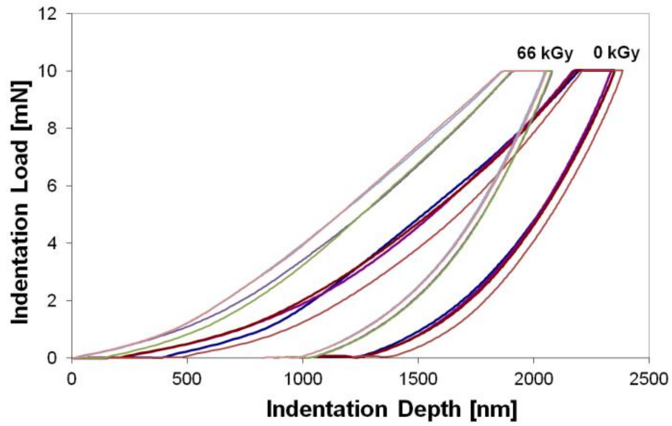

Fig. 11 Indentation load vs. Indentation depth

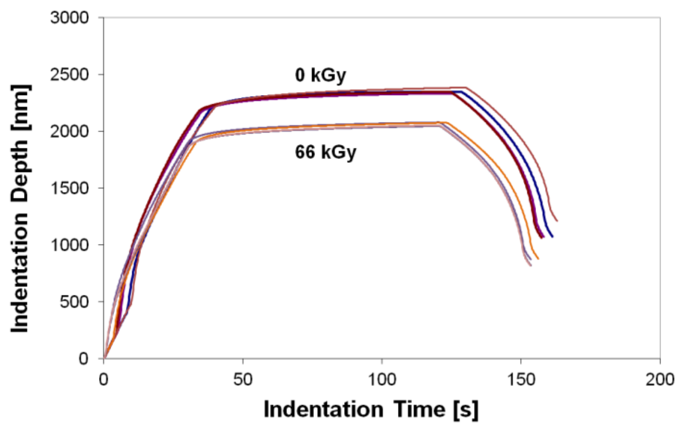

Fig. 12 Indentation depth vs. Indentation time

A. *Indentation load 10 mN*

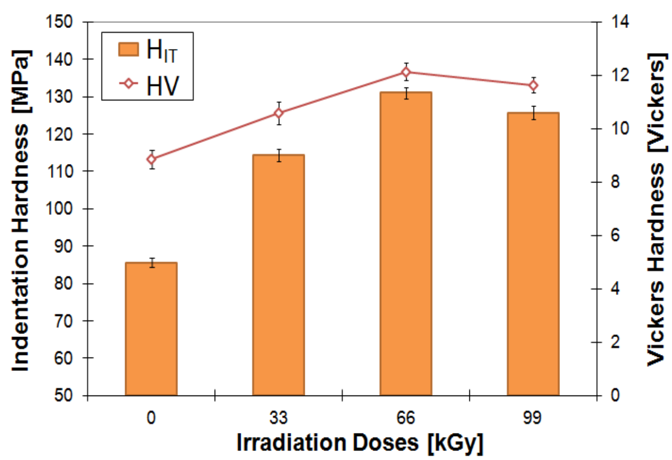

Fig. 13 Hardness H_{IT} of PA12 vs. irradiation doses

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 66 kGy (by 54% higher in comparison with the non-irradiated PA12), as can be seen at Fig. 13.

