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Effect of additives on thermal properties of electron beam irradiated LDPE foam

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Abstract. In this work, the effects of some additives such as TMPTMA, a multifunctional monomer, and ZnO as the activator on thermal properties of electron beam irradiated LDPE foam were investigated. LDPE foams were made via adding 5 phr of azodicarbonamide as the blowing agent (ACA), 1–5 phr of ZnO and 1–5 phr of TMPTMA to the low-density polyethylene (LDPE) and then cross-linked using the 10 MeV electron beam at the dose range of 20 to 100 kGy. Effects of activator, multifunctional monomer and irradiation on thermal properties such as melting and degradation temperatures in cross-linked polyethylene foam were investigated. The thermal properties were measured by differential scanning calorimetry system (DSC).

Key words: polyethylene foam • 10 MeV electron beam • crosslinking • thermal properties • multifunctional monomer • activator

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Introduction

Polyolefines are tough, flexible and resistant to chemicals and abrasion, and foams made from polyolefines inherit such properties. The key properties of polyolefine foams are resiliency, energy absorption, buoyancy, resistance to chemicals, low thermal conductivity, thermoformability and ease of fabrication. Among polyolefine foams, polyethylene foam is used in a wide range of area such as automotive, buoyancy, flotation and insulation [6].

Most commercial polyolefine foam products are prepared by expansion process. In the foaming process, viscosity suddenly decreases while heating above the melting point, and the generated gas from the foaming agent cannot be retained inside. This phenomenon causes difficulties in obtaining foams with good expansion ratio and consequently making it impossible to control the size and number of foam cells [6]. In processes where foam expansion is accomplished by heating, bubbles need to be stabilized by crosslinking. This is particularly true for a process employing a chemical blowing agent (CBA) that decomposes exothermically. Crosslinking stabilizes the expanding bubbles by sharply increasing the extensional viscosity of the polymer, thereby preventing cell walls from draining. Crosslinking not only stabilizes bubbles during expansion but also

enhance the resistance of the cellular product to thermal collapse. Polyolefines can be cross-linked by high energy radiation, peroxide, a multifunctional aside or an organo-functional silane. Some researchers investigated structure-property relationship in PE foams [3–5].

In the present study, the authors want to relate the effects of activator, multifunctional monomer and irradiation to the thermal properties of polyethylene foam. In our assumption, due to the fact that there is not so much documented information about the mentioned factors, this work can give some beneficial data to the readers.

Experimental

Materials

Low-density polyethylene (LDPE) supplied by Bandar Imam Petrochemical Company, Iran, (MFI: 2 g/10 min, density: 0.92 g/cm^3) were used in this investigation. Azodicarbonamide (ACA), made by MERCK Company, was used as blowing agent with degradation (or decomposition) temperature range of 200–220°C (Fig. 1), and trimethylolpropane-trimetacrylate (TMPTMA) was used as multifunctional monomer from Aldrich. Technical grade zinc oxide (ZnO) was used as activator from Pars Oxide Company, Iran.

Sample preparation

LDPE and other additives, in different ratios as shown in Table 1, were melt-mixing in an internal mixer (Cam-type Brabender Lab-Station, 350 ml, Germany) with a speed of 50 rpm at 120°C for 5 min. The obtained compound compression molded between polyester sheets at 120°C using a Dr Collin warm press instrument to prepare sheets with 2 ± 0.1 mm thickness [2].

Samples irradiation

The compression molded sheets were irradiated in air under the scanned beam of a high-energy electron accelerator, Rhodotron TT200 type. The system is provided with the 10 MeV electron beam energy, maximum available beam current of 8 mA, and a scan width of 100 cm at a scan frequency of 100 Hz. The irradiation was performed for the samples to obtain doses of 20 kGy up to 100 kGy with an acceptable dose distribution [7] and a constant dose rate due to using the same beam current. Furthermore, to prevent local overheating during the irradiation, the samples were irradiated on an aluminum pallet for 20 kGy in each cycle of irradiation using a conveyor system.

