Microhardness of polyamide 12 after crosslinking due to beta radiation

H. Vaskova, D. Manas, M. Ovsik, M. Manas and M. Stanek

Abstract**—**The paper presents an experimental study of the effect of beta radiation on properties of surface layer of polyamide 12. Irradiation of polymers initiates crosslinking process in the structure especially in micro-layers. Radiation doses of 0, 33, 66, 99, 132, 165 and 198 kGy were used for unfilled polyamide 12 with the 5% cross-linking agent (triallyl isocyanurate). Applied radiation doses caused different structural and micromechanical changes which have a significant effect on the final properties of the tested polyamide 12. Beta irradiation of the examined thermoplastic caused the growth of values of material parameters as microhardness or indentation modulus of elasticity, indentation creep etc. The improvement of micromechanical properties was measured by the instrumented microhardness test. Raman spectroscopy analysis as an innovative analytical method was carried out on the irradiated samples. As a spectroscopic vibrational method it has the potential to provide quite detailed information on the structure, what is useful for monitoring structural changes of materials. The correlation between results of both methods has been detected and studied.

Keywords**—**Beta radiation, crosslinking, microhardness, polyamide 12, Raman spectroscopy.

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 semi-crystalline to 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.

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

Fig. 1 Chemical formula of polyamide 12

The thermoplastics which are used for production of various types of products have very different properties. The main group presents standard polymers which are easy obtainable under favorable price conditions. The disadvantage of standard polymers is limited both by mechanical and thermal properties. The group of standard polymers is the most considerable one and its share in the production of all polymers is as high as 90%.

The engineering polymers form a very important group of polymers which offer much better properties in comparison with 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 10 % of all polymers.

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

One of the ways how to improve properties of polymer materials is a process of crosslinking for forming macromolecular spatial network within the structure. The process of networking can be running in many ways. Very progressive method is radiation crosslinking. Significant changes of HDPE mechanical and thermo-mechanical properties after irradiation are presented in [1]. Authors of [2] deal with the impact of a chemical agents on mechanical properties of radiation cross-linked polymers.

Radiation processing mainly involves the use of either electron beams from electron accelerators or gamma radiation from cobalt-60 sources. The radiation cross-linking of thermoplastic materials via electron beam or cobalt 60 (gamma rays) 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 [3, 4].

The main differences between beta and gamma rays are shown in Table 1. These differences lie in their different abilities of penetrating the irradiated material. Gamma rays

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H. Vaskova is with the Tomas Bata University in Zlin, Faculty of Applied Informatics, nam. T.G.Masaryka 5555, 760 01 Zlín, Czech (phone: +420 576 035 228; e-mail: vaskova@fai.utb.cz

D. Manas is with the Tomas Bata University in Zlin, Faculty of Technology, nam. T.G.Masaryka 5555, 760 01 Zlín, Czech (phone: +420 576 035 172; e-mail: dmanas@ft.utb.cz)

M. Ovsik, M. Manas and M. Stanek are with the Tomas Bata University in Zlin, Faculty of Technology, nam. T.G.Masaryka 5555, 760 01 Zlín, Czech (e-mail: ovsik@ft.utb.cz, manas@ft.utb.cz, stanek@ft.utb.cz).

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 dose can be applied within seconds, whereas several hours are required in the gamma radiation plant.

Table 1 The main differences between beta and gamma rays

MAIN DIFFERENCES	**Gamma rays**	**β electron accelerators**
Penetration ability	high	depends on the energy of the accelerated electrons
Time of required dose	several hours	seconds

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. Simultaneously, high voltage is generated in a pressure vessel filled with insulating gas. 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. A simplified scheme is shown in Fig. 2.

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 permits the application of different radiation doses from one product type to another. The dimensional stability, strength, chemical resistance and wear of polymers normally creates higher strength as well as reduced creep under load if the applied temperature is above the glass can be improved by irradiation. Irradiation cross-linking 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. Diagrams of gamma and beta irradiation are shown in Fig. 3.

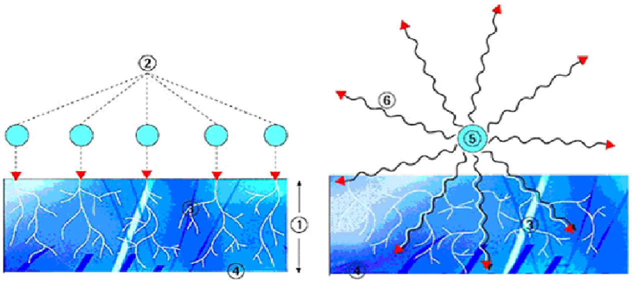

Fig. 3 Left: electron rays, 1 – penetration depth of electron, 2 – primary electron, 3 – secondary electron, 4 – irradiated material. Right: Gamma rays, 3 – secondary electrons, 4 – irradiated material, 5 – encapsulated Co – 60 radiation source, 6 – Gamma rays.

