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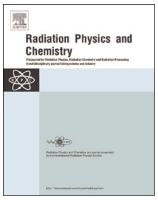

The effect of electron-beam irradiation and halogen-free flame retardants on properties of poly butylene terephthalate

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HIGHLIGHTS

- We investigated the effects of flame retardants and irradiation on the PBT's properties.
- After irradiation tensile strength improved but impact strength degraded.
- Irradiated PBT burned in a lower rate and less dripping than non-irradiated samples.
- Adding the flame retardants to PBT and crosslinking made it self-extinguishing.

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ABSTRACT

Engineering plastics like Poly (butylene terephthalate) due to their desirable properties have various industrial applications. Neat PBT is highly combustible, so it is necessary to improve significantly its fire retardancy to meet the fire safety requirements. The combustion performance of PBT can be improved by addition of appropriate flame retardant additives. In this study we have investigated the effect of halogen free flame retardants, i.e. melamine and aluminum phosphate, and instantaneously electron beam radiation-induced crosslinking in the presence of Triallyl cyanurate on various properties of PBT.

The results of gel content showed that a dose range of 200–400 kGy leads to high cross linked structure in this polymer. Also mechanical experiments showed that its structure became rigid and fragile due to irradiation. Radiation crosslinking of this polymer made its dielectric loss coefficient ten times lower than non-irradiated polymer, but had no effect on its dielectric constant. Moreover the addition of the fire retardant additives as impurity decreased the dielectric loss coefficient. TGA analysis in nitrogen exhibited that irradiation increases char formation and use of the fire retardant additives leads to reduction of onset temperature and formation of higher char quantity than pure PBT. According to the results of UL-94, irradiated samples burned with lower speed and less dripping in vertical and horizontal positions than pure polymer. Finally irradiation of the polymers containing fire retardant additives with a dose of 400 kGy led to self-extinguishing and non-dripping and reach to V-0 level in the UL-94 V.

1. Introduction

Poly (butylene terephthalate) is an engineering thermoplastic that has numerous industrial applications such as electronic and communication equipment, electrical connectors, industrial equipments, medical devices and automotive productions. It has high heat resistance as well as good mechanical strength and toughness. It is resistant to the oils, greases and cleaning fluids. This thermoplastic polyester easily burns and drips, thus flame retardancy in this polymer is of high interest and importance. There are numerous effective additives containing halogens for this purpose; but these additives produce toxic and corrosive gases and dark smoke during burning which may be harmful for human and environment (Gallucci and Patel, 2003; Xiao et al., 2006). Therefore, several studies have been performed on non-halogen additives such as phosphorus and nitrogen-based flame retardants like phosphines, phosphinates (Bakirtzis et al., 2009; Gallo et al., 2011), phosphonates (Balabanovich and Engelmann, 2003), red phosphorus (Balabanovich et al., 2004), phosphates (Ishikawa et al., 2004) and melamine compounds (Balabanovich, 2004)

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which were successfully used in PBT. Phosphorus acts as a flame retardant (FR) in both phases: in the gas phase due to release of phosphinic acid to the gas phase, and in solid phase as a char former (Gallucci and Patel, 2003; Braun et al., 2008). The addition of melamine to the polymers like PBT and polyamide 6 improves their fire retardant performance. The mode of its action is endothermic sublimation and vapor-phase dissociation. Moreover, melamine transforms to non-volatile products and ammonia (Balabanovich, 2004).

In a number of studies done in this concern, phosphorus compound in combination with nitrogen containing additives have successfully been used as fire retardants in PBT (Braun et al., 2008; Braun and Scharte, 2008; Ramani et al., 2009; Levchik et al., 1997).

Levchik and Weil (2005) have reviewed the publications of the last fifteen years on the flame retardancy of thermoplastic polyesters, especially poly (ethylene terephthalate) (PET) and poly (butylene terephthalate) (PBT).

In the recent years crosslinking reaction has been of high interest for improving the fire behaviour and other properties of polymers. The process of burning requires that large polymer chains to be broken down in order to give smaller molecules. Eventually, a stage is reached at which the produced molecules have sufficient volatility to escape the surface and enter the gas phase.

