Nanohardness of electron beam irradiated PMMA

P. Kratky, D. Manas, M. Manas, M. Stanek, M. Ovsik, K. Kyas, J. Navratil

***Abstract* —** The submitted paper presents the assessment of mechanical properties of the surface layer of modified polymethyl methacrylate. Modification of the surface layer was made by irradiation cross-linking on the surface, which enables modification of polymer materials and hence the change of their end-use properties. The process of mechanical stress is applied by nanohardness test. The surface layer of polymer material is modified by β – radiation. After the polymethyl methacrylate is subjected to radiation, changes of the surface layer at applied load are observed. Material properties of the created surface layer are measured by nanohardness test using the DSI method (Depth Sensing Indentation).

***Keywords* —** Crosslinking, irradiated, nano-hardness, PMMA.

I. INTRODUCTION

As polymers belong to constructive materials which find use at the most industry branches. The advantage is a low weight together with the excellent mechanical properties, very good chemical resistance and other properties, which assign them for various applications. Disadvantage is mainly low temperature stability which significantly reduces usage of these polymers.

Every properties improvement especially temperature stability helps to increase application possibilities. In addition, properties modification of standard polymers, which are relatively cheap products, gives them advantage for another usage. One of the possibilities of polymers improvement is their radiation cross-linking.

The irradiation cross-linking of thermoplastic materials via electron beam or cobalt 60 (gamma rays) is performed separately, after processing. Generally, ionizing radiation includes accelerated electrons, gamma rays and X-rays.1

Radiation processing with an electron beam offers several distinct advantages when compared with other radiation sources, particularly γ-rays and x-rays. The process is very fast, clean and can be controlled with much precision. There is no permanent radioactivity since the machine can be switched off. In contrast to γ-rays and x-rays, the electron beam can be steered relatively easily, thus allowing irradiation of a variety of physical shapes. The electron beam radiation process is practically free of waste products and therefore is no serious environmental hazard. The main difference between beta and gamma rays is in their different abilities to penetrate the irradiated material. Gamma rays have a high penetration capacity. The penetration capacity of electron rays depends on the energy of the accelerated electrons. Due to electron accelerators, the required dosage can be applied within seconds, whereas several hours are required in the gamma radiation plant. (Fig. 1). [1,2]

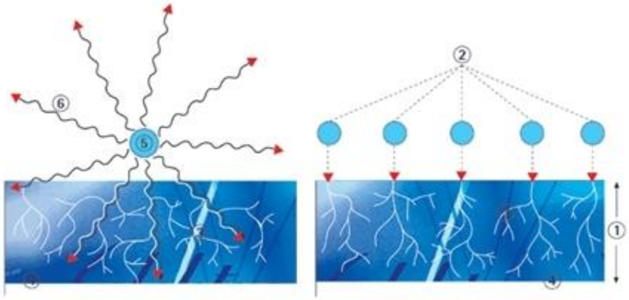

Fig. 1 Design of gamma rays (a) and electron rays (b), 1 – Penetration depth of an electron, 2 – Primary electron, 3 – Secondary electron, 4 – Irradiated material, 5 – Encapsulated Co – 60 Radiation source, 6 – Gamma rays [2]

Beta and gamma rays can be used for the irradiation of polyolefines, polyesters, halogen polymers and polyamides from the thermoplastics group, elastomers and thermoplastic elastomers. Some of them need the addition of a cross-linking agent. [1,6,7,8]

Radiation cross-linking usually improves strength, reduces creep, contributes to chemical resistance improvement and in many cases improves tribological properties. Effect of radiation cross-linking significantly improves temperature stability. Because of that, materials which belong to group of standard polymers can be used in applications, which would be in term of temperature stability intended only to constructive thermoplastic polymers.

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II. EXPERIMENTAL

For this experiment polymethyl methacrylate (PMMA) PTS - ACRYLEX CM - 207; PTS Plastics Technologie Service, Germany was used. The material already contained a special cross-linking agent TAIC - triallylisocyanurate (5 volume %), which should enable subsequent cross-linking by ionizing β – radiation. The prepared specimens were irradiated with doses of 15, 30 and 45 kGy at BGS Beta-Gamma Service GmbH & Co. KG, Germany [1-4].

The samples were made using the injection molding technology on the injection moulding machine ArburgAllrounder 420C. Processing temperature 200–240 °C, mold temperature 60 °C, injection pressure 80 MPa, injection rate 45 mm/s.

Instrumented nanohardness tests were done using a Nanoindentation Tester (NHT2) – Opx/Cpx, CSM Instruments (Switzerland) according to the CSN EN ISO 6507-1. Load and unload speed was 100 mN/min. After a holding time of 90 s at maximum load 50 mN the specimens were unloaded. The indentation hardness HIT was calculated as maximum load to the projected area of the hardness impression according to:

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

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.

