Micro-hardness of Glass Fiber-Filled PA6 Influenced by Beta Irradiation

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

Abstract—The presented article deals with the research of micro-mechanical properties in the surface layer of modified Polyamide 6 filled by 30% of glass fibers. These micro-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 purpose of the article is to consider to what extent the irradiation process influences the resulting micro-mechanical properties measured by the DSI method.

Keywords—polyamide 6, glass fiber, micro-hardness, irradiation, crosslinking, β – radiation.

I. INTRODUCTION

Plastic is one of the most utilized raw materials in our daily life and is a material of utmost importance. The use of polymeric materials is not new and they have been used since the ancient times. Some of these polymers are used as plastics in engineering. Currently, amongst the engineering materials, several polymers are used. The polyamide is distinguished as the most important of all [1] [2].

Polyamides (PA) are semi-crystalline polymers. A distinction is made between two types. Polyamides made of one basic material (PA 6) and polyamides, which are made of 2 basic materials (PA 66). Polyamides have very good mechanical properties, are particularly tough and have excellent sliding and wear characteristics [1] [3] [4] [5].

Polyamide 6 (PA 6) is the most common extruded polyamide and offers a balanced combination of all typical characteristics of this group of materials. Polyamides are characterized by their possessing of hightensile strength, elasticity, tenacity and resistance to abrasion. These mechanical properties are maintained even under high temperatures and therefore, the polyamides can be used in temperatures up to 200 °C in applications of short-term [1] [2] [6].

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. One application that has proved most useful over the years is radiation crosslinked components for the electrical industry, e.g. switch components, and the automotive industry, for instance components for the engine compartment [2] [7].

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] [4] [7] [10].

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. Also, in comparison to UV and visible radiation, they can penetrate considerably deeper into the

Martin Ovsik is with the Tomas Bata University in Zlin, nam. T. G. Masaryka 5555, 76001 Zlin, Czech Republic (phone: +420576035062; e-mail: ovsik@ft.utb.cz).

David Manas is with the Tomas Bata University in Zlin, nam. T. G. Masaryka 5555, 76001 Zlin, Czech Republic (e-mail: dmanas@ft.utb.cz).

Miroslav Manas is with the Tomas Bata University in Zlin, nam. T. G. Masaryka 5555, 76001 Zlin, Czech Republic (e-mail: manas@ft.utb.cz).

Michal Stanek is with the Tomas Bata University in Zlin, nam. T. G. Masaryka 5555, 76001 Zlin, Czech Republic (e-mail: stanek@ft.utb.cz).

Martin Bednarik is with the Tomas Bata University in Zlin, nam. T. G. Masaryka 5555, 76001 Zlin, Czech Republic (e-mail: mbednarik@ft.utb.cz).

Petr Kratky is with the Tomas Bata University in Zlin, nam. T. G. Masaryka 5555, 76001 Zlin, Czech Republic (e-mail: kratky@ft.utb.cz).

Ales Mizera is with the Tomas Bata University in Zlin, nam. T. G. Masaryka 5555, 76001 Zlin, Czech Republic (e-mail: mizera@ft.utb.cz).

material [10] [11].

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] [7].

Fig. 1 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 [1] [4] [7].
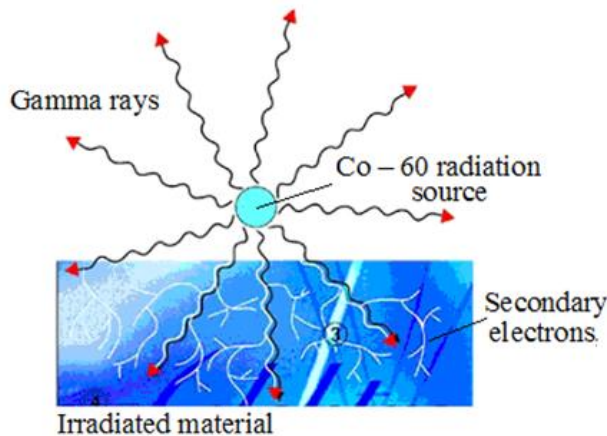

Fig. 2 Scheme of radiation crosslinking by gamma rays

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. 3. To reduce the dose required for crosslinking, crosslinking agents are used.
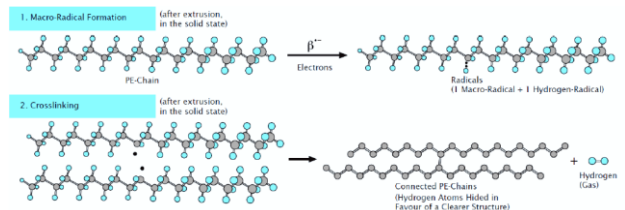

Fig. 3 Mechanism of radiation crosslinking

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 [1] [4].

