THE BEHAVIOUR OF CROSS-LINKING FILLED PBT MEASURED BY NANO-HARDNESS

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DOI: 10.17973/MMSJ.2016_10_201678
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Radiation crosslinking of filled PBT is a well-recognized modification of improving basic material characteristics. 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 behaviour. The specimens of 30% glass fiber filled PBT were made by injection moulding technology and irradiated by doses of beta radiation (0, 33, 66 and 99 kGy). The change of nano-mechanical properties is greatly manifested mainly in the surface layer of the modified PBT where a significant growth of nano-mechanical values can be observed. Indentation modulus increased from 1.1 to 1.8 GPa (increasing about 64%) and indentation hardness increased from 56 to 85 MPa (increasing about 52%).The results of the measurements showed considerable increase in nano-mechanical properties (indentation hardness, indentation elastic modulus, indentation creep) when beta radiation are used.

KEYWORDS
glass fiber, polybutylene terephthalate (PBT), cross-linking, nano-hardness, nano-indentation

1 INTRODUCTION

Polybutylene terephthalate (PBT) is a semi-crystalline thermoplastic of the polyester family, which crystallizes very slowly and is therefore available in an amorphous-transparent or crystalline-opaque condition, depending on the processing method.

PBT are characterized by their high strength and rigidity, dimensionally stable, low tendency to creep, very good frictional and wear resistance, good impact strength, very low coefficient of thermal expansion, good chemical resistance to acids, very good electrical characteristics, very low moisture absorption, good adhesion and welding ability. Furthermore, PBT, like all polyesters, has very good frictional and wearing properties. Compared to PET, PA6 has a better impact strength - particularly at low temperatures.

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. 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.

Common PBT, 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 PBT structure. The utility properties of PBT improve when the noncrystalline part of PBT is cross-linked.

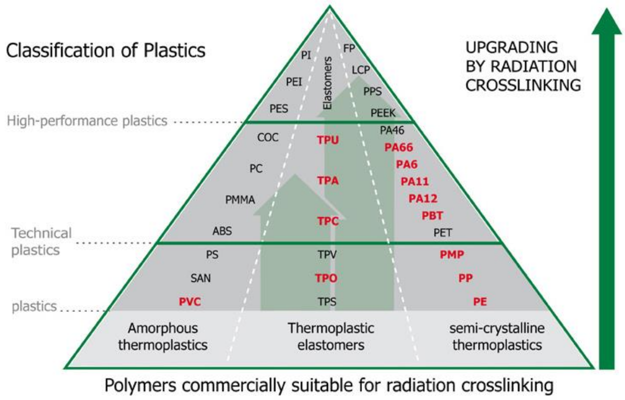

Figure 1. Upgrading by radiation cross-linking of PBT

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. The production of these types of polymers takes less than 1 % of all polymers (Fig. 1).

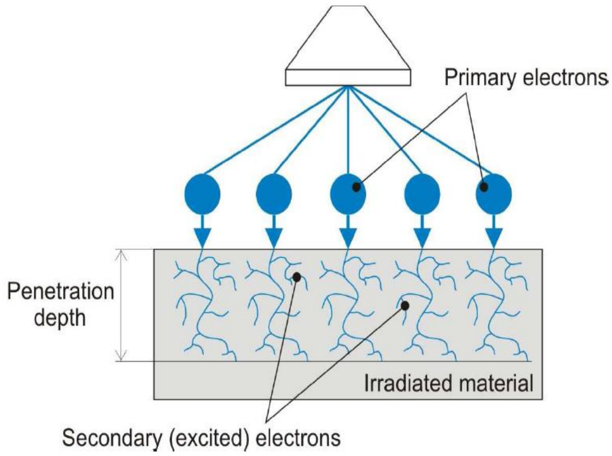

Figure 2. Design of Electron rays

The aim of this paper is to study the effect of ionizing radiation with different doses, on nano-mechanical properties of filled 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.

2 EXPERIMENTAL

2.1 *Material and methods*

For this experiment Polybutylene terephthalate PBT V-PTS-CREATEC-B3G6 filled by 30% glass fiber (PBT+30%GF), 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. The prepared specimens were irradiated with doses of 33, 66 and 99 kGy at BGS Beta-Gamma Service GmbH & Co. KG, Germany (fig. 3).

