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The influence of electron beam irradiation on the mechanical and thermal properties of Poly (ether-block-amide) blends

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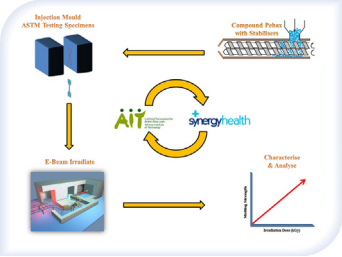
HIGHLIGHTS

- Mechanical properties of Pebax and Irganox 565 can be controlled by radiation dose
- Virgin Pebax and Pebax blended with Irgnaox B215 provides good radiation resistance
- MFI decreases gradually for the Virgin Pebax with an increase in radiation dose
- Molecular weight of Pebax and Irganox B215 is less effected by radiation dose
- Simultaneous chain scission and crosslinking/branching occurs during irradiation

GRAPHICAL ABSTRACT



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ABSTRACT

High energy electron beam irradiation of Poly (ether-block-amide) (Pebax) can induce modifications and/or degradation to transpire in the material subsequent to treatment. To minimise this, Pebax was blended with three stabilisers where each formulation was subjected to electron beam radiation at doses of 25, 50 and 75 kGy. Mechanical testing revealed that the virgin Pebax and the Pebax blended with Irganox B215 provided the best radiation resistance in terms of the tensile strength, elongation at break and Young's modulus. Upon increase in radiation dose from 25 to 75 kGy, a gradual diminution was observed for the melt flow index (MFI) of the virgin Pebax, whereas Pebax blended with Irganox B215 had a minute effect on the properties post irradiation. This study provides evidence that the stabilisers used can either promote undesirable effects or enhance the radiation resistance of Pebax material following radiation exposure.

1. Introduction

Pebax is a thermoplastic elastomer which is combined of linear chains of rigid aliphatic polyamide segments interspaced with flexible amorphous polyether segments. This copolymer is produced by a molten state polycondensation reaction from a diacarboxylic polyamide and a polyester diol (Cen et al., 2002; Friess et al., 2011). Properties for each of the copolymers are related to the relative content of polyether (PE) and polyamide (PA) and to their chemical characteristics. Pebax contains a phase separated microstructure in which the hard PA segment delivers the mechanical stability and contributes to crystallinity, while the soft PE segment acts as a permeable phase giving the material its high chain mobility (Bernardo et al., 2012; Kim et al., 2001; Le et al., 2011). This material is extensively used in the biomedical industry as it offers valuable properties such as elasticity and thermal stability at body

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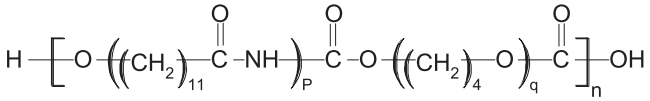
temperatures, where such applications range from catheter bodies to angioplasty balloons (Sjong et al., 2006). For medical device usage, it is of vital importance that the Pebax properties are not impaired by sterilisation using ionising irradiation techniques (Clayden and Pendlebury, 2001). During radiosterilisation of polymers, simultaneous chain scission and crosslinking can transpire where one process clearly predominates over the other. The preponderance of one process over another is determined by the overall structure of the polymer (Datta et al., 1998) and the irradiation processing conditions. It is possible to achieve stabilisation at the different stages of degradation by blending antioxidants, radical scavengers and hydroperoxide decomposers with a base polymer like Pebax. Hindered phenols are remarkably effective at protecting the physical properties of a polymer, however, at the expense of a yellowish colour formation (Klemchuk and Horng, 1991). While the hindered amine stabilisers (HAS) provide excellent resistance towards UV degradation and long term heat exposure. In recent years, the blending of phenolic antioxidants with various stabilisers has developed into an interesting field of research (Alariqi et al., 2007). Considering that synergistic mixtures (hindered amine stabilisers and primary and secondary antioxidants) of stabilisers for radiation stabilisation of Pebax have not being explored up until now, the current investigation will focus on identifying the improvements to the material after radiation exposure in terms of the mechanical and thermal properties.