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

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

The deduced modulus is calculated from the following equation:

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

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

$$E^* = \frac{1}{\frac{1}{E_r} - \frac{1 - v_i^2}{E_i}} \qquad (4)$$

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. [8] [12] [41].

Determination of indentation creep C_{IT}:

$$C_{IT} = \frac{h_2 - h_1}{h_1} \cdot 100 \qquad (5)$$

Where h_1 is representing 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. 2) [1] [7] [15].

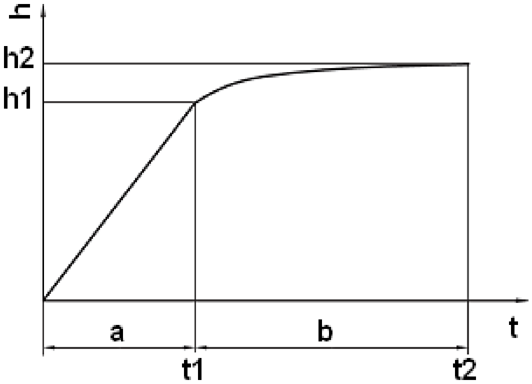

Fig. 2 Illustration of indentation creep parameters

Elastic part of the indentation work η_{IT} (Fig. 3):

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

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

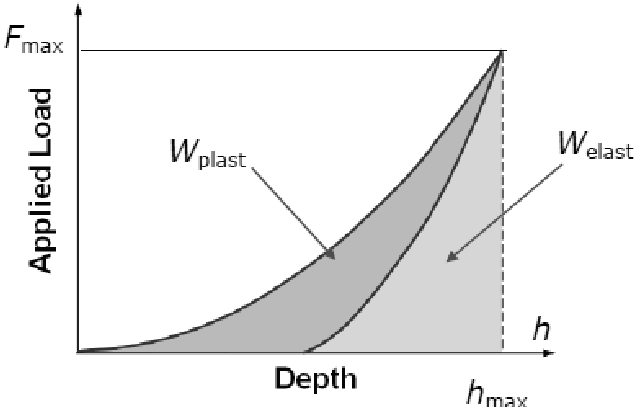

Fig. 3 Illustration of coefficient of back deformation

III. RESULTS AND DISCUSSION

For Instrumented nanohardness teset was used three different loads

A. *Indentation load 10 mN*

The values measured during the nanohardness test showed that the lowest values of indentation hardness were found for PMMA irradiated with dose of 45 kGy. On the contrary, the highest values of indentation hardness were obtained for the non-irradiated PMMA (by 12% higher in comparison with PMMA irradiated with dose of 45 kGy), as can be seen at Fig. 4.

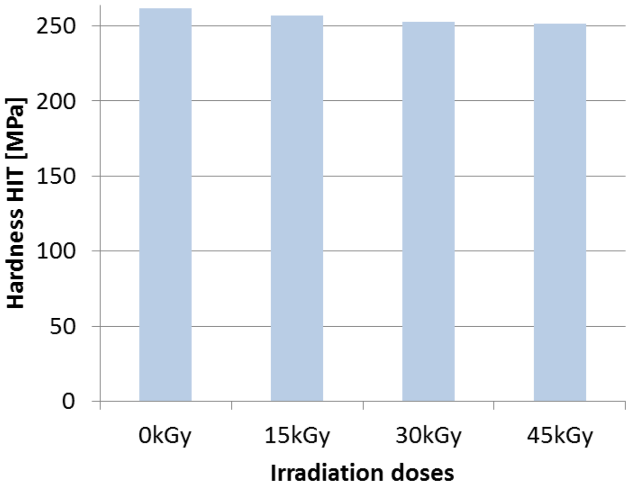

Fig. 4 Hardness HIT of PMMA vs. irradiation doses

Higher radiation dose does not influence significantly the nanohardness value. An indentation hardness increase of the surface layer is caused by irradiation cross-linking of the tested specimen, but total hardness decreasing due to degradation of basic material.

According to the results of measurements of nanohardness, it was found that the highest values of indentation modulus of elasticity were achieved at the non-irradiated PMMA (by 3% higher than compared with PMMA irradiated with dose of 45 kGy). On the contrary, the lowest values of the indentation modulus of elasticity were found for PMMA irradiated with dose of 45 kGy as is seen at Fig. 5.