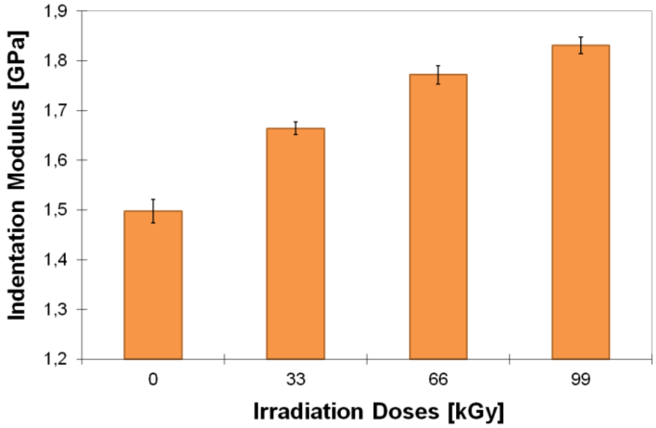

Fig. 14 Elastic modulus E_{IT} of PA12 vs. irradiation doses

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 99 kGy (by 22% 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. 14.

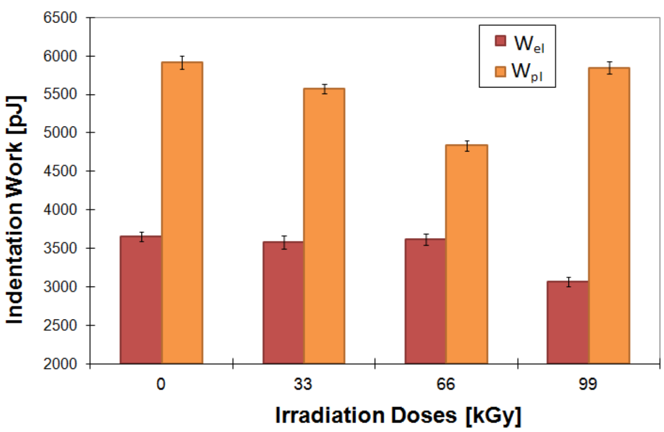

Fig. 15 Deformation work vs. irradiation dose

Other important material parameters obtained during the nano-hardness test were elastic (W_{el}) and plastic deformation work (W_{pl}). The greatest values of plastic and elastic deformation work were obtained for non-irradiated PA12. The lowest values of both elastic and plastic deformation work were obtained for PA12 irradiated with dose of 99 kGy. Radiation of specimens caused lower values of elastic as well as plastic deformation work which is apparent in Fig. 15.

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.

B. *Indentation load 50 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 66 kGy (by 35% higher in comparison with the non-irradiated PA12), as can be seen at Fig. 16.

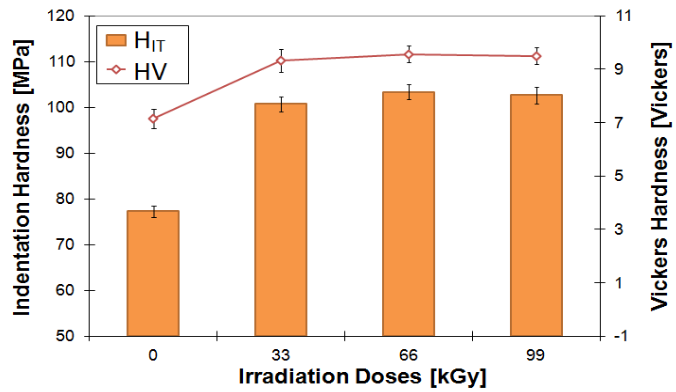

Fig. 16 Hardness H_{IT} of PA12 vs. irradiation doses

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 66 kGy (by 29% 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. 17.

