# Micro-hardness of Glass Fiber-Filled PBT Influenced by Beta Low Radiation Doses

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 PBT filled by 35% of glass fibers. The glass fiber-filled PBT modification was carried out with the aid of β - radiation at different radiation intensities and the resulting properties were measured with the aid of micro-indentation test by the DSI (Depth Sensing Indentation) method. 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*—**PBT, glass fiber, micro-indentation, hardness, crosslinking, β – radiation, Depth Sensing Indentation.

## I. INTRODUCTION

Polybutylene terephthalate (PBT) is a semi-crystalline thermoplastic of the polyester family, which crystallizes very slowly and is therefore available in an amorphous-transparent or crystalline-opaque condition, depending on the processing method [1].

PBT are characterized by their high strength and rigidity, dimensionally stable, low tendency to creep, very good frictional and wear resistance, good impact strength, very low coefficient of thermal expansion, good chemical resistance to acids, very good electrical characteristics, very low moisture absorption, good adhesion and welding ability. Furthermore, PBT, like all polyesters, has very good frictional and wearing properties. Compared to PET, PBT has a better impact strength - particularly at low temperatures [1] - [7].

The irradiation cross-linking of thermoplastic materials via electron beam or cobalt 60 (gamma rays) proceeds is proceeding separately after the processing. The cross-linking level can be adjusted by the irradiation dosage and often by means of a cross-linking booster [8] [9].

The main deference between β- and γ- rays is in their different abilities of penetrating the irradiated material. γ- rays have a high penetration capacity. The penetration capacity of electron rays depends on the energy of the accelerated electrons (Fig. 1) [10] [11].

Due to electron accelerators the required dose can be applied within seconds, whereas several hours are required in the γ-radiation plant (Fig. 2).

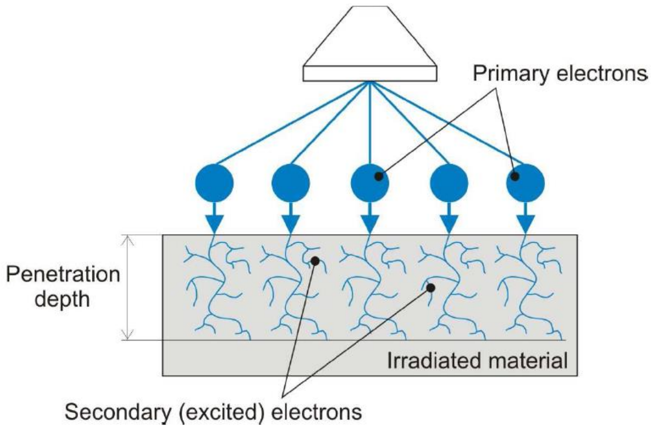

Fig. 1 Design of Electron rays

The electron accelerator operates on the principle of the Braun tube, whereby a hot cathode is heated in vacuum to such a degree that electrons are released [12].

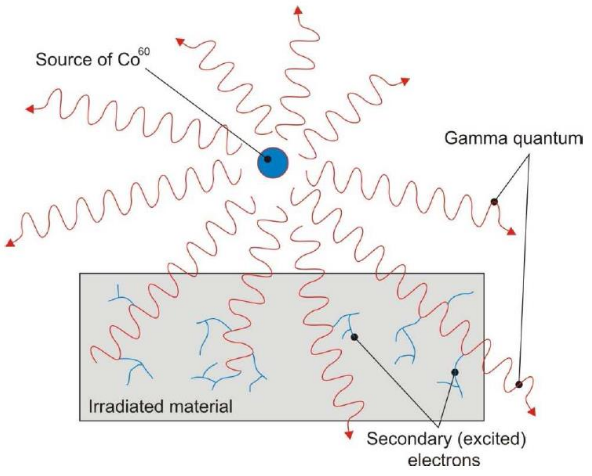

Fig. 2 Design of Gamma rays

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).

Simultaneously, high voltage is generated in a pressure vessel filled with insulating gas. The released electrons are accelerated in this vessel and made to fan out by means of a magnetic field, giving rise to a radiation field. The accelerated electrons emerge via a window (Titanium foil which occludes the vacuum) and are projected onto the product [13] - [15].