Vibrational methods are known for precise assessments of polymers already years. Infrared spectroscopy is in polymer and material science used for more than 25 years, Raman spectroscopy much less time. Although the basic principle, an inelastic light scattering on matter, was discovered at the beginning of the 20th century, the rebirth of this method is coming even in about last decade thanks to technical advancements. The use of the method includes in the area of polymers mostly research-oriented applications, but recently also routine analyses. Raman spectra can serve for identification of the material [7], the impurities, for processes monitoring or product quality control [8], e.g. in the paper [9] the capability of the access to the control of quasi real time in-

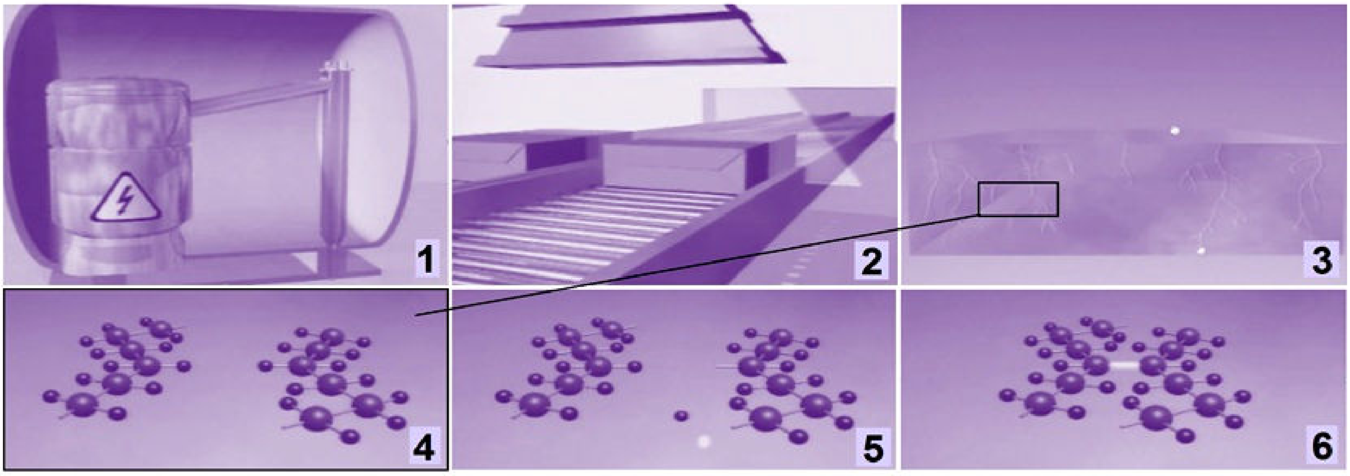

Fig. 2 Process of beta radiation. 1- the electron accelerator, 2 – palleted products are irradiated by a stream of fast moving (beta)electrons, 3, 4 – a structure of material is disrupted, 5 – hydrogen atoms are removed from their positions along chains leaving highly reactive site of free radicals, 6 – created crosslink between two chains.

situ studies of crosslinking reaction of epoxy resin is presented. Raman spectroscopy has been already used for studying material properties of polymers [10, 11]. To our best knowledge no reports on the use of Raman microscopy studying the irradiated PA12 microhardness are available.

Common PA12, when exposed to the effect of the radiation cross-linking, degrades and its mechanical properties deteriorate. With the cross-linking agent TAIC (triallyl isocyanurate) the cross-linking reaction occur in the structure of PA12. The utility properties of PA12 improve when the non-crystalline part of PA12 is cross-linked [5, 6].

This paper discusses the influence of radiation doses on the microhardness of beta-irradiated cross linked polyamide 12. Authors also propose Raman spectroscopy as a potential technique for studying structural changes in PA12 via irradiation.

