

Effect of environmentally-friendly flame retardants on fire resistance and mechanical properties of rigid polyurethane foams

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Abstract: In this paper the new compositions of polyurethane foams with reduced flammability containing environmentally friendly flame retardants, such as ammonium polyphosphate, melamine pyrophosphate, triethyl phosphate, bentonite and expanded graphite obtained with long fiber injection (LFI) method have been presented. The effect of the addition of various flame retardants and their mixtures on the fire resistance and mechanical properties of the foams has been determined. An improvement in fire resistance of the modified polyurethane compositions has been observed. Manufactured polyurethane foams containing flame retardants have been classified as materials with flammability class V-0. The addition of flame retardants has not significantly deteriorated mechanical properties of the investigated materials.

Keywords: polyurethane foams, flame retardants, resistance to fire, mechanical properties, apparent density.

Wpływ przyjaznych środowisku antypirenów na ognioodporność i właściwości mechaniczne sztywnych pianek poliuretanowych

Streszczenie: Metodą wtryskiwania długich włókien (LFI) otrzymano nowe kompozycje pianek poliuretanowych o ograniczonej palności, zawierające przyjazne środowisku środki zmniejszające palność, takie jak: polifosforan amonu, pirofosforan melaminy, fosforan trietylu, bentonit i grafit ekspandowany. Określono wpływ dodatku tych antypirenów i ich mieszanin na ognioodporność oraz właściwości mechaniczne pianek. W porównaniu z pianką poliuretanową bez dodatków, wszystkie modyfikowane kompozycje poliuretanowe wykazały poprawę ognioodporności i zostały sklasyfikowane jako materiały niepalne klasy V-0. Stwierdzono także, że dodatek antypirenów nie spowodował istotnego pogorszenia właściwości mechanicznych badanych materiałów.

Słowa kluczowe: pianki poliuretanowe, antypireny, ognioodporność, właściwości mechaniczne, gęstość pozorną.

Nowadays, automotive, construction and aviation industry focuses on reducing the weight of vehicles and machines. Thus, many structures are largely made from lightweight polymeric materials as well as polymer-based composites. An important role in constructions play rigid polyurethane (PUR) foams [1–3]. Due to their low fire resistance, they have to be appropriately modified. One of the basic methods for the preparation of PUR with reduced flammability is adding to them flame

retardants. So far, the most commonly applied flame retardants contained chlorine and bromine. During combustion of the foam containing halogen compounds, toxic gases and fumes cause environmental pollution, which threatens the health and life of humans. Regarding these risks, the European Union introduced restrictions on their application [4, 5]. Due to the environmental aspects the industry began to apply to PUR environmentally friendly flame retardants such as nanofillers, expanded graphite and phosphorus/nitrogen compounds. Environmentally friendly flame retardant additives help to reduce the amount of emitted toxic gases and fumes. Depending on the type of flame retardant there are several mechanisms of reducing the flammability of PUR foams. Phosphorus-nitrogen compounds are inhibitors of the combustion in the gas phase and form a glassy coating, limiting heat transfer to the interior of foam. Nanofillers

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(for example montmorillonite) in the composition form a barrier for emitted gaseous decomposition products of the polymer, whereas expanded graphite during the combustion forms a foamed carbon coating, hampering heat flow. To obtain the desired effect of fire resistance, to PUR foams should be introduced even 40 % of the flame retardant, what adversely affects the mechanical properties and increases the manufacturing costs. Utilizing a synergic effect occurring between different types of flame retardants, the flammability of PUR polymer matrix can be successfully limited by introducing a smaller amount of flame retardant additives [6–9].

The aim of the studies was to manufacture PUR foams with appropriate flame resistance while preserving the requested mechanical properties. To achieve the desired effect, various flame retardants in suitable proportions have been dispersed in the PUR matrix.

EXPERIMENTAL PART

Materials

For the synthesis of polyurethane foam, Elastoflex® E 3509 (BASF Polyurethanes GmbH) system has been selected. This system consists of polymeric methylene diphenyl diisocyanate (IsoPMDI 92140, BASF Polyurethanes GmbH) containing 31.5 % of NCO groups (viscosity $\eta = 219 \text{ mPa} \cdot \text{s}$, density at $25 \text{ }^\circ\text{C}$ $d_{25} = 1.23 \text{ g/cm}^3$) and the polyol component (Elastoflex® E 3509 Polyol, BASF Polyurethanes GmbH, $\eta = 1250 \text{ mPa} \cdot \text{s}$, $d_{25} = 1.12 \text{ g/cm}^3$) containing polyol, catalyst and stabilizing agents.

As the flame retardants the following compounds have been used:

- ammonium polyphosphate (APP, Tecnosintesi, Germany);
- melamine pyrophosphate (MPYP, Alwernia, Poland);
- triethyl phosphate (TEP, Clariant, Germany);
- expanded graphite (EG, Grafpol, Poland);
- bentonite modified benzyl(hydrogenated tallow alkyl)dimethyl ammonium chloride, (C, trade number Cloisite 10A, Byk, Germany);
- bentonite from Russian deposits (B, provided by a representative of Bento Group Minerals Company Poland Sp. z o.o., Gdynia) modified with butyl(triphenyl)phosphonium chloride (Xiamen Pioneer Technology c.o. Ltd., China).

