

Chemically crosslinked polyethylene foams of limited flammability (*Rapid Communication*)

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Abstract: A method to prepare chemically crosslinked polyethylene foams from a mixture consisting of polyethylene, foaming agent, crosslinking agent, antioxidant and flame retardant was discussed in this paper. The extrusion was carried out using a twin-screw extruder (temperature of barrel zones: 100, 110, 125 and 125 °C). Crosslinking process of the extruded material was performed at 160 °C for 5 min. The polyethylene films were foamed in silicon oil at 225 °C for 2 min. The influence of the content of flame retardant on density, hardness, flammability and tensile strength of the obtained foam was determined.

Keywords: polyethylene foams, chemical crosslinking, foaming, flame retardancy.

Chemicznie sieciowane pianki polietylenowe o ograniczonej palności

Streszczenie: Omówiono sposób otrzymywania chemicznie sieciowanych pianek polietylenowych z mieszaniny zawierającej polietylen, środek spieniający, środek sieciujący, antyutleniacz oraz środek ograniczający palność. Proces wytłaczania folii prowadzono w wytłaczarce dwuślimakowej (temperatury stref grzejnych cylindra: 100, 110, 125 i 125 °C). Proces sieciowania prowadzono w temperaturze 160 °C w ciągu 5 min. Folię poddano procesowi spieniania w oleju silikonowym w temperaturze 225 °C przez 2 min. Zbadano wpływ zawartości środka ograniczającego palność na gęstość, twardość, palność oraz wytrzymałość na rozciąganie otrzymanych pianek polietylenowych.

Słowa kluczowe: pianki polietylenowe, sieciowanie chemiczne, spienianie, uniepalnianie.

Chemically crosslinked polyethylene foams are characterized by good thermal insulation properties, low density, low thermal conductivity, high sound absorption and chemical resistance. These properties favour their wide use in construction, automotive, packaging industry and the sport [1, 2].

Chemically crosslinked foams are produced in five stages. The first stage involves obtaining a mixture of polymer with a crosslinking agent (*e.g.* dicumyl peroxide [3]), a chemical foaming agent and other additives (crosslinking processing aids, flame retardants, etc.). This step is carried out in a mixer. In the second step, the pellets are prepared in an extruder. When the film is extruded to form the pellets it is subjected to the process of crosslinking and foaming [4].

Polyethylene as the basic ingredient of chemically crosslinked foams belongs to the group of flammable materials. In order to obtain foams of reduced flammability, it is necessary to use a flame retardant, which reduces oxygen index (*OI*) of the polymer materials. This is especially important in the case of materials used in construction and transport, for which EU

directives introduce more stringent requirements regarding their flammability characteristics. For these reasons, the development of the composition and production technology of polymer composites of reduced flammability is of great interest for the industry [5].

In the recent years in the EU countries a tendency to reduce applying flame retardancy methods, which use chlorinated flame retardants, due to their toxicity to the environment is observed. These restrictions have triggered pursuit for alternative solutions. Nowadays, in the flame retardancy process there are halogen-free flame retardants such as Mg(OH)₂, Al(OH)₃ or organophosphates applied. The disadvantages of limiting use of the hydroxides as a flame retardants is necessary to use large quantities of the substances in order to obtain an adequate flame retarding effect, which leads to deterioration of material properties *e.g.* increase in density [6–9].

The objective of the study is to determine the effect of organophosphorus flame retardants on density, hardness, flammability and tensile strength of chemically crosslinked polyethylene foams.

EXPERIMENTAL PART

Materials

Low density polyethylene (PE-LD) of type Malen FGAN 23-D003 characterized by density $d = 0.922 \text{ g/cm}^3$

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and $MFR (190\text{ }^\circ\text{C}/2.16\text{ kg}) = 0.31\text{ g}/10\text{ min}$ was supplied by Lyondellbasell. The crosslinking agent was dicumyl peroxide of type Perkadox BC-FF (content of dicumyl peroxide >99 wt %) delivered by Akzo Nobel Chemicals. Azodicarbonamide of type Unicell D1500TSK delivered by Tramaco was used as a foaming agent. Irganox PS 802 FL (Ciba Specialty Chemicals) was used as antioxidant. The halogen-free flame retardant was based on organophosphorus compound (phosphorous content 14 %, nitrogen content 37 %, humidity content below 0.5 % [10]) with trade name AFLAMMIT PCO 800 and was supplied by Thor company.