The samples were made using the injection molding technology on the injection molding machine Arburg Allrounder 470H. Processing temperature 245–265 °C, mold temperature 70 °C, injection pressure 75 MPa, injection rate 65 mm/s.

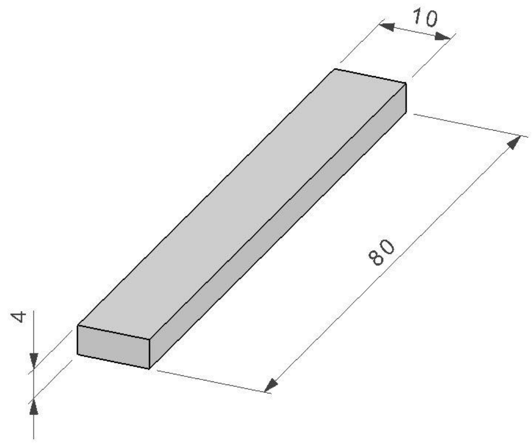

Figure 3. Dimension of sample.

2.2 Nano-indentation test

Nano-indentation test were done using a Nano-indentation tester (NHT) (fig. 5), CSM Instruments (Switzerland) according to the CSN EN ISO 14577. Load and unload speed was 100 mN/min. After a holding time of 90 s at maximum load 50 mN the specimens were unloaded. The specimens were glued on metallic sample holders.

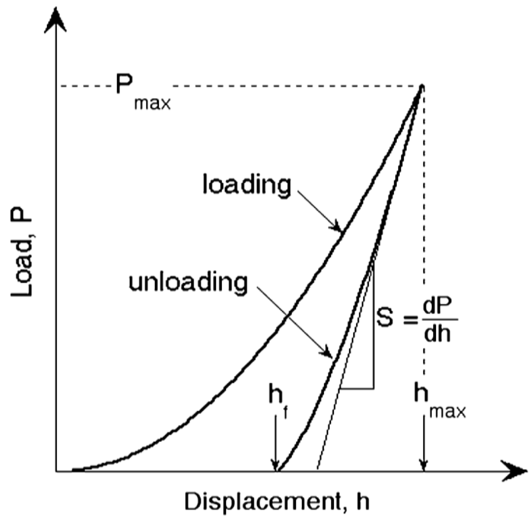

Figure 4. Schematic illustration of indentation curve

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

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

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 (fig. 4).

Figure 5. Nano-indentation tester

3 RESULTS AND DISCUSSION

The results of instrumented indentation are summarized in Table 1. The greatest values of nano-hardness test were obtained for PBT+30%GF irradiated with dose of 66 kGy.

Table 1. Summary of measured values

Irradiation doses	0kGy	33kGy	66kGy	99kGy
H_{IT} (MPa)	56.37	76.64	**84.79**	79.84
E_{IT} (GPa)	1.14	1.69	**1.82**	1.75
C_{IT} (%)	38.90	32.91	**28.13**	29.72
W_{el} (uJ)	1.81	1.30	**1.31**	1.34
W_{pl} (uJ)	3.07	2.53	**2.48**	2.54

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

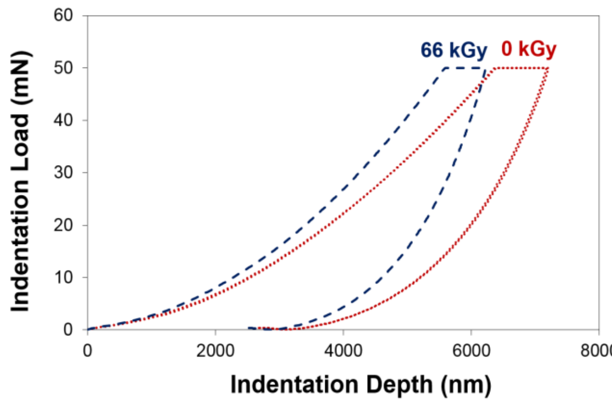

Figure 6. Indentation characteristic of irradiated

The fig. 6 and fig. 7 shows a very important correlation between the force and the depth of the indentation. The correlations provide very valuable information on the behaviour of tested material and the modified surface layer. The correlation between the force and the depth of the indentation in PBT+30%GF also proved very interesting. 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 PBT+30%GF showed considerably smaller depth of the impression of the indenter which can signify greater resistance of this layer to wear.

