Nano-indentation Test of Crosslinking Polyamide 11 by Electron Beam

M. Ovsik, M. Stanek, A Dockal, M. Reznicek and A. Skrobak

***Abstract*—**This article deals with the influence of electron beam radiation on nano-mechanical properties and the structure of polyamide 11. Crosslinking of polymers is a process, during which macromolecular chains start to connect to each other and the spatial network creates in the structure. During the action of the ionizing radiation two actions can occur: crosslinking and scission of macromolecules – degradation. Both these processes run parallel. Using the crosslinking technology the standard and construction polymer can obtain the more "expensive" high-tech polymeric materials properties and thus replace these materials in many applications. Tested material was irradiated by different doses of beta radiation (33, 66 and 99 kGy). The nano-mechanical properties were measured using DSI method, which fluently records the change of the indentation in time. From this dependence it is possible to determine nano-mechanical properties such as indentation hardness, indentation modulus etc. During results consideration it is obvious that irradiation acts on each polymer differently, but always when the optimal dose was found, nano-mechanical properties increased up to 34 %. The changes of nano-mechanical properties were confirmed by structural measurement when the change of hardness and modulus corresponded to gel content.

***Keywords*—**Polyamide 11, crosslinking, Electron Beam, nano-indentation, hardness.

I. Introduction

POLYAMIDE 11 (PA 11) is a semi-crystalline thermoplastic polymer belonging to the family of aliphatic polyamides well known as Nylon belonging to the most used polymeric materials. Polyamides are considered as construction polymers used in all branches of the plastics industry. Very often they are used in the automotive industry. Polyamides have excellent mechanical properties, high resistance against chemicals and abrasion etc. These polymers are often reinforced with the fibre glass to obtain better mechanical properties. Other of many possibilities how to improve mechanical properties of polyamides is to use ionizing beta radiation for creation of crosslinked bonds in the inner structure of the material. Radiation crosslinking using ionizing beta radiation is the safe, fast, clean process, free of waste with no environmental hazard. Our team investigated the influence of ionizing beta radiation on the micro-mechanical properties of PA 11. We found out that after irradiation of PA 11 with the doses of 0, 33, 66 and 99 kGy had this polymer the best micro-hardness at the dose of 99 kGy, the elastic modulus at the dose of 33 kGy and the indentation creep at the dose of 99 kGy was similar as in the case of non-irradiated samples [1].

Mária Porubská et al. investigated the influence of gamma irradiation in air and in the inert atmosphere on the unfilled or glass fibre reinforced PA 6. They measured the gel point around the dose of 300 kGy for both materials, but gel formation at higher doses is more effective for pure PA 6. Irradiation in air caused the increase of molecular weight, but the crosslinked portion was not obtained even at highest dose of radiation 500 kGy. The highest increase of impact strength was found out at PA in comparison to PA with glass fibres. The scientist Mária Porubská investigated again PA 6 after irradiation, this time using electron beam radiation. She found out that the crosslinking was more effective for pure PA in comparison with PA filled with the glass fibre [2].

A huge amount of articles is concentrated on the crosslinking of polyamides using various types of crosslinking, but there is a small amount of articles concentrated on crosslinking of PA 11 using electron beam radiation and subsequent investigation how micro-mechanical properties were changed after this irradiation [3, 4].

Common PA11, when exposed to the effect of the radiation crosslinking, degrades and its mechanical properties deteriorate. Using crosslinking agent TAIC (triallyl isocyanurate) produces a crosslinking reaction inside the PA11 structure. The utility properties of PA11 improve when the non-crystalline part of PA11 is crosslinked (Figure 1) [5, 7].
The thermoplastics which are used for production of various types of products have very different properties. Standard polymers which are easy obtainable with favorable price conditions belong to the main class. 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 polymers is as high as 90% [8, 9].

The main aim of this study is to compare changes in the

Martin Ovsik is with the Tomas Bata University in Zlin, nam. T. G. Masaryka 5555, 76001 Zlin, Czech Republic (e-mail: ovsik@utb.cz).
Michal Stanek is with the Tomas Bata University in Zlin, nam. T. G. Masaryka 5555, 76001 Zlin, Czech Republic (e-mail: stanek@utb.cz).
Adam Dockal is with the Tomas Bata University in Zlin, nam. T. G. Masaryka 5555, 76001 Zlin, Czech Republic (e-mail: adockal@utb.cz).
Martin Reznicek is with the Tomas Bata University in Zlin, nam. T. G. Masaryka 5555, 76001 Zlin, Czech Republic (e-mail: mreznicek@utb.cz).
Adam Skrobak is with the Tomas Bata University in Zlin, nam. T. G. Masaryka 5555, 76001 Zlin, Czech Republic (e-mail: skrobak@utb.cz).

nano-mechanical properties of irradiated polyamide 11. This work explores the potential improvements in nano-indentation properties and morphology of crosslinked polyamide 11 by ion beam treatment. These tested polymers find a broad application in many branches of industry and in daily life as well.