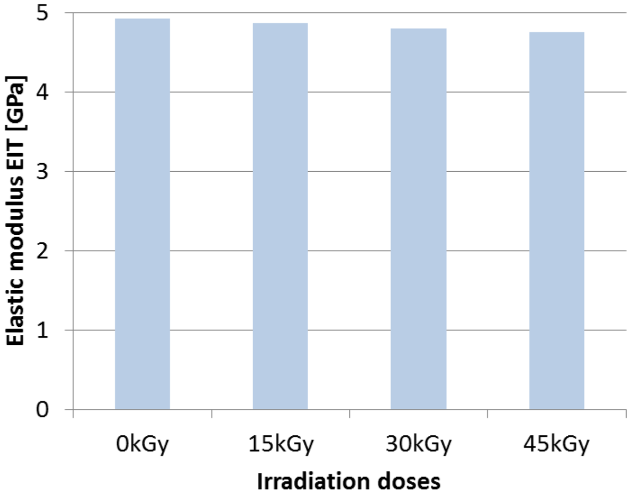

Fig. 5 Elastic modulus EIT of PMMA vs. irradiation doses

The lowest values of hardness Vickers were found for PMMA irradiated with dose of 45 kGy. On the contrary, the highest values of hardness Vickers were obtained for non-irradiated PMMA (by 3% higher in comparison with PMMA irradiated with dose of 45 kGy), as can be seen at Fig. 6.

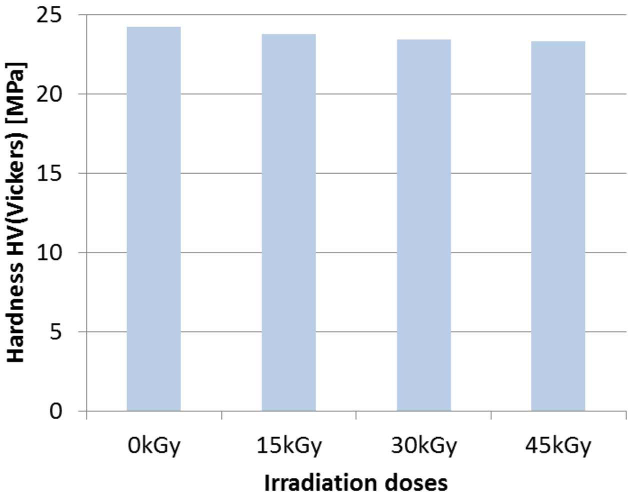

Fig. 6 Hardness Vickers of PMMA vs. irradiation doses

Other important material parameters obtained during the nanohardness 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. 5).

The greatest values of plastic and elastic deformation work were obtained for PMMA irradiated with dose of 30 kGy. The lowest values of plastic and elastic deformation work were obtained for the non-irradiated PMMA. Radiation of specimens caused higher values of elastic as well as plastic deformation work which is apparent in Fig. 7.

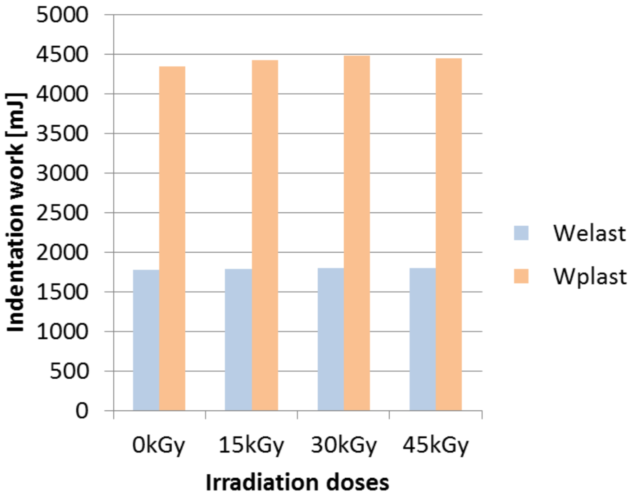

Fig. 7 Elastic and plastic deformation work of PMMA vs. irradiation doses

The greatest values of indentation creep were obtained for PMMA irradiated with dose of 30 kGy. The lowest values of indentation creep were obtained for non-irradiated PMMA.

Radiation of specimens caused increase of indentation creep and subsequent decrease of indentation creep which is apparent in Fig. 8.

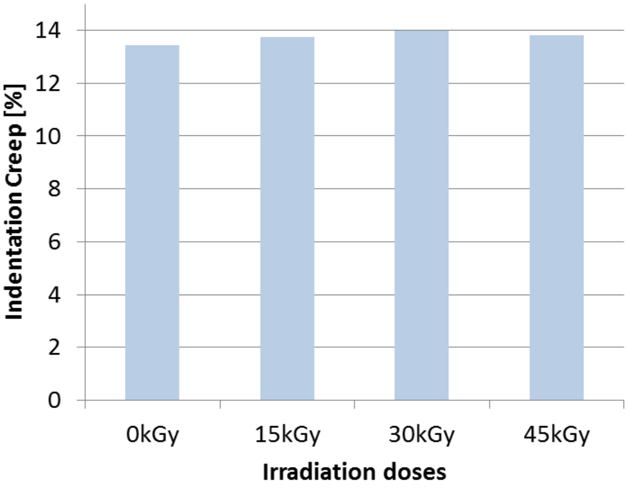

Fig. 8 Indentation Creep of PMMA vs. irradiation doses

The lowest values of back deformation coefficient n_{IT} were found for the PMMA irradiated with dose of 30 kGy. On the contrary, the highest values of back deformation coefficient n_{IT} were obtained for non-irradiated PMMA (by 12% higher in comparison with the PMMA irradiated with dose of 30 kGy), as can be seen at Fig. 9.