Preparation of samples

To modification of bentonite the procedure of modification of smectic clays using phosphonium salt was employed. This procedure has been previously patented [10, 11] and described in the literature [12].

Specimens of rigid PUR foams have been manufactured in the hot pressing process using a press which is part of the tooling in long fiber injection (LFI) process. At

the first step, the polyol component was mechanically mixed for 5 min with selected flame retardant additives. Then, the modified polyol component and the isocyanate were stirred together for 25 s. In the final step, the PUR mixture was poured into a mold heated to $65 \text{ }^\circ\text{C}$. The mold was closed under the pressure of 50 MPa, for 360 s. The same method was used to prepare the reference polyurethane sample without flame retardant. The compositions of manufactured foams are shown in Table 1.

T a b l e 1. Polyurethane compositions manufactured by hot pressing

| Symbol of sample | Flame retardant additives | Content of additive, wt % |
|------------------|--|---------------------------|
| PUR „0” | none | |
| PUR TE | triethyl phosphate | 4.0 |
| | expanded graphite | 4.0 |
| PUR ME | melamine pyrophosphate | 4.0 |
| | expanded graphite | 4.0 |
| PUR AE | ammonium polyphosphate | 4.0 |
| | expanded graphite | 4.0 |
| PUR CAE | bentonite modified benzyl(hydrogenated tallow alkyl)dimethyl ammonium chloride | 1.9 |
| | ammonium polyphosphate | 4.0 |
| | expanded graphite | 3.0 |
| PUR BAE | bentonite modified butyl(triphenyl)phosphonium chloride | 1.9 |
| | ammonium polyphosphate | 4.0 |
| | expanded graphite | 3.0 |

Testing methods

Apparent density (δ) is the mass per unit volume of a material, including the voids which are in the material. The apparent density was measured and calculated for plates with dimensions of $100 \times 100 \text{ mm}$ according to PN-EN 1602:2013-07 standard.

Limiting oxygen index (*LOI*) determines the minimum concentration of oxygen needed to maintain the flame of burning material [13]. The value of *LOI* is expressed in percentage and calculated according to the formula:

$$LOI = \frac{X_O}{X_O - X_N} \cdot 100 \% \quad (1)$$

where: X_O – oxygen volume flow, X_N – nitrogen volume flow [14].

Oxygen index tests were carried out on equipment manufactured by Fire Testing Technology Ltd. The study was carried out according to PN-EN ISO 4589-2:2006 standard. UL 94 tests for safety of flammability were carried out in a horizontal/vertical flame chamber manufactured by Fire Testing Technology Ltd. The tests were conducted on plates with dimensions of $127 \times 12.7 \text{ mm}$. The

flammability tests by flame burner consist in setting fire to the horizontally (UL 94 HB) or vertically (UL 94 V) placed samples. The study was carried out according to PN-EN 60695-11-10 standard. During UL 94 HB test the flame is set at the angle of 45° to sample for 30 seconds. In this method, the time in which the plate will burn at the measuring section is measured.

During UL 94 V test the flame is set twice, each time for 10 s. Flammability of the sample is determined on the basis of smoking and glowing time.

Smoke density was determined as deterioration of visibility due to smoke released during combustion of the material. Measurement of visibility deterioration was carried out for the samples with dimensions of 100 × 120 mm. During the test, the intensity of light beam (E) is measured. The initial intensity of light beam was (100 lx). The measurements were performed according to PN-K-02511: 2000 and UIC 564-2.

Tensile tests were carried out using a Zwick/Roell 1465 universal machine with a pre-load of 20 N and the initial speed of 2 mm/min. The tests were performed according to DIN EN ISO 527 standard.

RESULTS AND DISCUSSION

The results of apparent density measurements and flammability tests are presented in Table 2.

Table 2. Results of apparent density (δ) measurements and flammability tests (LOI, UL 94 V and UL 94 HB)

| Symbol of sample | δ , g/cm ³ | LOI, % | UL 94 V | UL 94 HB |
|------------------|------------------------------|--------|---------|----------|
| PUR „0” | 0.69 | 23.4 | — | HB |
| PUR TE | 0.70 | 30.8 | V-0 | HB |
| PUR ME | 0.69 | 29.3 | V-0 | HB |
| PUR AE | 0.71 | 30.5 | V-0 | HB |
| PUR CAE | 0.71 | 28.8 | V-0 | HB |
| PUR BAE | 0.70 | 29.8 | V-0 | HB |

The addition of flame retardants to polyurethane foams changed apparent density only slightly but significantly affects the fire resistance. The values of LOI for prepared compositions containing flame retardants were higher than 28 %, what allows to qualify them as flame resistant materials [15, 16]. This statement was also confirmed by the results obtained during the UL 94 V test. It was found that all compositions containing flame retardant additives can be classified as materials with flammability class V-0 (Table 2).

