Nano-mechanical Properties and Morphology of Irradiated Glass Fiber Filled Polypropylene

MICHAL STANEK, MARTIN OVSIK, DAVID MANAS, MARTIN REZNICEK
Department of Production Engineering
Tomas Bata University in Zlin
TGM 5555, 760 01 Zlin
CZECH REPUBLIC
ovsik@utb.cz http://www.utb.cz/ft-en

Abstract: - Cross-linking is a process in which polymer chains are associated through chemical bonds. Radiation, which penetrated through specimens and reacted with the cross-linking agent, gradually formed cross-linking (3D net), first in the surface layer and then in the total volume, which resulted in considerable changes in specimen behavior. This paper describes the effect of electron beam irradiation on the surface properties (nano-indentation test) of glass fiber filled polypropylene (30%). These nano-mechanical properties were measured by the DSI (Depth Sensing Indentation) method on samples which were non-irradiated and irradiated by low (33, 66 and 99 kGy) and high (132 and 165 kGy) doses of the β – radiation. Nano-indentation test was performed at (400mN) indentation loads. The purpose of the article is to consider to what extent the irradiation process influences the resulting nano-mechanical properties measured by the DSI method. The polypropylene tested showed significant changes of indentation hardness and modulus. The best results were achieved by irradiation at doses of 99 and 132 kGy (increase about 68%) by which the highest nano-mechanical properties of filled polypropylene were achieved. These changes were examined and confirmed by X-ray diffraction and Gel content.

Key-Words: - polypropylene, glass fiber, morphology, irradiation, nano-hardness, nano-indentation

1 Introduction

Polypropylene (PP) is a stereospecific polymer prepared by polymerization using an organometallic catalyst system. Commercial polypropylenes have up to 95% isotactic content, which means that pendant methyl groups are almost all on the same side of the chain [1].

When polypropylene is exposed to ionizing radiation, free radicals are formed and these cause chemical changes. Since PP is highly crystalline, these radicals are relatively immobile, and consequently may not be available for reaction for long periods of time [1-3]. As with other polyolefin, upon irradiation the free radicals are formed along with evolution of hydrogen gas. If the radical is formed on the pendant methyl, the resulting reaction is cross-linking. However, if the radical is formed in the main chain, the chain end may react with hydrogen, thus causing an irreversible scission. Although the processes of chain scission and cross-linking occur simultaneously, and even though the net effect is crosslinking, the overall effect is the loss of mechanical strength [1-6].

Radiation processing of polymers is a well-established and economical commercial method of precisely modifying the polymer properties. Cross-linking is a process in which polymer chains are associated through chemical bonds. Cross-linking is carried out by chemical reactions or radiation and in most cases the process is irreversible. Ionizing radiation includes high-energy electrons (electron beam - β-rays) (Fig. 1) and gamma rays (γ-rays) (Fig. 2). These not only are capable of converting monomeric and oligomeric liquids into solids, but also can produce major changes in properties of solid polymers. [4-8]

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 [1, 2, 9]. As a result, we can optimize properties of commodity and engineering polymers and impart them the properties of high performance polymers [11, 12].

Therefore, using of ionizing radiation has found a very wide range of applications in medicine,

agriculture and industry. Many scientists have examined the issues of polymer radiation cross-linking. They discovered that some of polymer materials exposed to the ionizing radiation tend to either improve or worsen their mechanical properties. It depends on chemical structure if polymers cross-link or degrade predominantly. Degradation is an undesirable process which may cause significant deterioration of crucial properties for some applications [11-14].

Common PP, 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 PP structure. The utility properties of PP improve when the non-crystalline part of PP is cross-linked.

