

Mechanical and thermomechanical properties of radiation modified poly(ethylene-octene)/Ni-Zn ferrite nanocomposites

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Abstract. Poly(ethylene-1-octene) copolymer (POE) composites filled with nickel-zinc ferrite nanoparticles have been modified by exposure to an electron beam at doses up to 500 kGy. The influence of radiation dose and ferrite content on mechanical properties has been investigated. Thermomechanical properties – thermorelaxation stresses formed in thermal heating and thermo residual stresses resulting in the process of full setting and cooling of materials have been investigated for radiation cross-linked oriented (extended up to 100%) composite samples. Increase of concentration of ferrite particles and increase of radiation dose affects a notable increase of elastic modulus and reduces the deformability in comparison to entire elastomer. Improvement of thermomechanical properties especially at low irradiation doses (100-150 kGy) have been detected for composites with increase of ferrite filler content up to 5 wt. %. It was found that gel content of POE increased up to 85% for pristine POE material with increase of irradiation dose up to 500 kGy due to the formation of cross-linked structure, increase of filler concentration up to 5 wt. % affect reduction in gel fraction due to uniform dispersion in amorphous (ethylene and substituted with hexyl branches) POE phases.

1. Introduction

Ethylene-octene copolymers (POE's) belong to a relatively new class of ethylene elastomers with high flexibility, rubber like mechanical properties and a processability of thermoplastics. Modification of cross-linkable polymer matrix like POE's by ionizing irradiation (γ -rays, accelerated electrons) can significantly improve durability of material [1]. Radiation modified cross-linkable thermoplastic polyolefins and their copolymers like metallocene-based POE's exhibit unique properties in comparison to unmodified materials: enhanced viscoelastic behavior above the melting point, increased thermal stability and improved mechanical, thermal and rheological properties as a reason of spatially formed cross-linked structure [1, 2].

There is importance from many industrial and engineering viewpoints due to the application of cross-linked POE in the manufacture of heat shrinkable materials (HSM), which are widely used in the cable and electric coatings, sealants and the other industrial elements as replacement of commonly known (HSM) based on low and high density polyethylene due to improved cross-linking efficiency of POE structures [2-4]. The previous studies have shown effect of small concentrations of liquid crystal polymers as reinforcement agents on mechanical and thermomechanical properties of HSM based on polyolefins [3]. It is predictable that inorganic filler particles are dispersing mainly in heterogeneous



amorphous phase where the formation of cross-links occur that may affect increase of tensile and thermomechanical properties of polymer. The inorganic nanoparticles may act similarly by affecting reinforcement of tensile and thermomechanical properties of radiation modified POE composites. However, the incorporation inorganic nanofillers in polymer matrices possess improvement of mechanical properties such as hardness, elastic modulus and tensile strength at both low and high temperatures, as well as may affect change in dielectric, thermal and other properties [4]. Such materials filled with ferrite nanoparticles may have applications in engineering fields as microwave absorbers, special construction materials, soft magnets and shape memory materials [4-5].

In this research, POE composites with zinc-nickel ferrite nanofiller have been made. The composites have been irradiated with ionising radiation (accelerated electrons), and their tensile, structural and thermomechanical properties have been investigated. It should be noted that radiation modified POE composites with ferrite nanoparticles have not been previously described in literature.

2. Materials and investigation methods

2.1. Materials

Poly(ethylene-1-octene) copolymer with 1-octene content equal to 17 wt. % (*ENGAGE 8540*) supplied by the Dow Chemical Company (density 0.908 g/cm³ and melt flow index 1.0 g/10 min) and nickel-zinc ferrite $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nano particles with a diameter 10-30 nm, density - 4.8 g/cm³ supplied by the Nanostructured & Amorphous Materials (USA) were used as the component materials. The composites of POE with concentrations of ferrite equal to 0, 2 and 5 wt. % were obtained by dual extrusion at 170-180°C and pressing at 190°C.

Irradiation of composite plates was performed by accelerated electrons (5MeV) in *LINAC LU4* (Latvia) in normal air at room temperature. The irradiation doses were 100, 150, 300 and 500 kGy.