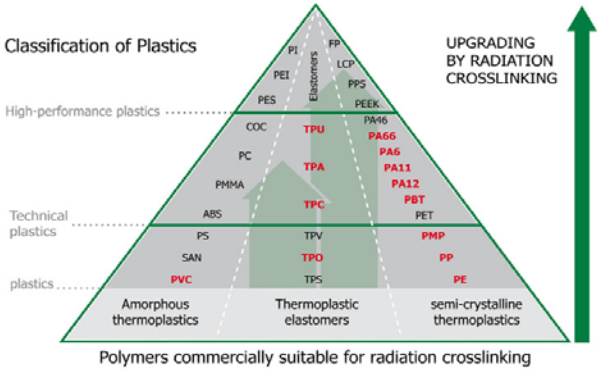

Fig. 1 Upgrading properties by radiation crosslinking

II. Experimental

The crosslinked material was chosen for the measurement of nano-indentation properties for comparison of various options. Polyamide 11 from the company PTS was chosen as a material. Testing samples were made from this material according to a standard ISO 527-2 1BA for the tensile test. The processes of injection molding and radiation crosslinking were performed with the minimum time gap to avoid the influence on the measurement surroundings.

A. Material

For this experiment polyamide 11 V-PTS-CREAMID11T*M600/13 (PTS Plastics Technologie Service, Germany) was used. The material already contained the special crosslinking agent TAIC - triallyl isocyanurate (6 volume %), which should enable subsequent crosslinking by ionizing β – radiation.

B. Sample preparation

Process conditions were set according to the manufacturer. These samples were moulded by the injection moulding machine ARBURG Allrouder 470H (Loßburg, Germany) according to the same process conditions.

Table 1 Process parameters.

Parameters	Unit	PA 11
Injection Pressure	MPa	65
Cooling Time	s	17
Mould Temperature	°C	60
Zone 1	°C	240
Zone 2	°C	250
Zone 3	°C	260
Zone 4	°C	270

The normalized specimens, with dimensions of (80 x 10 x 4) mm, were used. Process conditions; see Table 1.

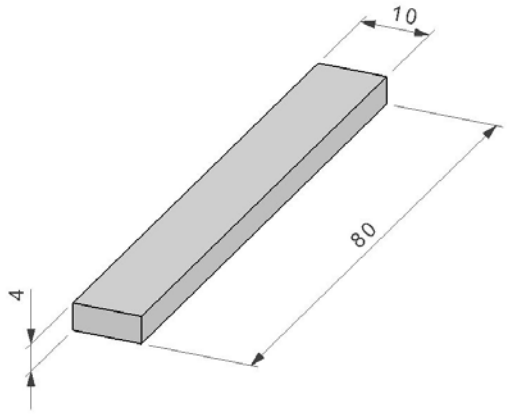

Fig. 2 Dimension of sample.

C. Irradiation process

The crosslinking causes the connection of polymeric chains to each other, most often using covalent bonds to form the spatial network. Test bodies were irradiated under industrial conditions on a commercially available irradiation device in a broader range of radiation doses (0, 33, 66 and 99 kGy) compared to the doses corresponding to the experience in the practice.

All samples were irradiated with electron (beta) rays (accelerated electrons - A Rhodotron R E-beam accelerator, electron energy 10 MeV) in the firm BGS Beta Gamma Service GmbH & Co, Saal am Danau – Germany.