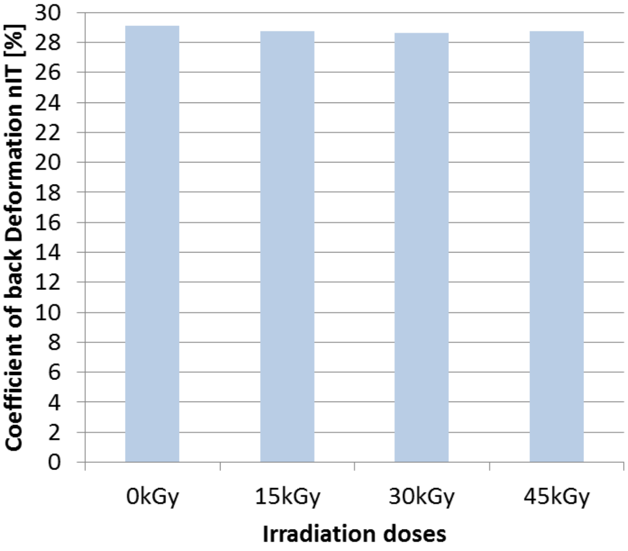

Fig. 9 Coefficient of back deformation n_{IT} vs. irradiation doses

B. Indentation load 50 mN

The values measured during the nanohardness test showed that the lowest values of indentation hardness were found for the PMMA irradiated by a dose of 45 kGy. On the contrary, the highest values of indentation hardness were obtained for PMMA irradiated by a dose of 15 kGy (by 6% higher in comparison with PMMA irradiated by a dose of 45 kGy), as can be seen at Fig. 10.

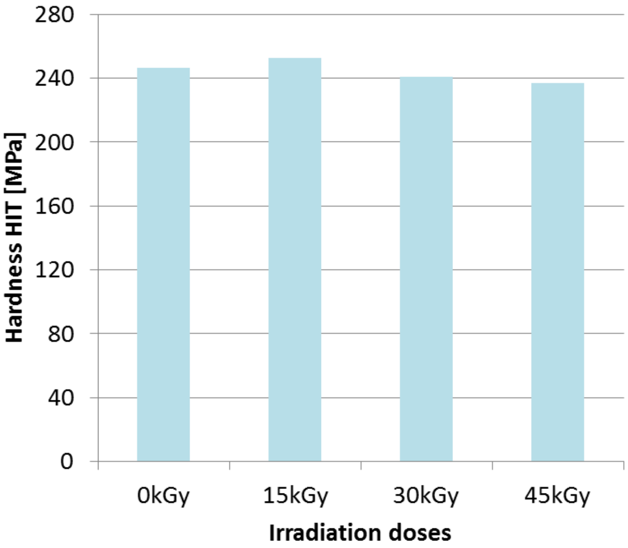

Fig. 10 Hardness HIT of PMMA vs. irradiation doses

Higher radiation dose does not influence significantly the nanohardness value. An indentation hardness increase of the surface layer is caused by irradiation cross-linking of the tested specimen, but total hardness decreasing due to degradation of basic material.

According to the results of measurements of nanohardness, it was found that the highest values of indentation modulus of elasticity were achieved at the non-irradiated PMMA (by 2% higher than compared with PMMA irradiated with dose of 45 kGy). On the contrary, the lowest values of the indentation modulus of elasticity were found for PMMA irradiated with dose of 45 kGy as is seen at Fig11.

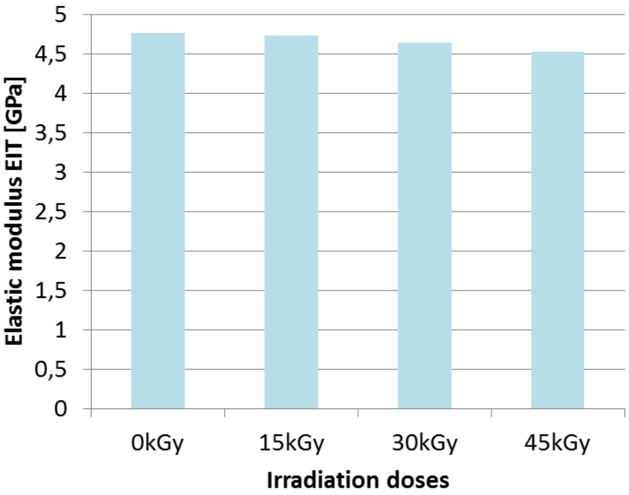

Fig. 11 Elastic modulus EIT of PMMA vs. irradiation doses

The lowest values of hardness Vickers were found for PMMA irradiated with dose of 45 kGy. On the contrary, the highest values of hardness Vickers were obtained for PMMA irradiated with dose of 15 kGy (by 3% higher in comparison with PMMA irradiated with dose of 45 kGy), as can be seen at Fig. 12.