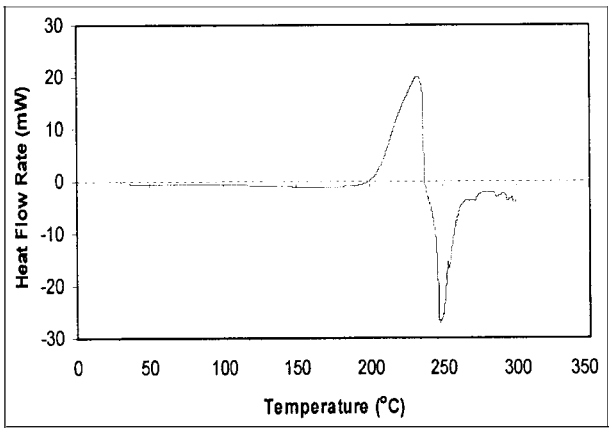

Fig. 1. DSC diagram of ACA. Degradation temperature range is 200–220°C.

Foaming method

In order to make foam, according to the degradation temperature of ACA, the samples were placed in an oven in the temperature range of 200 to 220°C. After accomplishing a series of trials, the optimum oven temperature was defined as 205°C. Samples then were placed in the oven at 205°C in order to obtain suitable foaming time. At the final stage, due to the fact that the surface appearance and quality of the samples prepared via oven were not so proper, the samples were prepared using the compression molding system to obtain the high quality foam.

Thermal analysis

The DSC tests were performed using a Shimadzu apparatus DSC-50 model, made in Japan. The samples were sealed in aluminum pans under nitrogen atmosphere in a temperature range between ambient temperatures up to 450°C at a heating rate of 10°C/min. The melting and the degradation temperatures of the samples were determined. According to the DSC diagram for the similar sample, the melting region in this experiment was defined as two temperatures of onset and end-set temperatures which are the beginning and ending temperatures of the melting region, respectively.

Results and discussion

At the first stage, in order to investigate the effect of absorbed dose on degradation and melting points of polyethylene foam, some flat sheet samples of PE and 5 phr of ACA [1] were prepared and irradiated in the range of 20 to 100 kGy (formulations 1 to 5 in Table 1). After foaming procedure, the samples were objected to DSC measurements. The melting and degradation temperatures were recorded vs. absorbed dose in Figs. 2 and 3, respectively. According to Fig. 2 increasing the absorbed dose did not change the end-set temperature significantly, whereas the onset temperature was changed in the range of 20 to 40 kGy and then became constant. Therefore, the absorbed dose of 50 kGy was chosen for the next experiment. Furthermore, the degradation temperature increases remarkably by raising in absorbed dose due to the irradiation. The degradation temperature increment at the chosen dose is about 30°C in compare with lower dose at which the foaming is

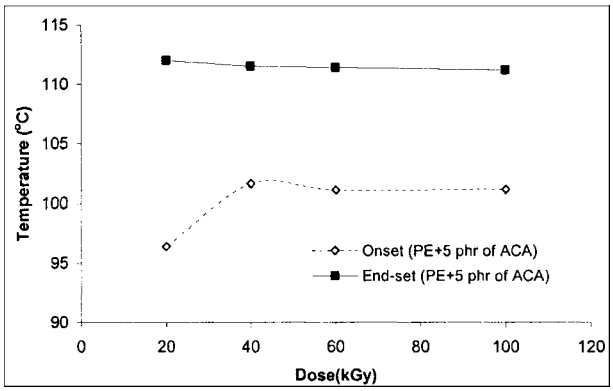

Fig. 2. Effect of radiation dose on melting temperature of LDPE foam samples.

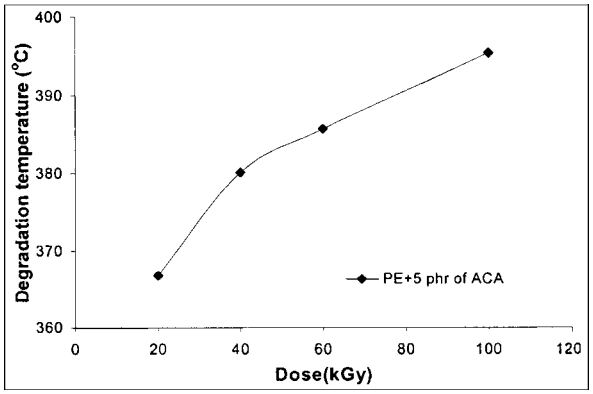

Fig. 3. Relationship between degradation temperature and radiation dose for LDPE foam samples.

possible (Fig. 3). As it is shown in the figures, there is not any data in the dose region less than 20 kGy. This is due to the fact that the gel content in the samples was too low and they were failed during the foaming process.

