

FIRE BEHAVIOUR AND THERMAL STABILITY OF FLEXIBLE POLYURETHANE FOAMS MODIFIED BY PHOSPHOROUS AND EXPANDABLE GRAPHITE ADDITION

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Abstract

The main purpose of these studies was to assess the possibility of reducing the flammability of flexible polyurethane foams modified by phosphorous and expandable graphite fillers and to verify the possibility of replacing a phosphorous additive with expandable graphite. Thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), cone calorimeter (CC) measurements and linear flammability tests were performed. The results indicate that the addition of expandable graphite and phosphorous filler could be a good method to improve the fire resistance of flexible polyurethane foams. In addition, replacing a portion of the phosphorous filler with expandable graphite makes it possible to lower the flammability of these foams.

1 Introduction

Polymers are a significant part of people's life. They are used in many industries, and they can be found almost everywhere. Polyurethanes are a large group of polymer materials. They can be produced in the form of coatings, foams, adhesives, fibres and elastomers, and they are used in many industries, e.g., in medicine, in the automotive industry and to produce furniture [1,2]. Flexible polyurethane foams (FPFs) are the main group of polyurethanes. They are produced mainly in a one-shot process, and they are used primarily in upholstered furniture [3,4]. The main problem with the use of FPFs is their high flammability caused by their low density, porosity, open-cell structure and other physical properties of FPFs, which depend on the components used in the production of FPFs (polyol, isocyanate, catalyst or surfactant) [5,6,7]. For this reason, a smouldering cigarette or an electrical failure in a home or car can rapidly lead to a fire. The decomposition of polyurethanes is always accompanied by the emission of toxic fumes and smoke. The amount of smoke evolved during combustion depends on many factors, including the ambient temperature, the type of ignition, the type of combustion and the availability of oxygen [8]. These fumes are dangerous to people's health. Therefore, FPFs must have a satisfactory degree of fire resistance to ensure people's safety. To meet these requirements, FPFs are modified physically or chemically. A very popular method of improving the fire resistance of FPFs is the addition of fillers that act as flame

retardants. For this purpose, different types of synthetic or natural fillers are used. Conventional fillers used in FPFs could be in the form of fibres, plates or particles, but fillers in the form of liquids and suspensions are also used. In recent years, it has become desirable to use halogen-free flame retardants and also to replace compounds containing chlorine or bromine [4,9,10]. The addition of each filler to FPFs has an influence on the properties of the final material. Generally, it leads to an increase of the weight and a decrease of the flexibility of FPFs, so it is important to use fillers, which makes it possible to reduce the flammability and to maintain the other properties of FPFs.

The main purpose of this research was to assess the possibility of reducing the flammability of FPFs modified by phosphorous and expandable graphite fillers and to verify the possibility of replacing the phosphorous additive with expandable graphite. Of the materials currently available on the market, phosphorous fillers are commonly used in FPFs. The phosphorous filler used in this work was filler from the Fyrol group named Fyrol PNx. Additives from the Fyrol group are commonly used to improve the fire resistance of polymer materials [10-12]. These compounds make it possible to obtain good results in terms of the reduction of flammability, but their cost reduces the ability to use them. Expandable graphite is a natural-origin product used mainly to improve the fire resistance of coatings, sealants, insulations and plastics. Expandable graphite is an environmentally friendly and physiologically neutral product formed from graphite ore through special physical and chemical treatments. Heating expandable graphite above 150°C causes a large volume expansion, and particles of expanded graphite are formed. The expanded graphite forms an insulating char layer, protecting the material against spreading of the flames to the deeper layers of the material. The main advantages of expandable graphite are its low cost, high resistance, chemical inertness and lack of risk of interaction with materials or catalysts. These properties make it possible to use this additive in many applications. Some studies have confirmed an improvement in the fire retardancy of polyurethane materials filled with expandable graphite [13-15]. In recent years, expandable graphite has been the subject of studies aimed at lowering the flammability of FPFs.

To assess the possibility of improving the thermal stability and fire-retardant properties of FPFs, the following measurements were carried out: thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), cone calorimeter (CC) measurements and linear flammability tests.

2 Materials and testing methods

2.1 Materials

Flexible polyurethane foams were prepared by the one-shot method. The polyol used to produce the flexible polyurethane foams was polyether. Toluene diisocyanate (TDI) was used as an isocyanate. Water was used as a blowing agent. Silicone surfactant, amine and tin-based catalysts were also used. As a fillers were used expandable graphite and phosphorous fillers. The expandable graphite (EG) was obtained from Sinograf in Poland. The particle size of the EG was approximately 0.18 mm, and the expansion was approximately 250. The phosphorous filler was obtained from ICL Industrial Products. It is a commercially available filler named Fyrol PNx (FPNX) that is used frequently in flexible polyurethane foams.

Four types of flexible polyurethane foam were tested in this study: flexible polyurethane foam (FPF), FPF + 15 wt % FPNx (FPF+FPNX), FPF + 15 wt % EG (FPF+EG) and FPF + 5 wt % FPNx + 10 wt % EG (FPF+FPNX+EG).

2.2 Testing methods

2.2.1 Thermogravimetric analysis

Thermogravimetric analysis was used to analyse the thermal stability of the prepared foams. The TGA was performed using a TA Instruments TGA Q500. Samples of approximately 10 mg were heated to 600°C at a heating rate of 10°C/min in a nitrogen atmosphere. The following parameters were set: temperature of 5 % mass loss ($T_{5\%}$, °C), temperature of 50 % mass loss ($T_{50\%}$, °C), temperature of the maximum rate of decomposition of the hard segments (T_{max1} , °C) and temperature of the maximum rate of decomposition of the soft segments (T_{max2} , °C).