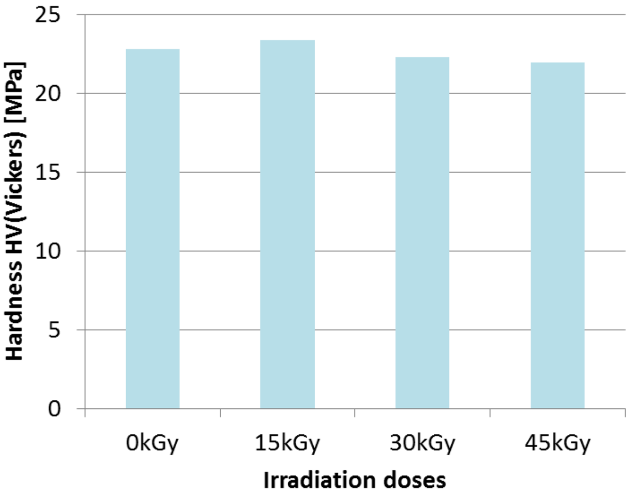

Fig. 12 Hardness Vickers of PMMA vs. irradiation doses

The greatest values of plastic and elastic deformation work were obtained for PMMA irradiated with dose of 45 kGy. The lowest values of elastic deformation work were obtained for non-irradiated PMMA. The lowest values of plastic deformation work were obtained for PMMA irradiated with dose of 15 kGy. The lowest values of plastic and elastic deformation work were obtained for the non-irradiated PMMA. Radiation of specimens caused higher values of elastic as well as plastic deformation work which is apparent in Fig. 13.

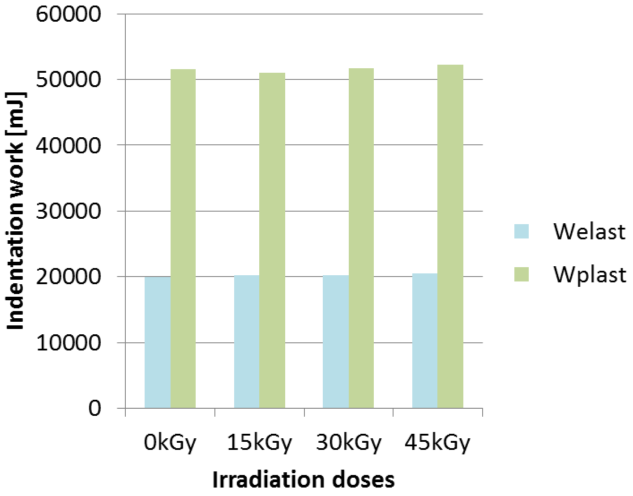

Fig. 13 Elastic and plastic deformation work of PMMA vs. irradiation doses

The greatest values of indentation creep were obtained for PMMA irradiated with dose of 15 kGy. The lowest values of indentation creep were obtained for PMMA irradiated with dose of 30 kGy.

Radiation of specimens caused increase of indentation creep and subsequent decrease of indentation creep which is apparent in Fig. 14.

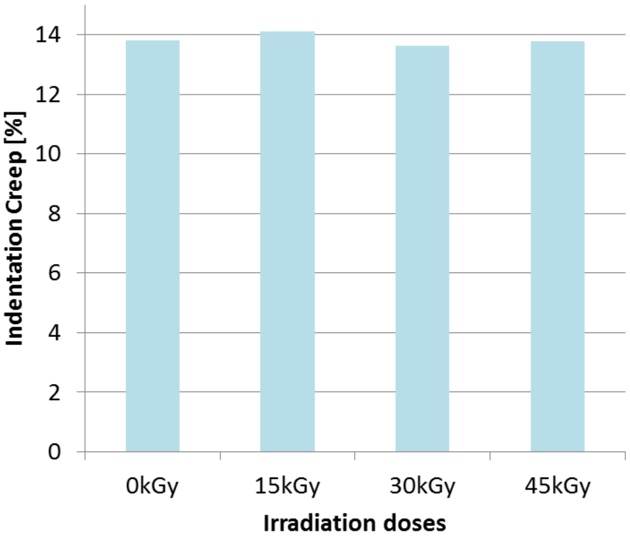

Fig. 14 Indentation Creep of PMMA vs. irradiation doses

The lowest values of back deformation coefficient n_{IT} were found for non-irradiated PMMA. On the contrary, the highest values of back deformation coefficient n_{IT} were obtained for PMMA irradiated by a dose of 15 kGy (by 2% higher in comparison with the non-irradiated PMMA), as can be seen at Fig. 15.