II. EXPERIMENTAL

A. Materials

For this experiment polyamide 12 V-PTS-Creamid-12-AMN 0 TLD Plastics Technology Service, Germany (unfilled, PA12+TAIC) was used. The material already contained the special cross-linking agent TAIC - triallyl isocyanurate (5% of volume), which should enable subsequent cross-linking by ionizing β – radiation. The prepared specimens were irradiated with doses of 33, 66, 99, 132,165 and 199 kGy at BGS Beta-Gamma Service GmbH & Co. KG, Germany [6, 12, 13].

B. Microhardness experiments

The samples were made using the injection molding technology on the injection molding machine Arburg Allrounder 420C. Processing temperature 210–250 °C, mold temperature 60 °C, injection pressure 80 MPa, injection rate 50 mm/s.

Instrumented microhardness tests were done using a Micro Combi Tester, CSM Instruments (Switzerland) according to the CSN EN ISO 6507-1. Load and unload speed was 1 N/min. After a holding time of 90 s at maximum load 0,5 N the specimens were unloaded. The indentation hardness H_{IT} was calculated as maximum load to the projected area of the hardness impression according to:

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

$$h_c = h_{\max} - \varepsilon \frac{F_{\max}}{S} \tag{2}$$

h_{max} is the indentation depth at force F_{max}, h_c is contact depth. In this study the Oliver and Pharr method was used to calculate the initial stiffness S and contact depth h_c. The specimens were glued on metallic sample holders [12, 13].

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

$$E_{IT} = \overline{E} \cdot (1 - v_s^{\,2}) \tag{3}$$

The Plane Strain Modulus $\overline{E}$ is calculated from following equation:

$$\overline{E} = \frac{1}{\frac{1}{E_r} - \frac{1 - v_i^{\,2}}{E_i}}, \tag{4}$$

Where

$$E_r = \frac{\sqrt{\pi S}}{2\beta\sqrt{A_p h_c}}. \tag{5}$$

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

Determination of indentation hardness C_{IT} is:

$$C_{IT} = \frac{h_2 - h_1}{h_1} \cdot 100 \tag{6}$$

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.

The elastic deformation work W_e determines the reaction of a 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. 4).

Elastic part of the indentation work η_{IT}:

$$\eta_{IT} = \frac{W_{elast}}{W_{total}} \cdot 100 \tag{7}$$

$$W_{total} = W_{elast} + W_{plast} \tag{8}$$

Plastic part W_{plast} / W_{total} follows as

$$100\% - \eta_{IT} \tag{9}$$

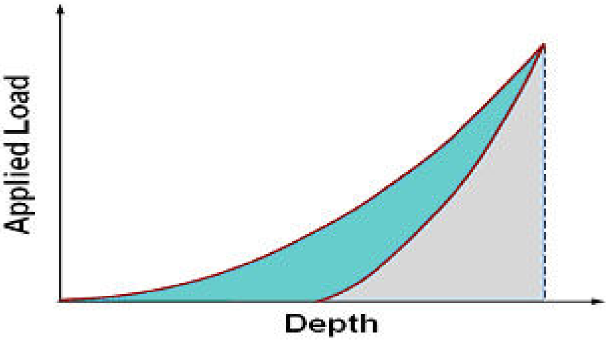

Fig. 4 Indentation work η_{IT}

C. Raman spectroscopy

Raman spectroscopy as an innovative analytical method has, in principle, the potential to answer many questions concerning chemical details of molecular structure. This feature makes Raman spectroscopy definitely proper for material identification. The key for the identification is a unique "fingerprint" Raman spectrum for every individual chemical element and its modification.

Raman spectroscopy brings over other techniques advantages as non-destructiveness, no special requirements for sample preparation, rapidity or contactless measurements what makes this analytical tool convenient, attractive and participating on the growth of its popularity worldwide.

InVia Basis Raman microscope from Renishaw was used for recording Raman spectra of irradiated samples. Argon ion laser with the excitation wavelength 514nm and maximum output power of 20 mW and 785 nm NIR diode laser with maximum output power 300 mW were used as light sources. A Leica DM 2500 confocal microscope with the resolution up to 2μm was coupled to the Raman spectrometer. All measurements were collected at 50x magnification, with 10s exposure time and 5 accumulations. Measurements from different spots of the same sample gave corresponding results. The samples were scanned in range 100 to 3200 cm^{-1} with 2 cm^{-1} spectral resolution.

The instruments used –Micro Combi Tester and Raman microscope are displayed in Fig. 5.