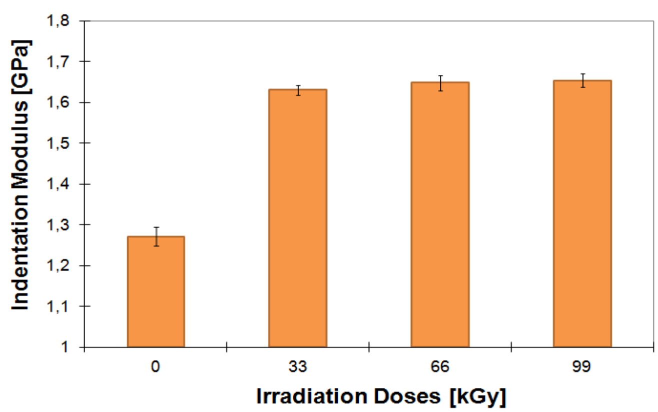

Fig. 17 Elastic modulus E_{IT} of PA12 vs. irradiation doses

The greatest values of elastic deformation work was obtained for non-irradiated PA12. The lowest values of elastic deformation work was obtained for PA12 irradiated with dose of 66 kGy. The lowest values of plastic deformation work was obtained for non-irradiated PA12. The greatest values of plastic deformation work was obtained for PA12 irradiated with dose of 33 kGy. Radiation of specimens caused lower values of elastic as well as plastic deformation work which is apparent in Fig. 18.

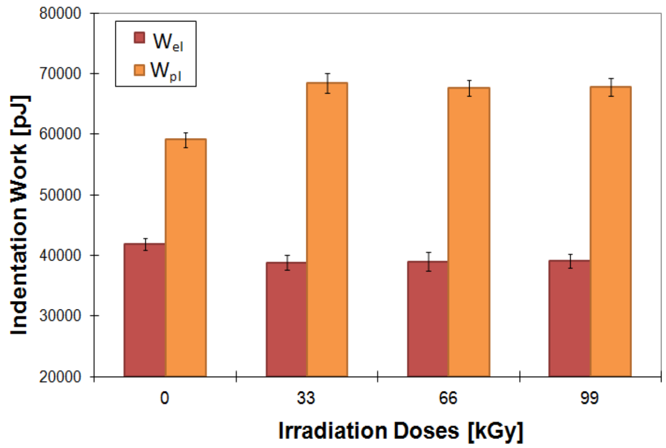

Fig. 18 Deformation work vs. irradiation dose

C. 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 66 kGy (by 48% higher in comparison with the non-irradiated PA12), as can be seen at Fig. 19.

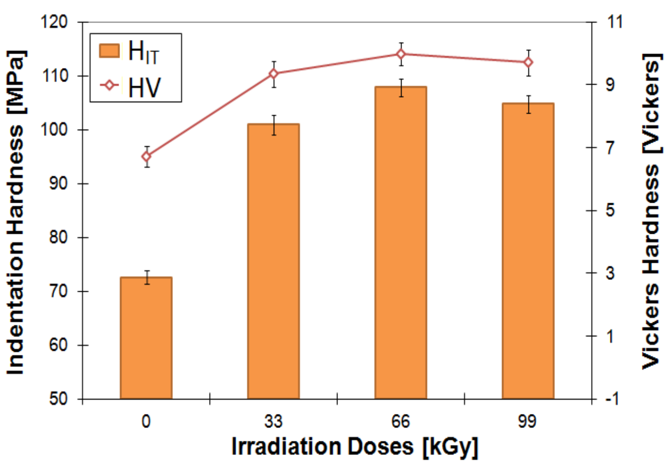

Fig. 19 Hardness H_{IT} of PA12 vs. irradiation doses

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 66 kGy (by 57% 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. 20.

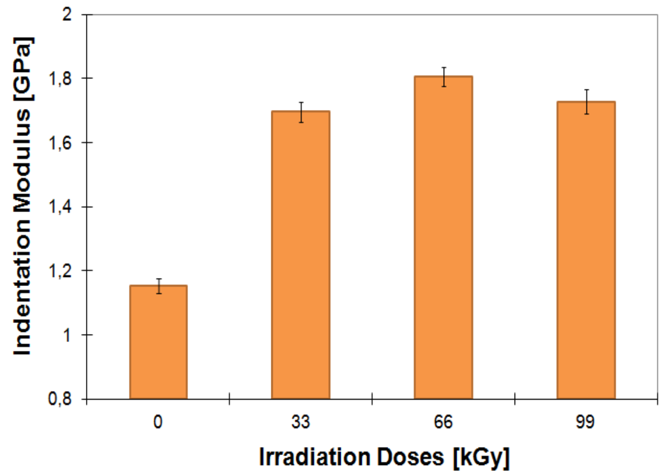

Fig. 20 Elastic modulus E_{IT} of PA12 vs. irradiation doses

The greatest values of plastic and elastic deformation work were obtained for non-irradiated PA12. The lowest values of both elastic and plastic deformation work were obtained for PA12 irradiated with dose of 66 kGy. Radiation of specimens caused lower values of elastic as well as plastic deformation work which is apparent in Fig. 21.