High performance polymers have the best mechanical and thermal properties but the share in production and use of all polymers is less than 1%.

Common PA6, 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 PA6 structure. The utility properties of PA6 improve when the noncrystalline part of PA6 is cross-linked [1] [7].

The aim of this paper is to study the effect of ionizing radiation with different doses, on micro-mechanical properties of polyamide 6 (PA 6) with 30% of fiberglass reinforcement 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. Irradiation

For this experiment polyamide PA6 V-PTS –Creamid-B63VN, filled by 30% glass fiber, that were supplied by PTS Plastics Technologie Service, Germany (filled by 30% glass fiber, PA6+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, 15, 30, 45, 66 and 99 kGy at BGS Beta-Gamma Service GmbH & Co. KG, Germany.

B. Injection molding

The samples were made using the injection molding technology on the injection moulding machine Arburg Allrounder 420C. Processing temperature 240–280 °C, mold temperature 75 °C, injection pressure 70 MPa, injection rate 45 mm/s.

C. Instrumented microhardness tests

Instrumented microhardness tests were done using a Nanoindentation tester (NHT), CSM Instruments (Switzerland) according to the CSN EN ISO 6507-1 (Fig. 4). Load and unload speed were 1 N/min, 2 N/min and 10 N/min.

After a holding time of 90 s at maximum load 0,5 N, 1 N and 5 N the specimens were unloaded.

Fig. 4 Micro-combi tester

The indentation hardness H_{IT} was calculated as maximum load to the projected area of the hardness impression according to [6] [11]:

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

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. 5).

Fig. 5 Schematic illustration of unloading process

The indentation modulus is calculated from the Plane Strain modulus using an estimated sample Poisson's ratio [6] [11]:

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

The reduced modulus and Plane Strain Modulus E* is calculated from the following equation [6] [7]:

$$E_r = \frac{\sqrt{\pi \cdot S}}{2 \cdot \beta \cdot \sqrt{A_p(h_c)}} \quad \text{and} \quad E^* = \frac{1}{\frac{1}{E_r} - \frac{1 - v_i^2}{E_i}} \quad (3)$$

Where E_i is the Elastic modulus of the indenter, E_r is the Reduced modulus of the indentation contact, v_i is the Poisson's ratio of the indenter.

Determination of indentation hardness C_{IT}:

$$C_{IT} = \frac{h_2 - h_1}{h_1} \cdot 100 \quad (4)$$

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. 6) [1] [4] [6].
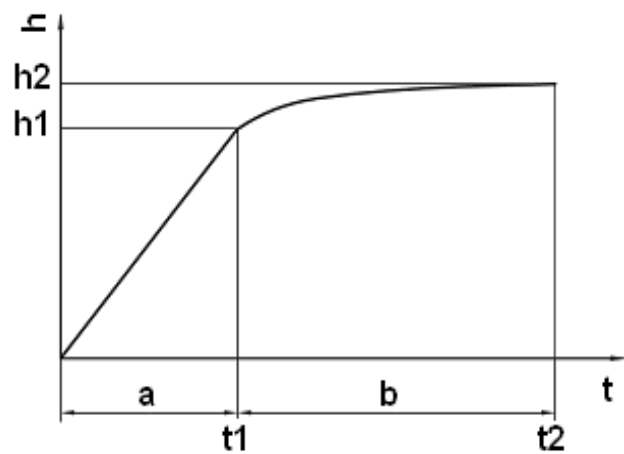

Fig. 6 Expression of indentation creep

Elastic part of the indentation work ηIT (Fig. 7):

$$\eta_{IT} = \frac{W_{elast}}{W_{total}} \cdot 100 \quad \text{with} \quad W_{total} = W_{elast} + W_{plast} \quad (5)$$

