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CHARACTERIZATION OF GAMMA IRRADIATED POLYPROPYLENE WITH PRODEGRADABLE ADDITIVE

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ABSTRACT

Compound of polypropylene that contains 1,5 % prodegradable additive D_2W has been prepared using a single screw extruder. The obtained blend was grinded and injected in the form of standard specimens for tensile testing. The samples thus manufactured were irradiated with different dosage of gamma radiation up to 476 kGy. The physical, mechanical, and rheological characteristics such as tensile strength, relative elongation and melt flow index were determined in accordance with the radiation dosage applied. The effect of the gamma radiation on the structure of the oxo degradable polypropylene was examined by IR spectroscopy and X-ray diffraction analysis.

Keywords: polypropylene, gamma irradiated, pro-degradant.

INTRODUCTION

It is recognized that purposeful changes in the material structure are achieved during irradiation with radioactive emissions due to the fact that the radiation can cause chemical reactions. Vulcanized rubber products, radiation-chemical synthesis of different compounds, etc. are products of this technology. The irradiation equipment for these purposes most often uses sources of gamma rays such as Cobalt - 60 and Cesium -137. They are also used for sterilization of different food products, seeds, medical instruments and others. Irradiation of a dose of about 10^7 rad increases the degree of polymerization in usual polyethylene by 60% as well as its thermal stability. The irradiation with gamma rays leads to co-polymerization of synthetic and natural polymers, such as wood, paper and cotton with styrene. Thus, wooden-plastic materials of high hardness and strength [1, 2] are produced by soaking wood with monomer and subsequent irradiation by gamma rays.

It is found that the radiation energy absorbed by some structural units of the polymer can be transmitted to others performing regrouping of the chemical bonds and rupturing of the weakest of them. There are ongoing processes of destruction and cross-linking which generally take place simultaneously but one of them prevails depending on the structure of the polymer. Polymers that contain a large number of chains of the type ($-CH_2-CH_2-$) show a higher tendency to cross-linking. During this process the molecular weight of the polymer increases, while its solubility in oils decreases. Various types of polyolefins can be referred to this type of polymers [3].

Brandi Keene et al. [4] irradiate polypropylene (PP) nonwoven textiles with different doses of gamma radiation up to 25 kGy. After the irradiation with c γ-radiation, the FTIR spectrum shows carbonyl groups increase. According to the authors the physical and mechanical properties of the polypropylene deteriorate after irradiation with 25 kGy.

Ries M. D et al. [5] find that the sterilization of ultra-high molecular weight polyethylene (UHMWPE) in an air medium leads to oxidation of the polymer at the surface and changes its degree of crystallinity, thus deteriorating its mechanical properties.

The sterilization of products (prosthesis) by UHMWPE with gamma radiation of a dose of 25 kGy can cause unpredictable changes in the properties and the durability of joint prosthesis [6, 7].

The literature survey on the mechanism of γ irradiation impact on the polymer structure and on the physical and mechanical properties shows two opposing tendencies in varying degree depending on the structure of the polyolefin, the dose and the intensity of irradiation and the conditions (environment) under which it is performed. These are the cross-linking that increases the mechanical strength and the oxidative destruction that weakens the material.

There is insufficient information on the effects of different doses of gamma radiation on the properties of oxodegradable polypropylene.

The main aim of the present study is to be subject samples of polypropylene with and without prodegradent to irradiation with gamma radiation to 50 Mad and to establish the influence of prodegradent on the processes induced by gamma radiation.

EXPERIMENTAL

The following materials were used:

- Polypropylene – Moplen EP440G, Impact Copolymer produced by LyondellBasell Industries;
- Pro-degradant d_2W produced by Symphony Environmental;

Preparation of test specimens

The polymer blends were prepared on a single screw extruder with L : D = 25. There was electrical resistance heating. The temperature was controlled with thermocouples and thermoregulatory. The temperature mode of extruding was selected depending on the composition of the extruded mixtures.

„Trusioma Kuasi" 25/32 injection molding machine was used to obtain „scoop" type specimens. The drive of the screw and the closing press was of a hydraulic mode. The heating of the material cylinder was achieved through electrical resistance, while the temperature was controlled by thermoregulators. The products were produced under the following temperature regime:

- temperature of first zone of 160°C
- temperature of second zone of 175°C
- temperature of third zone of 180°C

The timing of the injection cycles were:

- injection and holding under pressure - 3 s;
- cooling - 10 s.

A laboratory ultra-thermostat set to maintain 40°C temperature of the molding tool was used to control the temperature of the molding tool.