2.2. Methods

The tensile tests of composite specimens were performed at 20±2°C on a Tinius Olsen H1KS UTM at a deformation speed of 1 mm/min for determination of elastic modulus E and at a deformation speed of 50 mm/min for stress-strain characteristics in accordance to ISO 527-2 standard. 7 parallel specimens have been tested.

The gel content of the irradiated composite samples was determined by evaluation of the content of insoluble fraction of cross-linked materials after solvent extraction in refluxing xylene for 48h. The extracted samples were then dried at 80°C for 24 h and weighted. Percent gel fraction was calculated as per the equation (1), where f_g is the percent gel fraction, m_i – the initial sample weight, m_g – the weight of sample after the extraction of soluble fraction. Results have been shown as the average of three parallel samples for each composition with average weight of sample 0.2 g.

$$f_g = m_i / m_g \cdot 100\% \quad (1)$$

Thermomechanical behavior of the irradiated POE samples with 0 and 5 wt. % ferrite content, after their preliminary orientation by extension up to 100%, was investigated in the temperature range of 20 to 220°C. Specimens in the form of 5 x 5 x 2 mm strips were gradually heated and cooled under isometric conditions. The arising thermal relaxation σ_{TR} and residual thermal shrinkage σ_{RS} stresses were determined by a strain gage equipped with a 0.01 N sensitivity.

3. Results and discussion

3.1. Gel fraction

Figure 1 shows the effect of irradiation dose on gel content of pristine POE and POE composites with Ni-Zn ferrite content 2 and 5 wt. %. As a result of increase in spatial network formation (cross-linking

extent), gel content increases gradually with increment of irradiation dose for pristine POE and reaches the average value of about 85% at the maximum irradiation dose (500 kGy). The values of gel content reduced for composites with increase of Ni-Zn ferrite content and with increase of irradiation dose. For example, gel fraction at 100 kGy decreased from 29 up to 24% with increase of ferrite content from 0 up to 5 wt. %, but at 300 kGy it decreased about 1.3 times – from 73 up to 56%.

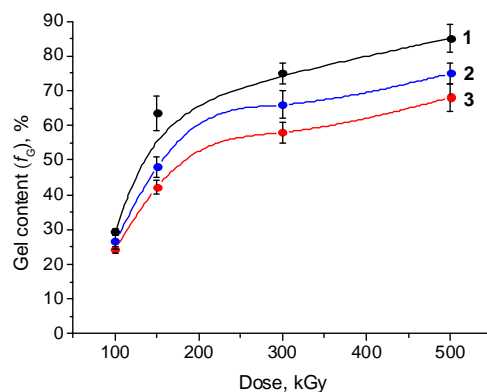


Figure 1. Gel fraction as a dependence of irradiation dose of POE-ferrite composites at ferrite concentrations 0 (1), 2 (2) and 5 (3) wt. %.

3.2. Tensile tests

The changes of tensile properties obtained from the stress-strain curves of unirradiated and irradiated up to 500 kGy POE composites are compared in Figure 2.

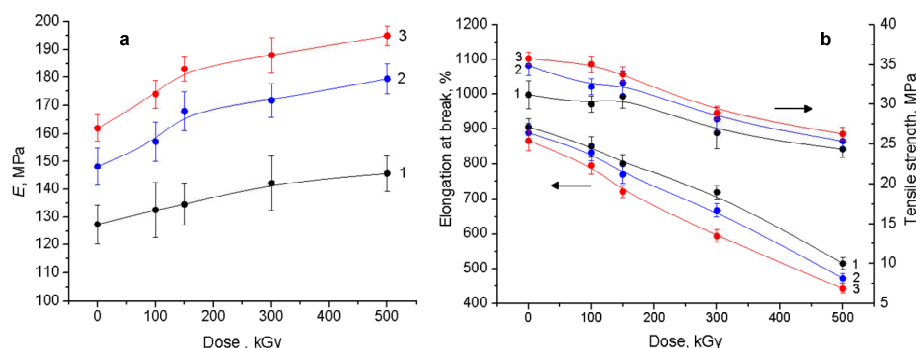


Figure 2. Elastic modulus (a), elongation at break and tensile strength (b) as a dependence of irradiation dose of POE-ferrite composites at ferrite concentrations 0 (1), 2 (2) and 5 (3) wt. %.