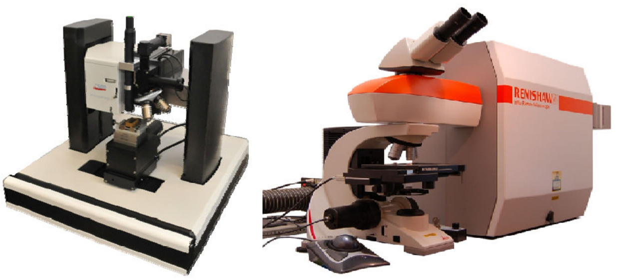

Fig. 5 Instruments used for instrumented microhardness tests (left) and acquiring Raman spectra (right).

III. RESULTS

A. Microhardness tests

During the microhardness test these material parameters were obtained:

- microhardness
- elastic modulus
- hardness Vickers
- indentation creep
- elastic/plastic deformation work

The results of the specific dependences are illustrated in Fig. 6 - 10. Firstly the microhardness test was performed at the maximum load 0,5 N. Secondly two other values of maximum load 1N and 5N were applied. Results from the three sets of measurement are displayed in Fig. 11 -16.

The values measured during the microhardness test showed that the lowest values of indentation hardness were found for the non-irradiated PA12. On the contrary, the highest values of indentation hardness were obtained for PA12 irradiated by a dose of 132 kGy (by 74% higher in comparison with the non-irradiated PA12), as can be seen in **Fig.6**.

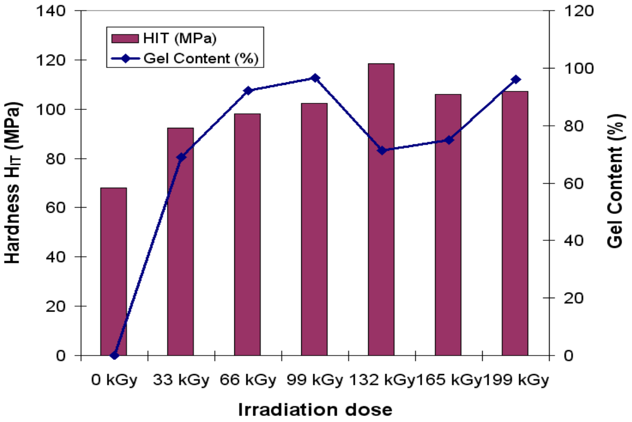

Fig. 6 Microhardness of PA12 versus β - radiation doses

According to results of measurements of microhardness, it was found that the highest values of indentation modulus of elasticity were achieved at the PA12 irradiated with dose of 132 kGy (by 67% 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 in Fig. 7.

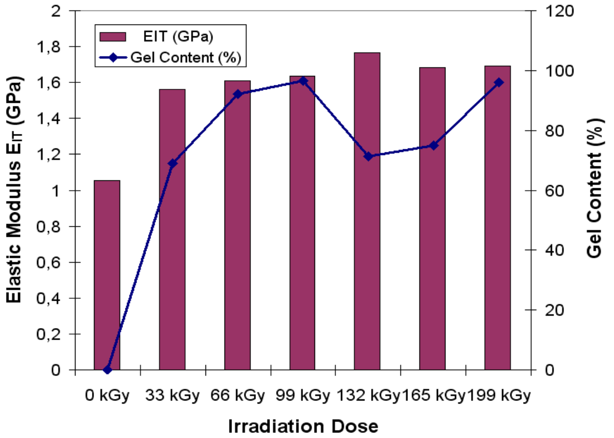

Fig. 7 Elastic modulus of PA12 versus β - radiation doses

The lowest values of hardness Vickers were found for the non-irradiated PA12. On the contrary, the highest values of hardness Vickers were obtained for PA12 irradiated by a dose of 132 kGy (by 74 % higher in comparison with the non-irradiated PA2), as can be seen at Fig. 8.

According to the results of measurements of microhardness, it was found that the lowest values of indentation creep were achieved at the PA12 irradiated with dose of 199 kGy (by 36% 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 at Fig. 9.