Irradiation technique

The obtaining of samples with different doses of irradiation was performed in "Bulgamma" irradiator (owned by "Sopharma") working with the radioactive isotope Cobalt-60. The device worked since 1990. It was validated by the manufacturer NORDION (Canada), a leader in irradiation facilities production. The irradiator in BULGAMMA was licensed and monitored by the Nuclear Regulatory Agency in the Republic of Bulgaria. The selected doses of irradiation were 100 kGy, 150 kGy, 250 kGy and 476 kGy.

The following indicators of samples characterization were examined:

The melt index – in accordance with BS EN ISO 1133/2006.

The tensile strength and elongation - *in accordance with* EN ISO 527/2012 standard.

The samples analysis was performed by *IR* – spectroscopy *using*

IRAffinity-1 "Shimadzu" for infrared spectroscopy with Fourier transformation.

It offered the highest ratio signal: noise (sensitivity) in its class of 30 000:1, with sensitivity of 0.5 cm^{-1} (according to research of Shimadzu from January, 2008). This high sensitivity was due to the high energy ceramic source of light, the temperature controlled highly sensitive DLATGS detector and the precise optical elements. In addition, the software standard for this instrument allowed processing and analysis of the spectral data.

The samples X-ray structural analysis was carried out using X-ray powder diffraction. The data obtained was recorded on TUR M62 diffractometer using Co Kα in the range of 2 θ 4 - 80° constantly scanning at 2° min^{-1}.

The relative degree of crystallinity γ, %) of the examined polypropylene samples was defined on the ground of the relation:

$$\chi_c = \frac{I_c}{I_a + I_c}.100, \%$$

where I_a was the area of the amorphous regions, while I_c was the area of the crystalline regions.

RESULTS AND DISCUSSION

Samples of polypropylene EP440G are prepared. One of these contains 1.5 % of pro-degradant D2W. The results referring to the melt flow index of the non-irradiated samples and those irradiated by different doses

Table 1. Melt flow index of polypropylene, irradiated with γ rays up to 476 kGy.

Dose, kGy	MFI of EP440G, g/10 min	MFI of EP440G+1.5 % D_2W, g/10 min
0	1.3	2.7
100	51.2	121
150	53	49
250	Not melting	Not melting
476	Partially melting	Partially melting

of gamma radiation up to 476 kGy are shown in Table 1.

The melt index of the EP440G material increases with increase of the irradiation dose up to 150 kGy. Most likely this is due to the prevailing processes of rupture of the macromolecular polypropylene chains. Cross-linking and as a result of this process occurs at higher doses of gamma radiation and the polymer does not melt.

Upon addition of 1.5 % pro-degradant D2W the processes of destruction and recombination occur more rapidly at a lower dose of gamma radiation. The most likely reason for this is the presence of even a small amount of oxygen in the airtight sealed specimen and the nature of prodegradent action.

IR spectrums of PP samples (with and without addition of pro-degradant D2W), exposed to γ-radiation dose 100 kGy and 476 kGy are shown in Fig.1. The main bands in the IR spectrums are as follows: (i) the bands at 2950 cm^{-1}, 2920 cm^{-1}, 2886 cm^{-1} correspond to asymmetric deformation oscillations of the CH_3 groups; (ii) the bands at 2837 cm^{-1} and 1456 cm-1 are related to asymmetric vibration oscillations for CH_3 and CH_2 groups; (iii) the bands at 1375 cm^{-1} and 1370 cm^{-1} are specific for symmetric vibration oscillations of CH3 groups; (iv) the bands in the area of 1166 cm-1-809 cm^{-1} correspond to deformation oscillations of the C-C, C-CH_3 groups.

The addition of pro-degradant leads to decrease of the intensity of the main bands, while the increase of the irradiation dose leads to the appearance of new bands in the area 2356 cm^{-1} - 2322 cm^{-1}. They are due to the valent oscillations of CH_2 groups, which probably can explain the fact that at the occurrence of cross-linking and absence of samples melting at increased irradiation dose. The process of destruction under γ-irradiation involves initiation, distribution and interruption. The reactions of initiation can affect different parts of PP-chain. The gamma rays' energy causes the rupture of covalent bonds. It can be assumed that there will be a rupture of the C-H bond in the methylene group in accordance with the possible mechanism of the process presented in Fig. 2.