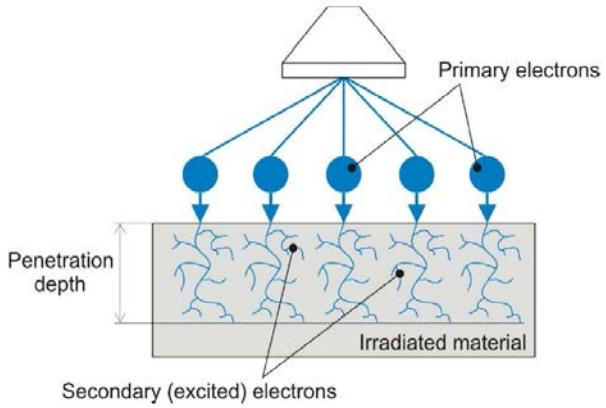

Fig. 1. Radiation crosslinking by electrons rays

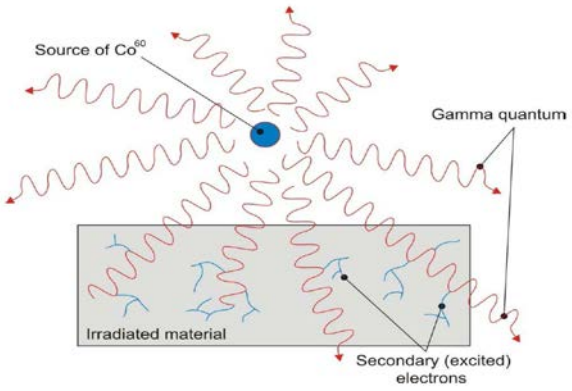

Fig. 2. Radiation crosslinking by Gamma rays

From the results of previous studies it is apparent, that the radiation crosslinking is very efficient method for modifying the final properties of the polymers. However, some knowledge remains unexplained so far, and therefore each new finding about the effect of radiation crosslinking on the properties of polymer materials may contribute to a better understanding of the issue and thus can extend the field of new applications [7-14].

As discussed above, nano-mechanical properties in the cross-linking polypropylene is affected by many structural, morphological and surface characteristics parameters. That is why, paper presented is focused on study of the effect of the irradiation by different doses in polypropylene. There are studied nano-mechanical properties combined with X-ray diffraction and Gel content.

2 Experimental

2.1 Material

For this experiment polypropylene PP PTS-Crealen-8G8HS*801natur filled by 30% glass fibers (PP + 30%GF), that were supplied by PTS Plastics Technology Service, Germany was used. The material already contained the special cross-linking agent TAIC - triallyl isocyanurate (6 volume %), which should enable subsequent cross-linking by ionizing β – radiation.

2.2 Sample preparation

The samples were made using the injection molding technology on the injection molding machine Arburg Allrounder 470H. Processing temperature 210–230 °C, mold temperature 55 °C, injection pressure 90 MPa, injection rate 50 mm/s. It was used normalized specimen measuring 80x10x4 mm (Fig. 3).

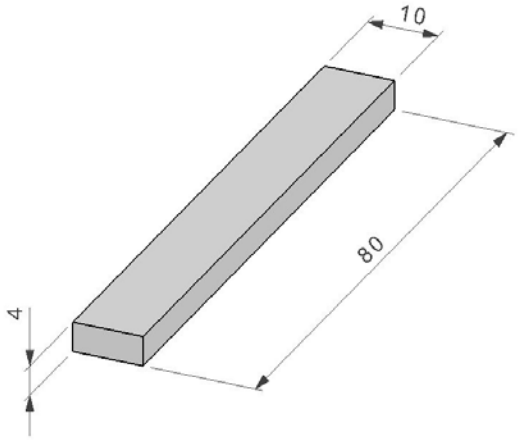

Fig. 3. Dimension of sample

2.3 Irradiation

All samples were irradiated with electron (beta) rays (electron energy 10 MeV, radiation dose: 33 kGy, 66 kGy, 99 kGy, 132 kGy and 165 kGy) in the firm BGS Beta Gamma Service GmbH & Co, Saal am Danau – Germany.

2.4 X-ray diffraction.

X-ray diffraction patterns were obtained using a PAN alytical X-pert Prof X-ray diffraction system (Netherlands). The CuKα radiation was Ni-filtered. The scans (4.5 ° 2 Q/min) in the reflection mode were taken in the range 5-30 ° 2Θ. The sample crystallinity X was calculated from the ratio of the crystal diffraction peaks and the total scattering areas.

2.5 Gel content

Gel test is done to find the content of non-filtered phase – gel of the given material according to standard ČSN EN 579. The portion of 1g (of material radiated by low radiation doses) weighed with a precision of three decimal places was mixed with 100–250 ml of solvent. Xylol was used for polypropylene because it dissolves the amorphous part of polypropylene, the cross-linking part does not dissolve. The mixture was extracted for 6h. Then solutes were separated by distillation. After removing the residual Xylol the cross-linked extract was rinsed by distilled water. The rinsed extract was dried for 6–8 h in vacuum at 100 °C. The dried and cooled residue was weighed again with precision to three decimal places and compared to the original weight of the portion. The result is stated in percentage as the degree of cross-linking.