D. Gel content

A gel test is conducted to determine the content of non-filtered phase-gel of the given material according to the CSN EN 579 standard. The portion of 1 g (of material radiated by radiation doses), weighed with a precision of three decimal places, was mixed with 100–250 mL of solvent. Xylol was used for testing the polymers because it dissolves the amorphous part of polymers; the crosslinking part does not dissolve. The mixture was extracted for 6 h. Then, the solutes were separated by distillation. After removing the residual xylol, the crosslinked extract was rinsed in distilled water. The rinsed extract was then dried for 8 h, under vacuum, at 100 °C. The dried and cooled residue was re-weighed, with a precision of three decimal places, and compared to the original weight of the portion. The result, stated in percentage, shows the degree of crosslinking:

$$G_i = \frac{m_3 - m_1}{m_2 - m_1} \cdot 100 \quad (1)$$

Where G_i is the degree of crosslinking of each specimen expressed in percentage, m_1 is the weight of the cag and lid in milligrams, m_2 is the total of weights of the original specimen,

cage and lid in milligrams, and m3 is the total of the weights of the residue of specimen, cage and lid in milligrams.

E. Nano-indentation test

Instrumented indentation represents a modern technique which, unlike the traditional hardness testing, does not rely on observation of the indent made by hard tip on the surface of the tested material. It rather continuously records the depth of penetration (h) into the material with respect to the actual applied load (P). The result is a loading, or P-h, curve as it is schematically shown in Fig. 3. From the known geometry of the tip and its material properties a number of data about the tested material can be inferred [13 -17].

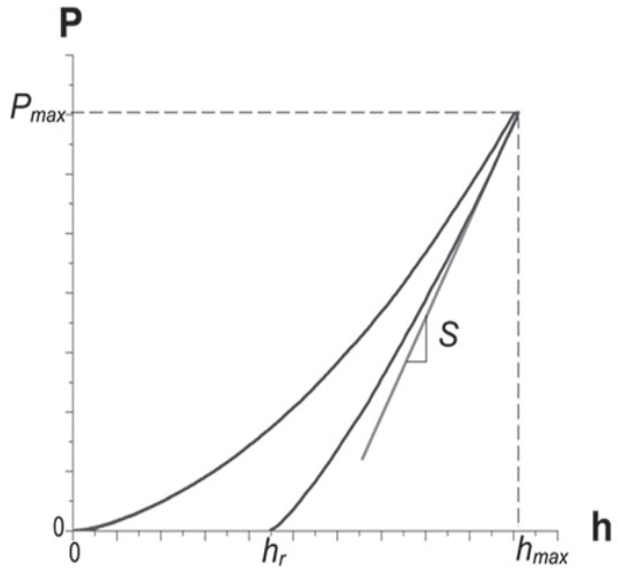

Fig. 3 Typical load (P) vs. penetration depth (h) curve of a load-unload instrumented indentation test, where the designation of various quantities is illustrated: the maximum load (Pmax), maximum penetration depth (hmax), residual depth (hr), and contact stiffness (S).

Nano-indentation properties was measured by means of Nano-Hardness Tester NHT^3 (Fig. 4) made by Anton Paar (Graz, Austria), according to the CSN EN ISO 14577 standard. On each material at least ten indents were made and the results were statistically treated. Standard simple loading-unloading mode was used. From the obtained "load vs. depth of penetration" curves values of nano-indentation properties were calculated according to Oliver and Pharr. The measurement parameters are shown in Table 2.

Table 2. Measurement parameters.

Parameters	Unit	Value
Maximum Load	mN	10
Load/Unload Speed	mN/min	20
Holding Time	s	90

Table 3. Process parameters.

Parameters	Unit	Value
Force	mN	0.1 - 500
Resolution	nN	0.02
Depth	um	200
Resolution	nm	0.001
International standards		ISO 14577, ASTM E2546

Fig. 4. Nano-indentation Tester NHT^3.

The indentation hardness (H_{IT}) was calculated as maximum load (F_{max}) to the projected area of the hardness impression (Ap) and the indentation modulus (E_{IT}) is calculated from the Plane Strain modulus (E*) using an estimated sample Poisson's ratio (ν) according to [10-15]:

$$H_{IT} = \frac{F_{\max}}{A_p} \tag{2}$$

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

Determination of indentation creep C_{IT} (Fig. 5), where h_1 is the indentation depth at time t_1 of reaching the test force (which is kept constant), h_2 is the indentation depth at time t_2 of holding the constant test force [15 -20].

$$C_{IT} = \frac{h_2 - h_1}{h_1} \cdot 100 \tag{3}$$

Measurement of all above mentioned properties was performed 10 times to ensure statistical correctness.