The X-ray diffractions obtained provide estimating the degree of crystallinity of the PP and PP with 1.5 % prodegradent are defined. The values obtained are as follows:

Dose, kGy	Degree of crystallinity of PP, %	Degree of crystallinity of PP whit 1.5 % D_2W
0	63.6	68.1
476	48.6	32.3

The crystallinity degree decrease is most likely due to the processes of degradation that lead to size reduction of the crystals and to increase of the amorphous region. The results referring to the change of the tensile strength depending on the absorbed γ radiation dose are presented in Fig. 3, while those for the relative elongation are illustrated in Fig. 4.

The tensile strength of the test samples decreases with increase of the radiation dose due to crystal structure disappearance and new amorphous supramolecular phase appearance. This leads to the manifestation of brittle destruction of the tested specimens with clearly expressed fracture appearance. Furthermore, the decrease of the strength may be due to the ongoing reactions of destruction.

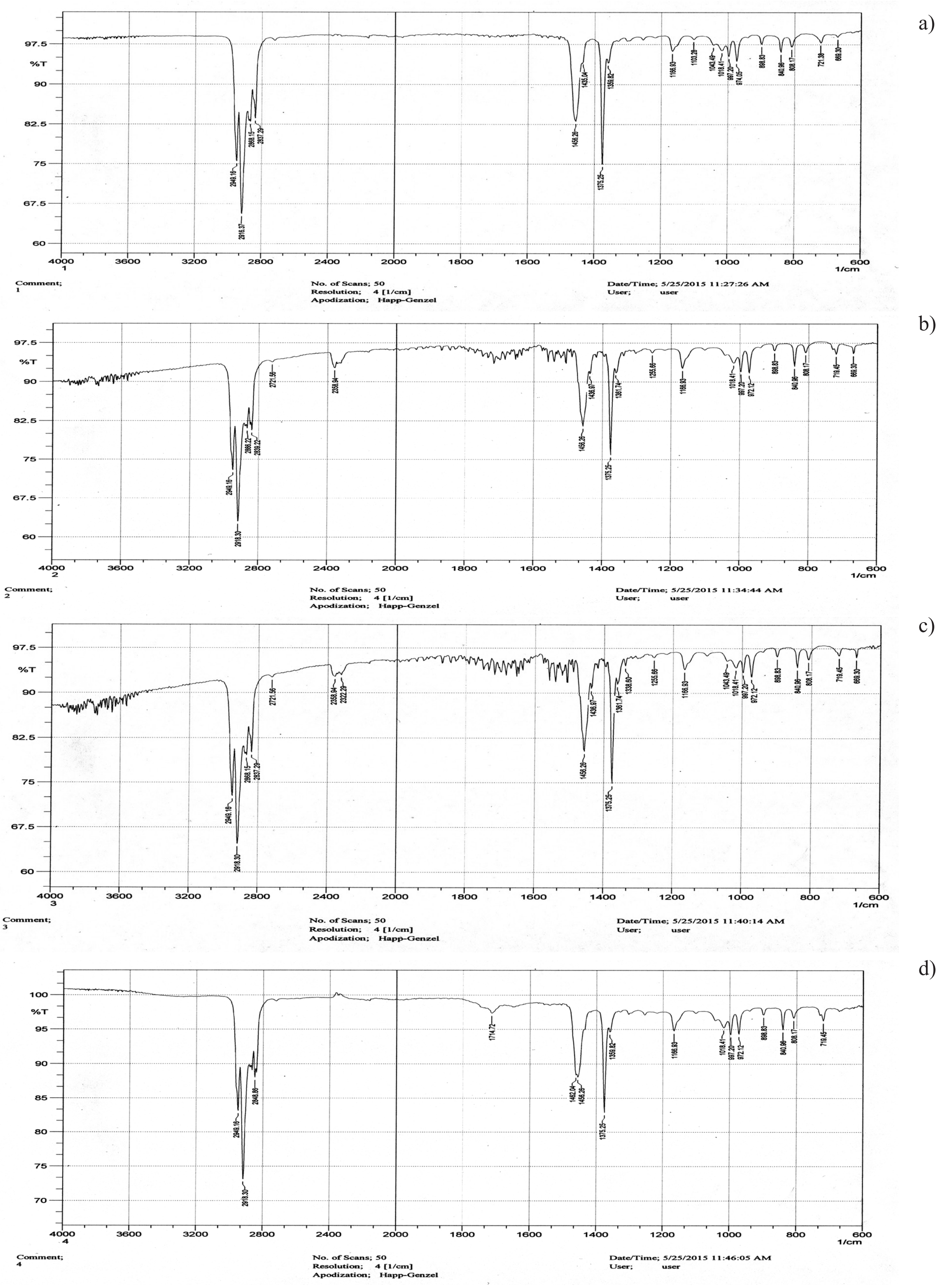

Fig. 1. IR spectrum of: a) PP, irradiated with 100 kGy; b) PP + 1.5 % D2W irradiated with 100 kGy; c) PP irradiated with 476 kGy; d) PP + 1.5 % D2W irradiated with kGy.