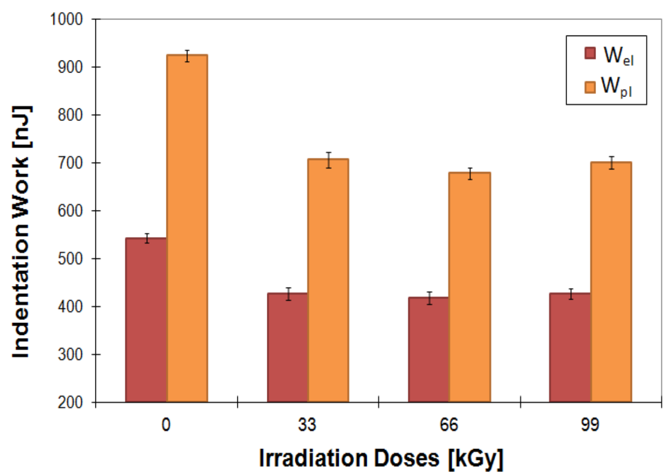

Fig. 21 Deformation work vs. irradiation dose

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.

D. Indentation load 10 mN, 50 mN and 250 mN

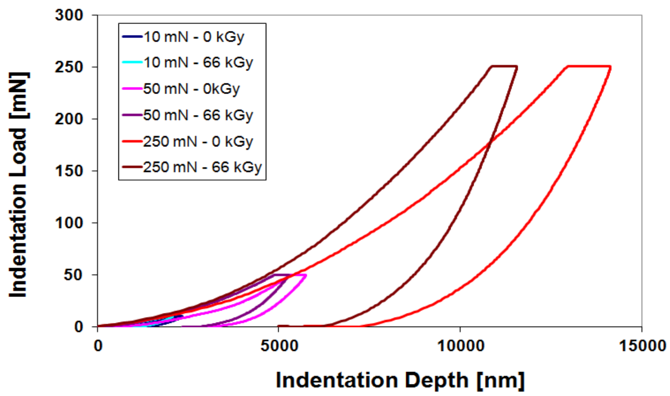

Fig. 22 Indentation load vs. Indentation depth

The figure 22 and 23 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.

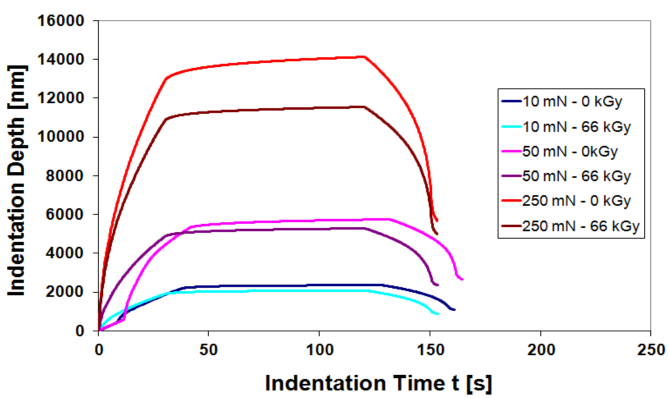

Fig. 23 Indentation depth vs. Indentation time

The load applied for nano-hardness test was 10 mN, 50 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 66 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 66 kGy compared to the non-irradiated specimen was found to be around 54% (Fig. 24).