2. Experimental

2.1. Materials

Pebax (polyether-block-amide) 6333 virgin medical grade polymer was manufactured by Arkema Ltd. (France) and purchased from the National Chemical Company (Ireland). A density of 1.01 g/cm^3 was specified for the material with a melting temperature of 169 °C. The material was supplied in granular form and was stored under vacuum at ambient temperature until use. Pebax contains linear chains of hard polyamide (PA) blocks covalently linked to soft polyether (PE) blocks via ester groups. The PE blocks have a molecular weight that varies from approximately 400 to 3000 g/mol, whereas the PA blocks have a molecular weight that varies from about 500 to 5000 g/mol (Sheth et al., 2003). The complex structural formula of this block copolymer is (Murray et al., 2013a):



Polymer stabilisers such as Irganox B215 (organo-phosphite and hindered phenolic antioxidant), Irganox 565 (multifunctional phenolic antioxidant) and Tinuvin 783 (hindered amide light stabiliser) were kindly supplied by Heterochem (Dist) Ltd. (Ireland). All material was used as received with no further treatment.

2.2. Hot melt extrusion

The compounding of the materials in this study was performed on a Micro 27 laboratory twinscrew extruder (Leistritiz Ltd.) which incorporated a screw diameter of 27 mm and a 38/1 length-to-diameter ratio. The temperature profile of the labscale extruder was established by means of nine temperature controllers attached along the length of the barrel. A tenth temperature controller located at the die was used to regulate the temperature of the die zone. Feeding of the polymer and additives was accomplished by independent K-Tron gravimetric feeders. In this study, four different batches of material were analysed: (1) Pebax at 100% denoted by P0, (2) Pebax at 99.8% and Irganox B215 at 0.2% denoted by PB215, (3) Pebax at 99.8% and Irganox 565 at 0.2% denoted by P565, and (4) Pebax at 99.8% and Tinuvin 783 at 0.2% denoted by P783.

2.3. Injection moulding and packaging

Drying of the virgin and compounded Pebax material was performed in accordance to the manufacturer's specifications (75 °C for 6 h). A moisture content test was conducted on the dried materials prior to injection moulding. This was to ensure the moisture content was below a specified limit (typically below 0.02%) to avoid defects during the processing of the samples. An Arburg injection moulder was utilised in manufacturing type IV (American society for testing and materials) ASTM D638 testing specimens. The machine had a maximum clamping force of 38 t with a screw diameter of 25 mm. Each of the samples i.e. tensile specimens and granules was placed into sealable low density polyethylene bags in order to contain it in a controlled environment. Sample size, density, weight and orientation remained identical for each bag during the packaging process to facilitate uniform irradiation (Murray et al., 2013b).

2.4. Electron beam irradiation

First, dose mapping was conducted on the virgin and compounded Pebax testing specimens to determine the maximum and minimum dose zones and process reproducibility. A Mevex high energy electron beam irradiator (combined 10/12 MeV unit, 20 kW) was used to irradiate the samples at doses of 25, 50 and 75 kGy. The dose rate was delivered at approximately 12.5 kGy per pass on each side of the samples to accomplish a consistent irradiation dose. All samples were irradiated at room temperature in the presence of air at the Synergy Health plant (Tullamore, Ireland) (Murray et al., 2012).

2.5. Tensile testing

Virgin and compounded Pebax dumbbell specimens were used to measure the tensile strength, Young's modulus and elongation at break. The experiment was carried out according to ASTM D638-03 (ASTM D638-03, 1994) with the exception of implementing a crosshead speed of 500 mm/min. An Instron 3365 universal testing machine was employed to conduct each experiment where a 5 kN load cell was applied during the experiments with a gripper distance of 40 mm. Five tests were executed for each dose range and the mean was obtained from each of the five results.

2.6. Melt flow index

Melt flow index (MFI) values of the non-irradiated and irradiated Pebax granules were measured according to ASTM standard D 1238 (ASTM D638-03, 1994) by means of a CEAST Melt Flow Quick Index. MFI measurements were performed at a temperature of 235 °C under a 1 kg weight. The melted material flowed through an orifice of 2.00 mm diameter for 10 min and the values were reported in g/10 min.

3. Results and discussion

3.1. Tensile testing

The results of the tensile strength, elongation at break and Young's modulus of virgin and compounded Pebax are illustrated in Figs. 1–3, subsequent to a range of electron beam irradiation doses. In each case, the non-irradiated virgin Pebax was used as the control sample when analysing the results. Represented in Fig. 1 is the tensile