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 |

Cobalt 60 serves as the source of radiation in the gamma radiation plant. Many of these radiation sources are arranged in a frame in such a way that the radiation field is as uniform as possible. The palleted products are conveyed through the radiation field. The radiation dose is applied gradually, that is to say, in several stages, whereby the palleted products are conveyed around the Co – 60 radiation sources several times. This process also allows the application of different radiation doses from one product type to another. The dimensional stability, strength, chemical resistance and wear of polymers can be improved by irradiation. Irradiation cross-linking normally creates higher strength as well as reduced creep under load if the application temperature is above the glass transition temperature (Tg) and below the former melting point. Irradiation cross-linking leads to a huge improvement in resistance to most of the chemicals and it often leads to the improvement of the wear behavior (Table 1.) [14] [16].

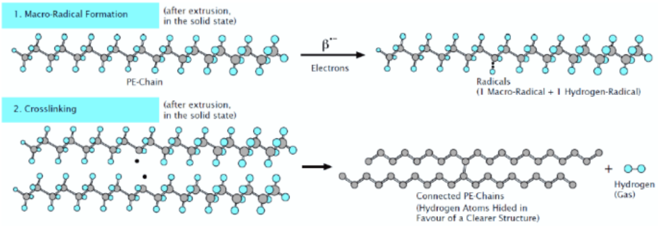

Fig. 3 Mechanism of radiation crosslinking

Common PBT, 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 PBT structure. The utility properties of PBT improve when the noncrystalline part of PBT is cross-linked (Fig. 3).

The aim of this paper is to study the effect of ionizing radiation with different doses, on micro-mechanical properties of PBT with 35% 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 Polybutylene terephthalate PBT V-PTS-CREATEC-B3HZC * M800/25, PTS Plastics Technology Service, Germany (filled by 35% glass fiber (35%GF), PBT+TAIC) was used. The prepared specimens were irradiated with doses of 0, 33, 66, and 99 kGy at BGS Beta-Gamma Service GmbH & Co. KG, Germany.

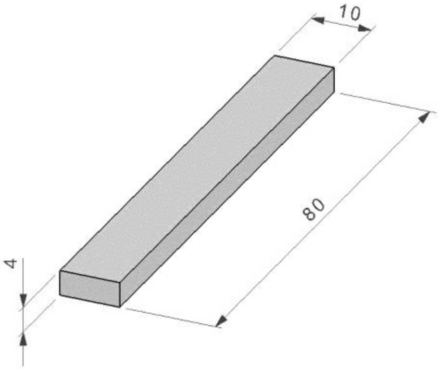

Fig. 4 Dimension of sample

### B. Injection molding

The samples were made using the injection molding technology on the injection moulding machine Arburg Allrounder 420C (Fig. 4). Processing temperature 230–260 °C, mold temperature 75 °C, injection pressure 85 MPa, injection rate 60 mm/s.

### C. Instrumented microhardness tests

Instrumented microhardness 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 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. 5).

The indentation hardness $H_{IT}$ was calculated as maximum load to the projected area of the hardness impression according to [17]:

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

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. 6).

Fig. 5 Indentation tester

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

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

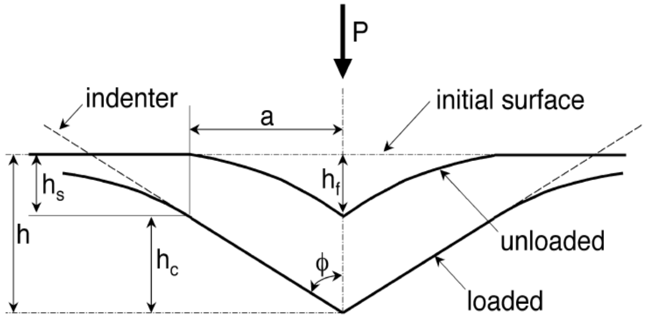

Fig. 6 Schematic illustration of unloading process

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

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

Where $E_i$ is the Elastic modulus of the indenter, $E_r$ is the Reduced modulus of the indentation contact, $\nu_i$ is the Poisson´s ratio of the indenter.

Determination of indentation hardness $C_{IT}$:

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

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 [1] [4] [6].