Sample preparation

At the initial stage, the mixture consisting of polyethylene, crosslinking and foaming agent, anti-oxidant and heat stabilizer was prepared using a Brabender planetary mixer. Extrusion process of pellets was realized using a co-rotating twin-screw extruder with screw configuration like in [11]. The temperature profile along the barrel was: 100, 110, 125 and 125 °C. The polymer film was obtained by the lab equipment consisting of the single screw extruder type Plasti-Corder PLV 151 (Brabender) with the flat die and polishing rolls. The screw parameters were: working length 25D and compression ratio 3:1. Furthermore, the experimental stand was equipped with a device for measuring temperature of the heating zone of the plasticizing system and the head. Screw rotation speed was 75 rpm.

The crosslinking process was carried out in the oven of type SLW 53 (POL-EKO) at the temperature 160 °C for 5 min, while the foaming process was conducted in silicone oil bath at 225 °C for 2 min. The compositions of individual compounds are showed in Table 1.

Table 1. The composition of prepared polyethylene foams

Symbol of sample	Content, wt %			
	dicumyl peroxide	foaming agent	flame retardant	anti-oxidant
P-0	0.8	15	0	0.2
P-2	0.8	15	2	0.2
P-6	0.8	15	6	0.2
P-10	0.8	15	10	0.2
P-14	0.8	15	14	0.2
P-18	0.8	15	18	0.2
P-22	0.8	15	22	0.2

Methods of testing

Total apparent density (ρ_a) was determined from crosslinked and foamed samples (dimension of samples was approximately 50 × 50 mm) — three samples for each film. Density and dimensions of samples were measured in accordance with PN-EN ISO 845:2010 and PN-EN ISO 1923:1995.

Hardness tests were performed basing on the standard PN-ISO 868:2005 using a durometer Shore A type WPM (Thür.Industriewerk Rauenstein).

Tensile test of samples (5 measurements for each sample) were performed using testing machine type TIRAtest 27025. The research was performed in the machine direction (MD) according to PN-EN ISO 527-1:2012 and PN-EN ISO 527-3:1998.

The study of flammability by measurements of oxygen index (OI) was based on PN-C-89020:1976.

RESULTS AND DISCUSSION

The effect of flame retardant content on the density and hardness is shown in Table 2. As expected, the density and hardness of the foam increased with increasing flame retardant concentration. The highest density was obtained for foams (P-22) made from composition consisting of 22 % of flame retardant. The foams of lowest density (0.06 g/cm³) were samples P-0 and P-2. The apparent density of P-22 foam was almost ten times higher than the density of foams P-0 and P-2.

Table 2. Values of hardness and densities of prepared polyethylene foams

Symbol of samples	Density, g/cm ³	Hardness, ShA
P-0	0.06 ± 0.01	—
P-2	0.06 ± 0.01	—
P-6	0.37 ± 0.04	62 ± 2
P-10	0.44 ± 0.04	72 ± 2
P-14	0.44 ± 0.08	73 ± 2
P-18	0.53 ± 0.02	77 ± 1
P-22	0.57 ± 0.05	81 ± 2

Determination of the hardness of P-0 and P-2 foams was not possible because the foams were characterized by the highest degree of foaming as compared to the other samples. From above mentioned foams, P-6 foam was characterized by the lowest value of hardness equal to 62 ShA. The highest hardness was obtained for foam with the highest content of flame retardant (22 wt %). The hardness of this foam was about 30 % higher than the hardness of the foam containing 6 wt % of this component.

The influence of flame retardant content on OI is shown in Fig. 1. The lowest OI value was obtained for the foam without flame retardant. The obtained value of OI was equal to 27 % and was higher than for the crosslinked PE-LD ($OI = 20.4\text{ \%}$ [8]). It can be a result of the crosslinking process [8] and the use of silicone oil in the foaming process, which is non-flammable. Silicone oil penetrates into the pores of the foam and probably increases the value of OI .