The UL 94 HB test results allow to classify investigated PUR foams containing flame retardants to flammability class HB, because each sample went out before the measuring point. However, as it is shown in Fig. 1, there were significant differences in the time the flame went out.

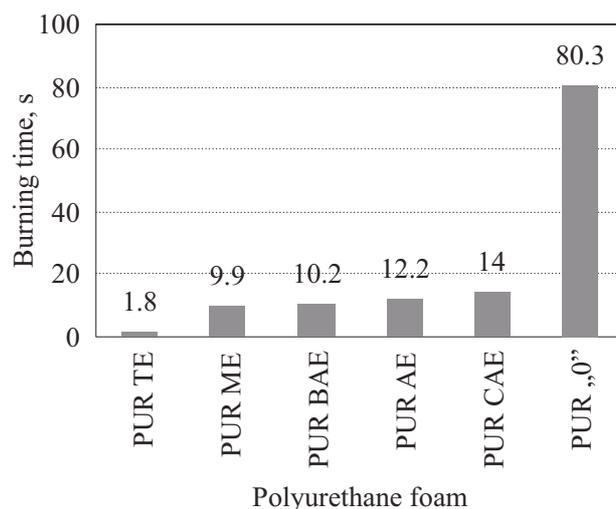


Fig. 1. Burning time of prepared polyurethane foams during UL 94 HB test

After comparison of burning times of the manufactured compositions, it was found that samples containing any flame retardants went out several times faster than polyurethane foam without flame retardants. After analyzing the results it was observed that the burning time of the composition containing expanded graphite and liquid phosphate salt (PUR TE) is shorter than the time for samples containing flame retardants only in the powder form. The explanation for such differences in results may be the fact that the homogenization of flame retardants in polyol was much better caused by the liquid form of phosphorus salt. It was also observed that one of the polyurethane foams containing three flame retardant components (PUR CAE) has had the longest burning time of all the modified foams. The reason for this is the worst homogenization of additives with a polyol. All three fillers used in this composition were in the powder form.

Results of light beam intensity measurements used in smoke density test are shown in Table 3.

Table 3. Results of light beam intensity (E) measurements

| Symbol of sample | E , lx |
|------------------|----------|
| PUR „0” | 0.8 |
| PUR TE | 4.8 |
| PUR ME | 30.9 |
| PUR AE | 23.7 |
| PUR CAE | 22.0 |
| PUR BAE | 27.0 |

Smoke density test results show, that the addition of flame retardants can increase the transparency of smoke and visibility during the burning of the polyurethane foams. It was observed that the smallest improvement in smoke density was obtained for the composition containing graphite and triethyl phosphate (PUR TE). The most

significant improvement has been observed for the sample with graphite and melamine polyphosphate additives (PUR ME).

Table 4. Results of mechanical tests of manufactured PUR foams

| Symbol of sample | Young's modulus, MPa | Tensile strength MPa | Strain, % |
|------------------|----------------------|----------------------|-----------|
| PUR „0” | 1181 | 17.9 | 1.91 |
| PUR TE | 1229 | 15.8 | 1.63 |
| PUR ME | 1302 | 13.8 | 1.27 |
| PUR AE | 1468 | 14.5 | 1.17 |
| PUR CAE | 1305 | 16.4 | 1.70 |
| PUR BAE | 1300 | 15.9 | 1.73 |

The results of tensile tests are collected in Table 4. Modified PUR foams show slightly lower tensile strength than unmodified reference sample. Among all compositions containing flame retardants, the highest tensile strength, differing slightly from the unmodified foam, has sample containing ammonium polyphosphate, expanded graphite and modified bentonite (PUR CAE). It is caused by the addition to the composition of bentonite which has a beneficial effect as filler reducing the flammability of the PUR and improving the strength properties of the material [17].

CONCLUSIONS

All prepared PUR foams containing flame retardants are characterized by acceptable resistance to flame. Burning time values obtained during the UL 94 HB test lead to the conclusion that the foam containing flame retardants in liquid form (triethyl phosphate) has the best flame resistance, most likely due to the easier and better homogenization of flame retardant additives and polyol. Modification of polyurethane foams using suitably selected composition of flame retardants may also improve the transparency of the fumes released during the combustion of material. In this test the highest values were obtained for the foam containing melamine pyrophosphate and expanded graphite. Attention should be paid to changes of tensile properties of modified polyurethanes relative to the unmodified foams. The addition of flame retardant caused only slight worsening of tensile strength of the investigated polyurethane foams. The utilizing of suitably selected flame retardants for PUR foams

allows to manufacture a lightweight foam materials characterized by high flame resistance with satisfying mechanical properties. Analysis of all tests leads to the conclusion that the best is a composition marked as PUR BAE. This PUR foam was characterized by increased fire resistance and decreased smoke density with only small decrease in mechanical properties.

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