Elastic part of the indentation work $\eta_{IT}$ (Fig. 7):

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

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

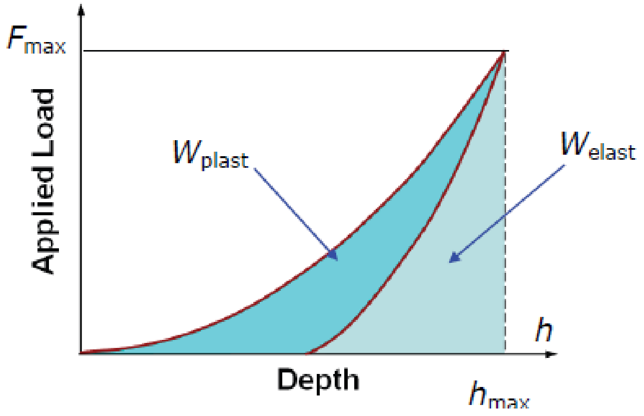

Fig. 7 Indentation work $\eta_{IT}$

## III. RESULTS AND DISCUSSION

Micro-indentation characteristics determined by DSI method are depicted in Fig. 8 and Fig. 9. They characterize course of loading force in dependence on indenter penetration depth, which gives an idea about course of instantaneous values of observed micro-mechanical properties.

The correlation between the force and the depth of the micro-indentation in glass fiber-filled PBT 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 (66 kGy) glass fiber-filled PBT showed considerably smaller depth of the impression of the indenter which can signify greater resistance of this layer to wear.

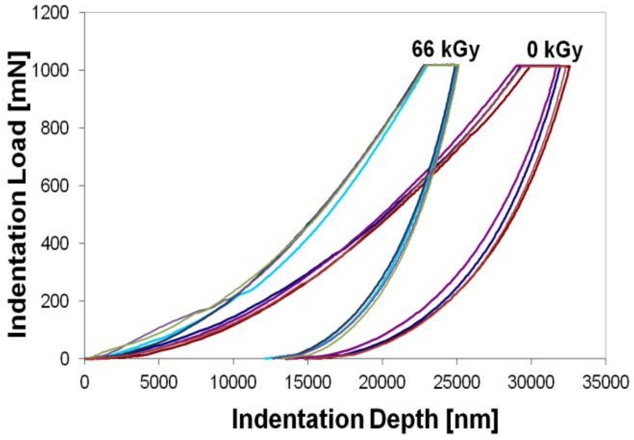

Fig. 8 Indentation load vs. Indentation depth

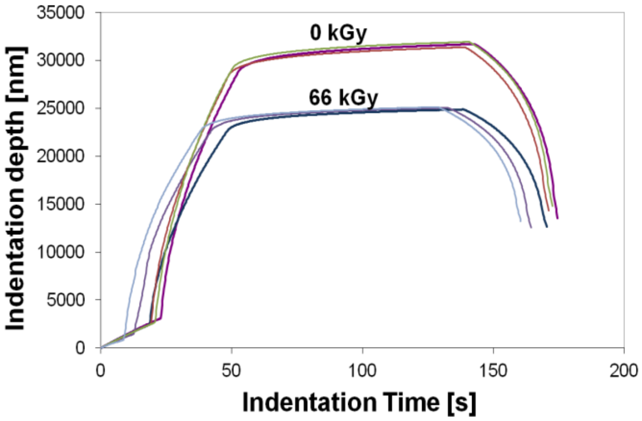

Fig. 9 Indentation depth vs. Indentation time

## A. *Indentation load 0.5N*

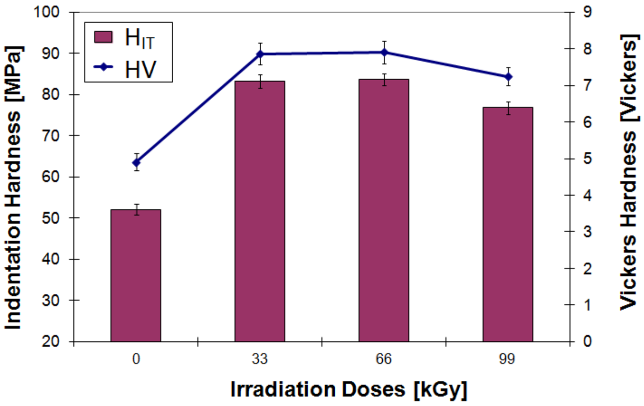

Fig. 10 Hardness $H_{IT}$ of PBT vs. irradiation doses

The values measured during the micro-indentation test showed that the lowest values of indentation hardness and Vickers hardness were found for the non-irradiated 35% GF PBT. On the contrary, the highest values of indentation hardness and Vickers hardness were obtained for PBT irradiated by a dose of 66 kGy (by 64% higher in comparison with the non-irradiated PBT), as can be seen at Fig. 10.