Where G_i is the degree of cross-linking of each specimen expressed in percentage, m1 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 m_3 is the total of the weights of the residue of specimen, cage and lid in milligrams.

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

2.5 Nano-indentation

Nano-indentation test were performed using a Nano-indentation tester (Fig. 4), CSM Instruments (Switzerland) according to the CSN EN ISO 14577. The tip is made of diamond having the shape of a cube corner (Vickers). In the present study, the maximum load used was 400 mN and loading rate (and unloading rate) was 800 mN/min. A holding time was 90 s at the indentation and 21600 s at the creep.

The indentation hardness H_{IT} was calculated as maximum load to the projected area of the hardness impression according to [5-7]:

$$H_{IT} = \frac{F_{\max}}{A_p} \qquad (2)$$

$$h_c = h_{\max} - \varepsilon \frac{F_{\max}}{S} \qquad (3)$$

,where h_{max} is the indentation depth at F_{max}, h_c is contact depth. In this study the Oliver and Pharr method was used calculate the initial stiffness (S), contact depth (h_c). The specimens were glued on metallic sample holders (Fig. 5).

Fig. 4. Nano-indentation tester

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

$$E_{IT} = E^* \cdot (1 - \nu_s^2) \qquad (4)$$

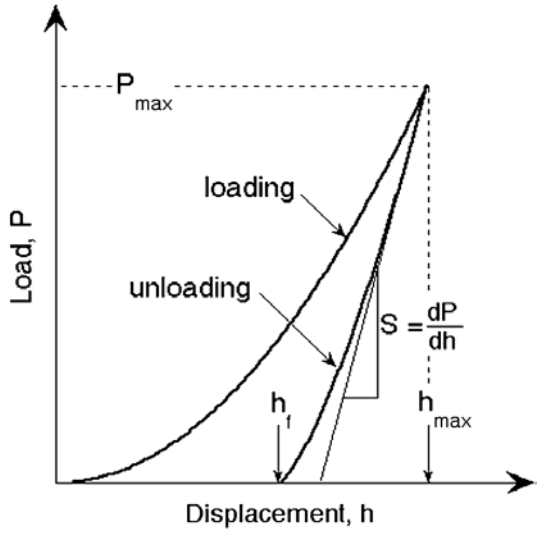

Fig. 5. Schematic illustration of indentation curve

Determination of indentation hardness C_{IT}, where h_1 is the indentation depth at time t_1 of reaching the

test force (which is kept constant), h_2 is the indentation depth at time t_2 of holding the constant test force (Fig. 6) [4-8]:

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

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

3 Results and discusion

Comparison of nano-mechanical properties (indentation hardness, indentation modulus, Vickers hardness, indentation creep and deformation work) of PP30GF before and after irradiation (33kGy, 66kGy, 99kGy 132kGy and 165kGy is given in the Fig. 9 to Fig. 10. The measured results clearly show, that irradiation increases micro-mechanical properties of PP30GF for all tested indentation load. Values of nano-mechanical properties correspond to the changes were examined and confirmed by X-ray diffraction and Gel content , is given in the Fig. 6, Fig. 7 and Fig. 8.

3.1 X-ray diffraction

Figure 6 shows typical X-ray diffraction of the non-irradiated and irradiated polypropylene. The results of the crystallinity for non-radiated and irradiated PP30GF are shown in the Fig. 7. The values measured show some heterogeneity of the crystallinity at individual radiation doses. When applying β-radiation the structure of PP30GF undergoes decrease of the crystalline phase.

The smallest value of crystallinity was found in the case of the PP 30GF irradiated at the dose of 66 kGy. On the contrary the highest value of crystallinity (Fig. 7) was measured at non-irradiated and the irradiated at dose of 165 kGy.

The process of irradiation causes physical and chemical changes in the structure of PP 30GF. They are mainly changes of crystalline and amorphous phase. The measurement results show clearly that as the irradiation dose increases, the crystallinity decreases. During the amorphous phase cross-linking occurs which results in creation of very solid areas as well as considerable growth of nano-hardness values. Higher irradiation doses do not cause greater cross-linking but rather disruption of links resulting in degradation of the irradiated material.