The increase of flame retardant content slightly raises OI , but for the content higher than 14 wt % OI remains practically constant. Polymeric materials containing

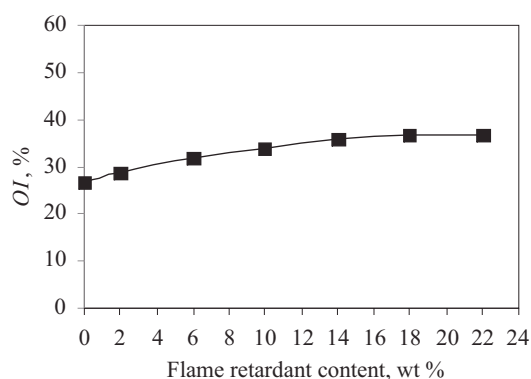


Fig. 1. The effect of flame retardant content on oxygen index (OI) of foams

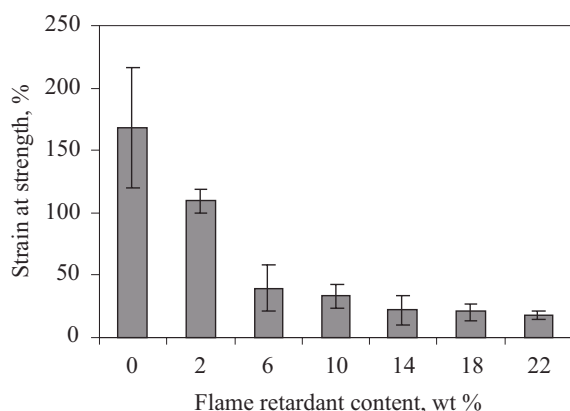


Fig. 2. The effect of flame retardant content on strain at strength of foams

organophosphates thermally decompose during combustion and release the phosphoric acid. This acid causes dehydrogenation of the polymer, which formed a protective coke layer [6].

The dependency of strain at maximum tensile stress of chemically crosslinked foams on the content of flame retardant is presented in Fig. 2. The smallest strain at tensile strength equal to 16.1 % was obtained for the foam containing 22 wt % of the flame retardant. The highest strain

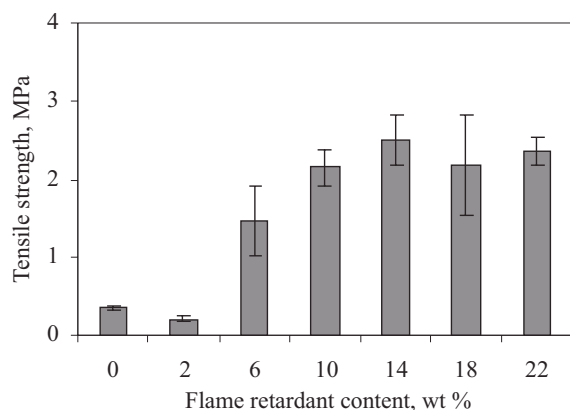


Fig. 3. The effect of flame retardant content on tensile strength of foams

at tensile strength was noticed for the foams without any flame retardant. Strain for these foams was approximately nine times higher than the strain for the foam containing 22 wt % of this agent.

The effect of flame retardant content on the tensile strength of foams is shown in Fig. 3. The lowest value of the tensile strength equal to 0.21 MPa was obtained for the foam containing 2 wt % of the flame retardant and the highest for the foam containing 14 wt %. The strength of this foam was 12 times greater than the strength of foam containing 2 wt % of this agent. It must be noticed that reducing the materials density by foaming process also decreases the tensile strength. The low density is characterized by large share of void structures, which decreases their tensile strength.

CONCLUSION

This research and extrusion tests lead to the conclusion that the preparation process of chemically crosslinked foams of reduced flammability conducted in five stages allows to obtain low density foams (0.06 g/cm³, the degree of foaming 15).

It was observed that the addition of the flame retardant causes the increase of OI value from 24 to 37 %. Chemically crosslinked polyethylene foams with 2 % of the flame retardant are practically nonflammable. Too high content of flame retardant reduces the quality of foams' surface.

The foaming process using silicone oil causes the surface of foams greasy what reduces their commercial application.

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