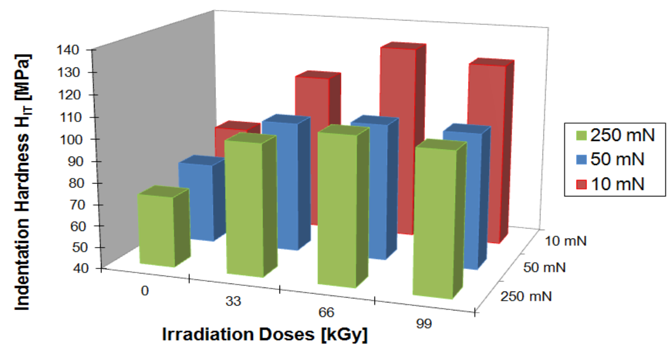

Fig. 24 Hardness H_{IT} of PA12 vs. irradiation doses

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 66 and 99 kGy, when applying all three loads (10 mN, 50 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 57% in the tested specimen (66 kGy) compared to the non-irradiated specimen (Fig. 25).

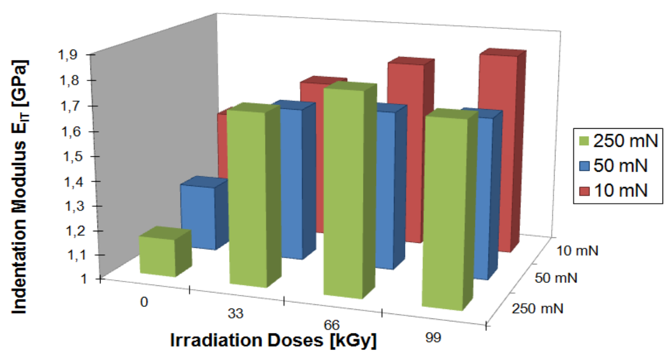

Fig. 25 Elastic modulus E_{IT} of PA12 vs. irradiation doses

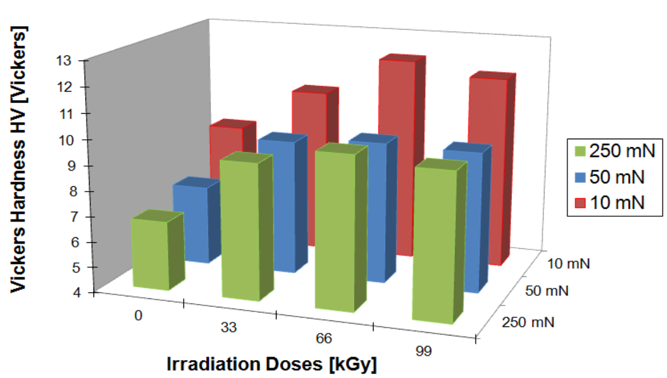

Fig. 26 Hardness Vickers of PA12 vs. irradiation doses

The results of elastic and plastic deformation work showed that the highest values at nano-hardness test were found for non-irradiated specimens. The specimens subjected to beta radiation showed lower values of both elastic and plastic deformation work. The decrease in values of deformation work needed to deform the tested materials indicates changes of structure caused by radiation of the tested PA12. The greatest changes between irradiated and non-irradiated specimen were found at 250 mN load. The increased radiation dose caused a slight drop of values of deformation work. This corresponded with the reverse relaxation coefficient η_{IT}, which showed higher values for irradiated specimens and the lowest value for non-irradiated specimens (Fig. 27).