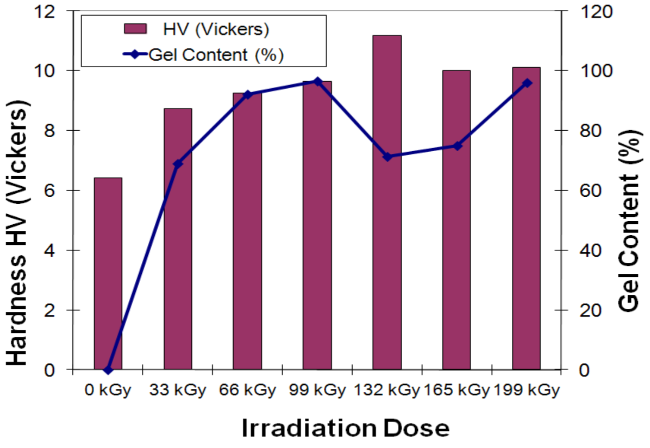

Fig. 8 Hardness Vickers of PA12 versus β - radiation doses

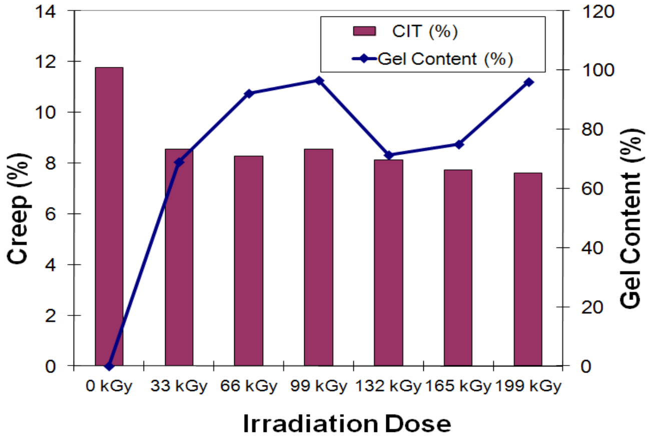

Fig. 9 Indentation creep of PA12 versus β - radiation doses

Other important material parameters obtained during the microhardness test were elastic and plastic deformation work.

The highest 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 a dose of 199 kGy. Radiation of specimens caused lower values of elastic as well as plastic deformation work which is apparent in Fig. 10.

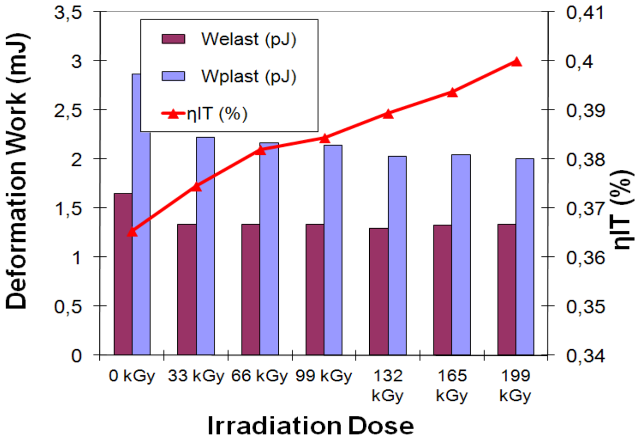

Fig. 10 Deformation work of PA versus β - radiation doses

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 PA12. The highest values were measured at irradiation doses of 199 kGy. The smallest values were found at non-irradiated PA12.

B. Microhardness tests – different loads

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 polyamide 12 modified by beta radiation. The measurement results show that the highest value of microhardness at all loads applied was found when the radiation dose was 132 kGy, see Fig. 11. When higher radiation doses were applied, microhardness values declined, 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 semi-crystalline structure of tested polyamide 12. The increase in microhardness of the surface layer at the dose of 132 kGy compared to the non-irradiated specimen was found to be around 57%.

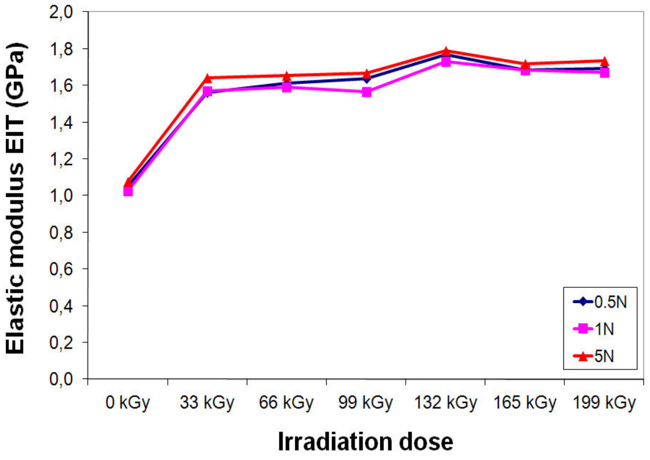

Fig. 11 Elastic modulus of PA12 versus β - radiation doses for three different values of load.

