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Effect of low doses beta irradiation on thermal, micro and macro mechanical properties of irradiated polypropylene

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HIGHLIGHTS

- Improvement of micromechanical properties of PP radiated by low beta radiation doses was found to be threefold.
- Macromechanical properties of radiated PP was improved by 28%.
- Heat resistance in modified PP was twofold.
- The low radiation doses cause structural changes.
- Low radiation doses cause relative changes in representation of hydroxyl and carbonyl groups.

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ABSTRACT

The influence of beta radiation on the change of structure and selected properties (both mechanical and heat properties) of polymer materials has been proved. Medium and high doses of beta radiation influence both macro-mechanical and thermal properties of polypropylene in a positive as well as negative way. The use of low doses of beta radiation for polypropylene and its influence on the changes of micro, macro mechanical and thermal properties was thoroughly studied. The specimen were produced by injection technology and subjected to low doses of beta radiation of 0, 15 and 33 kGy The changes of structure, micro, macro and thermal mechanical properties were evaluated by FTIR, WAXS, DSC, tensile test, impact test, microhardness test and thermomechanical analysis. The results of measurements showed a considerable improvement (threefold) of micro mechanical properties (microhardness) of low beta radiation doses. It was also proved that macro and thermomechanical properties of polypropylene modified by low beta radiation doses improved.

1. Introduction

Irradiation of a polymer by different radiations leads to several physicochemical changes, a few of which include scissioning and or crosslinking, carbonization, conjugation, oxidation, creation of defects, generation of low molecular weight fragments and evolution of gases. These changes induce considerable modifications in mechanical, electrical, thermal and optical properties of polymers and are qualitatively or quantitatively based on properties of radiation and the polymer (Mathakari et al., 2008; Cleland et al., 2003; Chmielewski et al., 2005).

Polypropylene is a versatile, low cost, chemically stable and lightweight polymer, which offers attractive mechanical, electrical and thermal properties due to its relative higher degree of crystallinity. This is used in many applications such as radiation-sterilized medical and pharmaceutical components, food packaging materials and cosmetics (Chapiro, 1995; Fintzou et al., 2006; Svorcik et al., 1997). A literature survey indicates that effects of 14.89 MeV electron irradiation on polyethylene and polystyrene in the dose range of 57.6–576 kGy showed a greater red shift in absorption edge of polyethylene as compared to polystyrene (Mishra et al., 2001; Abdel-Hamid, 2005). Whereas, the enhancement in the thermal properties, dielectric constant, dielectric loss and crystallinity of 2 MeV and 1.5 MeV electron irradiated polypropylene has also shown considerable modifications. However, more investigations are needed as far as the radiation energy, mode of energy deposition and energy densities are concerned. In particular, the effects of high energy pulsed electron irradiation on mechanical properties such as surface hardness and surface roughness of polypropylene needs more attention (Radwan, 2007;

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Yagoubi et al., 1999; Dorschner et al., 1998). Out of several types of radiations that can be used for radiation processing, high-energy electrons are of particular interest, especially for polymers, due to their high dose rates and consequently high-energy deposition in lesser time intervals. This not only achieves high process rates, but also allows crosslinking, as oxidation effects are relatively weak at the high dose rates. Moreover, electron beam irradiation also offers facility of easy control, maintenance of steady dose rate without any depletion and homogeneous energy deposition (Uzuna et al., 2005; Chvatalova et al., 2009; Manas et al., 2013; Oliver and Pharr, 1992).

The improvement of both mechanical properties and thermal stability of PP after radiation crosslinking is described also by Shukushima (Shukushima et al., 2001) but the way of sample preparation is quite different in this case. In research work described in this article the samples preparation by injection molding is in fact the same as real plastic parts production in industrial scale. Therefore the results of this research are very easy applicable in praxis.

The present work deals with the influence of low doses β-radiation on the thermal, micro-macro mechanical properties of irradiated cross-linked polypropylene.

2. Experimental

2.1. Material

For this experiment isotactic polypropylene PTS—Crealen EP-2300L1-M800; PTS Plastics Technologie Service, Germany (unfilled, iPP+TAIC, MFR—230 °C/2.16 kg–6 g/10 min) was used. The material already contained a special cross-linking agent TAIC—triallylisocyanurate (6 vol%), which should enable subsequent cross-linking by ionizing β-radiation. Irradiation was carried out in the company BGS Beta Gamma Service GmbH & Co, KG, Saal am Donau, Germany with the electron rays, electron energy 10 MeV, doses minimum of 0, 15, and 33 kGy on air by the ambient temperature (Manas et al., 2008; Ovsik et al., 2012).

2.2. Samples preparation

The samples were made using the injection molding technology on the injection molding machine ArburgAllrounder 420C. Processing temperature range 210–240 °C, mold temperature 50 °C, injection pressure 80 MPa, injection rate 50 mm/s (Ragan et al., 2012).

2.3. Microhardness

Instrumented microhardness tests were done using a Micro Combi Tester, CSM Instruments (Switzerland) according to the CSN EN ISO 6507-1. 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 indentation hardness H_{IT} was calculated as maximum load to the projected area of the hardness impression according to

$$H_{IT} = \frac{F_{\max}}{A_p} \tag{A1}$$

$$h_c = h_{\max} - \varepsilon \frac{F_{\max}}{S} \tag{A2}$$

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 to calculate the initial stiffness and contact depth (h_c). The specimens were glued on metallic sample holders (Manas et al., 2013; Oliver and Pharr, 1992).

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 Cu*K*α radiation was Ni-filtered. The scans (4.5 2Θ/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.

Crystall size L_{110} of α 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 2Θ was chosen (Manas et al., 2013).

2.5. TMA (Thermo mechanical analysis)

Thermomechanical analysis ČSN ISO 306 VST/A 10 means measuring resistance of a needle to polymer material at different temperatures according to Vicata. The specimen of a rectangular shape $4 \times 10 \times 10$ mm ($h \times b \times l$) was inserted to a measuring device and loaded by a constant force of 10 N. Pre-heating of the specimen was 50 °C for the period of 1 min. The following heating was from 50 °C to 400 °C at 20 °C/min. Relationship of the depth of the imprint and temperature was monitored (Oliani et al., 2010).

2.6. 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°). 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 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 (Otaguro et al., 2010; Lalande and Gardette, 2004).

2.7. Impact test

The impact tests were done using a Zwick 513 Pendulum Impact Tester (Germany) according to the CSN EN ISO 179-2. Drop energy was 25 J (Oliani et al., 2010; Manas et al., 2008).

2.8. Optical microscopy

Zeiss NU-2 optical microscope (Germany) with polarized light was used to study morphology of the crystallized specimens. The samples with thickness 25 μm were placed on the microscope stage and observed in the polarized light. Micrographs of the observed structure were taken using a SONY F-717 digital camera. Common graphic software was used for editing of final images (Nedkrov et al., 1991).

2.9. Tensile testing

A Zwick 1456 multipurpose tester (Germany) was used according standard CSN EN ISO 527-1, 527-2 for the tensile testing of injection-molded testing specimens with a gauge length of 80 mm. The specimens were strained at room temperature up to break at a test speed of 10 mm/min. From the stress–strain traces, strength at break and elongation at break were derived. Besides, the elastic modulus was evaluated using a Zwick external