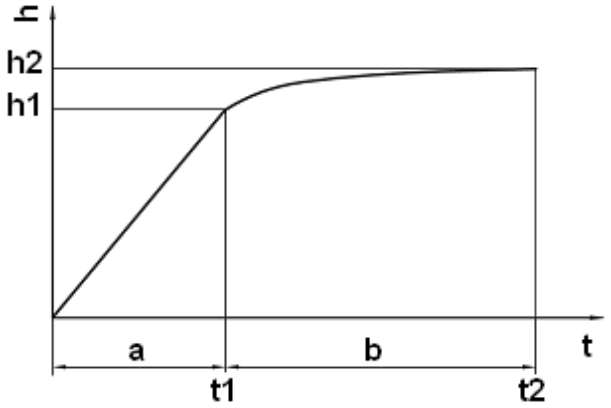

Fig. 5. Expression of indentation creep, a - Application of the test force, b - Test force kept constant from t_1 to t_2.

F. Wide-angle X-ray scattering

Wide-angle X-ray diffraction patterns were obtained using a PANalytical X´Pert PRO X-ray diffraction system (Netherlands). The CuKα radiation was Ni-filtered. The scans (4.5 ° 2 Θ/min) in the reflection mode were taken in the range 5–30 ° 2 Θ. The sample crystallinity (X) was calculated from the ratio of the crystal diffraction peaks and the total scattering areas.

Crystall size L110 of α most intensive peak at 110 was calculated using Scherrer equation. As a standard "perfect" crystal terephthalic acid with the peak at 2 Θ = 17.4 ° and the half maximum breadth 0.3 ° 2 α was chosen.

G. Fourier transformed infrared spectroscopy (FTIR)

Infrared spectra were measured by ATR technology using single reflection ATR (GladiATR, PIKE Technologies), which was equipped with diamond crystal of refractive index of 2.4 and impact angle 45°). Spectra were measured by FTIR spectrometer Nicolet 6700 FTIR (Thermo Nicolet Instruments Co., Madison, USA) blown with dry air. Spectra were measured at the definition of 2 cm-1 using 64 scans. Pure ATR diamond crystal was used for the background and ATR correction was used for the adjustment of spectra. Manipulation with spectra was done using OMNIC Software 8.2. Each specimen was measured 2 times on each side.

III. Results and Discussion

For the nano-mechanical properties measurement the polyamide 11 was selected for radiation crosslinking. The main reason of this selection is this easy modification by beta radiation and this often application in the technical practice. For confirmation of the results and changes of nano-mechanical properties of tested polymers using DSI method, structural measurements were done. These properties were always 10 times measured at polymers. The influence of radiation dose on nano-mechanical properties of tested polymers was compared.

The measured values of the ultra-nano indentation test were obtained for PA 11 irradiated with beta rays as shown in Table 4.

Table 4. Nano-indentation values

Parameters	Unit	0 kGy	33kGy	66kGy	99kGy
Gel Con.	%	0,00	33,00	87,00	76,00
H_{IT}	MPa	153,38	156,08	205,19	176,46
HV_{IT}	Vickers	14,21	14,46	19,00	16,34
E_{IT}	GPa	2,11	2,16	2,50	2,18
C_{IT}	%	7,55	6,76	6,35	7,01

Nano-indentation characteristics determined by DSI method are depicted in Figure 6. From Figure 6, there is evident the change of the properties of polyamide 11 with addition of crosslinking agent before and after irradiation by different doses. Figure characterizes the dependence of the indentation depth on time of the application of the constant loading force, while indentation curves give the possibility to obtain indentation hardness, indentation modulus and the size of deformation, elastic, plastic and total work needed to formation of the indentation.