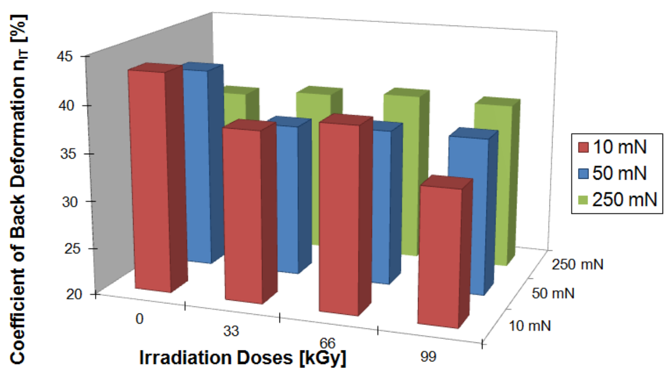

Fig. 27 Deformation work of PA12 vs. irradiation dose

E. *Creep behaviour*

From Figure 28, it is obvious that irradiation has a positive effect on the creep behaviour of the PA12 tested. The highest difference in indentation creep was found for an irradiation dosage of 66 kGy.

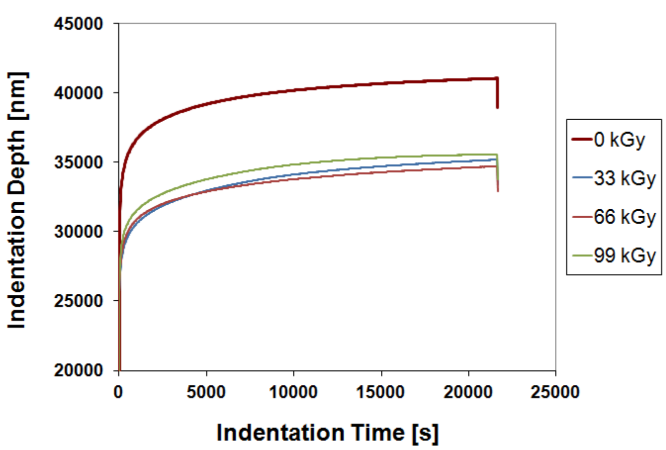

Fig. 28 Indentation creep of PA12

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 54% 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. 29.

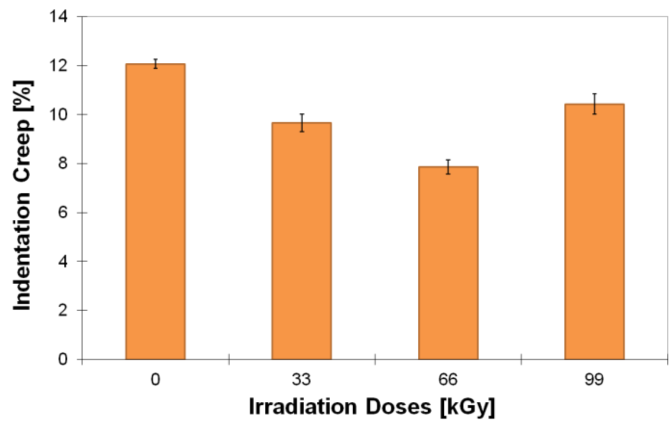

Fig. 29 Creep of PA12 vs. irradiation doses

IV. Conclusion

The article is the assessment of mechanical properties (nano-hardness) of the surface layer of modified PA12. The surface layer of the polymer material such as PA12 is modified by β – radiation with doses of 33, 66 and 99 kGy.

Irradiation of PA12 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.
- The highest values of indentation hardness and indentation modulus were achieved at the glass PA12 irradiated with dose of 66 kGy.
- 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.

Instrumented nano-hardness test of polyamide 12 beta irradiated samples was performed. After the beta radiation the amorphous part was cross linked what was accompanied with the radical increase of nano-hardness and indentation modulus of elasticity. The largest increase was observed in both cases using the doses of 66 kGy. The properties of surface layer of polyamide 12 were modified significantly by beta radiation improved. The nano-hardness values were increased by 54%. Stiffness of surface layer increased significantly by 57% as a result of radiation. The creep values of irradiated polyamide 12 decreased by 54% on average. 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. The highest values of nano-mechanical properties were reached at radiation dose of 66 kGy. With higher radiation doses, the resulting values of nano-mechanical properties decreased and then showed constant values.