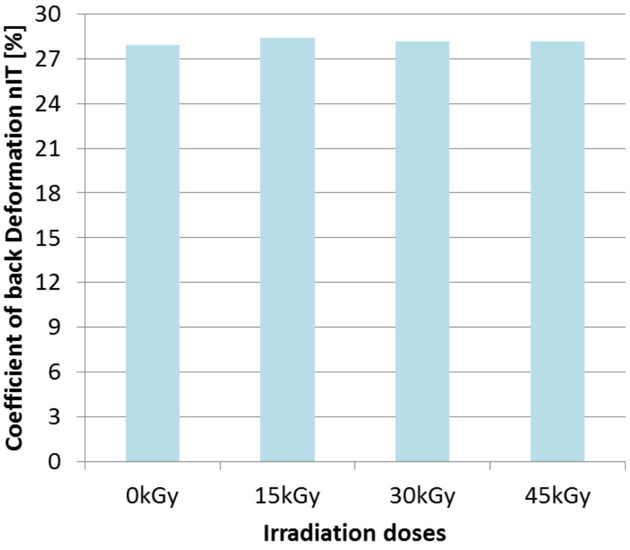

Fig. 15 Coefficient of back deformation n_{IT} vs. irradiation doses

C. *Indentation load 250 mN*

The values measured during the nanohardness test showed that the lowest values of indentation hardness were found for the PMMA irradiated by a dose of 45 kGy. On the contrary, the highest values of indentation hardness were obtained for PMMA irradiated by a dose of 15 kGy (by 17% higher in comparison with PMMA irradiated by a dose of 45 kGy), as can be seen at Fig.16.

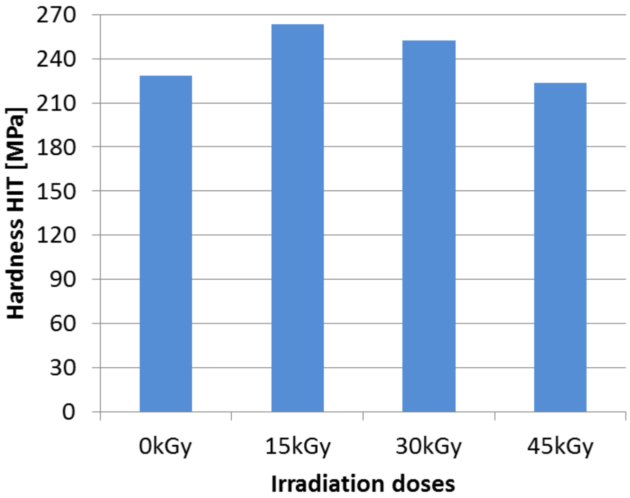

Fig. 16 Hardness HIT of PMMA vs. irradiation doses

Higher radiation dose does not influence significantly the nanohardness value. An indentation hardness increase of the surface layer is caused by irradiation cross-linking of the tested specimen, but total hardness decreasing due to degradation of basic material.

According to the results of measurements of nanohardness, it was found that the highest values of indentation modulus of elasticity were achieved at PMMA irradiated with dose of 15 kGy (by 10% higher than compared with PMMA irradiated with dose of 45 kGy). On the contrary, the lowest values of the indentation modulus of elasticity were found for PMMA irradiated with dose of 45 kGy as is seen at Fig 17.

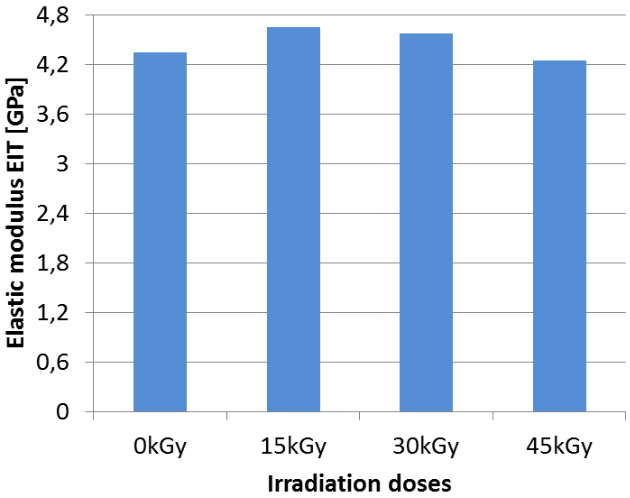

Fig. 17 Elastic modulus EIT of PMMA vs. irradiation doses

The lowest values of hardness Vickers were found for PMMA irradiated with dose of 45 kGy. On the contrary, the highest values of hardness Vickers were obtained for PMMA irradiated with dose of 15 kGy (by 17% higher in comparison with PMMA irradiated with dose of 45 kGy), as can be seen at Fig. 18.

