

# MECHANICAL PROPERTIES OF LOW DENSITY POLYETHYLENE (LDPE) IRRADIATED BY LOW DOSES BETA IRRADIATION MEASUREMENT BY ULTRA NANOINDENATION TEST

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The influence of low doses of beta radiation on the changes in the structure and selected properties (mechanical and thermal) polymers were proved. Using low doses of beta radiation for low density polyethylene (LDPE) and its influence on the changes of mechanical properties of ultra nanohardness has not been studied in detail so far. The specimens of low density polyethylene (LDPE) were made by injection moulding technology and irradiated by low doses of beta radiation (0, 33, 66 and 99 kGy). The changes in the microstructure and micromechanical properties of surface layer were evaluated using FTIR, WAXS and instrumented ultra nanohardness test. The results of the measurements showed considerable increase in mechanical properties (indentation hardness, indentation elastic modulus) when the low doses of beta radiation are used.

## KEYWORDS

low density polyethylene (LDPE), cross-linking, ultranano-hardness, surface layer

## 1 INTRODUCTION

Cross-linking is a process in which polymer chains are associated through chemical bonds [Woods 1974]. Cross-linking is carried out by chemical reactions or radiation and in most cases the process is irreversible [Barlow 1979]. Ionizing radiation includes high-energy electrons (electron beam -  $\beta$ -rays) (Fig. 1). These not only are capable of converting monomeric and oligomeric liquids into solids, but also can produce major changes in properties of solid polymers.

The engineering polymers are a very important group of polymers which offer much better properties in comparison to those of standard polymers. Both mechanical and thermal properties are much better than in case of standard polymers [Pharr 1998, Oliver 2004]. The production of these types of polymers takes less than 1 % of all polymers (Fig. 2).

Nowadays, polyethylene is one of the most widely used polymers [Drobny 2003]. The manufacture and processing of polyethylene have significantly increased within the last decade. The reason of this increase is not only the world-wide economic growth but also expansion of this polymer into the new industrial sectors [Ragan 2012, Zamfirova 2010]. Increasing need in the polyethylene consumption brings about increased

interest and activities connected to the exploitation of the recycled materials.

During recycling, polyethylene undergoes repeated cycles of processing combined with the periods of "aging", in which the polymer is used as a final product. The combination of these processes, hence, influences properties of the recycled material [Behalek 2013, Dobransky 2015 and 2016]. In order to assure quality of the final products manufactured from the recycled material, the properties of the repeatedly processed material have to be investigated and understood to predict its performance during processing and product performance during the subsequent life-cycles.

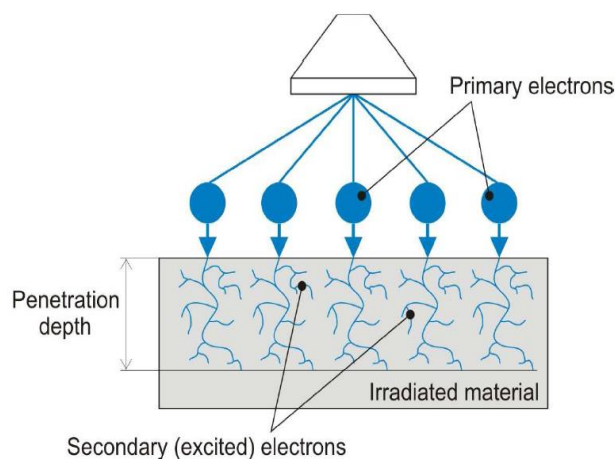


Figure 1. Design of Electron rays

Mechano-chemical degradation, in general, comprises the processes related to breaking of chemical bonds in polymer, which may be induced by mechanical stress, increased temperature and oxygen presence. Each of these factors, either solely or in mutual combination, influences resulting properties of polyethylene. The commonly accepted degradation mechanism of polyethylene involves the chain scission caused by thermo-mechanical stress, which induces formation of macro-radicals. At the low oxygen content, the macro-radicals will react with each other forming polymer branches and unsaturated groups. At the high oxygen content, macro-radicals react with oxygen enhancing thus formation of free radicals attacking polymer chains and resulting in chain scission and molar mass decrease [Manas 2015].