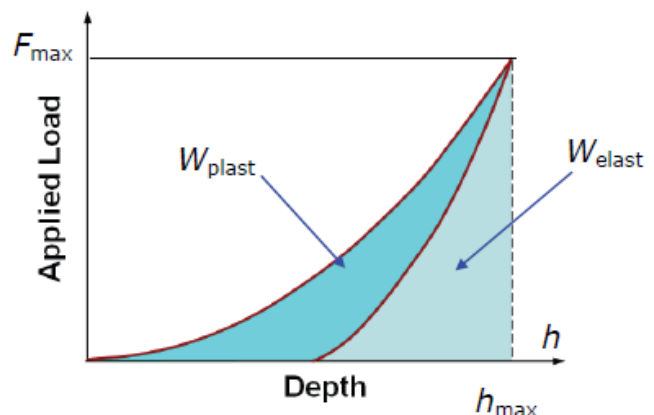Plastic part W_{plast} / W_{total} follows as 100% - ηIT (6)

Fig. 7 Indentation work η_{IT}

III.   RESULTS AND DISCUSSION

The figure 8 and 9 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 glass fiber-filled polyamide 6 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 indentor in the surface layer. On the contrary, the irradiated glass fiber-filled polyamide 6 showed considerably smaller depth of the impression of the indentor which can signify greater resistance of this layer to wear.

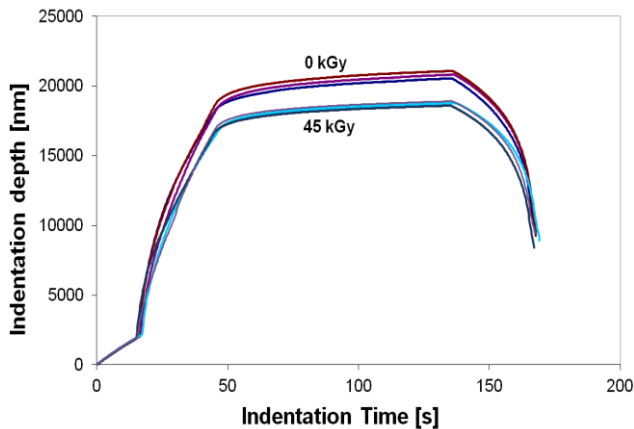Fig. 8 Indentation load vs. Indentation depth

Fig. 9 Indentation depth vs. Indentation time

A.   Indentation load 0.5N

The values measured during the microhardness test showed that the lowest values of indentation hardness and Vickers hardness were found for the non-irradiated glass fiber-filled PA6. On the contrary, the highest values of indentation hardness and Vickers hardness were obtained for glass fiber-filled PA6 irradiated by a dose of 66 kGy (by 23% higher in comparison with the non-irradiated glass fiber-filled PA6), as can be seen at Fig. 10.
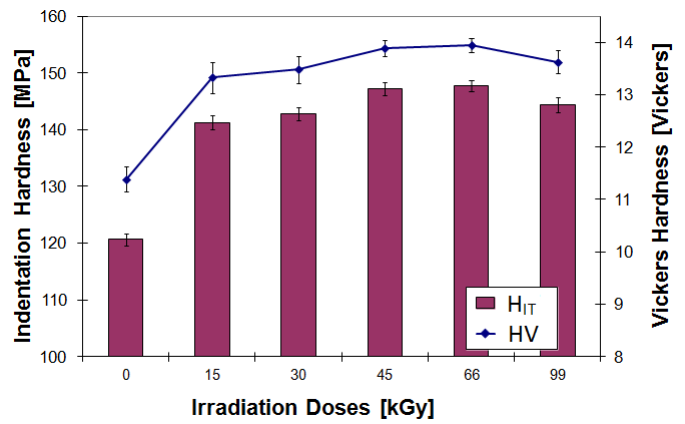

Fig. 10 Hardness H_{IT} of PA6 vs. irradiation doses

Higher radiation dose does not influence significantly the microhardness value. An indentation hardness increase of the surface layer is caused by irradiation cross-linking of the tested specimen. A closer look at the microhardness results reveals that when the highest radiation doses are used, microhardness decreases which can be caused by radiation indusced degradation of the material.