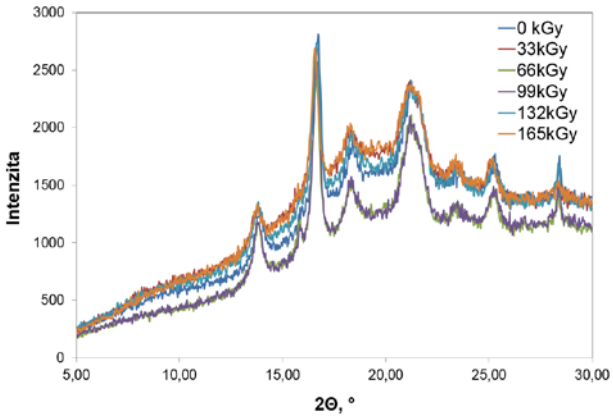

Fig. 6. X – ray diffractograms of PP30GF

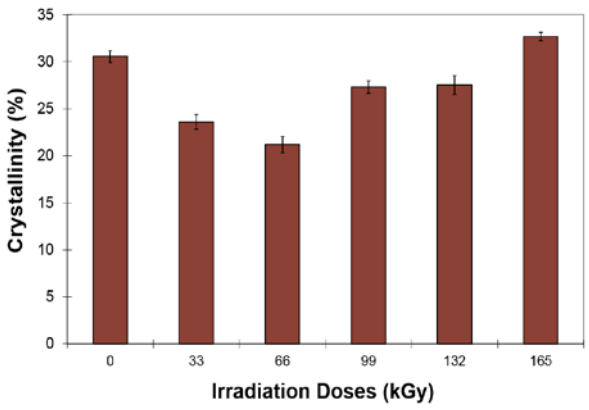

Fig. 7. Crystallinity of PP30GF

3.1 Gel Content

The results of the gel content for non-radiated and irradiated PP30GF are listed in Table 1. Gel content showed the highest values at radiation dose of 99 kGy at which it reached 67.0% degree of cross-linking (Figure 8). Specimens irradiated by 66 kGy and 132 kGy radiation dose showed very similar value 66.8% and 66.5% degree of cross-linking.

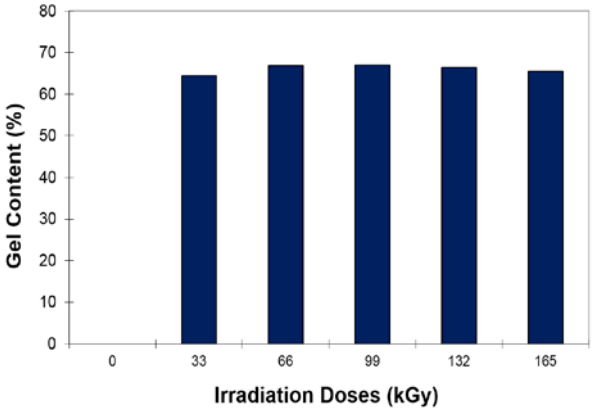

Fig. 8. Gel content of PP30GF

3.2 Nano-indentation

Radiation cross-linking creates changes in the PP 30GF structure by creating 3D net. Beta radiation gradually penetrates more deeply into the PP 30GF structure through the surface layer. The surface layer undergoes changes which have a considerable influence on the nano-mechanical properties of PP 30GF.

Nano-indentation characteristics determined by DSI method are depicted in Fig. 9 and 10. They characterize course of loading force in dependence on indentor penetration depth, which gives an idea about course of instantaneous values of observed nano-mechanical properties.