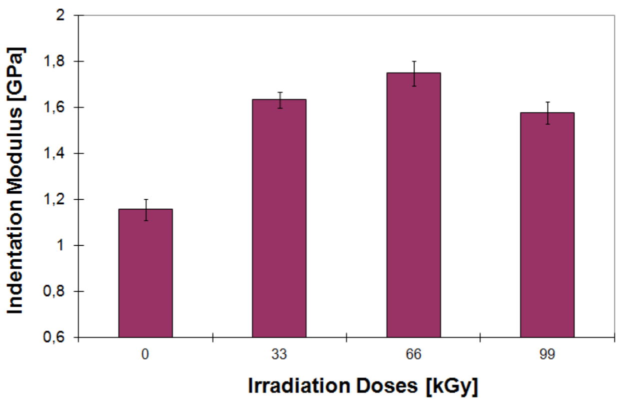

Fig. 11 Elastic modulus $E_{IT}$ of PBT vs. irradiation doses

According to the results of measurements of micro-indentation test, it was found that the highest values of indentation modulus of elasticity were achieved at the glass fiber-filled PBT irradiated with dose of 66 kGy (by 50% higher than compared with non-irradiated PBT). On the contrary, the lowest values of the indentation modulus of elasticity were found for non-irradiated PBT as is seen at Fig. 11.

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

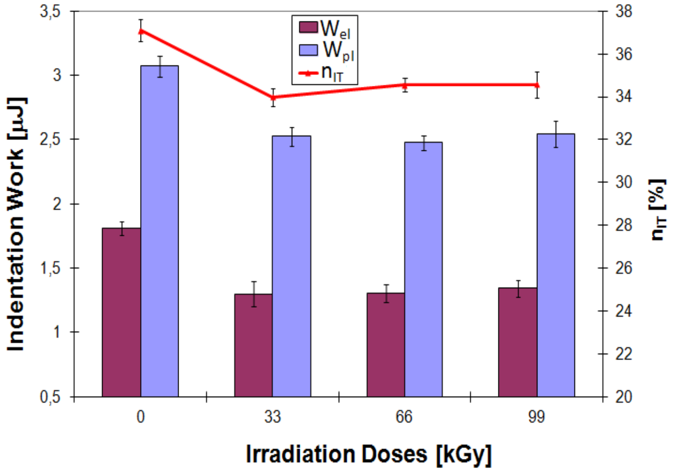

Fig. 12 Deformation work vs. irradiation dose

Other important material parameters obtained during the microhardness test were elastic and plastic deformation work. The elastic deformation work $W_{el}$ determines the reaction of material to applied (multiaxial) load with reversible deformation. The plastic part of the deformation work $W_{pl}$ 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 PBT. The lowest values of both elastic and plastic deformation work were obtained for glass fiber-filled PBT 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. 12.

Next to plastic and elastic deformation work, the coefficient of back deformation $\eta_{IT}$ is especially important for the assessment of the structure of the irradiated glass fiber-filled PBT. The highest values were measured at non-irradiated glass fiber-filled PBT. The smallest values were found at irradiation doses of 33 kGy.

### *B. Indentation load 1N*

The values measured during the micro-indentation test showed that the lowest values of indentation hardness and Vickers hardness were found for the non-irradiated 35% GF PBT. On the contrary, the highest values of indentation hardness and Vickers hardness were obtained for PBT irradiated by a dose of 66 kGy (by 53% higher in comparison with the non-irradiated PBT), as can be seen at Fig. 13.