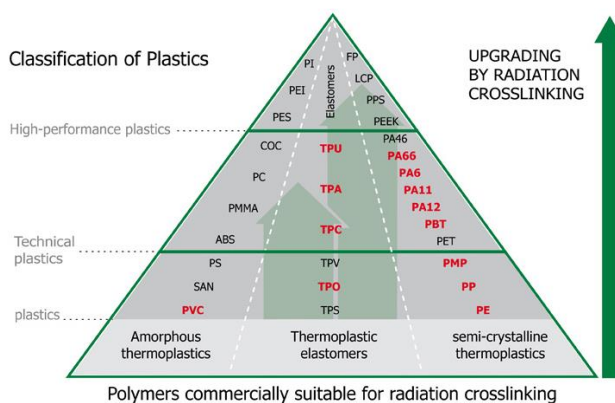


Figure 2. Upgrading by radiation cross-linking of LDPE

It is generally supposed that exposure of polymer melt to oxygen, known as thermo oxidation, affects the polyethylene degradation more significantly than the mechanical stress during extrusion. The theory and mechanism of the

polyethylene degradation is discussed in several monographs and papers. It is believed that general degradation mechanism during thermo oxidation is roughly similar both for low density polyethylene (LDPE) and high density polyethylene (HDPE). However, the course of degradation depends strongly on the polymer type and polymer treatment during processing. As the degradation predominantly takes place in the amorphous phase of these semi-crystalline polymers, the difference between degradation course of LDPE and HDPE, possessing the different degree of crystallinity, is obvious [Ovsik 2012, 2014 and 2015].

Mechanical thermo-oxidative degradation of high density polyethylene has been studied for example in a twinscrew extruder using Philips and Ziegler-Natta HDPE types. The results of the study show an increase of the polymer molar mass after five processing cycles in extruder at 200 and 240 °C, respectively, as evaluated from the shift of the molar mass distribution curves towards a high molar mass region. The shift is more pronounced at high temperature and when using the HDPE of Philips type. The results of the study published in, suggest; however, that HDPE did not degrade to any significant degree during 10 extrusion cycles, as concluded from the measurements of elongation at break, oxygen induction temperature, melt flow index and number average molar mass determined by gel permeation chromatography (GPC).

The interaction of polymers with energetic ion or atom beams is of theoretical and practical interest. The related physical and chemical changes induced with high yields may lead to large modifications in the various characteristics of polymers. These include electrical and optical properties, surface wettability, adhesive bonding, biocompatibility, surface hardness and wear resistance, etc. In particular, there are several studies on the various effects induced in polyethylene (PE) by ion beams.

The aim of this paper is to study the effect of ionizing radiation with low doses beta irradiation, on mechanical properties of surface layer of low-density polyethylene (LDPE) and compare these results with those of non-irradiated samples.

## 2 EXPERIMENTAL

### 2.1 Material and methods

For this experiment low density polyethylene (DOW LDPE 780E) (unfilled, LDPE) was used. Irradiation was carried out in the company BGS Beta Gamma Service GmbH & Co, KG, Saal an der Donau, Germany with the electron rays, electron energy 10 MeV, doses minimum of 0, 33, 66 and 99 kGy on air by the ambient temperature.