According to the results of measurements of microhardness, it was found that the highest values of indentation modulus of elasticity were achieved at the glass fiber-filled PA6 irradiated with dose of 66 kGy (by 20% higher than compared with non-irradiated glass fiber-filled PA6). On the contrary, the lowest values of the indentation modulus of elasticity were found for non-irradiated glass fiber-filled PA6 as is seen at Fig. 11.
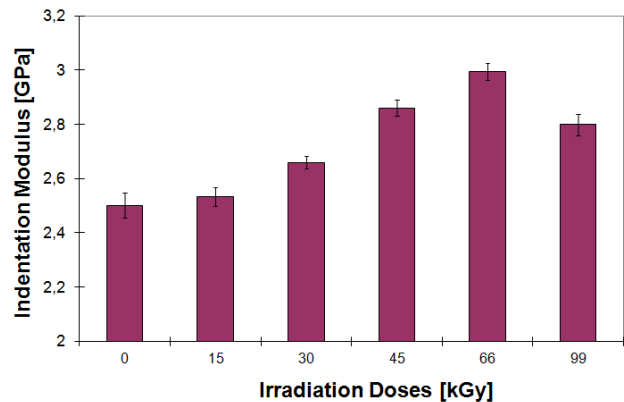

Fig. 11 Elastic modulus E_{IT} of PA6 vs. irradiation doses

Other important material parameters obtained during the microhardness test were elastic and plastic deformation work. The elastic deformation work We determines the reaction of material to applied (multiaxial) load with reversible deformation. The plastic part of the deformation work Wpl defines toughness of the tested material (surface layer) and its resistance to plastic deformation (Fig. 12).

The greatest values of plastic and elastic deformation work were obtained for non-irradiated glass fiber-filled PA6. The lowest values of both elastic and plastic deformation work

were obtained for glass fiber-filled PA6 irradiated with dose of 15 kGy. Radiation of specimens caused lower values of elastic as well as plastic deformation work which is apparent in Fig. 12.

Next to plastic and elastic deformation work, the coefficient of back deformation η_{IT} is especially important for the assessment of the structure of the irradiated glass fiber-filled PA6. The highest values were measured at non-irradiated glass fiber-filled PA6. The smallest values were found at irradiation doses of 15 and 99 kGy.

Fig. 12 Deformation work vs. irradiation dose

B. *Indentation load 1N*

The values measured during the microhardness test showed that the lowest values of indentation hardness and Vickers hardness were found for the non-irradiated glass fiber-filled PA6. On the contrary, the highest values of indentation hardness and Vickers hardness were obtained for glass fiber-filled PA6 irradiated by a dose of 66 kGy (by 20% higher in comparison with the non-irradiated glass fiber-filled PA6), as can be seen at Fig. 13.
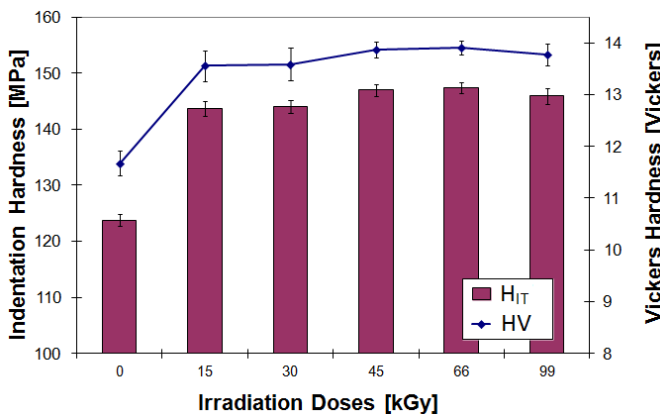

Fig. 13 Hardness H_{IT} of PA6 vs. irradiation doses

Higher radiation dose does not influence significantly the microhardness value. An indentation hardness increase of the surface layer is caused by irradiation cross-linking of the tested specimen. A closer look at the microhardness results reveals that when the highest radiation doses are used, microhardness

decreases which can be caused by radiation indusced degradation of the material.