In order to investigate the effect of activator, some sheet samples according to the formulations 6 to 8 included in Table 1 (PE, 5 phr of ACA and 1, 3 and 5 phr of ZnO), were prepared and irradiated at a 50 kGy dose. Then, the samples were investigated by DSC test

Table 1. Different mixing formulations

No.	LDPE (phr)	ACA (phr)	ZnO (phr)	TMPTMA (phr)	Dose (kGy)
1	100	5	0	0	20
2	100	5	0	0	40
3	100	5	0	0	60
4	100	5	0	0	80
5	100	5	0	0	100
6	100	5	1	0	50
7	100	5	3	0	50
8	100	5	5	0	50
9	100	5	5	1	50
10	100	5	5	3	50
11	100	5	5	5	50

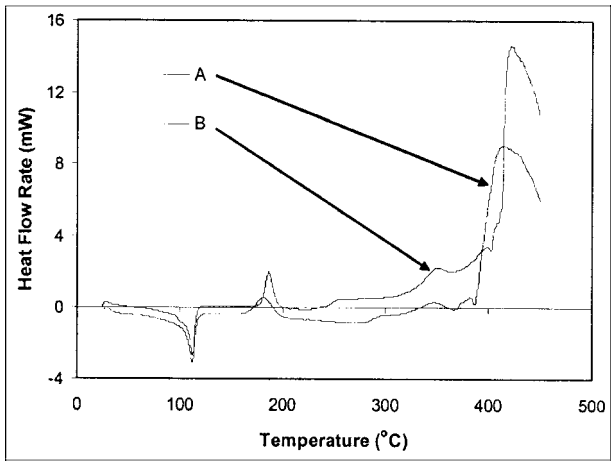

Fig. 4. DSC diagram of LDPE foam samples irradiated at 50 kGy; A – PE + 5 phr of ACA + (1–5) phr of ZnO; B – PE + 5 phr of ACA + 5 phr of ZnO + 1 phr of TMPTMA.

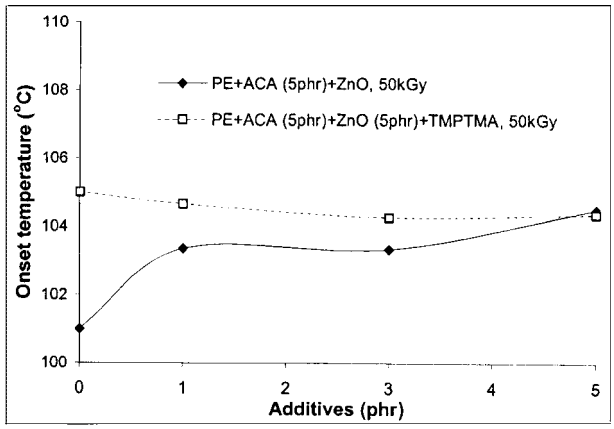

Fig. 5. Effect of additives (ZnO, TMPTMA) on T_{mi} for cross-linked LDPE foam samples, which were irradiated at 50 kGy.

(Fig. 4). It can be seen that ZnO did not make any noticeable effect on the onset and end-set temperature of the melting region (Figs. 5 and 6). But it is important that ZnO has a significant effect on the degradation point of ACA and decreases it from about 205°C to

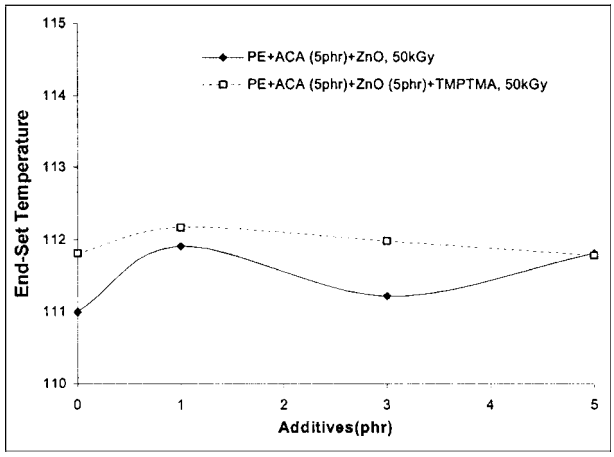

Fig. 6. Effect of additives (ZnO, TMPTMA) on melting end-set temperature of cross-linked LDPE foam samples, which were irradiated at 50 kGy.