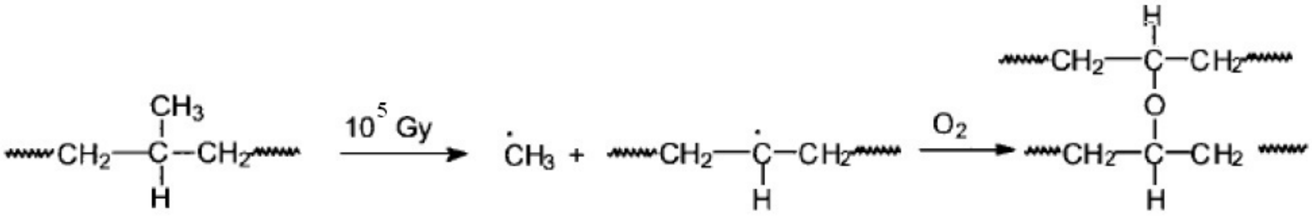

Fig. 2. Probable mechanism of reactions, in polypropylene under high dose γ irradiation.

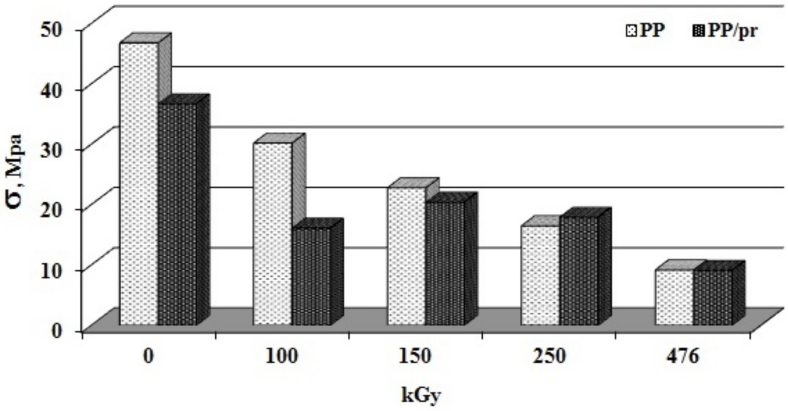

Fig. 3. Alteration of tensile strength, depending on irradiation dose.

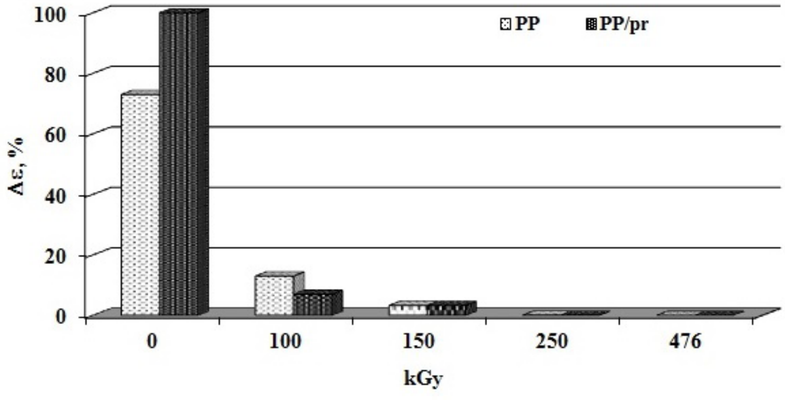

Fig. 4. Alteration of relative elongation at break, depending on irradiation dose.

Adding prodegradent does not change the behavior of PP upon irradiation with gamma radiation, but the processes of degradation and cross-linking occur at lower doses of irradiation

The gamma irradiation of polypropylene causes a spontaneous reaction of cross-linking and rupture of the chains. These effects are observed in varying degrees for all irradiation doses.

CONCLUSIONS

"Scoop" type samples are produced by injection molding using PP and oxo degradable PP. They are irradiated by different doses of γ-radiation reaching up to 476 kGy. It is found that two opposite tendencies are observed during the γ-irradiation - destruction of the macromolecules and cross-linking due to forming of new chemical bonds between the molecules groups. The processes of destruction and recombination occur rapidly in presence of prodegradent, besides at lower doses of gamma radiation. This assertion is supported by the melt index and mechanical tests results.

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