MATEC Web of Conferences **76**, 02018 (2016) DOI: 10.1051/matecconf/20167602018
CSCC 2016

Micro-hardness of surface layer of irradiated Polybutene Terephthalate (PBT)

David Manas[1,a], Miroslav Manas[1], Martin Ovsik[1], Michal Stanek[1], Lenka Chvatalova[1], Pavel Stoklasek[1] and Lenka Hylova[1]

[1]*Tomas Bata University in Zlin, Nam. T.G.Masaryka 5555, Zlin, 760 01, Czech Republic*

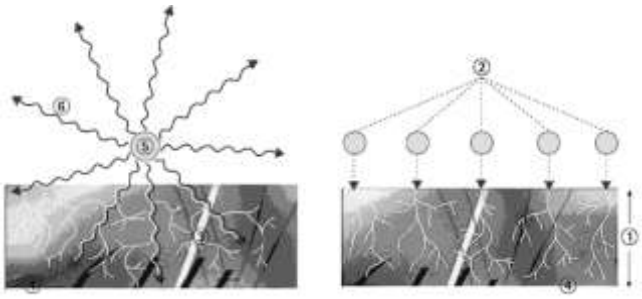
Abstract. Using high doses of beta radiation for polybutylene terephthalate (PBT) and its influence on the changes of micromechanical properties of surface layer has not been studied in detail so far. The specimens of PBT were made by injection moulding technology and irradiated by high doses of beta radiation (0, 132, 165 and 198 kGy). The changes in the microstructure and micromechanical properties of surface layer were evaluated using WAXS and instrumented microhardness test. The results of the measurements showed considerable increase in micromechanical properties (indentation hardness, indentation elastic modulus) when high doses of beta radiation are used.

1 Introduction

Poly (butylene terephthalate), PBT, is a commercially important engineering polymer with a wide range of applications such as injection molding and extrusion. As a member of the polyester family, it is also often used as the matrix material in glass fiber reinforced composites, having attractive mechanical properties, good moldability and fast crystallization rate. PBT has some processing advantages over its chemical relative, poly (ethylene terephthalate), PET. The melting temperature of PBT is about 230°C, which is lower than PET, (ca. 270°C), allowing PBT to be processed at lower temperatures. In addition, PBT has a lower glass transition temperature, a faster crystallization rate [1-8].

And it is widely used as fiber, textile, bottle, video tape, food trays and automobile components, such as connectors. However, the disadvantages such as relatively low notched impact strength, poor photo-stability and low deformation temperature obstruct the application of PBT. Therefore, modification of PBT becomes an important consideration.

The most effective and feasible method to solve the high notch sensitivity of PBT problem is to blend it with appropriate elastomeric materials, which is often called polymer-polymer alloying technique. In order to improve compatibility of the blends, reactive modifiers were selectively applied because they can react with the carboxylic or hydroxyl end groups of PBT molecular chains. Among these reactive modifiers, core-shell structured particles functionalized with epoxy groups were usually chosen for PBT blend systems. Therefore, many research efforts have been put into improving the impact strength of PBT [3-10]. The principle of the radiation process is the ability of the high energy radiation to produce reactive cationts, anoints and free radicals in the material. The industrial application of the radiation process (Figure 1) on polymer and composites includes polymerization, crosslink-linking and degradation. The radiation process involves mainly the use of either electron beam from electron accelerators or gamma radiation from Cobalt – 60 sources.



a) b)

Figure 1. Design of Gamma rays (a) and Electron rays (b).

a) 3 – secondary electrons, 4 – irradiated material, 5 – encapsulated Co – 60 radiation source, 6 – Gamma rays

b) 1 – penetration depth of electron, 2 – primary electron, 3 – secondary electron, 4 – irradiated materiál

The aim of this paper is to study the effect of ionizing radiation with different doses, on microhardness of surface layer 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 [3-10].

[a] Corresponding author: dmanas@ft.utb.cz

2 Experimental

2.1 Micro-indentation test

For this experiment polybutylene terephthalate (PBT) V-PTS-CREATEC-B3HZC * M800/25 nature; PTS Plastics Technologie Service, Germany was used. The material already contained a special cross-linking agent TAIC—triallylisocyanurate (6 volume %), which should enable subsequent cross-linking by ionizing β-radiation. Irradiation was carried out in the company BGS Beta Gamma Service GmbH & Co, KG, Germany with the electron rays, electron energy 10 MeV, doses minimum of 0, 132, 165 and 198 kGy on air the ambient temperature.