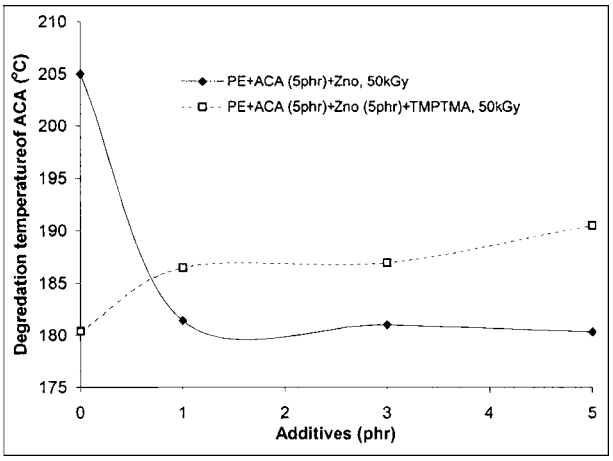

Fig. 7. Effect of additives (ZnO, TMPTMA) on ACA degradation temperature in LDPE foams which were irradiated at 50 kGy.

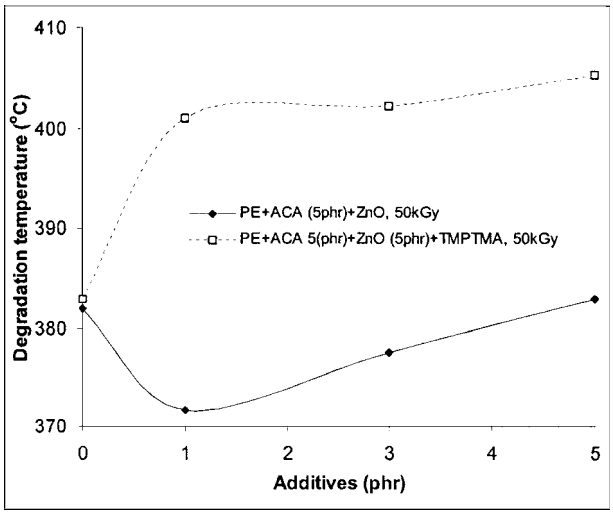

Fig. 8. Effect of additives (ZnO, TMPTMA) on degradation temperature of LDPE foam samples, which were cross-linked at 50 kGy.

180°C (Fig. 7). On the other hand, 1 phr of ZnO reduced the degradation temperature about 10°C, but it will be increased again up to near the same point using 5 phr of ZnO (Fig. 8). Therefore, 5 phr of ZnO were used for the next stage as the best percentage.

At the final stage, the formulations 9, 10 and 11 were prepared to investigate the TMPTMA effect on the degradation and melting temperatures of samples after irradiation and foaming procedure. The typical DSC diagram for the same formulation is shown in Fig. 4. It is obvious in Figs. 5 and 6 that TMPTMA do not have any significant effect on the onset and end-set temperatures of melting region. But it enhances the ACA degradation temperature up to 10°C (Fig. 7). Furthermore, foam sample degradation temperature increases remarkably by enhancement of TMPTMA amount, whereas degradation temperature will increase about 20°C by adding 1 phr of TMPTMA in the samples.

Conclusions

1. The end-set temperature of melting region for the PE foams does not change due to the irradiation, whereas the onset point increases at low doses (about 20 to 40 kGy).
2. The degradation temperature of PE foams increases remarkably up to 100 kGy. This thermal resistance extension arises from crosslinking of PE foams due to the radiation.
3. ZnO and TMPTMA do not have any significant effect on the onset and end-set temperatures of the melting region in PE foams.
4. ZnO decreases the ACA degradation temperature. This is the result of transient complex formation of the Zn-carboxylic.
5. Degradation temperature of the PE foam increases remarkably by TMPTMA augment. This enhancement arises from crosslinking scale increasing.
6. The optimum condition to get the best result can be obtained by formulation no. 9 (Table 1), which is LDPE (100 phr) + ACA (5 phr) + ZnO (5 phr) + TMPTMA (1 phr), and 50 kGy dose under the 10 MeV electron beam radiation.

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