This scenario indicates that in order to prevent the combustion of a polymer, breakdown to small molecules must be prevented and instead the polymer chains aggregate to produce the crosslinked polymer (Wilkie et al., 1989). In principle, crosslinking reduces the molecular mobility and increases the number of bonds required to be broken in a material to exhibit mass loss (Qiang and Wilkie, 2000). Intermolecular crosslink also leads to increasing the char formation when the irradiated polymer is heated (Balabanovich et al., 1999; Wilkie, 1999).

Radiation-induced crosslinking is one of the suitable methods to crosslink polymers because of its advantages in comparison with chemical methods. Radiation crosslinking occurs at room temperature or at temperature up to about 60 °C. This pure physical process is technically and economically feasible, since after execution of this method no residues of chemical substances exist, while there are some residues after chemical solutions (Chmielewski et al., 2005).

Balabanovich et al. investigated the effect of irradiation on the flame behaviour of PBT. They reported that PBT similar to polyamide-6 and polyamide 6, 6, can be made fire retardant to some extent by the addition of red phosphorus and irradiation by 60Co gamma rays. It turned out that a minimum phosphorus load of 12.5 wt% is required to achieve non-dripping and V-1 rating in the UL-94 test (Balabanovich et al., 2004).

In this study we investigated the effects of electron beam irradiation and addition of halogen free flame retardant additives (10 wt% melamine and 10 wt% aluminum phosphate) on flame retardancy as well as mechanical, electrical and thermal properties of PBT.

2. Experimental

2.1. Materials

The PBT (Poly butylene terephthalate) used in this study was a commercial product of Razin polymer, I. R. Iran (Razadur-K116). Triallyl cyanurate (TAC), melamine, phenol and 1, 2-Dichlorobenzol was supplied from Merck Co, Germany. Aluminum phosphate was provided by Aldrich Co, USA.

Table 1
Composition of formulations (wt%).

Material	PBT	TAC	Melamine	Aluminum phosphate
PBT	100	–	–	–
PBT/TAC	96	4	–	–
PBT/FRs[a]	80	–	10	10
PBT/TAC/FRs	76	4	10	10

[a] FRs: melamine and aluminum phosphate.

2.2. Samples preparation

PBT/additives samples were prepared by using internal mixer 350-E made by Brabender Company. The mixing was carried out at 80 rpm and 240 °C. Before processing, PBT was dried in the vacuum oven at 80 °C for 15 h. The samples formulations are given in Table 1.

2.3. Irradiation

The irradiation was carried out in air by using Rhodotron-TT200 10 MeV electron beam. Irradiation was done on a conveyor belt with variable speed in the rage of 260–640 cm/min and dose per pass of 25 kGy. Samples have been irradiated to total absorbed doses of 200, 300 and 400 kGy at room temperature in room temperature of 25 °C.

The dosimetry method was Cellulose Triacetate (CTA) in which absorbed dose was measured based on a change in optical absorbance in the CTA dosimeter film. In accordance with standard test method ASTM51650-13, CTA dosimeter film is particularly useful in absorbed dose mapping because it is available in a strip format and if measured using a strip measurement device, it can provide a dose map with higher resolution than using discrete points. Because of small thickness of the samples, a uniform dose distribution has been considered. After determining the optimum dose for radiation-induced crosslinking, some tests were carried out on all samples before and after being irradiated by optimum dose.

2.4. Gel content

According to ASTM D-2765, the gel content of the irradiated samples was determined by extraction with phenol/1, 2-Dichlorobenzol (50/50) as solvent at room temperature for 48 h. The gel content denotes the ratio of the mass of the sample after extraction to the mass before extraction by using Eq. (1), where W_0 is the initial weight of the sample and W is its final weight of samples after extraction.

$$\%\,gel\ content = \left[1 - \left(\frac{W - W_0}{W_0}\right)\right] \times 100 \tag{1}$$

Three samples of each formulation were measured and the average was determined.

2.5. Tensile behavior and impact strength

Tensile strength in accordance with standard test method ASTM D-638 was determined. This test was determined by using HIWA200 machine at 50 mm/min speed of testing and at room temperature. Five specimens were tested and the average of values was reported. Notched izod impact was carried out with HIWA301 machine according to ASTM D-256.

2.6. Thermogravimetric analysis

TGA studies were carried out by using a Shimadzu DTG-50H instrument in the presence of nitrogen atmosphere at a heating