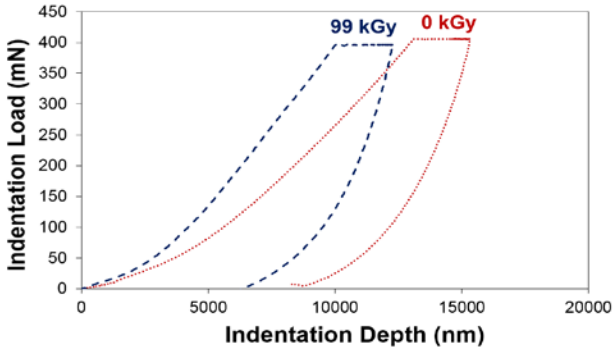

Fig. 9. Indentation characteristic of PP30GF

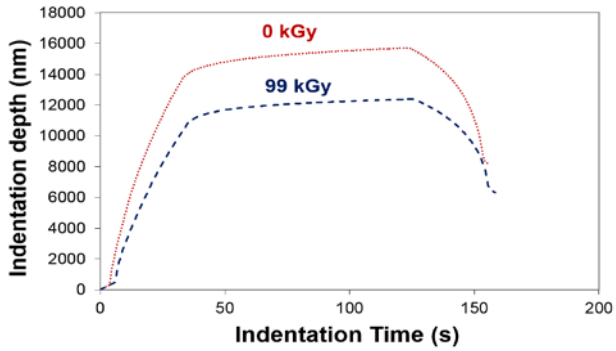

Fig. 10. Indentation characteristic of PP30GF

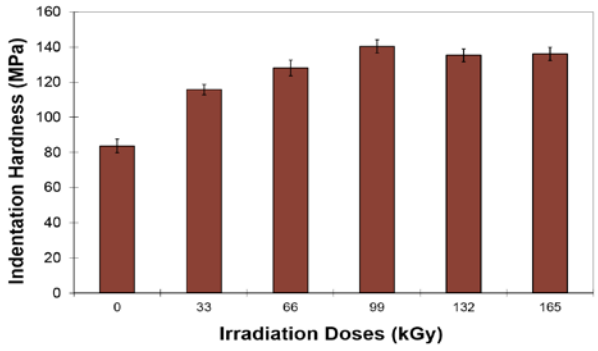

Fig. 11. Indentation hardness (H_{IT})

It demonstrated the influence of radiation on the change of nano-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 PP30GF showed considerably smaller depth of the impression of the indenter which can signify greater resistance of this layer to wear (Fig. 9 and Fig. 10).

The values measured during the nano-indentation test showed that the lowest values of indentation hardness and Vickers hardness (H_{IT} = 83.7 MPa, HV_{IT} = 7.9 Vickers) were found for the non-irradiated PP30GF. On the contrary, the highest values of indentation hardness and Vickers hardness (H_{IT} = 140.3 MPa, HV_{IT} = 13.2 Vickers) were obtained for PP30GF irradiated by a dose of 99 kGy (by 68% higher in comparison with the non-irradiated PP30GF), as can be seen at Fig. 11, 12.

In the case of indentation modulus the highest value was found for PP30GF irradiated by the radiation dose of 99 kGy (E_{IT} = 2.8 GPa). The smallest value of indentation modulus was found for non-irradiated PP30GF (E_{IT} = 1.9 GPa). The increase of the value of PP30GF irradiated by the radiation dose of 99 kGy was by 47% in comparison to the non-irradiated PP30GF (Fig. 13).

Very important values were found for indentation creep (C_{IT}). The lowest value of indentation creep was measured at radiation dose of 165 kGy (C_{IT} = 13.2%). The highest indentation creep value measured at non-irradiated and irradiated dose of 99 kGy (C_{IT} = 16.2%). Decrease in creep values was 23% for irradiated PP30GF compared to the non-irradiated one as is seen at Fig. 14.

Radiation cross-linking creates changes in the PP30GF structure by creating 3D net. Beta radiation gradually penetrates more deeply into the PP30GF structure through the surface layer. The surface layer undergoes changes which have a considerable influence on the nano-mechanical properties of PP30GF.

Similar development was recorded for elastic and plastic deformation work illustrated in Fig. 15. The results of measurements show clearly that the lowest values of deformation work were measured on the sample irradiated by 132 kGy and 165 kGy doses (W_{el} = 0.7 µJ, W_{pl} = 1.6 µJ), while the highest values were reached on non-irradiated PP30GF (W_{el} = 0.9 µJ, W_{pl} = 2.2 µJ). A significant decrease of deformation work (25% and 36%) was recorded at the radiation dose of 165 kGy compared to the non-irradiated PP30GF. Radiation of specimens caused

lower values of elastic as well as plastic deformation work which is apparent in Fig. 15.