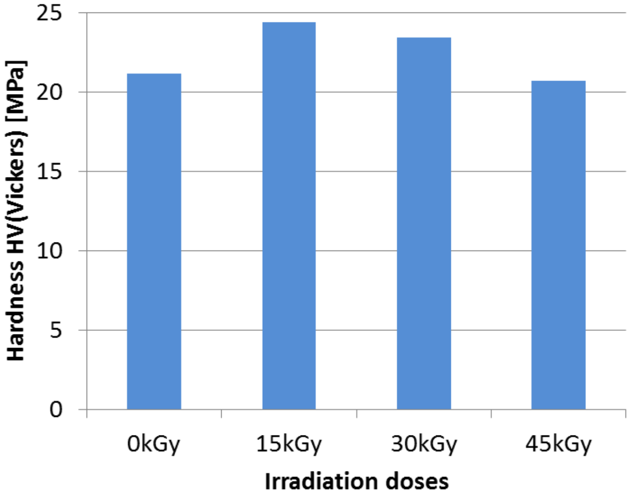

Fig. 18 Hardness Vickers of PMMA vs. irradiation doses

The greatest values of elastic deformation work were obtained for PMMA irradiated with dose of 45 kGy. The greatest values of plastic deformation work were obtained for non-irradiated PMMA. The lowest values of elastic deformation work were obtained for PMMA irradiated with dose of 30 kGy. The lowest values of plastic deformation work were obtained for PMMA irradiated with dose of 15 kGy. Radiation of specimens caused lower values of plastic a higher values of elastic deformation work which is apparent in Fig. 19.

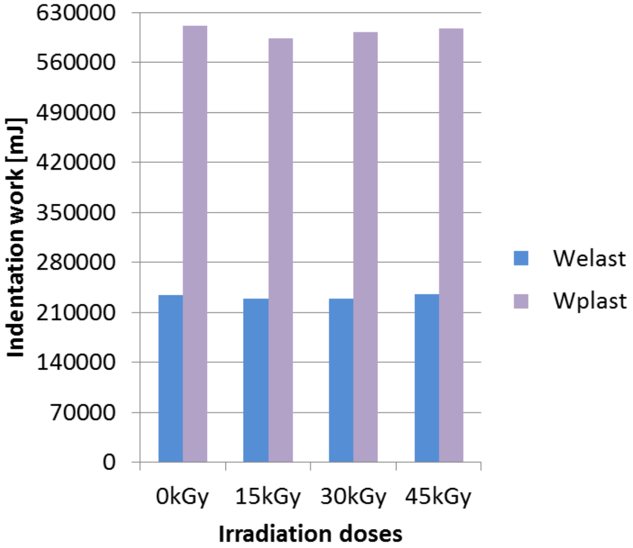

Fig. 19 Elastic and plastic deformation work of PMMA vs. irradiation doses

The greatest values of indentation creep were obtained for PMMA irradiated with dose of 30 kGy. The lowest values of indentation creep were obtained for PMMA irradiated with dose of 30 kGy.

Radiation of specimens caused increase of indentation creep and subsequent decrease of indentation creep which is apparent in Fig. 20.

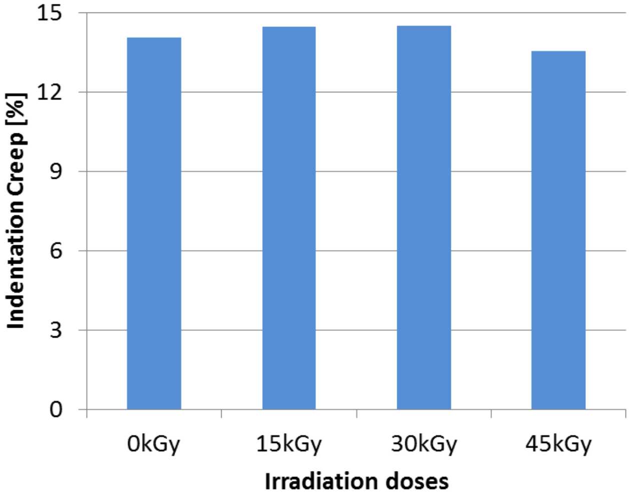

Fig. 20 Indentation Creep of PMMA vs. irradiation doses

The lowest values of back deformation coefficient n_{IT} were found for the PMMA irradiated with dose of 30 kGy. On the contrary, the highest values of back deformation coefficient n_{IT} were obtained for PMMA irradiated by a dose of 45 kGy (by 2% higher in comparison with the PMMA irradiated with dose of 30 kGy), as can be seen at Fig. 21.

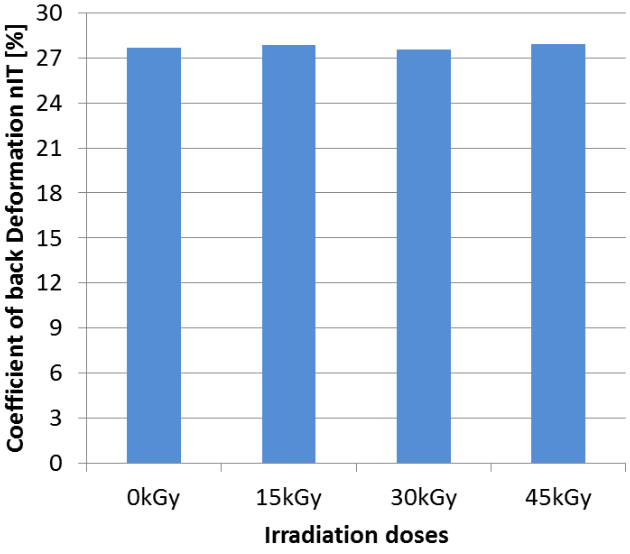

Fig. 21 Coefficient of back deformation n_{IT} vs. irradiation doses

IV. CONCLUSION

For measurement with load of 10mN we obtained lowest indentation depth for non-irradiated PMMA. The greatest values were obtained for PMMA irradiated with dose of 15 kGy, as can be seen at Fig. 22.