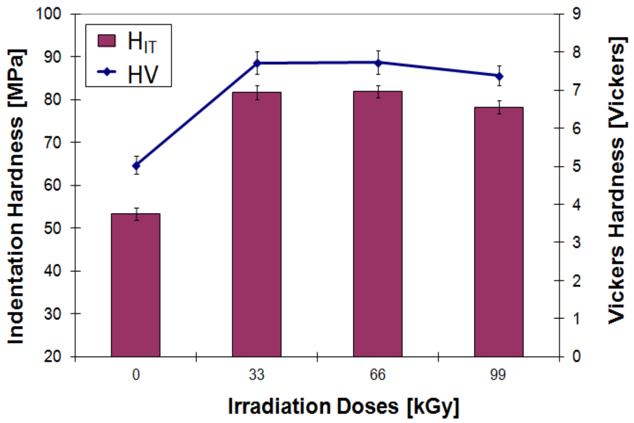

Fig. 13 Hardness $H_{IT}$ of PBT vs. irradiation doses

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 micro-indentation test, it was found that the highest values of indentation modulus of elasticity were achieved at the glass fiber-filled PBT irradiated with dose of 66 kGy (by 42% higher than compared with non-irradiated PBT). On the contrary, the lowest values of the indentation modulus of elasticity were found for non-irradiated PBT as is seen at Fig. 14.

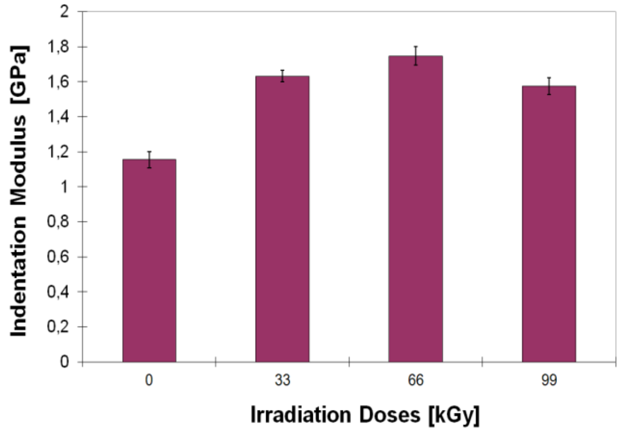

Fig. 14 Elastic modulus $E_{IT}$ of PBT vs. irradiation doses

The greatest values of both deformation works were obtained for non-irradiated 35% GF PBT. The lowest values of $W_{el}$, $W_{pl}$ and $n_{IT}$ were obtained for PBT 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. 15.

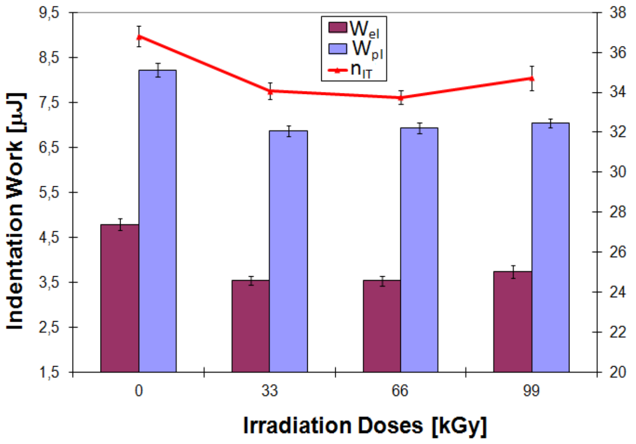

Fig. 15 Deformation work vs. irradiation dose

### *C. Indentation load 5N*

The values measured during the micro-indentation test showed that the lowest values of indentation hardness and Vickers hardness were found for the non-irradiated glass fiber-filled PBT. On the contrary, the highest values of indentation hardness and Vickers hardness were obtained for glass fiber-filled PBT irradiated by a dose of 66 kGy (by 47% higher in comparison with the non-irradiated glass fiber-filled PBT), as can be seen at Fig. 16.