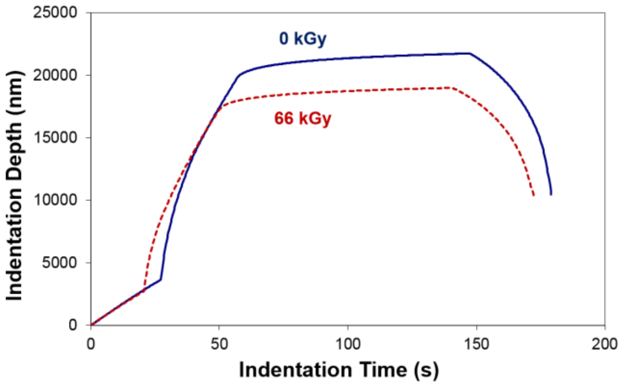

Figure 7. Indentation characteristic of irradiated

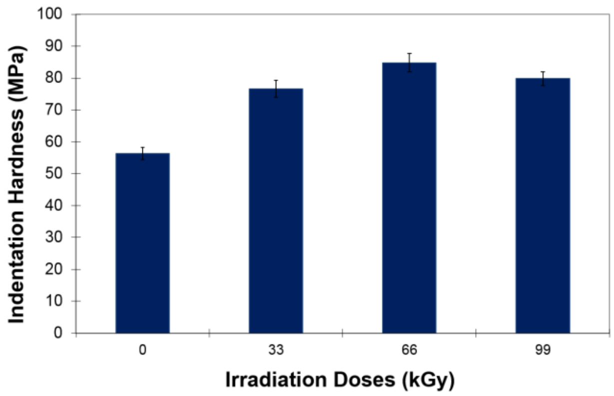

Figure 8. Indentation hardness vs. irradiation doses

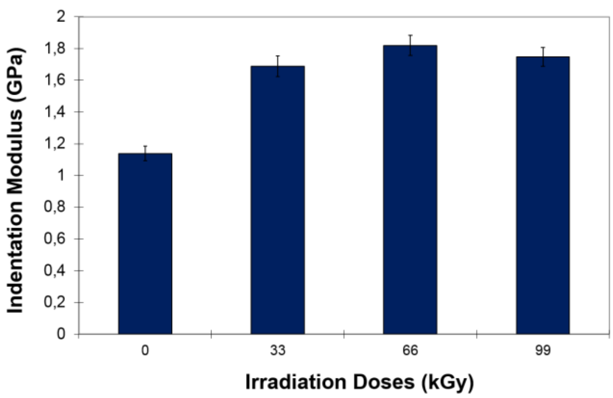

Figure 9. Indentation modulus vs. irradiation doses

Nano-indentation test of PBT+30%GF modified by beta radiation showed that the highest values of indentation hardness was found for PBT+30%GF modified by the radiation dose of 66 kGy (H_{IT} = 85 MPa). The smallest value of indentation hardness was found for non-irradiated PBT+30%GF (H_{IT} = 56 MPa). The increase of indentation hardness value for PBT+30%GF irradiated by the dose of 66 kGy was by 52% (Fig. 8) in comparison with the non-irradiated PBT+30%GF.

According to the results of nano-indentation test, it was found that the highest values of indentation modulus were achieved at the PBT+30%GF irradiated with dose of 66 kGy (E_{IT} = 1.8 GPa) (by 64% higher than compared with non-irradiated PBT). On the contrary, the lowest values of the indentation modulus were found for non-irradiated PBT+30%GF (E_{IT} = 1.1 GPa), as is seen at Fig. 9.