The results of nano-mechanical properties of surface layer of modified PA12 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.

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REFERENCES

[1] D. Manas, M. Hribova, M. Manas, M. Ovsik, M. Stanek, D. Samek, “The effect of beta irradiation on morfology and micro hardness of polypropylene thin layers“, 2012, *Thin Solid Films*, Volume 530, pp. 49-52. ISSN 0040-6090.

[2] M. Stanek, D. Manas, M. Manas, O. Suba, “OptimizationofInjection Molding Process“, *International Journal of Mathematics and Computers in Simulation*, Volume 5, Issue 5, 2011, p. 413-421

[3] M. Manas, D. Manas, M. Stanek, S. Sanda, V. Pata,Improvement of Mechanical Properties of the TPE by Irradiation“, 2011, *Chemicke listy*, Volume 105, Issue 17, pp. S828-S829

[4] M. Ovsik, D. Manas, M. Manas, M. Stanek, M. Hribova, K. Kocman, D. Samek, “Irradiated Polypropylene Studied by Microhardness and WAXS“, 2012, *Chemicke listy*, Volume 106, pp. S507-510. ISSN 0009-2770.

[5] M. Manas, M. Stanek, D. Manas, M. Danek, Z. Holik, “Modification of polyamides properties by irradiation”, *Chemicke listy*, Volume 103, 2009, p.24-26.

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

[7] M. Ovsik, D. Manas, M. Manas, M. Stanek, S. Sanda, K. Kyas:*“ Microhardness of PA6 Influenced by Beta Low Irradiation Doses“, International Journal of Mathematics and Computers in Simulation*, Volume 6, Issue 6, 2012, p. 575-583, ISSN 1998-0159.

[8] Manas D., Manas M., Stanek M., Danek M.: *Arch. Mater. Sci. Eng.*, 32 (2), 2008, pp. 69-76.

[9] Chvatalova L.; Navratilova J.; Cermak R.; Raab M., Obadal M.: *Macromolecules*, 42, 2009, 7413-7417.

[10] Wei, Z., Lu, Y., Meng, Y., Zhang, L. 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

[11] D. Janacova, H. Charvatova, K. Kolomaznik, V. Vasek, P. Mokrejs, “Solving of Non-Stationary Heat Transfer in a Plane Plate”, in Proc. *13th WSEAS International Conference on Automatic Control, Modelling &Simulation*, Lanzarote, CanaryIslands 2011, p.287-291

[12] H. Vaskova, V. Kresalek, „Raman Spectroscopy of Epoxy Resin Crosslinking“, in Proc. *13th WSEAS International Conference on Automatic Control, Modelling &Simulation*, Lanzarote, CanaryIslands 2011, p.357-360.

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

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

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

[16] Buckle, H. 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.

[17] D. Manas, M. Manas, M.Stanek, S. Sanda, V. Pata, “Thermal Effects on Steels at Different Methodsof Separation“, 2011, *Chemicke listy*, Volume 105, Issue 17, pp. S713-S715

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

[19] Manas, D., Stanek, M., Manas, M., Pata V., Javorik, J., “Influence of Mechanical Properties on Wear of Heavily Stressed Rubber Parts”, *KGK – Kautschuk Gummi Kunststoffe*, 62. Jahrgang, 2009, p.240-245.

[20] J. Javorik, D. Manas, “The Specimen Optimization for the Equibiaxial Test of Elastomers*,” in Proc. 13th WSEAS International Conference on Automatic Control, Modelling & Simulation*, Lanzarote, Spain, 2011, pp. 121-124.

[21] M. Stanek, D. Manas, M. Manas, J. Javorik, “Simulation of Injection Molding Process by Cadmould Rubber“, *International Journal of Mathematics and Computers in Simulation*, Volume 5, Issue 5, 2011, p. 422-429.

[22] V. Pata, D. Manas, M. Manas, M. Stanek, “Visulation of the Wear Test of Rubber Materials”, *Chemicke listy*, Volume 105, 2011, pp.290-292.