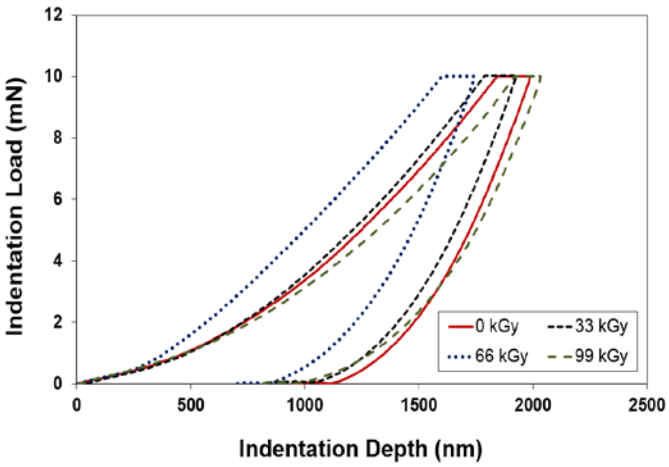

Fig. 6. Indentation load vs. Indentation depth

Graphic evaluation of measured results of indentation hardness in the dependence on different radiation doses for polyamide 11 are shown in Figure 7. From measured values of indentation hardness follows that radiation crosslinking at polyamide 11 takes effect by higher hardness at tested polymers. The lowest value of indentation hardness was found at non-irradiated PA 11 (153.4 MPa). The highest value of indentation hardness was measured at PA 11 irradiated at the dose of 66 kGy. The difference in hardness at tested PA 11 (205.2 MPa) was approximately 34 %. According Figure 7 it is clear that indentation hardness at tested polymers is strongly influenced by beta radiation. The values drop of hardness after application of radiation doses higher than 66 kGy is probably

caused by material degradation after irradiation.

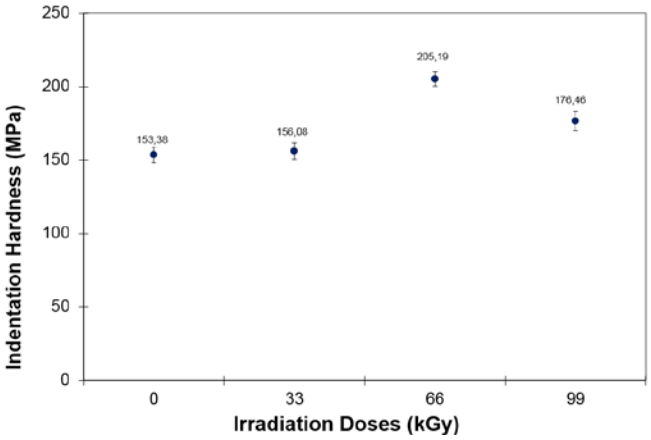

Fig. 7. Indentation hardness vs. Irradiation doses

PA 11 indentation modulus increased with the radiation dose up to maximum at the dose of 66 kGy (2.5 GPa) what is approximately higher by 19 % in comparison with non-irradiated PA 11 (2.1 GPa). The higher radiation dose, the lower values of indentation modulus (Figure 8).

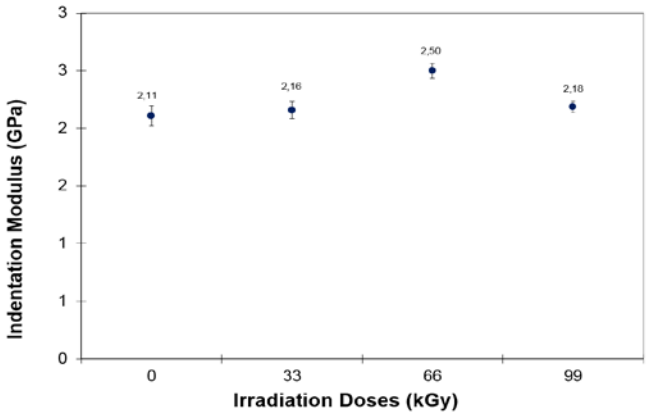

Fig. 8. Indentation modulus vs. Irradiation doses

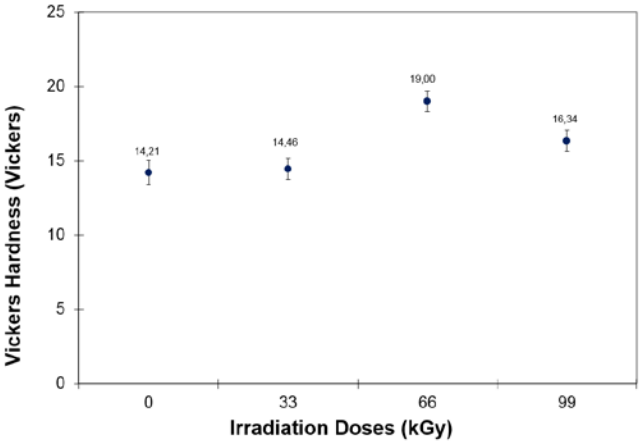

Fig. 9. Vickers hardness vs. Irradiation doses

Radiation crosslinking of PA 11 manifests by significant increasing of hardness values as is visible in Figure 9. The lowest values of Vickers hardness were measured at non-irradiated PA 11 (14.2 Vickers). On the contrary the highest values were achieved at PA 11 irradiated by the dose of 66 kGy (19.0 Vickers). The difference in hardness at both tested samples was approximately 34 %. The hardness increase is caused by crosslinking as a result of irradiation of the test body. The drop of both values after application of radiation doses higher than 66 kGy is probably caused by the material degradation after irradiation.