When observing the changes of stiffness (Fig 12) of the surface layer measured by microhardness test it was proved that the maximum value of stiffness was found at radiation dose of 132 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. Values of microhardness decreased at 1N load. In general it can be said that stiffness of the surface layer increased by 59% in the tested specimen (132 kGy) compared to the non-irradiated specimen.

Very important values were found for indentation creep at all applied loads as displayed in Fig. 13. With higher radiation doses the values of indentation creep dropped. The lowest value of creep was measured at radiation dose of 198 kGy. The highest creep value was found for non-irradiated polyamide 12. The creep values reached similar values at all applied loads. Decrease in creep values was 35% for irradiated polyamide 12 compared to the non-irradiated one.

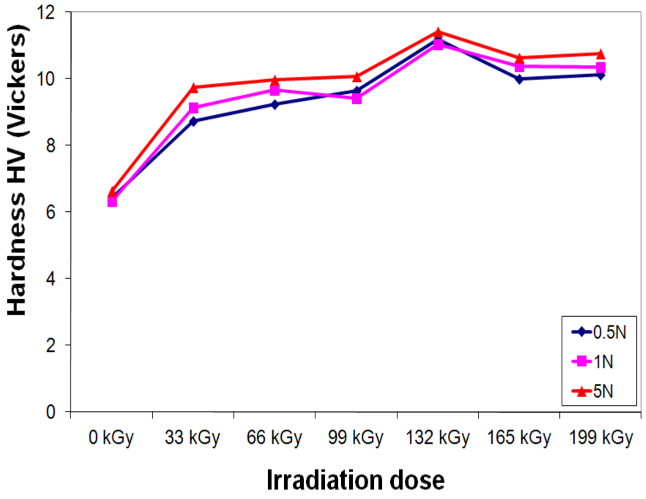

Fig. 12 Hardness Vickers of PA12 versus β - radiation doses for three different values of load.

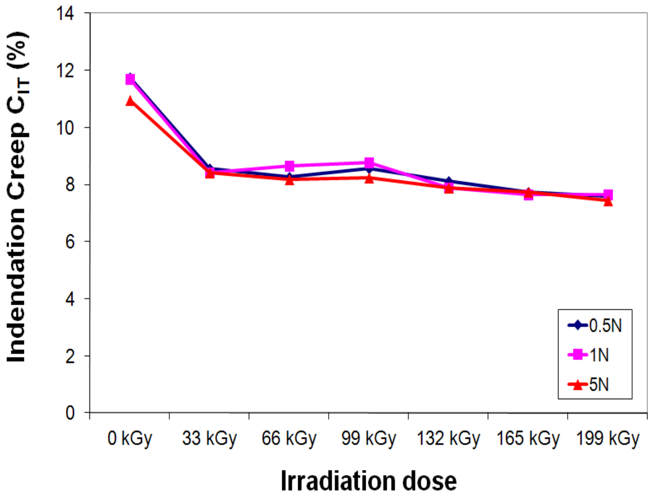

Fig. 13 Indentation Creep of PA12 versus β - radiation doses for three different values of load.

The results of elastic and deformation work, Fig. 14 and Fig 15 show 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 polyamide 12. 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 as is shown in Fig. 16.

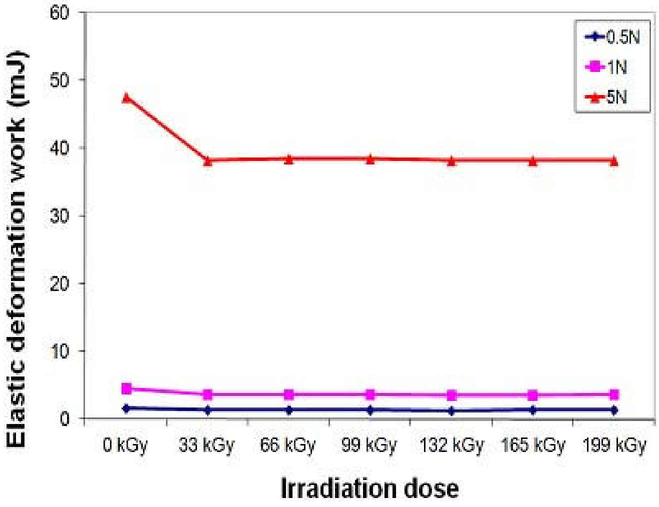

Fig. 14 Elastic deformation work of PA12 versus β - radiation doses for three different values of load.