The samples (Figure 2) were made using the injection molding technology on the injection moulding machine Arburg Allrounder 420C. Processing temperature 245–295 °C, mold temperature 85 °C, injection pressure 80 MPa, injection rate 45 mm/s. [7-17]

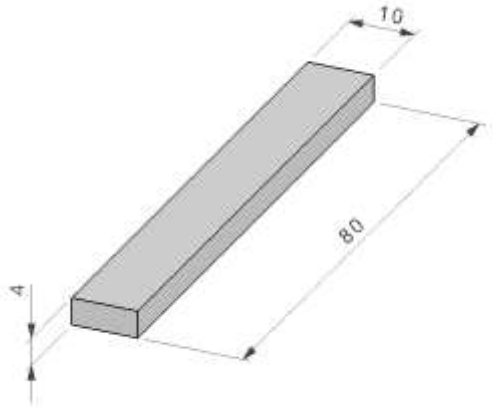


Figure 2. Dimension of sample.

2.2 Micro-indentation test

Micro-indentation test was done using a Micro Combi Tester (Figure 3), CSM Instruments (Switzerland) according to the CSN EN ISO 14577. Load and unload speed was 2 N/min. After a holding time of 90 s at maximum load 1 N the specimens were unloaded. The specimens were glued on metallic sample holders. Poisson's ratio (ν) of the polymer was 0.3. The indentation hardness (H_{IT}) was calculated as maximum load (F_{max}) to the projected area of the hardness impression (A_p) according to: [7-17]

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

2.3 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 L100 of α most intensive peak at 100 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 Θ was chosen [7-17].

Figure 3. Nano-indentation tester.

3 Results and discussion

The development of micromechanical properties of irradiated polybutylene terephthalate was characterized by the instrumented test of microhardness (H_{IT}), as can be seen in Figure 4. The lowest values (84 MPa) of microhardness were found on polybutylene terephthalate irradiated with radiation dose of 198 kGy radiation dose, while the highest value of microhardness (110 MPa) was measured at 165 kGy radiation dose. The values (93 MPa) of microhardness were found on non-irradiated polybutylene terephthalate. The increase of microhardness at 165 kGy radiation dose was by 18 % compared to the non-irradiated polybutylene terephthalate.

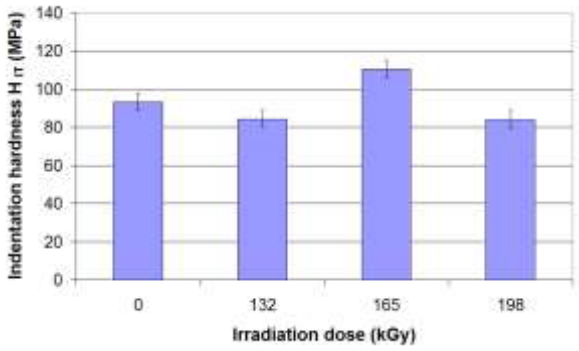


Figure 4. Indentation hardness H_{IT} vs. irradiation doses.

Similar development was recorded for microstiffness of specimens represented by the elastic modulus of indentation (E_{IT}) illustrated in Figure 5. The results of measurements show clearly that the lowest values of microstiffness were measured on the polybutylene terephthalate (1.23 GPa) irradiated with radiation dose of 198 kGy, while the highest values were reached in polybutylene terephthalate irradiated by 165 kGy dose (1.72 GPa). The value (1.54 MPa) of microstiffness were found on non-irradiated polybutylene terephthalate. A significant decrease of microstiffness (11 %) was recorded at the radiation dose of 33 kGy compared to the non-irradiated polybutylene terephthalate.

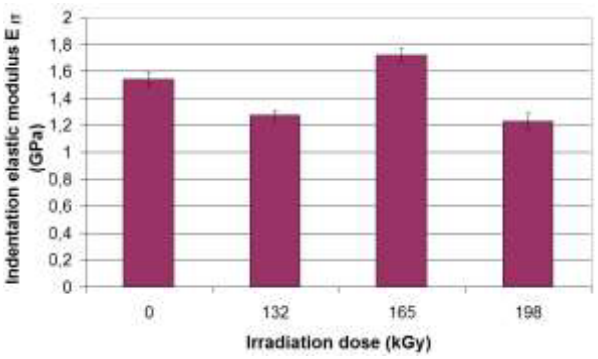


Figure 5. Indentation elastic modulus E_{IT} vs. irradiation doses.