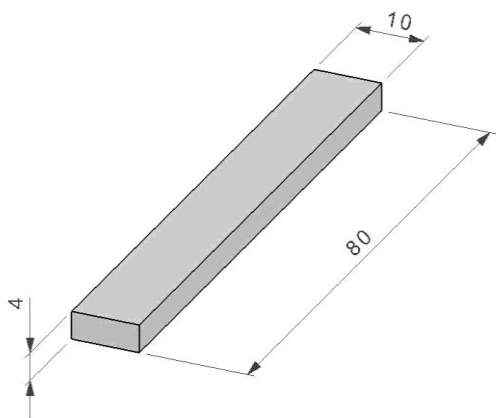


Figure 3. Dimensions of sample

The samples with dimensions, which are displayed in Fig. 3, were made using the injection moulding technology on the injection moulding machine Arburg Allrounder 420C. Processing temperature range 210–240 °C, mold temperature 50 °C, injection pressure 80 MPa, injection rate 50 mm/s

### 2.2 Ultra nanoindentation test

Nano-indentation test were done using an Ultra Nanoindentation Tester (UNHT) (Fig. 4), CSM Instruments (Switzerland) according to the CSN EN ISO 14577. Load and unload speed was 1000 µN/min. After a holding time of 90 s at maximum load 500 µN the specimens were unloaded. The specimens were glued on metallic sample holders.

$$H_{IT} = \frac{F_{\max}}{A_p} \quad (1)$$

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

The indentation hardness ( $H_{IT}$ ) was calculated as maximum load ( $F_{\max}$ ) to the projected area of the hardness impression ( $A_p$ ) and the indentation modulus ( $E_{IT}$ ) is calculated from the Plane Strain modulus ( $E^*$ ) using an estimated sample Poisson's ratio.



Figure 4. Ultra Nanoindentation tester

### 2.3 Gel Content

Gel test is done to find the content of non-filtered phase – gel of the given material according to standard CSN EN 579. The portion of 1 g (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 LDPE because it dissolves the amorphous part of LDPE, the crosslinking part does not dissolve. The mixture was extracted for 6 hours. Then solutes were separated by distillation. After removing the residual Xylol the crosslinked extract was rinsed by distilled water. The rinsed extract was dried for 6 - 8 hours 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 crosslinking.

$$G_i = \frac{m_3 - m_1}{m_2 - m_1} \cdot 100 \quad (3)$$

Where,

$G_i$  is the degree of crosslinking of each specimen expressed in percentage  
 $m_1$  is the weight of the cage and lid in milligrams  
 $m_2$  is the total of weights of the original specimen, cage and lid in milligrams  
 $m_3$  is the total of the weights of the residue of specimen, cage and lid in milligrams.  
The result of  $G_i$  is rounded to the nearest whole number

## 2.4 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  $\text{CuK}\alpha$  radiation was Ni-filtered. The scans ( $4.5^\circ \times 2^\circ/\text{min}$ ) in the reflection mode were taken in the range  $5\text{--}30^\circ \times 2^\circ$ . The sample crystallinity ( $X$ ) was calculated from the ratio of the crystal diffraction peaks and the total scattering areas. Crystal size  $L_{110}$  of  $\alpha$  most intensive peak at 110 was calculated using Scherrer equation. As a standard "perfect" crystal terephthalic acid with the peak at  $2\Theta = 17.4^\circ$  and the half maximum breadth  $0.3^\circ \times 2^\circ$  was chosen.

## 2.5 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  $45^\circ$ ). 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  $2\text{ cm}^{-1}$  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.

## 3 RESULTS AND DISCUSSION

The development of micromechanical properties of irradiated low density polyethylene (LDPE) was characterized by the instrumented test of ultra nanohardness, as can be seen in Fig. 5. The highest values (51.02 MPa) of indentation hardness ( $H_{IT}$ ) were found at 66 kGy radiation dose. The lowest value of indentation hardness (47.13 MPa) was measured on irradiated low density polyethylene (LDPE) sample at 33 kGy. The increase of indentation hardness at 66 kGy radiation dose was by 6 % compared to the non-irradiated low density polyethylene (LDPE).