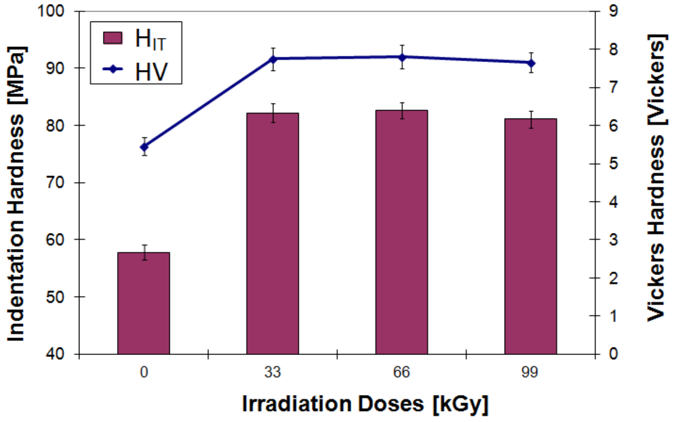

Fig. 16 Hardness $H_{IT}$ of PBT vs. irradiation doses

According to the results of measurements of micro-indentation test, it was found that the highest values of indentation modulus of elasticity were achieved at the glass fiber-filled PBT irradiated with dose of 66 kGy (by 50% higher than compared with non-irradiated PBT). On the contrary, the lowest values of the indentation modulus of elasticity were found for non-irradiated PBT as is seen at Fig. 17.

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.

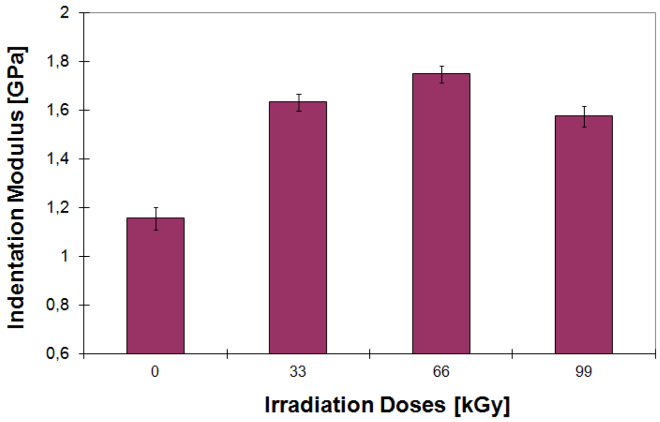

Fig. 17 Elastic modulus $E_{IT}$ of PBT vs. irradiation doses

The greatest values of plastic and elastic deformation work were obtained for non-irradiated glass fiber-filled PBT. The lowest values of both elastic and plastic deformation work were obtained for glass fiber-filled PBT 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. 18.

Next to plastic and elastic deformation work, the coefficient of back deformation $\eta_{IT}$ is especially important for the assessment of the structure of the irradiated glass fiber-filled PBT. The highest values were measured at irradiation doses of 99 kGy glass fiber-filled PBT. The smallest values were found at irradiation doses of 33 kGy.