Other important material parameters obtained during the micro-hardness test were elastic and plastic deformation work. The mechanical work W_{total} induced by the indentation is only partly consumed as plastic deformation work W_{plast}. During the removal of the test force the remaining part is set free as work of the elastic reverse deformation W_{elast}.

Very important values were found for indentation creep (C_{IT}). For materials which creeps as polymers, a basic calculation of that creep can be measure during a pause at the maximum force. The creep is the relative change of the indentation depth when the test force is kept constant measured by instrumented test of microhardness showed (Figure 6) that the highest creep values were measured on non-irradiated polybutylene terephthalate (7.8 %), while the lowest creep value was found in polybutylene terephthalate irradiated by 198 kGy dose (5.7 %). The creep dropped by 27 % as a result of radiation, which represents a considerable increase of surface layer resistance.

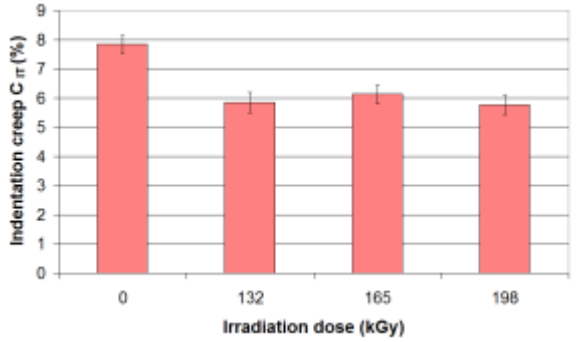


Figure 6. Indentation creep C_{IT} vs. irradiation doses.

The highest values of plastic deformation work were obtained for non-irradiated polybutylene terephthalate. The highest values of elastic deformation work were obtained for polybutylene terephthalate irradiated with radiation dose of 198 kGy. The lowest values of W_{el}, W_{pl} were obtained for polybutylene terephthalate irradiated with dose of 165 kGy. Radiation of specimens caused lower values of plastic deformation work which is in Figure 7.

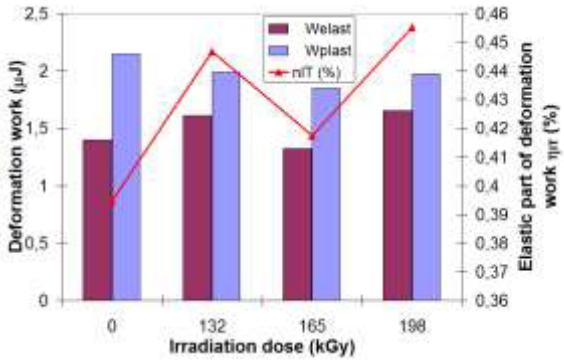


Figure 7. Deformation work vs. irradiation dose.

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

When applying β-radiation the structure of polypropylene undergoes loss and then a grow of the crystalline phase. 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 29-33 %). Cross-linking occurs in the remaining noncrystalline part which has a significant influence on the mechanical properties of the surface layer. The greatest size (Figure 9) of crystalline phase was found in the case at the radiation dose of 165 kGy (33 %). The lowest size of crystalline phase was found in the case at the radiation dose of 132 kGy (29 %). On the contrary the smaller size of crystalline phase was measured at non-irradiated (31 %). Its influence on the mechanical behavior is insignificant.

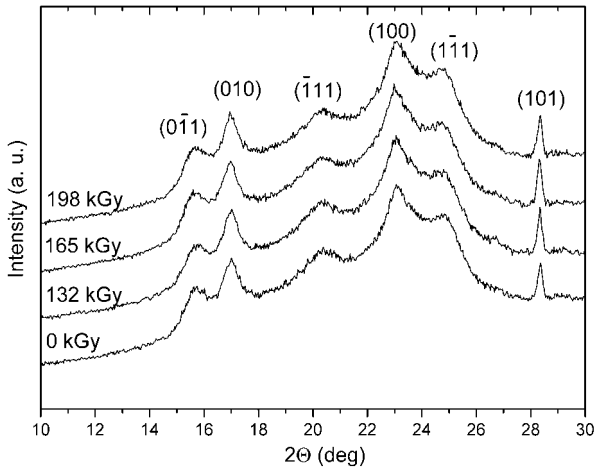


Figure 8. X- ray diffraction non-irradiated and irradiated PBT.

