IMPROVEMENT OF POLYMER SURFACE LAYER BY ELECTRON RADIATION

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This article deals with improving properties of surface layer of varying polymer products. Surface layer of the tested polymer was influenced by electron radiation with varying intensity. This resulted in improved resistance to wear due to creation of 3D network within the polymer structure. The properties were measured by instrumented test using a contemporary ultra-nano indentation device. The acquired data was then evaluated by OLIVER & PHARR method. Irradiation of surface layer caused a 16 % (26 %) improvement of mechanical properties in comparison to the unaltered material.

KEYWORDS

Radiation, electron beam, cross-linking, ultra-nano hardness, indentation

1 INTRODUCTION

As is well known, the industrial cross-linking of polymers can help to improve the material properties of polymers, such as mechanical, thermal and chemical properties. [Gehring 2000]

Beta radiation cross-linking is mostly used for treatment of the insulation cables, heat-shrinking sheets, tires, foams, tubes, etc. [Makuuchi 2012]

Polybutylene terephthalate (PBT) is a semi-crystalline thermoplastic material, which belongs to the polyester family. PBT is a polymer which owns great material properties such as high strength and rigidity, low creep, high dimensional stability, good impact strength, wear and frictional resistance, low moisture absorption, good chemical resistance etc. This polymer is commonly used in the automotive, textile, electric industry and for production of consumer products. It is also desirable to modify PBT using fillers or blend it together with other polymeric materials. [Metanawin 2015]

It is possible to crosslink polymers many ways, but the most common ways are gamma and beta rays. The main difference between these two kinds of rays is their ability to penetrate the crosslinked material. The penetration of beta rays depends on the energy of accelerated electrons, while the penetration capacity of gamma rays is generally high. [Drobny 2003]

The scientists from Brazil tried to create the biodegradable poly(lactic acid)/PBT polymer with the concentration of 3, 5, and 10 wt % of PBT, which produced in a twinscrew extruder. As a compatibilizer they used the addition of ethylene–glycidyl methacrylate copolymer. [Santos 2018]

There are many research papers concentrated on the possible modification and improvement of PBT using fillers, other polymers etc. [Li 2017], [Shrivastava 2016]

This study is concentrated on the ultra-nano-mechanical properties of irradiated glass fiber filed PBT (PBT 35%GF) and it is simultaneously follow-up research on our previous research. The aim of this paper is to study the effect of ionizing radiation with different doses, on ultra-nano mechanical properties of PBT and compare these results with those of non-irradiated samples. The study is carried out due to the ever-growing employment of this type of polymer (PBT).

2 EXPERIMENTAL

2.1 Material

A construction material PBT filled with 35% of glass fibres was chosen as a test subject for this experiment. It is used in numerous technical applications within the automotive industry. The material is labelled PBT V-PTSCREATEC-B3HZC * M800/25 and was obtained from company PTS. The material was enriched by 5% of cross-linking agent TAIC (triallyl isocyanurat) and afterwards irradiated by ionizing radiation which led to a creation of 3D network. The cross-linking agent allows a formation of the 3D network, thus increasing mechanical properties of the tested polymer.

2.2 Sample preparation

Samples were manufactured according to the ČSN EN ISO 179 standard with dimensions (80 x 10 x 4) mm (Figure 1). It was done on injection moulding machine Arburg Allrounder 470H and the parameters of the process can be seen in table 1. Before the tested material (in form of granules) was used, it had to be dried by a device labelled TERMOLIFT, as recommended by the manufacturer (Table 1).

Parameters	Unit	PBT 35%GF
Injection Pressure	MPa	65
Cooling Time	s	20
Mould Temperature	°C	65
Zone 1	°C	270
Zone 2	°C	275
Zone 3	°C	280
Zone 4	°C	285

Table 1: Process parameters

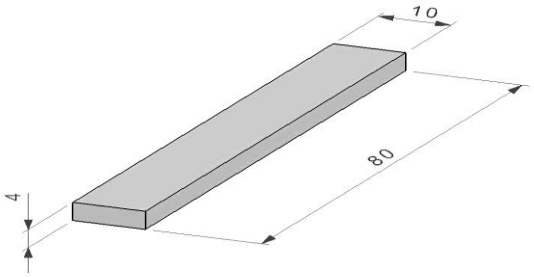

Figure 1: Dimension of sample

2.3 Irradiation

The irradiation of test subjects was performed in Germany in cooperation with company BGS (Beta- Gamma- Service) GmbH and Co, KG located in Saal an der Donau.

As a source of electron beta radiation a high voltage accelerator Rhodotron with maximum energy 10 MeV was chosen. Dosages of radiation were 33, 66 and 99 kGy. One pass in accelerator irradiated the test subject with a dosage of 33 kGy. In order to reduce the thermal stress of test subject, the irradiation with high dosages was done in more steps.