According to the results of measurements of microhardness, it was found that the highest values of indentation modulus of elasticity were achieved at the glass fiber-filled PA6 irradiated with dose of 45 kGy (by 17% higher than compared with non-irradiated glass fiber-filled PA6). On the contrary, the lowest values of the indentation modulus of elasticity were found for non-irradiated glass fiber-filled PA6 as is seen at Fig. 14.
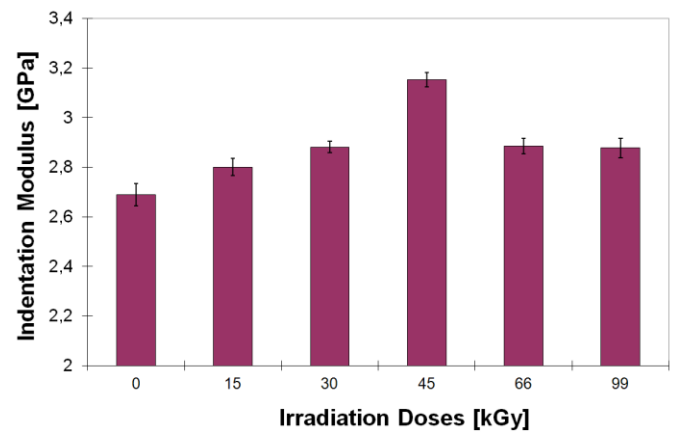

Fig. 14 Elastic modulus E_{IT} of PA6 vs. irradiation doses

The greatest values of plastic and elastic deformation work were obtained for non-irradiated glass fiber-filled PA6. The lowest values of both elastic and plastic deformation work were obtained for glass fiber-filled PA6 irradiated with dose of 15 kGy. Radiation of specimens caused lower values of elastic as well as plastic deformation work which is apparent in Fig. 15.

Next to plastic and elastic deformation work, the coefficient of back deformation η_{IT} is especially important for the assessment of the structure of the irradiated glass fiber-filled PA6. The highest values were measured at non-irradiated glass fiber-filled PA6. The smallest values were found at irradiation doses of 15 kGy.
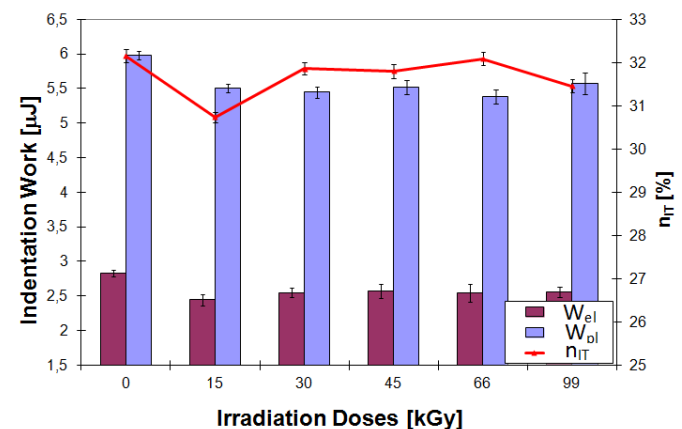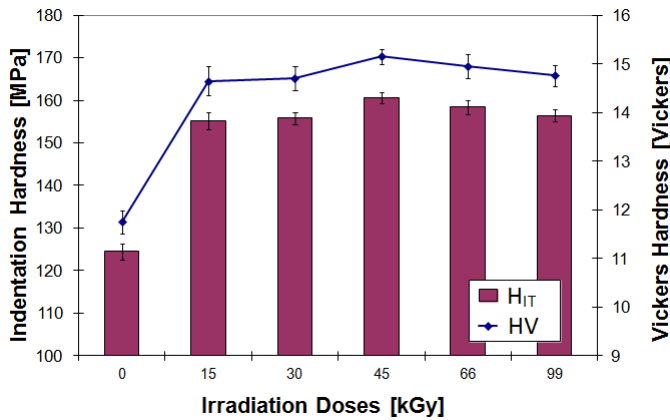

Fig. 15 Deformation work vs. irradiation dose

C. Indentation load 5N

The values measured during the microhardness test showed that the lowest values of indentation hardness and Vickers hardness were found for the non-irradiated glass fiber-filled PA6. On the contrary, the highest values of indentation hardness and Vickers hardness were obtained for glass fiber-filled PA6 irradiated by a dose of 45 kGy (by 28% higher in comparison with the non-irradiated glass fiber-filled PA6), as can be seen at Fig. 16.

Fig. 16 Hardness H_{IT} of PA6 vs. irradiation doses

Higher radiation dose does not influence significantly the microhardness value. An indentation hardness increase of the surface layer is caused by irradiation cross-linking of the tested specimen. A closer look at the microhardness results reveals that when the highest radiation doses are used, microhardness decreases which can be caused by radiation indusced degradation of the material.