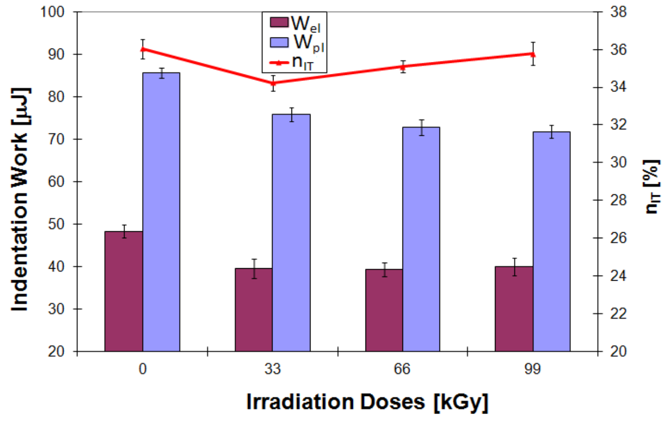

Fig. 18 Deformation work vs. irradiation dose

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

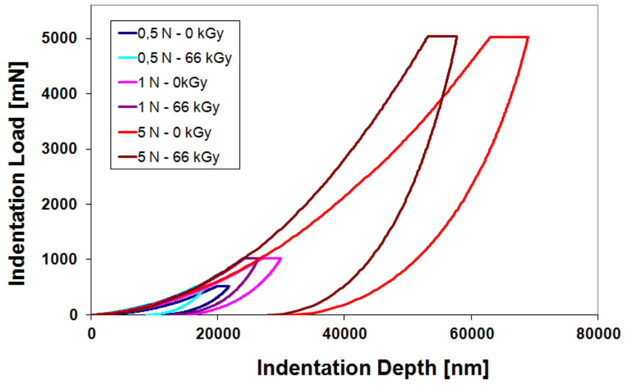

Fig. 19 Indentation load vs. Indentation depth

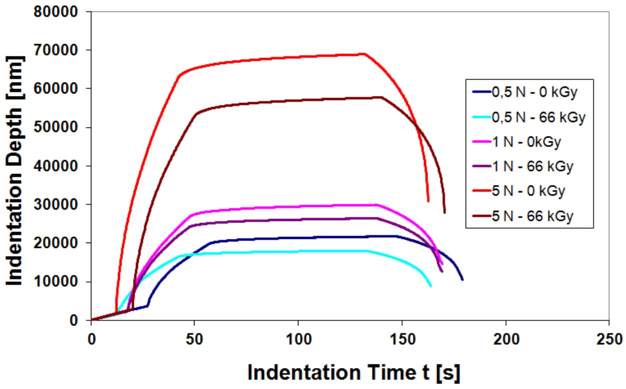

Fig. 20 Indentation depth vs. Indentation time

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 PBT showed considerably smaller depth of the impression of the indentor which can signify greater resistance of this layer to wear.

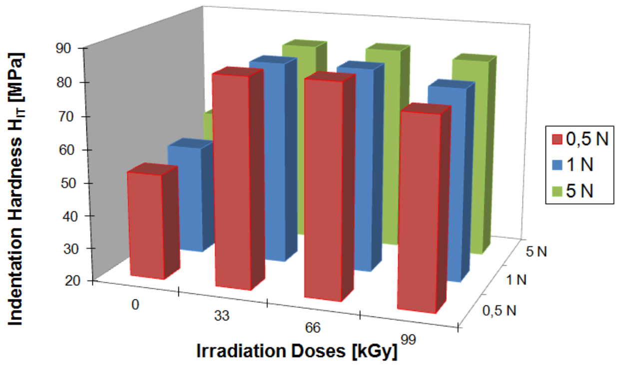

Fig. 21 Hardness $H_{IT}$ of PBT vs. irradiation doses

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 PBT 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 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 PBT 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 64% (Fig. 21).

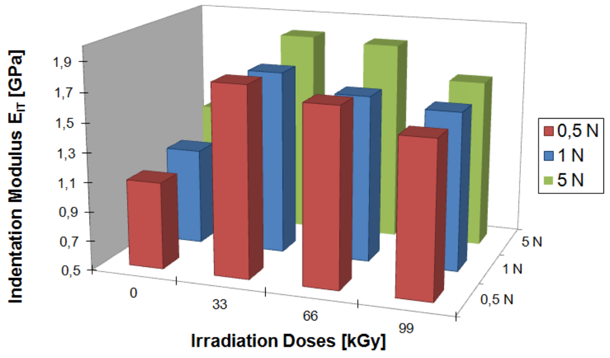

Fig. 22 Elastic modulus $E_{IT}$ of PBT vs. irradiation doses

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 50% in the tested specimen (66 kGy) compared to the non-irradiated specimen (Fig. 22).

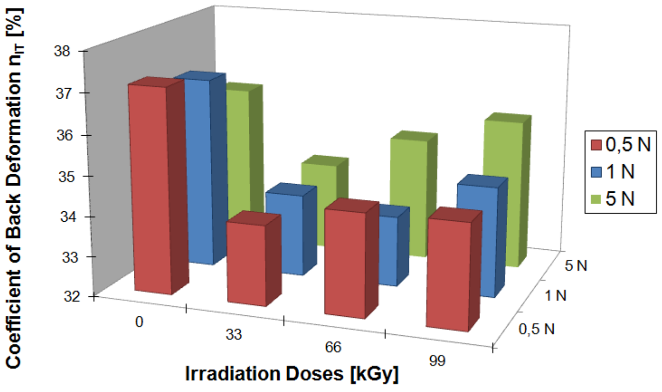

Fig. 23 Deformation work of PBT vs. irradiation dose

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 PBT. 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 $\eta_{IT}$, which showed higher values for irradiated specimens and the lowest value for non-irradiated specimens (Fig. 23).