The DSI method is determined not only for nano-indentation hardness and modulus of polymers. From the results it is possible to obtain a lot of other results for comprehensive assessment of the mechanical behaviour of polymers. The basic source of information the indentation characteristics obtained during measurement recorded the run of loading force in the dependence of the depth of the indenter penetration is. The importance of indentation characteristics is going to be presented on the base of the change of mechanical behaviour of tested polymers generated by radiation crosslinking comparison.

The time run of the indentation depth is the important run of measurement for the purpose of the determination of the creep behaviour of polymers (nano-indentation creep), which is determined from the difference of the loading after achieving of the indentation depth which is holding on the constant level and after time when the indentation depth was held on the constant level (Fig. 10).

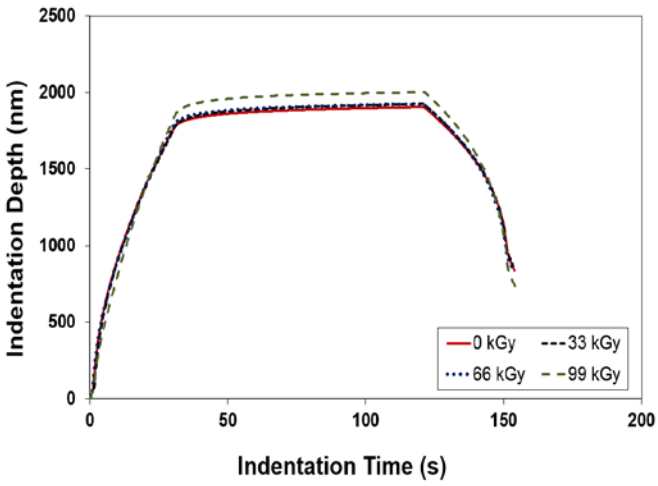

Fig. 10. Indentation depth vs. Indentation time

The PA 11 showed the decrease of indentation creep C_{IT} with the increase of the radiation dose (Fig. 11). At PA 11 the minimal value was measured at the dose of 66 kGy (6.4 %) with the increase of C_{IT} value by 19 % in comparison with non-irradiated PA 11. The higher radiation dose the upper C_{IT} value. The highest value of indentation creep was found at the non-irradiated material (7.6 GPa).

The gel test is carried out for the purpose of measurement of non-filterable phase content – the gel of given material according to the standard EN ISO 579. The determination of the gel content at Polyamide 11 in the dependence on applied dose of radiation is obvious from the Figure 12.

Figure 12 shows the resultant content of PA 11 gel. The trend in this material is similar to nano-mechanical properties trend, there is also a significant increase in the gel content at a radiation dose of 66 kGy (87%) and with an increasing radiation dose the gel content is slightly decreased up to a maximum radiation dose of 99 kGy where the gel content was measured at 76%. These results correspond to the measurement of nano-mechanical properties, where the highest values were measured at the radiation dose of 66 kGy.

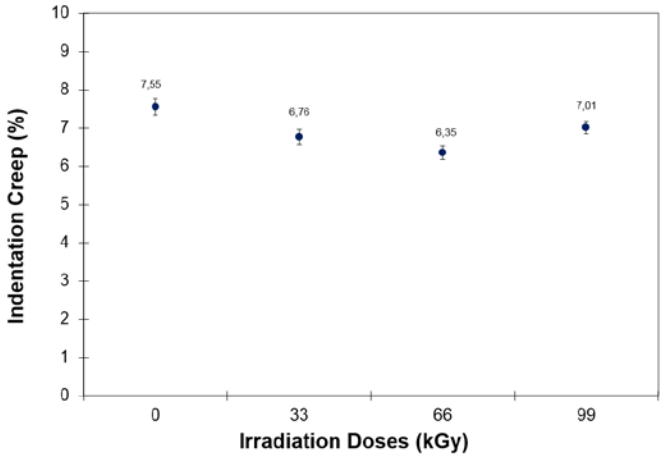

Fig. 11. Indentation creep vs. Irradiation doses

The accuracy of the gel content measurement is largely dependent on the robustness of the filter screen used, and so the resulting "micro gels" of the material in the lower radiation dose can pass through the filter sieve, so they are not counted in the total gel content. However, they already play a significant role in the measured properties.