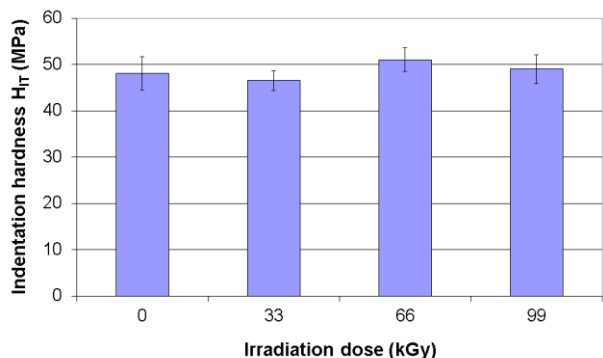


Figure 5. Indentation hardness  $H_{IT}$  of LDPE vs. irradiation doses

The results of the elastic indentation modulus ( $E_{IT}$ ) measurements illustrated in Fig. 6., which shows clearly that the lowest values of stiffness were measured low density

polyethylene (LDPE) irradiated by 0 kGy dose (0.34 GPa), while the highest values were reached in low density polyethylene (LDPE) irradiated by 66 kGy dose (0.42 GPa). A significant increase of stiffness (23 %) was recorded at the radiation dose of 66 kGy compared to the non-irradiated low density polyethylene (LDPE).

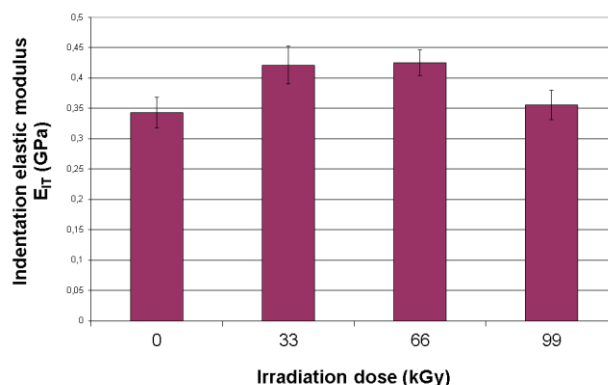


Figure 6. Indentation elastic modulus  $E_{IT}$  of LDPE vs. irradiation doses

Irradiation doses	0 kGy	33 kGy	66 kGy	99 kGy
Gel content (%)	0	0	28	54

Table 1. Gel content of LDPE vs. irradiation doses

Plastic ( $W_{\text{plast}}$ ) and elastic ( $W_{\text{elast}}$ ) deformation measured during ultra nanohardness test also showed (Fig. 7) that the lowest values of plastic deformation work were measured at the radiation dose of 66 kGy, while the highest values of plastic deformation work were found at the radiation dose of 33 kGy. Elastic part of deformation work (reverse relaxation coefficient ( $\eta_{IT}$ )) measured by instrumented test of ultra nanohardness showed that the highest creep values were measured on non-irradiated low density polyethylene, while the lowest creep value was found in low density polyethylene (LDPE) irradiated by 33 kGy dose.

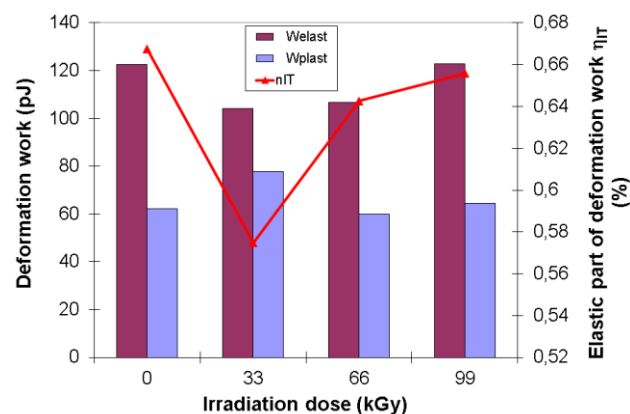


Figure 7. Deformation work of LDPE vs. irradiation doses

Sample LDPE	$X_{X\text{-ray}}$ , %, $\pm 1\%$
0 kGy	34.21
33 kGy	36.99
66 kGy	38.38
99 kGy	35.58

Table 2. X-ray diffraction of non-irradiated and irradiated LDPE

Material deformation in time under constant stress (indentation creep) measurement by instrumented test of ultra nanohardness is shown in Fig. 8. The highest creep values were

measured at the radiation dose of 33 kGy (6.12 %), while the lowest creep value was found in low density polyethylene irradiated by 66 kGy dose (5.21 %). The creep dropped by 10 % as a result of radiation, which represents a considerable increase of surface layer resistance.