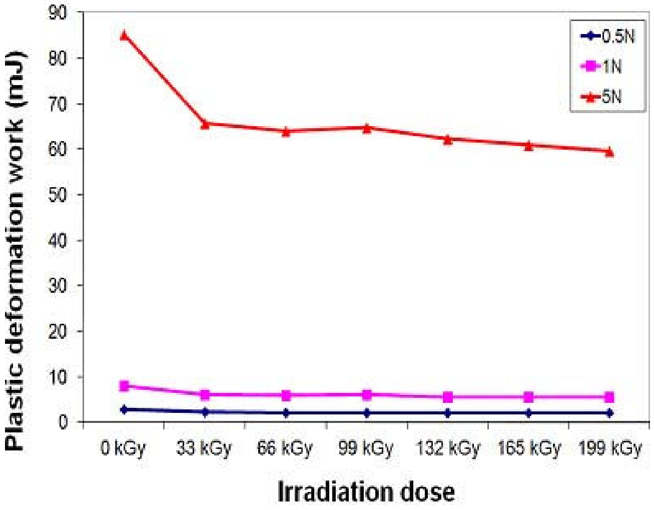

Fig. 15 Plastic deformation work of PA12 versus β - radiation doses for three different values of load

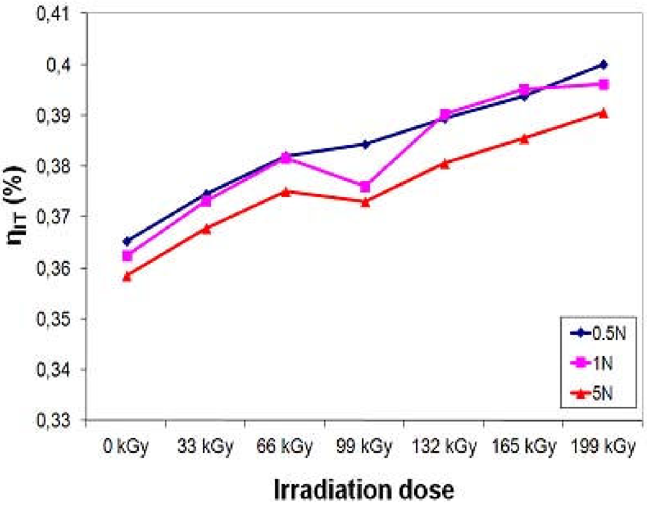

Fig. 16 Elastic part deformation work of PA12 versus β - radiation doses for three different values of load

The surfaces of non-irradiated PA12 and beta-irradiated sample with the dose of 132 kGy obtained by Leica microscope with the 20x objective are displayed in Fig. 17.

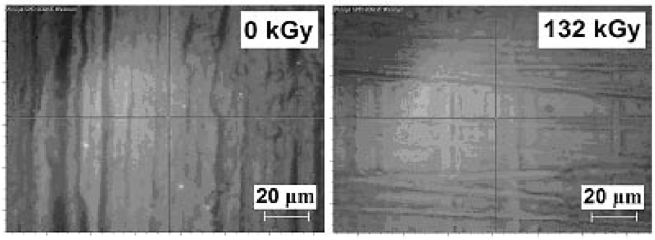

Fig. 17 Surface of non-irradiated and beta-irradiated (132kGy) PA12

C. Raman spectra of PA12

Raman spectra of PA12 were recorded using laser with 514nm excitation wavelength, but as Fig. 18 shows, there appeared fluorescence covering spectra of irradiated samples.

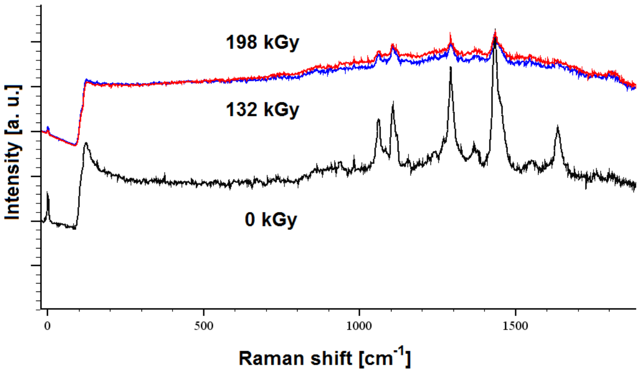

Fig. 18 Raman spectra of β-irradiated PA12 in the low frequency region using the 514 nm Ar^+ laser

To reduce fluorescence 785nm line of diode laser was used. Obtained spectra with labeled peaks are displayed in Fig. 19. Individual measured values of significant Raman shifts are listed in Table 2**.** Peaks were identified and the Raman vibrational modes for the peaks are assigned. Results are in accordance with previous articles [10, 11].