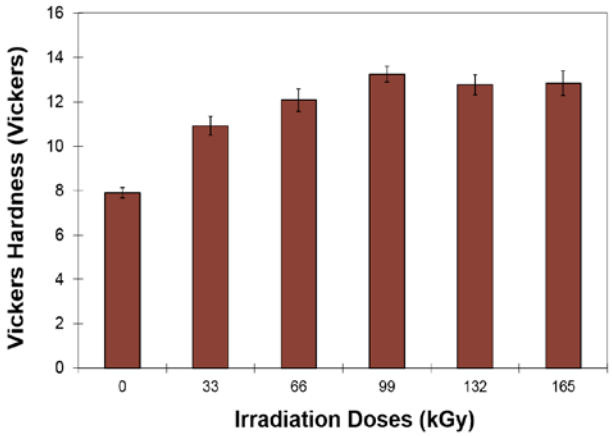

Fig. 12. Vickers hardness (HV_{IT})

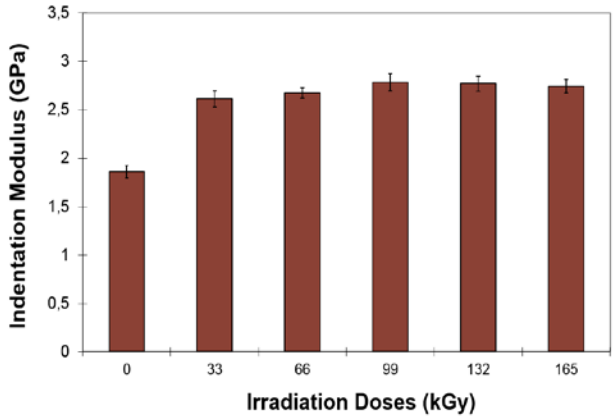

Fig. 13. Indentation Modulus (E_{IT})

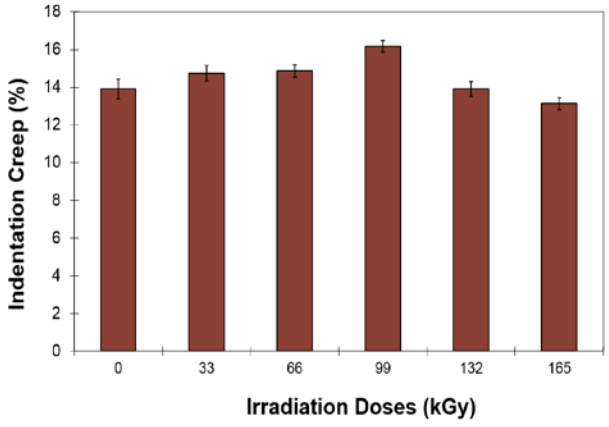

Fig. 14. Indentation creep (C_{IT})

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

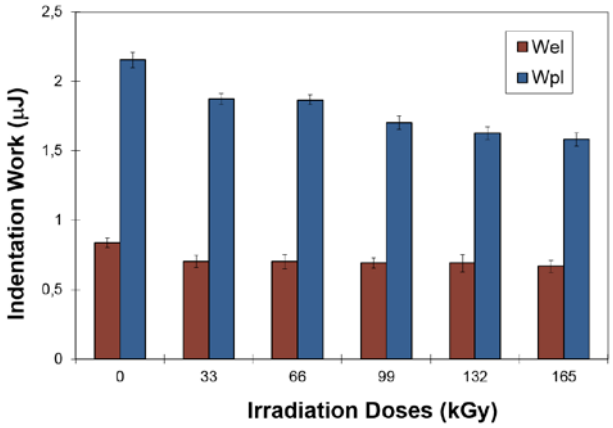

Fig. 15. Elastic and plastic part of deformation work

Table 1. Summary of measured values (400mN)

	0kGy	33kGy	66kGy
H_{IT} (Mpa)	83,69	115,69	127,98
HV_{IT} (Vickers)	7,90	10,92	12,08
E_{IT} (Gpa)	1,86	2,61	2,67
Wel (uJ)	0,84	0,70	0,70
Wpl (uJ)	2,15	1,87	1,87
C_{IT} (%)	13,90	14,76	14,87
Gel Content (%)	0,00	64,40	66,80
	99kGy	**132kGy**	**165kGy**
H_{IT} (Mpa)	140,32	135,20	136,03
HV_{IT} (Vickers)	13,24	12,76	12,84
E_{IT} (Gpa)	2,79	2,77	2,75
Wel (uJ)	0,69	0,69	0,67
Wpl (uJ)	1,70	1,63	1,58
C_{IT} (%)	16,17	13,91	13,12
Gel Content (%)	**67,00**	66,50	65,50

The results of the nano-mechanical properties for non-radiated and irradiated PP30GF are listed in Table 1. The greatest values of nano-hardness test were obtained for PP30GF irradiated with dose of 99 kGy.