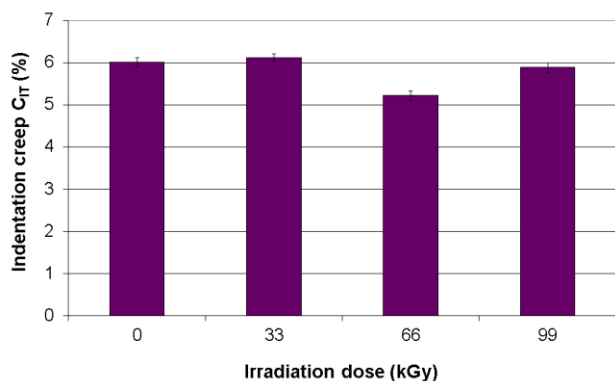


Figure 8. Indentation creep  $C_{IT}$  of LDPE vs. irradiation doses

Radiation, which penetrated through specimens, 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. 3D net together with crystalline phase caused changes mainly in the surface layer, which led to a significant increase of indentation hardness and stiffness of surface layer. This caused higher resistance of surface layer to wear, scratch, etc. Also, the creep values decreased as a result of changes made after the specimens were subjected to beta radiation.

Gel content showed the highest values at radiation dose of 99 kGy at which it reached 54 % degree of cross-linking, while the lowest value of degree of cross-linking was measured on non-irradiated and also on irradiated LDPE sample at 33 kGy (Table 1).

In the Fig. 9 is displayed typical X-ray diffraction spectrum of the non-irradiated and irradiated low density polyethylene (LDPE). There is an apparent presence of  $\alpha$ -phase in the non-irradiated specimen. The greatest grow of  $\alpha$ -phase is seen at the radiation dose of 66 kGy.

When applying  $\beta$ -radiation the structure of low density polyethylene undergoes loss and then growth of the crystalline phase (Table 2). 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 34.21-38.38 %). The greatest size of crystalline phase was found in the case at the radiation dose of 66 kGy (38.38 %). The lowest size of crystalline phase was found in the case at non-irradiated (34.21 %). Its influence on the mechanical behavior is insignificant, because of that cross-linking occurs in the remaining noncrystalline part which has a significant influence on the mechanical properties of the surface layer.

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. 10). For evaluation hydroxyl groups we used an area of the strip integrated in the area of  $3680-3126\text{ cm}^{-1}$ , (Each specimen was measured twice on both sides). For evaluation carbonyl groups we used an area of the strip integrated in the area of  $1816-1500\text{ cm}^{-1}$ , (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.

The smallest values of relative change of representation of hydroxyl and carbonyl groups were found at radiation dose of 0 kGy. At this dose the worse values of mechanical properties of the tested low density polyethylene (LDPE) were measured. The greatest change was found at radiation dose of 66 kGy. These changes of the structure correspond with the changes of mechanical properties of modified low density polyethylene (LDPE) by beta radiation.