## E. *Creep behaviour*

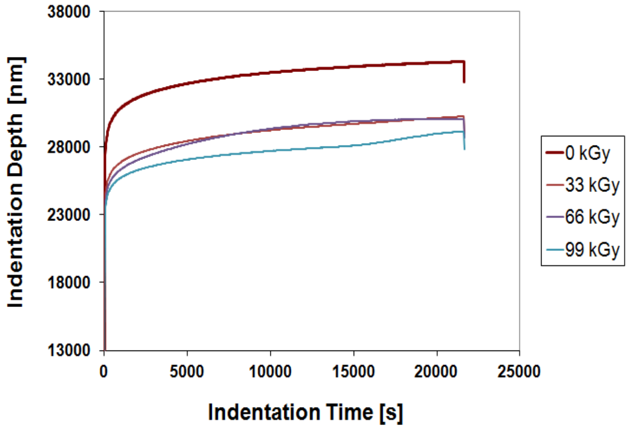

Fig. 24 Creep of glass fiber-filled PBT

From Figure 24, it is obvious that irradiation has a positive effect on the creep behaviour of the glass fiber-filled PBT tested. The highest difference in indentation creep was found for an irradiation dosage of 66 kGy.

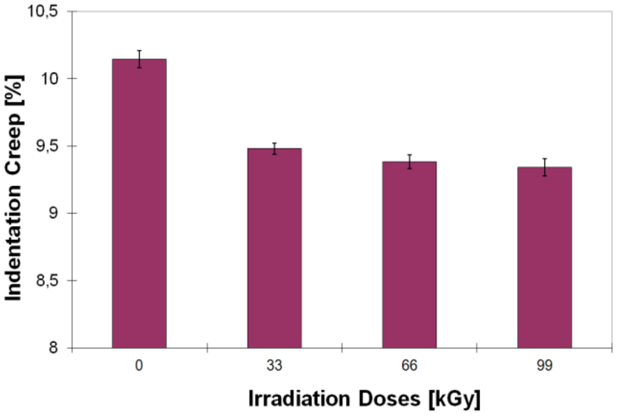

Fig. 25 Creep of glass fiber-filled PBT vs. irradiation doses

The values measured during the micro-indentation test showed that the lowest values of indentation creep were achieved at the PBT irradiated with dose of 66 kGy (by 9% lower than compared with non-irradiated 35% GF PBT). On the contrary, the highest values of the indentation creep were found for non-irradiated glass fiber-filled PBT as is seen at Fig. 25.

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

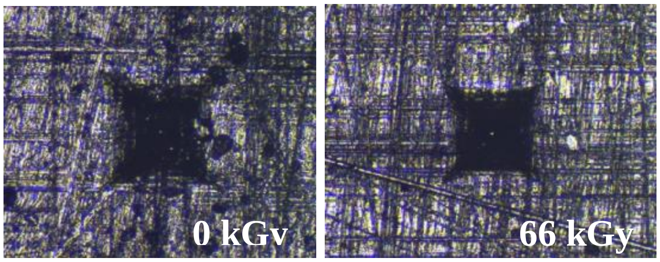

Fig. 26 Vickers indentation produced on PBT

The figure 26 shows the difference in the indentation of non-irradiated 35 % GF PBT and 35% GF PBT irradiated at doses of 66 kGy.

## IV. CONCLUSION

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

The properties of surface layer of glass fiber-filled PBT modified by beta radiation improved significantly. The micro-hardness values increased by about 64%. Stiffness of surface layer increased significantly by 50% as a result of radiation. The creep values decreased by 9% on average for irradiated glass fiber-filled PBT. 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 micro-mechanical properties were reached at radiation dose of 66 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 micro-mechanical properties of surface layer of modified glass fiber-filled PBT 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.

## ACKNOWLEDGMENT

This paper is supported by the internal grant of TBU in Zlin No. IGA/FT/2013/020 funded from the resources of specific university research and by the European Regional Development Fund under the project CEBIA-Tech No. CZ.1.05/2.1.00/03.0089 and Technology Agency of the Czech Republic as a part of the project called TA03010724 AV and EV LED luminaire with a higher degree of protection.

## 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] 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.

[8] 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.

[9] 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.

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

[12] 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.

[13] 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.

[14] 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.

[15] 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.

[16] 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.

[17] 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.