2.4 *Nano-indentation test*

An Ultra-nano indentation tester (UNHT³) manufactured by company ANTHON PAAR was used to evaluate the effect of the radiation dosages upon properties of surface layers of the tested polymer (Figure 2). Measurements were executed in compliance with ČSN EN ISO 14577 standard and tested parameters were evaluated by OLIVER and PHARR method. BERKOVICZ was used as a penetration body. Table 2 displays parameters used for measurements.

Parameters	Unit	Value
Maximum Load	uN	500
Load/Unload Speed	uN/min	1000
Holding Time	s	90

Table 2: Measurement parameters

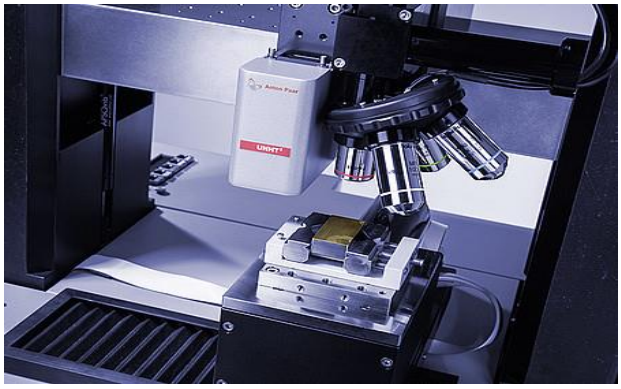

Figure 2: Nano-indentation tester

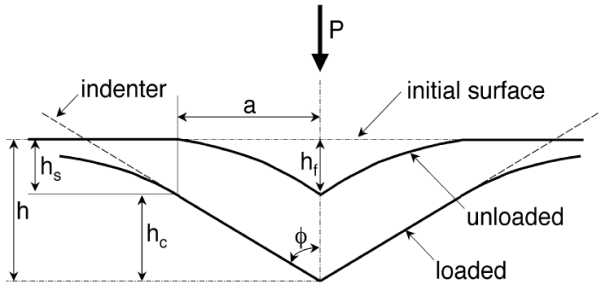

Figure 3: Schematic illustration of indentation curve

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

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

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 (hc). The specimens were glued on metallic sample holders (Figure 3). **[Oliver 2004]**

The indentation modulus is calculated from the Plane Strain modulus using an estimated sample Poisson's ratio: **[Ovsik 2015]**

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

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: **[Pharr 1998]**

$$C_{IT} = \frac{h_2 - h_1}{h_1} \cdot 100 \tag{4}$$

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

3 RESULTS AND DISCUSSION

Cross-linking is a chemical process in which a creation of a 3D network within the structure of linear polymers is initiated by ionizing radiation. These chemical reactions lead to permanent change of the structure (3D network) of the polymer. The ionizing radiation forms active centers that react with each other. The surface layer undergoes changes which have a considerable influence on the ultra-nano mechanical properties of PBT.

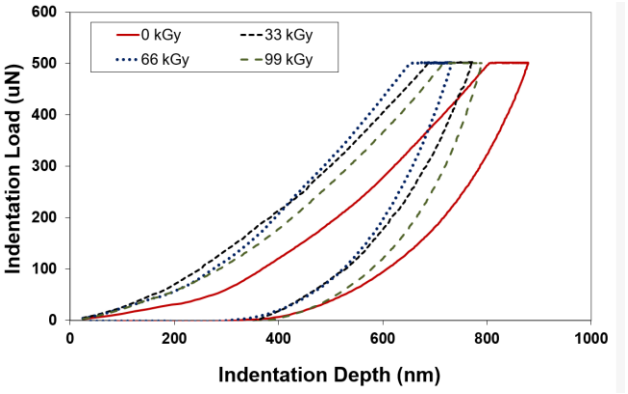

Figure 4: Indentation characteristic of irradiated PBT

Results of the instrumented ultra-nano hardness test are values of force (P) and depth (h). The most commonly used method to calculate hardness and elastic modulus is OLIVER and PHARR.

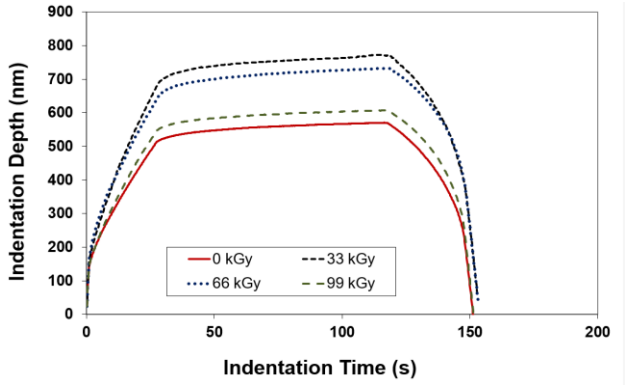

Figure 5: Indentation characteristic of irradiated PBT

The method is based on principles of elastic-plastic loading and elastic deloading. Measured elementary properties are maximum loading force Pmax, maximum indentation depth hmax and stiffness S, which is defined as tangent direction of the beginning area of the deloading curve. Figure 4 shows the dependence of the indentation force on the depth of the indentation. This dependence is used to determine mechanical

properties of surface layers. Varying properties of tested materials are apparent.