[23] M. Adamek, M. Matysek, P. Neumann, “Modeling of the Microflow Senzor”, i*n Proc. 13th WSEAS International Conference on Automatic Control*, Modelling & Simulation, Lanzarote, Canary Islands, 2011, p.137-140.

[24] M. Stanek, D. Manas, M. Manas, O. Suba, “Optimization of Injection Molding Process by MPX,” *in Proc. 13th WSEAS International Conference on Automatic Control, Modelling & Simulation*, p.212-216.

[25] Manas, M.; Manas, D.; Stanek, M.; Mizera, A.; Ovsik, M. Modification of polymer properties by irradiation properties of thermoplastic elastomer after radiation cross-linking. *Asian Journal of Chemistry*, 2013, Volume 25, Issue 9, s. 5124-5128. ISSN 09707077.

[26] Ovsik, M., Manas, D., Manas, M., Stanek, M., Kyas, K., Bednarik, M., Mizera, A. “Microhardness of HDPE influenced by Beta Irradiation“, *International Journal of Mathematics and Computers in Simulation*, Volume 6, Issue 6, 2012, p. 566-574, ISSN 1998-0159.

[27] T. Sysala, O. Vrzal, “A Real Models Laboratory and an Elevator Model Controlled through Programmable Controller (PLC)”, *in Proc. 13th WSEAS International Conference on Automatic Control, Modelling & Simulation*, Lanzarote, Canary Islands, 2011, p.365-368.

[28] Stanek, M., Manas, M., Manas, D., “Mold Cavity Roughness vs. Flow of Polymer”, *Novel Trends in Rheology III*, AIP, 2009, pp.75-85.

[29] Manas, D., Stanek, M., Manas, M., Pata V., Javorik, J., “Influence of Mechanical Properties on Wear of Heavily Stressed Rubber Parts”, *KGK – Kautschuk Gummi Kunststoffe*, 62. Jahrgang, 2009, p.240-245.

[30] Ovsik, M., Manas, D., Manas, M., Stanek, M., Kyas, K., Bednarik, M., Mizera, A. “Microhardness of HDPE influenced by Beta Irradiation“, *International Journal of Mathematics and Computers in Simulation*, Volume 6, Issue 6, 2012, p. 566-574, ISSN 1998-0159.

[31] Ovsik, M., Manas, D., Manas, M., Stanek, M., Bednarik, M., Kratky, P., “Effect of Beta Low Irradiation Doses on the Indentation Hardness of Glass Fiber-Filled Polypropylene“, 2013, *Chemicke listy*, Volume 107, pp. 68-70. ISSN 0009-2770.

[32] Herbert, E. G., Oliver, W. C., Pharr, G. M. Nanoindentation and the dynamic characterization of viscoelastic solids. *Journal of physics D: Applied Physic*s. 2008.

[33] Huang, Y., Zhang, F., Hwang, K. C., Nix, W. D., Pharr, G. M., Feng, G. A model of size effects in nano-indentation. *Journal of the Mechanics and Physics of Solids*. 2006, Vol. 54, p. 1668–1686.

[34] Ovsik, M., Manas, D., Manas, M., Stanek, M., Bednarik, M., Kratky, P., Mizera, A. “Effect of Beta Low Irradiation Doses on the Nano-Indentation Hardness of PBT”, *in Proc. 17th WSEAS International Conference on System*, Rhodes Island, Greece, 2013, pp. 230-234. ISBN 978-960-474-314-8.

[35] Ovsik, M., Manas, D., Manas, M., Stanek, M., Kyas, K., Bednarik, M., Mizera, A. “Effect of Beta Irradiation on the Microhardness of HDPE,” *in Proc. 16th WSEAS International Conference on Circuits & Systems*, Kos Island, Greece, 2012, pp. 285-288. ISBN 978-1-61804-108-1.