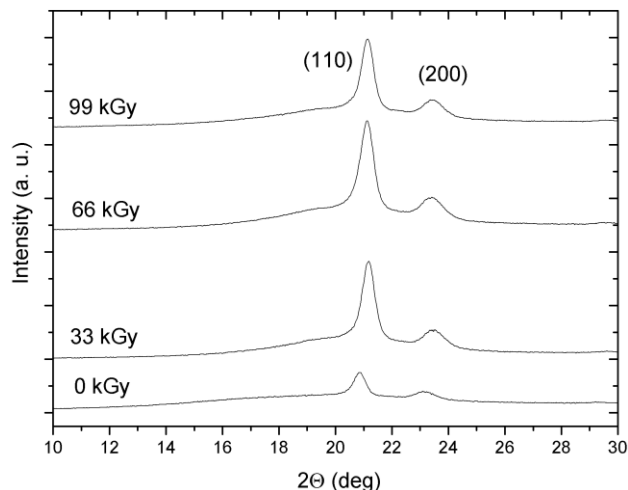


Figure 9. X-ray diffraction of non-irradiated and irradiated LDPE

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

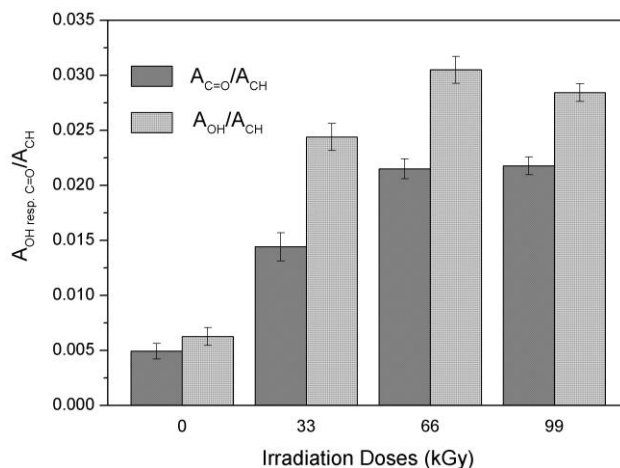


Figure 10. Change in the relative representation of hydroxyl and carbonyl groups of LDPE in relation to the irradiation doses

#### 4 CONCLUSIONS

The experimental study deals with the effect of modification of the surface layer by irradiation cross-linking on the properties of the surface layer of low density polyethylene (LDPE). Low density polyethylene was modified by beta irradiation at doses of 0, 33, 66 and 99 kGy. The changes of mechanical properties

were found at the radiation dose of 66 kGy for indentation hardness and elastic modulus (which increased by 6% and 23%) compared to the non-irradiated low density polyethylene. Improvement of mechanical properties in nano and macro scale of radiated low density polyethylene (LDPE) has a great significance also for industry. The modified low density polyethylene shifts to the group of materials which have considerably better properties. Its nanomechanical properties make low density polyethylene ideal for a wide application in the areas where higher resistance to wear, scratch are required.

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#### REFERENCES

- [Barlow 1979] Barlow, A. et al. 1979. Radiation processing of polyethylene. *Radiat. Phys. Chem.* 14, (1979) 783.
- [Behalek 2013] Behalek, L. and Dobransky, J. Conformal cooling of the injection moulds. *Applied Mechanics and Materials*. Vol. 308 (2013). pp. 127-132. ISSN 1660-9336.
- [Drobny 2003] Drobny, J. G. *Radiation Technology for Polymers*, CRC Press, New York, (2003).
- [Dobransky 2015] Dobransky, J. et al. Examination of Material Manufactured by Direct Metal Laser Sintering (DMLS). *Metalurgija*. Vol. 54. No. 3 (2015). pp. 477-480. ISSN 0543-5846.
- [Dobransky 2016] Dobransky, J. et al. Determination of the EOS Maragingsteel MS1 Material Resistance at Low Temperatures. *Metalurgija*. Vol. 55. No. 3 (2016). pp. 449-452. ISSN 0543-5846.
- [Manas 2015] 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*, (2015) 114, pp. 25-30.

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

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

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

[Ovsik 2014] Ovsik, M. et al. Effect of beta low irradiation doses on the filled PA66 measured by micro-indentation test. *Advanced Materials Research*, 1025-1026, (2014), pp. 415-418.

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

[Ragan 2012] Ragan, E. et al. Dynamic of Taking out Molding Parts at Injection Molding. *Metalurgija*. Vol. 51. No. 4 (2012). pp. 567-570. ISSN 0543-5846.

[Woods 1974] Woods, R. J., and Picaev, A. K. *Applied radiation chemistry: radiation processing*. New York: John Wiley, 1994.

[Zamfirova 2010] Zamfirova, G. et al. Microindentation study of Electron Beam Irradiated Polyamide Samples. *Chemicke Listy*, 104 (2010), 283-286.

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