Figure 5 displays the dependence of the depth of the indentation on the time of the indentation. It provides means to calculate creep behavior, which can be used to describe how surface layer behaves when exposed to long term constant load.

The measured values of the ultra-nano indentation test were obtained for PBT irradiated with beta rays as shown in Table 3.

Parameters	Unit	0 kGy	33kGy	66kGy	99kGy
Indentation Depth	nm	727,67	746,81	698,04	692,23
Indentation Hardness	MPa	54,86	49,65	63,04	63,38
Vickers Hardness	Vickers	5,08	4,60	5,84	5,87
Indentation Modulus	GPa	0,93	0,90	1,17	1,14
W_{el}	pJ	59,18	54,66	63,59	52,56
W_{pl}	pJ	93,48	118,77	95,60	101,97
Indentation creep	%	12,14	12,35	11,86	11,84

Table 3: Summary of measured values

Products made from PBT polymer are required to have good surface quality as well as wear resistance. Electron radiation is one of many technologies that can increase the longevity of the surface layer. The main parameter used for description of surface layer properties is the depth of the indentation. As can be seen in figure 6, the depth of the indentation of the tested PBT can be tracked by ultra-nano indentation technology.

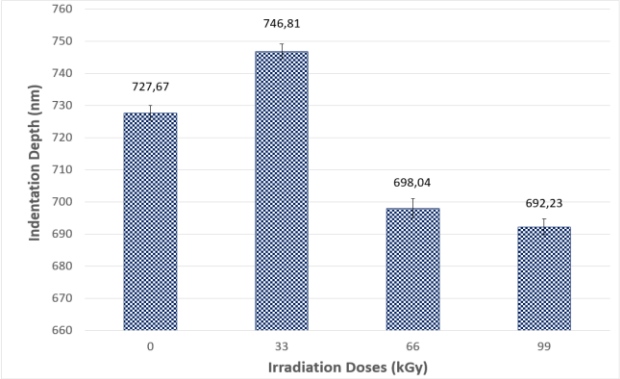

Figure 6: **Indentation depth of irradiated PBT**

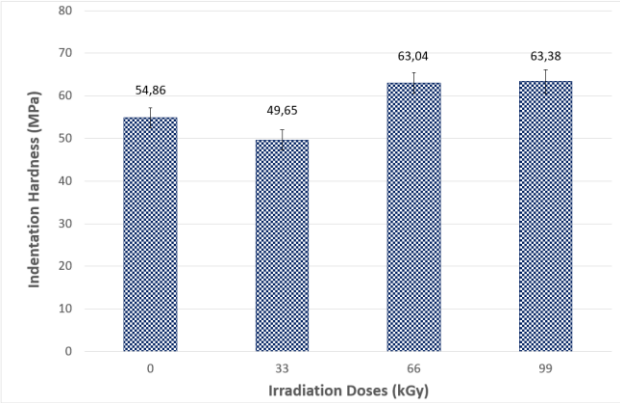

Figure 7: **Indentation hardness of irradiated PBT**

Graphic evaluation of measured results of indentation hardness in the dependence on different radiation doses for PBT are shown in Figure 7. From measured values of ultra-nano indentation hardness follows that radiation crosslinking at PBT takes effect by higher hardness at tested polymers. The lowest value of indentation hardness was found at non-irradiated PBT (54.8 MPa). The highest value of indentation hardness was measured at PBT irradiated at the dose of 99 kGy. The difference in hardness at tested PBT (63.4 MPa) was approximately 16 %. 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 99 kGy is probably caused by material degradation after irradiation.