According to the results of measurements of microhardness, it was found that the highest values of indentation modulus of elasticity were achieved at the glass fiber-filled PA6 irradiated with dose of 45 kGy (by 24% higher than compared with non-irradiated glass fiber-filled PA6). On the contrary, the lowest values of the indentation modulus of elasticity were found for non-irradiated glass fiber-filled PA6 as is seen at Fig. 17.
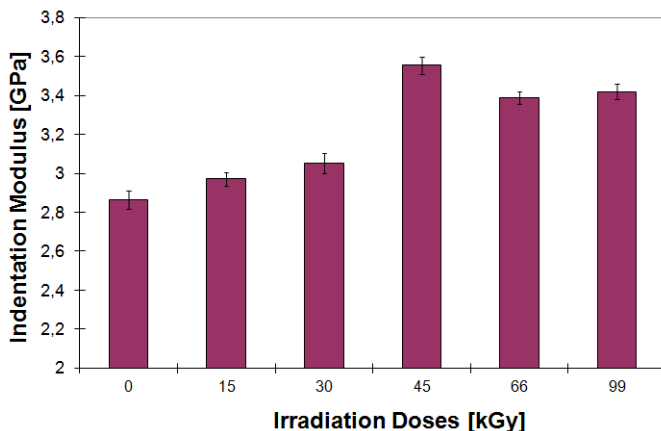

Fig. 17 Elastic modulus E_{IT} of PA6 vs. irradiation doses

The greatest values of plastic and elastic deformation work were obtained for non-irradiated glass fiber-filled PA6. The lowest values of both elastic and plastic deformation work were obtained for glass fiber-filled PA6 irradiated with dose of 45 kGy. Radiation of specimens caused lower values of elastic as well as plastic deformation work which is apparent in Fig. 18.

Next to plastic and elastic deformation work, the coefficient of back deformation η_{IT} is especially important for the assessment of the structure of the irradiated glass fiber-filled PA6. The highest values were measured at irradiation doses of 45 kGy glass fiber-filled PA6. The smallest values were found at irradiation doses of 99 kGy.
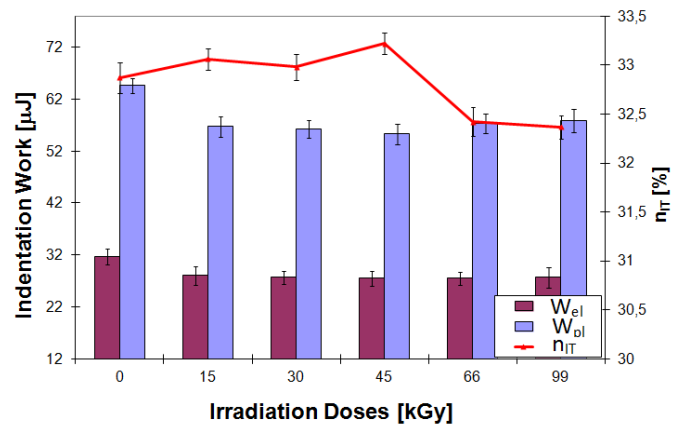

Fig. 18 Deformation work vs. irradiation dose

D. Indentation load 0.5N, 1N and 5N

The figure 19 and 20 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 glass fiber-filled PA6 showed considerably smaller depth of the impression of the indentor which can signify greater resistance of this layer to wear.
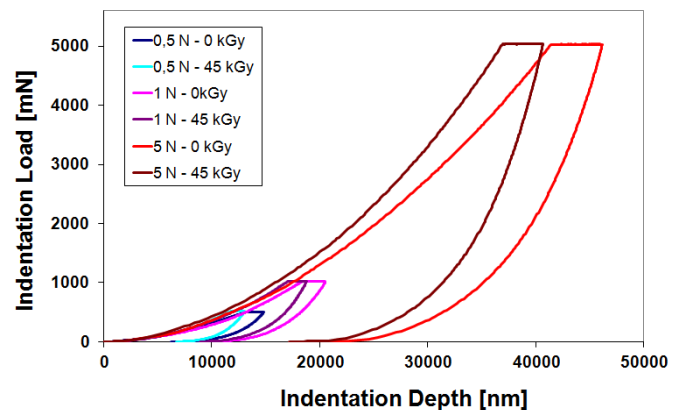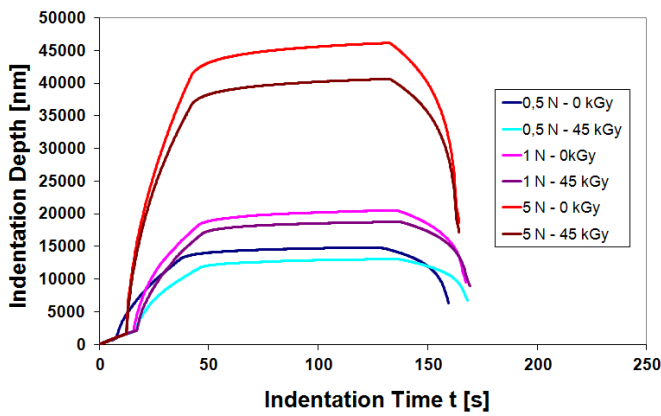