4 Conclusion

This research paper investigates influence of modified polymer material (beta radiation) on the nano-indentation test. The surface layer of PP30GF

is modified by β – radiation with doses of 33, 66, 99, 132 and 165 kGy.

Radiation, which penetrated through specimens and reacted with the cross-linking agent, gradually formed cross-linking (3D net), first in the surface layer and then in the total volume, which resulted in considerable changes in specimen behavior.

Irradiation of PP30GF with a β - radiation influences the nano-mechanical properties in the following way:

• Radiation of specimens caused improvement values of indentation hardness and indentation modulus.

• In the case of indentation hardness was achieved of the highest increase (for PP30GF) at irradiation doses of 99 kGy (a hike of approximately 68 % (referring to: Fig. 11). In the case of indentation modulus was achieved of the highest increase at irradiation doses of 99kGy (PP30GF) (a hike of approximately 47 %) (referring to: Fig. 13). In the case of indentation creep was achieved of the highest decrease at 165kGy (a drop of approximately 23 %) (referring to: Fig. 14).

• Higher radiation dose does not influence the indentation hardness and indentation modulus significantly, on the contrary due to degradation processes the properties deteriorate.

• Values of indentation hardness and indentation modulus correspond to the deformation works.

• The changes were examined and confirmed by X-ray diffraction and Gel content.

The results of nano-mechanical properties of surface layer of modified PP30GF 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/2017/010 funded from the resources of specific university research and by the Ministry of Education, Youth and Sports of the Czech Republic within the National Sustainability Programme project No. LO1303 (MSMT-7778/2014) and also by the European Regional Development Fund under the project CEBIA-Tech No. CZ.1.05/2.1.00/03.0089.

References:

[1] J.G. Drobny, *Radiation Technology for Polymers*, CRC Press, New York, 2003.

[2] Manas, D., et al. Effect of low doses beta irradiation on micromechanical properties of surface layer of injection molded polypropylene composite. *Radiation Physics and Chemistry*, 114, 2015, pp. 25-30.

[3] W.C. Oliver, W.C. and Pharr, G.M. Measurement of Hardness and Elastic Modulus by Instrumented Indentation. *Journal of Materials Research* 19 (1), 2004, pp. 1564 – 1583.

[4] Ovsik, M., et al. Irradiated Polypropylene Studied by Microhardness and WAXS, *Chemicke listy*, 106 2012, pp. 507-510.

[5] Ovsik, M., et al. Micro-indentation test and morphology of electron beam irradiated HDPE. *Key Engineering Materials*, 662, 2015, pp. 189-192.

[6] Pharr, G.M. Measurement of mechanical properties by ultra-low load indentation. *Materials Science and Engineering*, 1998.

[7] O. N. Tretinikov, S. Ogata, Y. Ikada, Surface Crosslinking of Polyethylene by Electron Beam Irradiation in Air, *Polymer* 39 24, 1998, pp. 6115 - 6120.

[8] G. Zamfirova, V. Gaydarov, T. Zaharescu, L. G. Silva, Microindentation study of Electron Beam Irradiated Polyamide Samples, *Chemicke Listy* 104, 2010, pp. 283-286.

[9] Behalek, L. and Dobránsky, J. Conformal cooling of the injection moulds. *Applied Mechanics and Materials.* Vol. 308, 2013. pp. 127-132.

[10] Dobransky, J., et al. Solving Depressions Formed During Production of Plastic Molding. *Metalurgija.* Vol. 54. No. 3, 2015. pp. 496-498.

[11] Dobransky, J., et al. Comparison of Cooling Variants by Simulation Software. *Advanced Materials Research.* Vol. 801, 2013. pp. 75-80.

[12] 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, *Journal of Applied Polymer Science* 124 (6) , 2012, pp. 4564-4571.

[13] 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, pp. 1049-1058.

[14] 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, pp. 566-574,