The figure 8 shows typical X-ray diffraction spectrum of the non-irradiated and irradiated polybutylene terephthalate. 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 198 kGy (Figure 8).

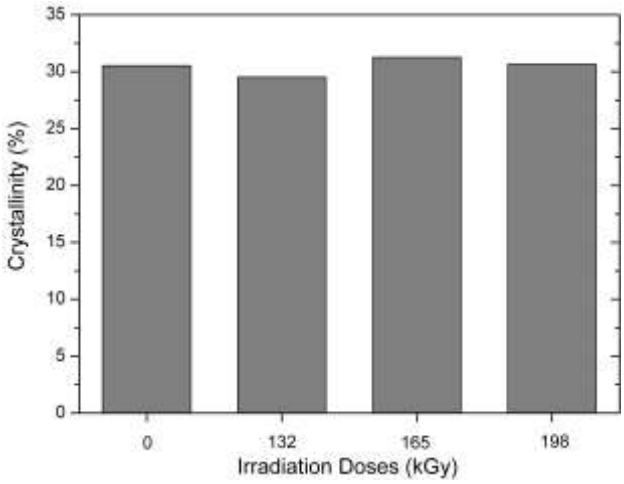


Figure 9. The crystallinity of non-radiated and irradiated PBT.

4 Conclusion

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 polybutylene terephthalate. Polybutylene terephthalate was modified by beta irradiation at doses of 0, 132, 165, 198 kGy. The changes of micromechanical properties were found at the radiation dose of 198 kGy for indentation creep (which decreased by 27%) compared to the non-irradiated polybutylene terephthalate.

Improvement of mechanical properties in micro and macro scale of radiated polybutylene terephthalate has a great significance also for industry. The modified polybutylene terephthalate shifts to the group of materials which have considerably better properties. Its micromechanical properties make polybutylene terephthalate ideal for a wide application in the areas where higher resistance to wear, scratch are required.

Acknowledgment

This work was supported 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 and 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

References

1. Dj. Gheysari, Eur. Polym. J. **37** (2001) 295-302, (2001)
2. K. Makuuchi, S. Cheng. Wiley, Hoboken, 2011.
3. J.G. Drobny, Elsevier, Oxford, 2013.
4. D. Dobrotə, Energy Procedia, **100**, 1160-1166, (2015)
5. G. Zamfirova, V. Gaydarov, T. Zaharescu, L. G. Silva. Chemicke Listy, **104**, 283-286, (2010)
6. D. Manas, M. Hribova, M. Manas, M. Ovsik,M. Stanek, Thin Solid Films, **530**, 49-52,(2013)
7. O. Uzuna, U. Kölemena, S. Çelebi, N. Güçlü, Journal of the European Ceramic Society. **25**, 969–977, (2005).
8. W. C. Oliver, G. M. Pharr. J Mater Res, **7**. (6) 1564–1583, (1992)
9. E. Ragan, P. Baron, J. Dobránsky. Advanced Materials Research 383-390, 2813-2818, (2012).
10. H. Wang, L. Xu, R. Li, J. Hu, M. Wang, G. Wu, Radiation Physics and Chemistry, **125**, 41-49, (2016)
11. J. Dobránsky, L. Běhálek, P. Baron, Key Engineering Materials, **669,** 36-43, (2016)
12. Dobransky, J., Běhalek, L., Baron, P., Kočiško, M., Simkulet, V., Vojnova, E., Briančin, J. Metalurgija, **55** (3), pp. 449-452, (2016)
13. Dobránsky, J., Kočiško, M., Baron, P., Simkulet, V., Běhálek, L., Vojnová, E., Nováková Marcinčinová, Ľ. Metalurgija, **55** (3), pp. 477-480, (2016)
14. J. Čop, L. Fojtl, O. Bílek, V. Pata, Manufacturing Technology, **16** (2), pp. 334-338, (2016)
15. Singh, P. Kishore, M. Singh, A. Srivastava, Radiation Effects and Defects in Solids, **170** (10), 845-853, (2015)
16. S. Kashyap, D. Datta, International Journal of Plastics Technology, **19** (1), 1-18, (2015)
17. S. Zhang, R. Dubay, M. Charest, Expert Systems with Applications, **42** (6), 2919-2927, (2015)