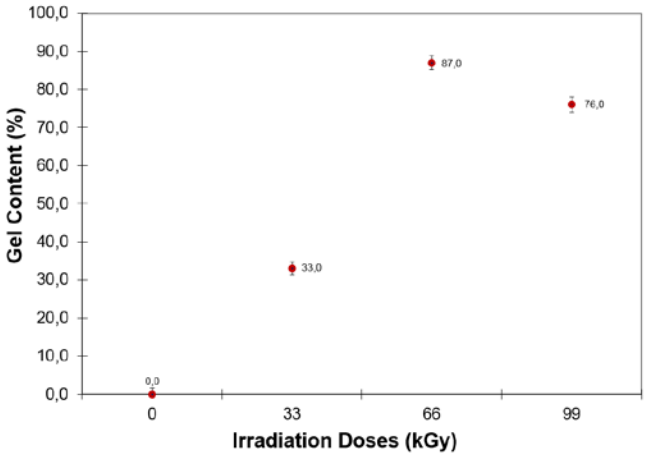

Fig. 12. Gel content vs. Irradiation doses

Table 5. X-ray diffraction of PA 11

Irradiation doses (kGy)	$X_{x\text{-}ray}$, %, ±1%
0	35
33	38
66	40
99	37

The figure 13 and show typical X-ray diffraction spectrum of the non-irradiated and irradiated polyamide 11 (PA 11). There is an apparent presence of α-phase in the non-irradiated specimen. The greatest grow of α-phase is seen at the radiation dose of 33 kGy (Fig. 14).

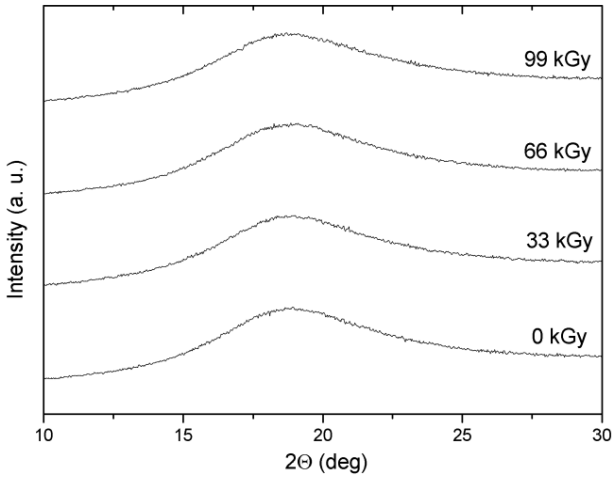

Fig. 13. X-ray diffraction of non-irradiated and irradiated PA11

When applying β-radiation the structure of polyamide 11 undergoes loss and then a grow of the crystalline phase (Table 5). It can be assumed that the size of individual crystals will correspond with the loss of crystalline phase (crystalline value X calculated lay in the range 35-40 %). The greatest size of crystalline phase was found in the case at the radiation dose of 66 kGy (40 %). The lowest size of crystalline phase was found in the case at non-irradiated (35 %). Its influence on the mechanical behavior is insignificant. Cross-linking occurs in the remaining noncrystalline part which has a significant influence on the mechanical properties of the surface layer. Its influence on the mechanical behavior is insignificant.

The infra-red spectroscopy, IR, is the versatile method to follow chemical modifications in a polymeric material. Studies carried through by some researchers presented the formation of carbonyl groups.

The results of the infrared spectroscopy showed changes of relative representation of hydroxyl and carbonyl groups in relation to the radiation dose (Fig. 14). For evaluation hydroxyl groups we used an area of the strip integrated in the area of 3570-3006 cm^{-1}, (Each specimen was measured twice on both sides). For evaluation carbonyl groups we used an area of the strip integrated in the area of 1768-1483 cm^{-1}, (Each specimen was measured twice on both sides). When the

specimen is irradiated, it leads to oxidation on C-H bonds and formation of oxygenic functional groups.