Fig. 19 Indentation load vs. Indentation depth

Fig. 20 Indentation depth vs. Indentation time

The load applied for microhardness test was 0.5N, 1N and 5N. We observed the effect of the load on the resulting properties of the surface layer of glass fiber-filled PA6 modified by beta radiation. The measurement results show that at all loads applied the highest value of microhardness was found when the radiation dose was 45 and 66 kGy. When higher radiation doses are applied, microhardness values decline, showing constant values. At higher loads there is a slight but not significant microhardness values. They range within statistical discrepancy. The increase in microhardness values at 5N load is caused by deeper penetration of the indentor, thus reaching semicrystalline structure of glass fiber-filled PA6 tested. The increase in microhardness of the surface layer at the dose of 66 kGy compared to the non-irradiated specimen was found to be around 28% (Fig. 21).
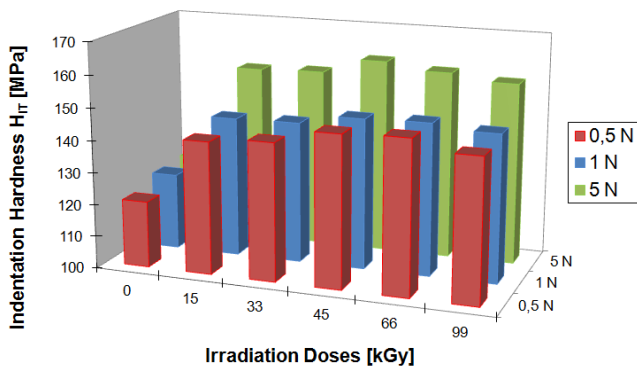

Fig. 21 Hardness H_{IT} of PA6 vs. irradiation doses

When observing the changes of stiffness of the surface layer measured by microhardness test it was proved that the maximum value of stiffness was found at radiation dose of 66 kGy, when applying all three loads (0.5N, 1N, 5N). 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 24% in the tested specimen (45 kGy) compared to the non-irradiated specimen (Fig. 22).
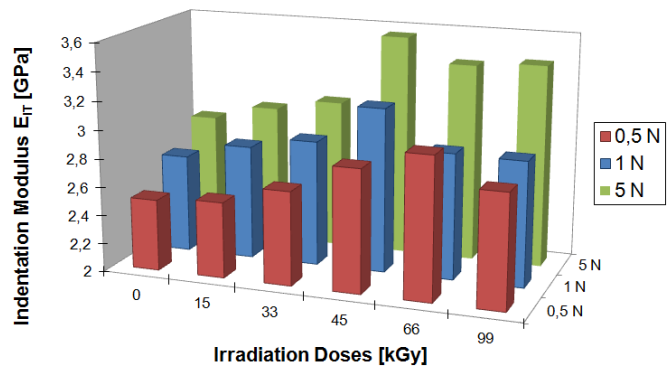

Fig. 22 Elastic modulus E_{IT} of PA6 vs. irradiation doses
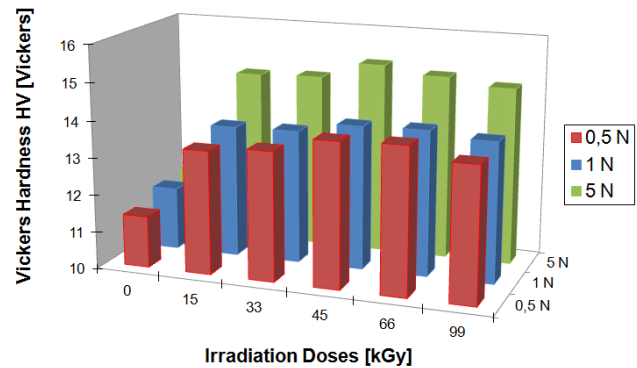