Incorporation of ferrite up to 5 wt. % in POE matrix affected increase of elastic modulus 1.27 times (elastic modulus increased from 127 ± 6 MPa up to 162 ± 5 MPa), increase of tensile strength 1.15 times and reduction of elongation at break 1.13 times.

Increment of elastic modulus with improvement of ferrite content up to 5 wt. % increased up to irradiation dose equal to 150 kGy, at which the modulus increased about 1.34 times. That is also seen in case of tensile strength and deformation at break that reach the optimal properties at 150 kGy, comparing composites with increment of ferrite content.

3.3. Thermomechanical properties

Thermomechanical curves of irradiated pristine POE and POE composites with ferrite content 2 and 5 wt. % are shown in Figure 3. The increase of thermorelaxation stress values coincides with increment of gel fraction due to increase of cross-linking. An improvement of thermorelaxation

stresses σ_{TR} for irradiated up to 100 kGy composites with increase in ferrite content from 0 to 2 and 5 wt. %: the values of σ_{TR} increase from 0.33 to 0.4 MPa with increase of ferrite content up to 5 m.%.

The behavior of isometrical heating of thermomechanical curves at 100 kGy indicates an improvement of mechanical stresses with a maximum stress at orientation temperature (140°C) that increases with increment of ferrite content, a small increment of thermal shrinkage stresses also has been indicated. Increment of thermorelaxation stresses reduces with increase of irradiation dose comparing the pristine POE and it's composite with 5 wt. % that coincides with changes of mechanical properties.

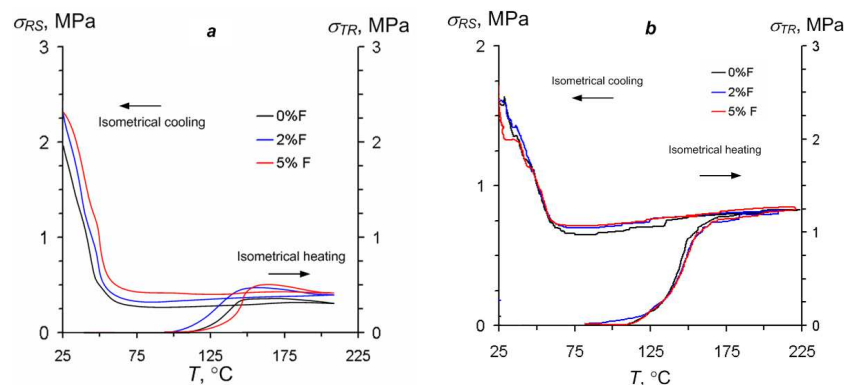


Figure 3. Thermomechanical curves of irradiated at 100 kGy and 300 kGy (b) oriented up to 100% POE-ferrite composites: dependence of thermorelaxation (σ_{TR}) and residual shrinkage (σ_{RS}) stresses at different ferrite content in composites

4. Conclusions

Structure properties of unirradiated and irradiated up to 500 kGy poly(ethylene-1-octene) composites filled with 0-5 wt.% Ni-Zn ferrite filler indicate a complex role of chain structure and crystallinity, irradiation dose and the content of ferrite particles on cross-linking efficiency of POE copolymers.

The mechanic study allow one to confirm first the reinforcement effect of Ni-Zn ferrite nanofiller for unirradiated POE elastomer composites and secondary an increase of cross-linking with increase of irradiation dose from 100 up to 500 kGy that affects increased stiffness, tensile strength and reduction of deformation at break, that even at dose as high as 500 kGy has relatively high values. Thermoshrinkable materials based on electron beam cross-linked POE composites with 0-5 wt. % Ni-Zn ferrite with improved mechanical and thermomechanical properties have been created after irradiation up to 100-150 kGy. A small effect of reinforcement of ferrite nanofiller on increase of thermorelaxation stresses has been reached for irradiated up to 100 kGy POE composites that reduces with increment of irradiation dose. That is explained with macromolecular cross-linking in POE's matrix interphase level at 300-500 kGy doses.

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