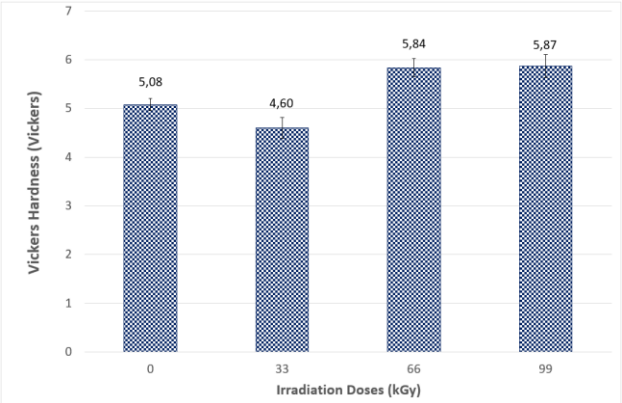

Figure 8: **Vickers hardness of irradiated PBT**

Indentation modulus is an important parameter used to describe a surface toughness of the tested PBT. The tangent direction of the de-loading curve is used to determine the indentation modulus, which corresponds with elastic (Young) modulus. Results of the indentation hardness were similar to those of indentation modulus, which mostly corresponds with indentation hardness (Figure 7). Highest values of the indentation modulus, approximately 26% higher in comparison to an unaltered material, were measured in PBT irradiated by a dosage of 66 kGy. In contrary, lowest values of the indentation modulus were measured in the unaltered material, as is evident from figure 9.

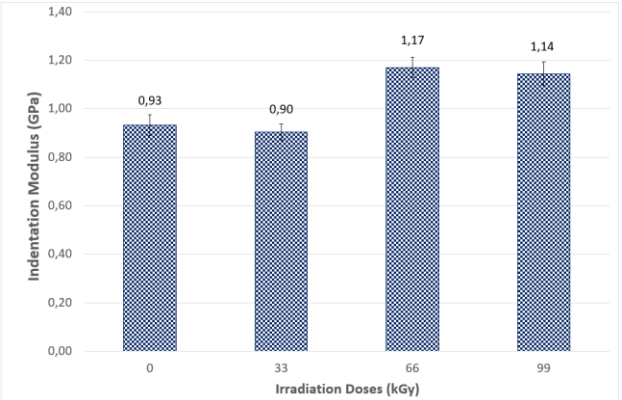

Figure 9: **Indentation modulus of irradiated PBT**

Important parameter for rating the surface layer of tested material is deformation work. Deformation work is divided into two components, plastic and elastic. Highest value of elastic deformation work was measured in original unaltered material (59.2 pJ), on the other high as dosage got higher, elastic deformation work got lower, where lowest value was 63.6 pJ measured in material irradiated by 66 kGy of radiation.

Plastic part of deformation work is main part of whole deformation work. Original unaltered material value of plastic

part of work was 93.5 pJ. Lowest value of plastic work was measured in PBT sample irradiated by 33 kGy of radiation and it was 118.8 pJ. This article describes influence of beta radiation on surface properties of tested polymer (PBT), which was modified by electron radiation. Surface was irradiated by 33 kGy, 66 kGy and 99 kGy of radiation.

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

Higher radiation dose does not significantly influence the ultra-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 ultra-nano hardness results shows that when the highest radiation doses are used, ultra-nano mechanical properties decrease. This can be caused by degradation of the material induced by radiation.

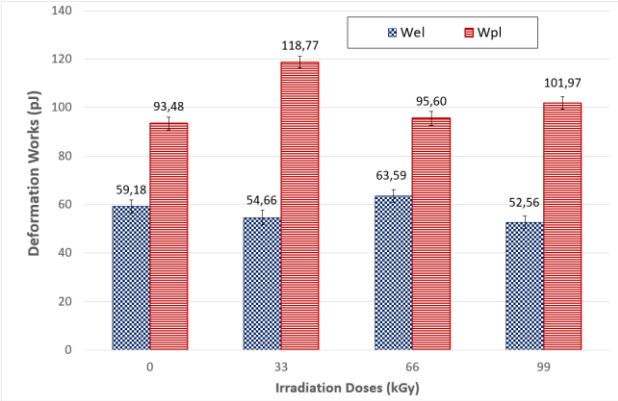

Figure 10: **Deformation works of irradiated PBT**

4 CONCLUSIONS

As the measured data show, radiation cross-linking significantly effects mechanical behavior of polymers. Due to the irradiation process, polymers can either undergo degradation or cross-linking. These changes are in process simultaneously, which is why choosing the right amount of radiation to achieve the best properties for any given application is important. Another factor that has to be taken into consideration is price, which is higher for bigger amounts of radiation. To study the effect of radiation on properties of polymers, a PBT with 35% glass fibers content was chosen and afterwards irradiated by dosages of 33, 66 and 99 kGy.

Results of the ultra-nano instrumented hardness test show that mechanical properties of the surface layer were improved with increasing amounts of radiation. For the material exposed to 99 kGy of radiation, the indentation and Vickers hardness was improved by 16%, while the elastic modulus rose by 26%. Elastic and plastic deformation work was improved as well.

These findings about radiation cross-linking of materials could lead to lower prices of final polymer products by replacing the unaltered material with material modified by radiation cross-linking. The modified material can have some properties that are similar with base material. Since the radiation cross-linking is conducted after the processing of the polymer, the manufacture process remains the same. Advantage of this fact is that any requested properties can be achieved after the granulate manufacture process.

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