Fig. 23 Hardness Vickers of PA6 vs. irradiation doses

The results of elastic and plastic deformation work showed that the highest values at microhardness 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 glass fiber-filled PA6. The greatest changes between irradiated and non-irradiated specimen were found at 5N 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. 24).
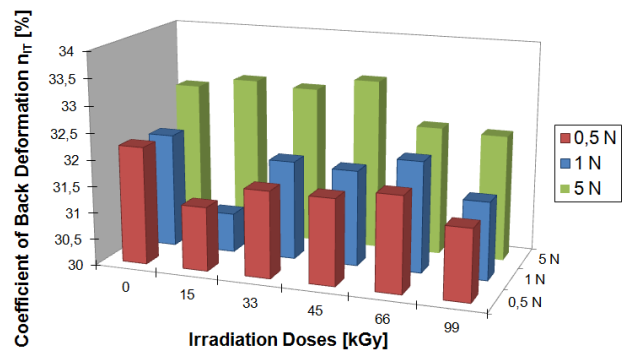

Fig. 24 Deformation work of PA6 vs. irradiation dose

E. Creep behaviour

From Figure 25, it is obvious that irradiation has a positive effect on the creep behaviour of the glass fiber-filled PA6 tested. The highest difference in indentation creep was found for an irradiation dosage of 45 kGy.
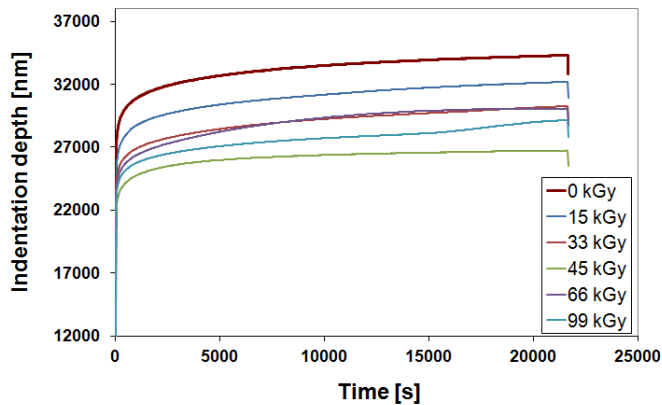

Fig. 25 Creep of glass fiber-filled PA6

According to the results of measurements of microhardness, it was found that the lowest values of indentation creep were achieved at the glass fiber-filled PA6 irradiated with dose of 30 kGy (by 13% lower than compared with non-irradiated glass fiber-filled PA6). On the contrary, the highest values of the indentation creep were found for non-irradiated PA6 as is seen on Fig. 26.
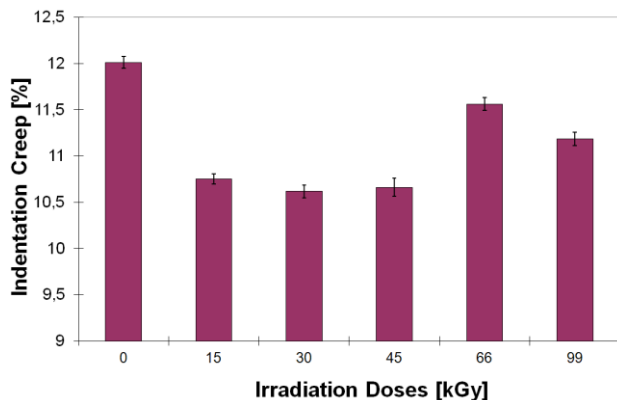

Fig. 26 Creep of glass fiber-filled PA6 vs. irradiation doses

IV. CONCLUSION

The article is the assessment of mechanical properties (microhardness) of the surface layer of modified glass fiber-filled PA6. The surface layer of the polymer material such as glass fiber-filled PA6is modified by β – radiation with doses of 15, 30, 45, 66 and 99 kGy.

Irradiation of glass fiber-filled Polyamide 6 with a β - radiation influences the micro-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 fiber-filled PA6 irradiated with dose of 45 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.

The results of micromechanical properties of surface layer of modified glass fiber-filled PA6 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] 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] 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.

[9] 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.

[10] 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.

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