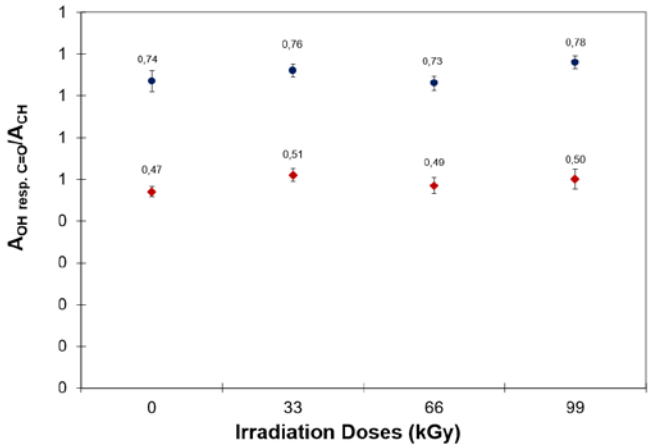

Fig. 14. Change in the relative representation of carbonyl groups of PA11 in relation to the irradiation doses

The smallest values of relative change of representation of hydroxyl and carbonyl groups were found at radiation dose of 0 kGy. At these doses the worse values of mechanical properties of surface layer of the tested polyamide 11 (PA 11) were measured. The greatest change was found at radiation dose of 33 kGy (At this dose the best values of mechanical properties of surface layer of the tested polyamide 11 (PA 11) were measured). These changes of the structure correspond with the changes of mechanical properties of modified polyamide 11 (PA 11) beta radiation.

IV. Conclusions

From the results it is evident that beta radiation crosslinking has a influence on nano-mechanical properties of polymers (PA 11). Nano-mechanical properties (indentation hardness, indentation modulus, Vickers hardness, deformation works) were measured using DSI method at all tested polymers. Polyamide 11 irradiated at the dose of 66 kGy reached the biggest changes of tested properties in comparison with non-irradiated materials. Nevertheless, it is necessary to mention that the final dose of radiation is always necessary to consider thoroughly with respect to the efficiency of the irradiation process. In some cases it is possible to choose also the lower radiation dose with comparable reached results of modification. Thanks to different applied radiation doses the improvement of usual material properties occurs, thereby the cheaper commodity or construction material can replace more expensive construction or special polymers.

The results of nano-mechanical properties were supported by the measurement of the structure, where measurements of gel test were performed. The Gel content confirmed the influence of radiation doses on the structure of studied polymers. From the measurements it can be stated that the highest changes were achieved by polyamide 11 examined at higher doses of radiation.

It should also be noted that a higher dose of radiation intensity does not necessarily mean a higher improvement in desired properties. For a particular application and material, it is always necessary to look for a suitable dose of radiation intensity.

Acknowledgment

This work was supported by the European Regional Development Fund under the project CEBIA-Tech Instrumentation No. CZ.1.05/2.1.00/19.0376 and by the Ministry of Education, Youth and Sports of the Czech Republic within the National Sustainability Program project no. LO1303 (MSMT-7778/2014). Moreover, it was supported by the Internal Grant Agency of TBU in Zlin: no. IGA/FT/2019/002.

References

[1] T. Yu, J. Chen, F. Wu, J. Rocks, Mater. Sci. Forum 815, (2015).
[2] Drobny J.G., Radiation Technology for Polymers (CRC Press, New York, 2003).
[3] G. Zamfirova, V. Gaydarov, T. Zaharescu, L. G. Silva, Chemicke Listy 104 (2010).
[4] T. Metanawin, A. Jamjumrus, S. Metanawin, Morphology, MATEC Web of Conferences 30, (2015).
[5] M. Ovsik, L. Hylova, D. Manas, M. Manas, M. Stanek, MATEC Web of Conferences 76, (2016).
[6] D. Manas, M. Manas, M. Ovsik, M. Stanek, L. Chvatalova, P. Stoklasek, L. Hylova, MATEC Web of Conferences 76, (2016)
[7] A. Barlow, et al. Radiat. Phys. Chem. 14, (2015)
[8] R. J. Woods, A. K. Picaev, Applied radiation chemistry: radiation processing (New York: John Wiley, 1994)
[9] E. Ragan, et al. Metalurgija 51, 4 (2012)
[10] D. Manas, M. Ovsik, A. Mizera, M. Manas, L. Hylova, M. Bednarik, M. Stanek, Polymers 10, 2 (2018)
[11] M. Ovsik, M. Stanek, M. Reznicek, MATEC Web of Conferences 125, (2017)
[12] W.C. Oliver, G.M. Pharr, J. Mater. Res., 19. (2004)
[13] M. Stanek, M. Ovsik, D. Manas, M. Reznicek, WSEAS Transactions on Applied and Theoretical Mechanics 12, (2017)
[14] 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.
[15] Oliver, W. C., Pharr, G. M. Measurement of hardness and elastic modulus by instrumented indentation. *Journal of Materials Research*. 2004, Vol. 19, no. 1.
[16] 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.
[17] 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.
[18] 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.
[19] 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.
[20] 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.