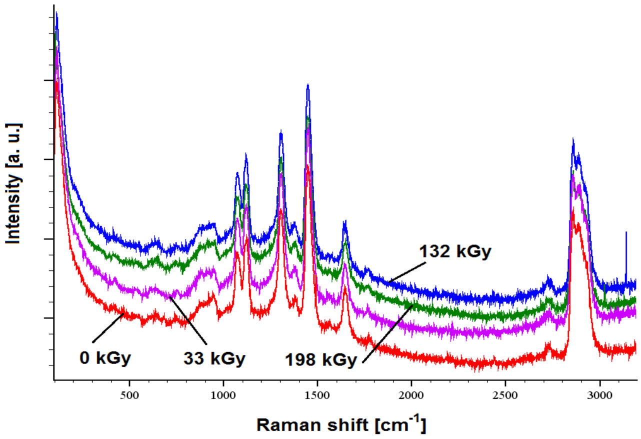

Fig. 19 Raman spectra of non-irradiated and β-irradiated PA12 using the 785nm NIR diode laser.

Table 2 Peak assignments for the Raman vibrational modes

Raman shift [cm^{-1}]		Functional groups
Measured NIR laser	Literature [7, 8]	
620	620	Amide VI (N-H)
632	630	Amide IV (C=O)
950	948	C-CO stretch
1075	1062	C-C stretch (backbone)
1123	1128	C-C stretch (backbone)
1308	1296	CH_2 twist
1378	1374	CH_2 wag
1452	1437	CH_2 bend
1638	1634	Amide I C=O stretch
2862	2850	CH_2 sym. stretch
2890	2886	CH_2 sym. stretch
outside the range	3301	N-H stretch

Difference in doses of irradiation causes different degree of cross-linking, and also the quantity of links, what affects the resulting microhardness of samples. Intensity of Raman signal is proportional to the amount of individual bonds in the material. Comparative results for intensities progression of selected Raman vibrational modes for differently irradiated samples are shown in Fig 20.

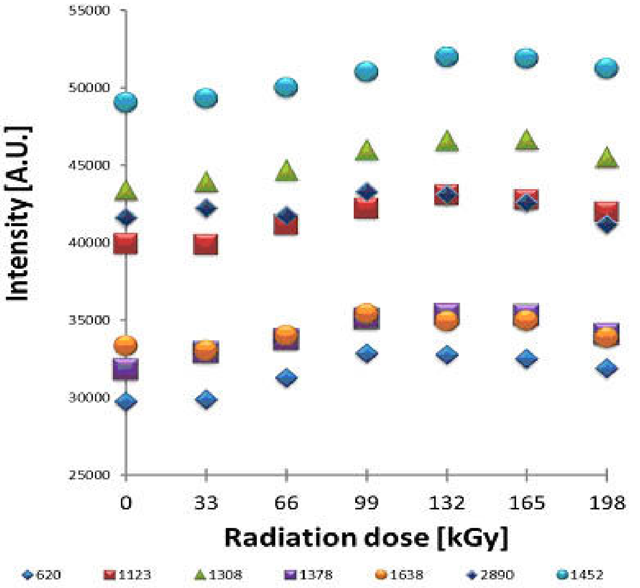

Fig. 20 The effect of β -radiation on change of intensity relations

IV. CONCLUSION

Instrumented microhardness 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 microhardness and indentation modulus of elasticity. The largest increase was observed in both cases using the doses of 132kGy. Results also showed that Raman spectroscopy is applicable for the progression of microhardness of PA12 irradiated samples assessment.

The properties of surface layer of polyamide 12 were modified significantly by beta radiation improved. The microhardness values were increased by 57%. Stiffness of surface layer increased significantly by 59% as a result of radiation. The creep values of irradiated polyamide 12 decreased by 33% 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 micromechanical properties were reached at radiation dose of 132 kGy. With higher radiation doses, the resulting values of micromechanical properties decreased and then showed constant values.

The results of micromechanical properties of surface layer of modified polyamide 12 show, that it can be used in more difficult applications in some industrial fields, in particular where there are high requirements for strength, stiffness and hardness of surface layer which appears to be the most suitable area of application. 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 12 modified by beta radiation is a suitable alternative to commonly used materials in the automotive and electrical industry.

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