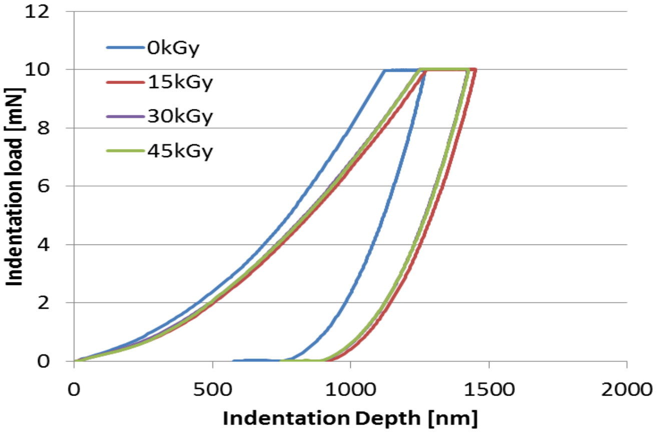

Fig. 22 Indentation load vs. Indentation depth

For measurement with load of 50mN we obtained lowest indentation depth for PMMA irradiated with dose of 30 kGy. The greatest values were obtained for non-irradiated PMMA, as can be seen at Fig. 23.

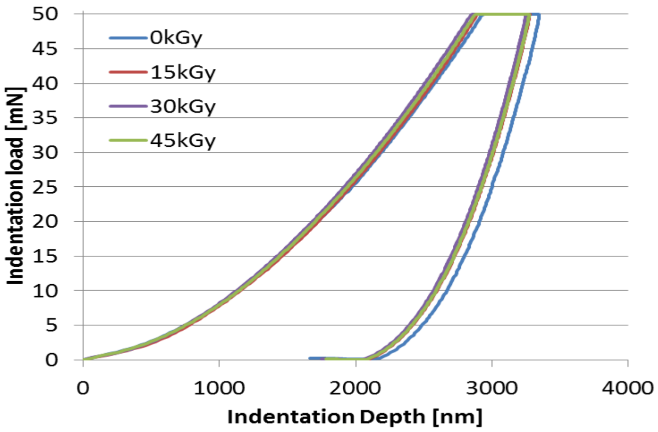

Fig. 23 Indentation load vs. Indentation depth

For measurement with load of 250mN we obtained lowest indentation depth for non-irradiated PMMA. The greatest values were obtained for PMMA irradiated with dose of 45 kGy, as can be seen at Fig. 24.

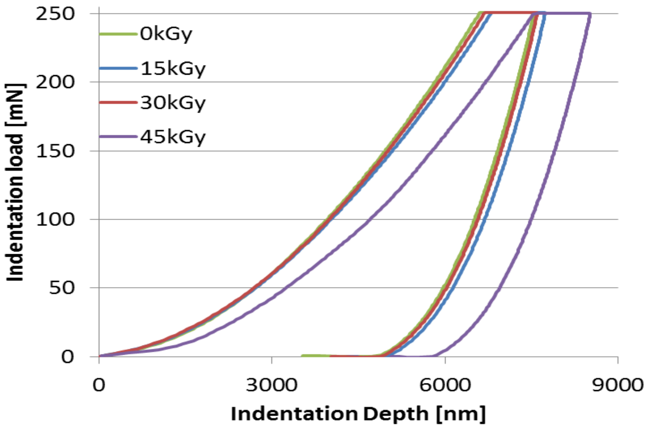

Fig. 24 Indentation load vs. Indentation depth

The properties of surface layer of Polymethyl methacrylate modified by beta radiation improved significantly. The nanohardness values increased about 10% at higher load as 10mN. Stiffness of surface layer increased significantly by 6% as a result of radiation. Changes of behavior in the surface layer were confirmed by final values of plastic deformation work whose values decreased in correlation with the increasing radiation dose. Elastic deformation was increasing with radiation dose. The highest values of micromechanical properties were reached at radiation dose of 15 kGy. The results of nanomechanical properties of surface layer of modified polymethyl methacrylate 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. The resistance of surface layer to wear makes its use suitable for the production of gears, friction parts of machinery and as alternative to some metal materials. Thanks to its low weight polyamide 11 modified by beta radiation is a suitable alternative to commonly used materials in the car and electrical industry.

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