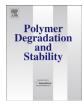
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# Tailoring of the thermal, mechanical and dielectric properties of the polypropylene foams using gamma-irradiation



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#### ABSTRACT

This study investigate the influence of gamma-irradiation (GI) doses from 0 up to 50 kGy on the polypropylene (PP) foams, mainly the impact on their structural and physical properties. It was found that structural properties were not significantly changed and the cellular structure of the PP foams sustain the same, while the thermal properties were significantly enhanced with increasing GI doses, due to the present cross-linking created within the irradiation. The cross-linking was confirmed also by the swelling measurements. The dielectric properties shows the three time increase of capacitance with increasing GI doses, due to the additional charges created in the foam voids by GI. Investigated mechanical properties in case of tensile tests as well as dynamical mechanical analysis proved, that enhanced behaviour was observed only in case of samples with irradiated by low doses, 1 kGy and 5 kGy, respectively, while the higher doses significantly decrease these ones, due to the present scission confirmed by FTIR and other investigations. Finally, it was found the competition between the cross-linking of the PP foam and present scission due to the applied GI and therefore the physical properties can be easily tailored.

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#### 1. Introduction

Polypropylene (PP) is one of a common polyolefin used in various applications such as food packaging [1], automotive industry [2], furniture [3] or tufted carpets [4]. However nowadays, when the natural resources for polymer synthesis started to be more expensive and their harvesting is rather demanding, the general meaning fall to produce the materials of the same usability. but consumption of the material should be lower. The partial solution for this case is preparation of the polymer foams [5,6]. Past decade there is a enormous increase of the various polymer foams produced for the mentioned applications. Biaxially oriented polypropylene (BOPP) is frequently used in the food packaging, due to its cellular structure and good permeability properties [7]. This kind of material (PP foam) was produced also by Savolainen [8], however for different application. Pajanen et al. performed the charging of the PP foam using corona discharge treatment, which resulted in polymer electret film with interesting application in mechanical energy harvesting [9]. Also other polymeric material were soon

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recognized to be used as a mechanical energy harvesters such as PVDF [10–12]. However, the low cost, light weight, chemical stability and easy processability makes this polymer one of the easiest materials to be used for this purpose. Therefore, the understanding of the morphology, physical and mechanical properties of them are the key to produce the material with required properties.

The material with good mechanical energy harvesting performance should have low Young's modulus and high d<sub>33</sub> coefficients. This can be achieved by addition of various organic and inorganic fillers [13-15] in order to increase the amount of the dipoles present in the material that moving when they are mechanically stimulated [16,17]. Another possibility is the treatment with  $\gamma$ irradiation (GI), when the additional charges can be entrapped in the voids of the material and was not done so far. Moreover, GI is a well-known tool used as a sterilization technique for polymers used in medical applications [18] as well as food packaging [19]. This technique was employed from 1960s and lot of research has been done on the investigations how GI influence the properties of treated samples [20–22] Moreover such technique can be utilized to improve the selected physical and mechanical properties various polymers [23,24]. The GI has further advantage of regular energy distribution, facile maintain and well-controlled doses regulation. Moreover, the GI can cause cross-linking reactions in polymers [25],

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their scission [26] and branching [27] at the same time, and depend on the applied doses [28], and atmosphere when irradiation take place [29]. Final properties of a specific material can be controlled by adjustment of these parameters. In this case the free radicals produced through the radiation process can cause oxidation and degradation of the materials. The oxidation happens less frequently in the crystalline regions as less oxygen can be diffused in these regions compared to the amorphous regions [30]. However, the effect of radiation on polymers and especially PP have been published before by many studies [31–33] but up to our knowledge no such studies have been done so far for PP foams.

Therefore, the aim of this study is to investigate the effect of gamma irradiation (GI) on commercial PP electret foam since this treatment can improve some physical and mechanical properties. Here the GI doses up to 50 kGy were utilized in order to minimized the degradation and maximize the cross-linking impact of the samples. The influence of the GI on the morphology of the samples as well as thermal, mechanical and dielectric properties was investigated in order to understand the changes in the structure and relate it to the change in the gamma irradiation doses.

#### 2. Experimental

#### 2.1. Materials

Polypropylene (PP) polymer electret film with 120  $\mu m$  in thickness, prepared by blow-moulding technique (EMFIT, Finland) used in this study. Xylene, reagent grade (Sigma Aldrich, USA) was used as a solvent for the swelling, gel content and GPC investigations.

#### 2.2. Preparation of the GI samples

The PP electret film was cut into small pieces with the following dimensions  $100 \times 100$  mm. Samples were individually placed into the  $^{60}$ Co gamma cell, (Atomic Energy, Canada Co. Ltd.). Irradiation was performed under air environment. Five different doses were applied to the samples with irradiation rate of 1.17 kGy/hour (Table 1). Samples were irradiated in relatively low doses, since higher doses can increase the scission in the material [17–19].