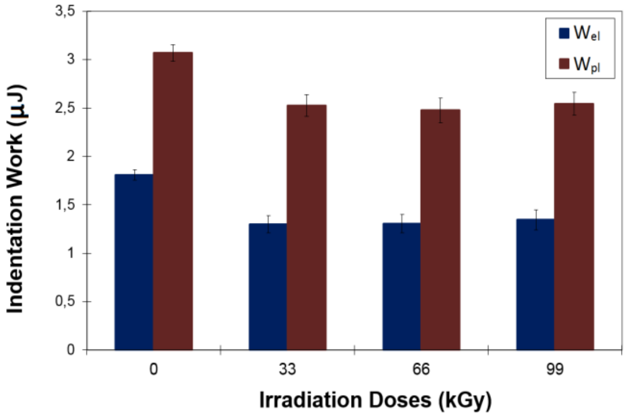

Figure 10. Indentation deformation work vs. irradiation doses

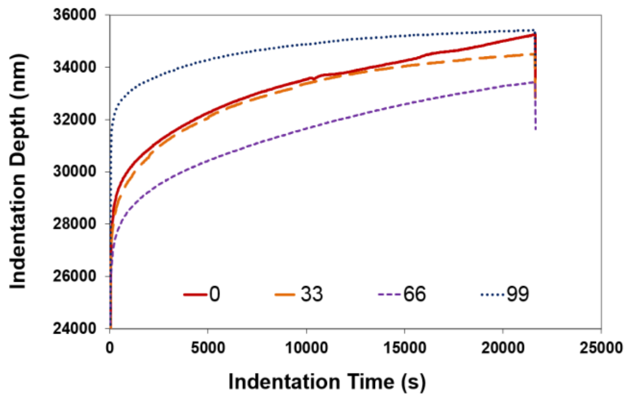

Figure 11. Indentation characteristic of irradiated - creep

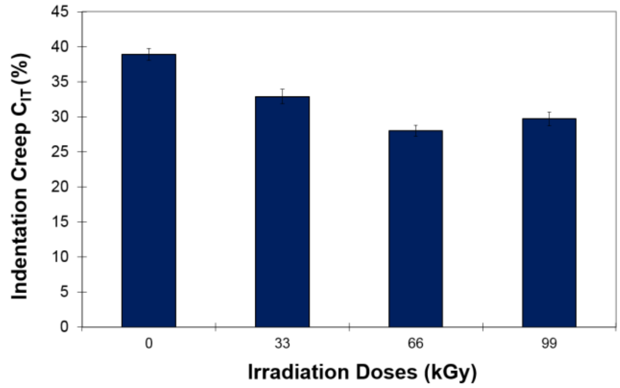

Figure 12. Indentation creep vs. irradiation doses

Higher radiation dose does not influence significantly the 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 nano-hardness results reveals that when the highest radiation doses are used, nano-hardness decreases which can be caused by radiation induced degradation of the material.

Interesting results were found for elastic and plastic part of deformation work. The highest value of elastic and plastic deformation work was measured for non-irradiated PBT+30%GF. The lowest value at both deformation work was found when the highest value of radiation dose of 66 kGy was applied (Fig. 10).

Very important values were found for indentation creep (C_{IT}). The lowest value of indentation creep was measured at radiation dose of 66 kGy (C_{IT} = 28.1%). The highest indentation creep value measured at non-irradiated PBT+30%GF (C_{IT} = 38.9%). Decrease in creep values was 39% for irradiated PBT+30%GF compared to the non-irradiated one as is seen at figure 11 and figure 12.

4 CONCLUSIONS

This research paper investigates influence of modified polymer material (beta radiation) on the nano-indentation test. The surface layer of PBT+30%GF is modified by β – radiation with doses of 33, 66 and 99 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.

The nano-mechanical properties of surface layer of PBT+30%GF modified by beta radiation improved significantly. The nano-hardness values increased by about 52% (66 kGy). Stiffness of surface layer increased significantly by 64% (66kGy) as a result of radiation. Also different depths of indentation in the surface layer of tested specimen were significantly different. The highest values of nano-mechanical properties were reached at radiation dose of 66 kGy. It also proved the fact that higher doses of radiation do not have very positive effects on the nano-mechanical properties, on the contrary due to degradation processes the properties deteriorate.

Improvement of nano-mechanical properties of radiated PBT+30%GF has a great significance also for industry. The modified PBT+30%GF shifts to the group of materials which have considerably better properties. Its nano-mechanical properties make PBT+30%GF ideal for a wide application in the areas where higher resistance to wear, creep are required. Commonly manufactured PBT+30%GF can hardly fulfil these criteria.

ACKNOWLEDGMENTS

This paper is supported by the internal grant of TBU in Zlin No. IGA/FT/2016/010 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.

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