#### 2.3. Characterization

Crystalline phases of powder samples were characterized by the X-ray diffractometer X'Pert PRO X-ray (PANalytical, The Netherlands) with a Cu-K $\alpha$  X-ray source ( $\lambda=1.5418$  Å) in the diffraction angle range of  $2\theta=5-85^{\circ}$ . Infrared spectroscopy measurement were performed using FTIR 670 Nicolet (Thermo Scientific, USA) in ATR mode. The data were collected in the range from 4000 to 500 cm<sup>-1</sup> wavenumber. Cross-sections of the irradiated samples were investigated using Scanning electron microscopy (SEM), images were obtained using FEI Quanta 200 Environmental Scanning Electron Microscope (ESEM) with a resolution of 5 nm and a magnification X200K in order to investigate the influence of the gamma irradiation on the foam structure. Positron lifetime measurements were carried out using a conventional fast-fast coincidence lifetime system consisting of two plastic scintillation detectors and corresponding electronics with a time resolution of

**Table 1**Samples treated with various doses of gamma irradiation.

Sample name	S0	S1	S5	S12.5	S25	S50
Radiation doses (kGy)	0	1	5	12.5	25	50

172 ps. Lifetime spectra of all unirradiated and irradiated samples were collected at room temperature and then analyzed. Gel permeation chromatography (GPC) at elevated temperature was used for determination of molecular weight, polydispersity index using Agilent GPC PL-GPC 220, (Agilent, Japan), equipped with viscosity detector providing absolute values of molecular weights. Samples were dissolved in Xylene at 150 °C temperature. The flow rate was 1 mL min<sup>-1</sup> and soluble polymer chains were analyzed from the molecular weight and polydispersity index point of view.

#### 2.4. Thermal properties

TGA measurements were performed using Perkin Elmer Pyris 6 TGA (Perkin Elmer, USA) at temperature range from  $50\,^{\circ}\text{C}$  to  $800\,^{\circ}\text{C}$  at heating rate of  $10\,^{\circ}\text{C}$ /min under nitrogen atmosphere. DSC measurements were performed with Perkin Elmer model DSC 8500 (Perkin Elmer, USA) at temperature range from  $-50\,^{\circ}\text{C}$  to  $220\,^{\circ}\text{C}$  at heating rate  $10\,^{\circ}\text{C}$ /min under nitrogen atmosphere with two cycles of heating and cooling,. Second scan was evaluated in order to investigate the change of the melting temperature Tm. The weight of the samples varies from 2.2 to 2.5 mg.

#### 2.5. Swelling properties

Irradiated samples were immersed into xylene at room temperature and weighted with an analytical balance (Sartorius, Germany) with 0.1 mg precision in various periods of time from 15 up to 240 min. The swelling Q (%) were evaluated using Eq. (1).

$$Q = \left(\frac{m - m_0}{m_0}\right) \cdot 100 \tag{1}$$

where  $m_0$  is the mass of unswelled sample and m is the mass of the samples at various periods of time.

#### 2.6. Mechanical properties

The tensile tests were performed according to the ASTM D 882-10 using Universal tensile testing machine (Lloyd, USA). The samples were cut into rectangular shapes in winding direction (1st direction) and blowing direction (2nd direction) Fig. 1. Also the anisotropy of the tensile properties was observed. DMA testing in tensile mode was performed by RSA-G2 (TA Instruments, USA) in the room temperature and air atmosphere. All measurements were performed at linear viscoelastic range and the mechanical behaviour was investigated in the frequency range from 0.1 Hz up to 10 Hz. The samples were in form of thin stripes with length of 3.5 cm and width of 4 mm. The investigation of the mechanical properties in the broad temperature range (20 °C–80 °C) was performed at 0.05% strain deformation and frequency of 1 Hz.

#### 2.7. Dielectric properties

The same PP electret foam unirradiated and irradiated with squared shape of 27 mm  $\times$  27 mm and 0.08 mm of thickness were used for investigation of the dielectric properties utilizing a Broadband Dielectric Impedance Analyzer Concept 40 (Novocontrol, Germany) in the frequency range from 0.1 Hz to 10 MHz and temperature range from  $-100~^{\circ}\text{C}$  and  $100~^{\circ}\text{C}$  in order to obtain the properties in the potential application window. The amplitude of applied AC voltage was 1 V. The standard sample cell BDS 1200 employing the RC model of the sample was used to determine complex impedance and based on this and dimensions of the sample the capacitance was obtained as crucial following characteristic.

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