2.2.2 Dynamic mechanical analysis

A dynamic mechanical analysis was performed in a DMA Q800 from TA Instruments. Samples with dimensions of 10 × 10 × 5 mm were tested using a multi-frequency mode with a compression clamp. The samples were heated at a heating rate of 3°C/min from -100°C to 60°C. The frequency was 5 Hz. Storage modulus (SM, MPa) and glass transition temperatures (T_g , °C) values were set from this measurement.

2.2.3 Cone calorimeter

Cone calorimeter measurements were carried out according to ISO 5660. The square specimens with dimensions of 100 × 100 × 20 mm were tested in a horizontal orientation. The samples were irradiated at 50 kW/m². The air flow rate was 24 l/s. The following parameters were analysed: the heat release rate (HRR, kW/m²), the peak of heat release rate (PHRR, kW/m²), the time at which the peak of heat release rate takes place (tPHRR, s), the mean effective heat of combustion (EHC, MJ/kg) and the CO/CO₂ weight ratio (CO/CO₂, kg/kg).

2.2.4 Linear flammability

Linear flammability tests were carried out according to PN ISO 3795:1996. Samples were exposed to the action of a low-energy flame. During this test, the time to flame extinguishment or the time to burning of the whole foam was defined.

3 Results

3.1 Thermogravimetric analysis

TGA is the most popular method for analysing the thermal stability of polymer materials. The TG and DTG thermograms of tested foams are shown in Figure 1 and Figure 2.

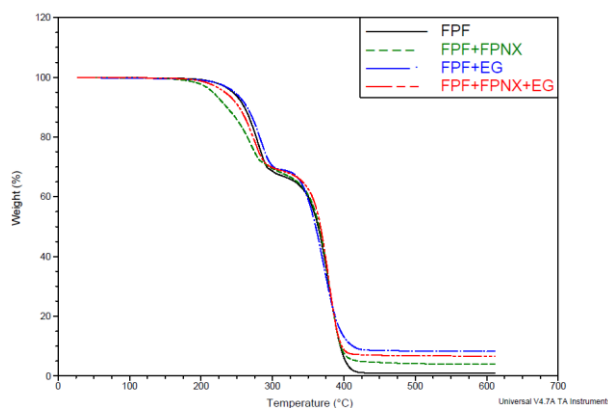


Figure 1. TG curves of tested materials.

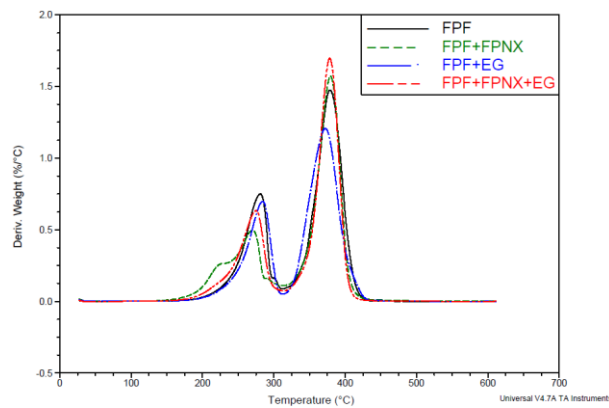


Figure 2. DTG curves of tested materials.

The modification of FPF by FPNX and EG results in changes in the degradation process. FPNX addition shifts the TG and DTG curves to the left, and EG addition tends to shift these curves slightly to the right. This behaviour could be observed, especially in the first step of the degradation process (first peak in the DTG curves). The greatest difference occurs for FPF+FPNX.

Material	T _{5%} [°C]	T _{50%} [°C]	Tmax ₁ [°C]	Tmax ₂ [°C]
FPF	245,39 ± 0,88	362,63 ± 1,21	281,57 ± 0,73	378,94 ± 1,13
FPF+FPNX	216,22 ± 0,36	366,23 ± 1,19	269,68 ± 0,04	380,74 ± 1,67
FPF+EG	247,60 ± 0,69	360,84 ± 0,68	283,86 ± 0,40	373,28 ± 1,37
FPF+FPNX+EG	233,52 ± 0,55	367,34 ± 0,11	274,38 ± 0,38	378,49 ± 0,09

Table 1. Selected results obtained from TG and DTG curves of tested materials.

The results of selected parameters obtained from the TG and DTG curves are presented in Table 1. The temperature of 5% mass loss (T_{5%}) is defined as the temperature at the beginning of the sample's decomposition process. FPF+FPNX yielded the lowest value of T_{5%}, while FPF+EG yielded the highest value. This result indicates that significant deterioration of the thermal stability occurs in FPF modified by the addition of FPNX. This deterioration could be related to some inappropriate changes in the chemical structure of FPF resulting from the addition of this filler. EG can be treated as a filler that improves the thermal stability of FPF. This may be related to the properties of EG, which is known as a chemically inert additive. The temperature of 50% mass loss (T_{50%}) corresponds with the temperature range of the decomposition of the soft segments in a material. The highest value of this temperature was observed for FPF+FPNX+EG. Degradation of each tested foam occurs in two well-defined steps. Tmax₁ is defined as the temperature of the maximum rate of decomposition of rigid segments, and Tmax₂ is defined as the temperature of the maximum rate of decomposition of the soft segments in polyurethane. The addition of FPNX leads to a decrease in the Tmax₁ value and an increase in the Tmax₂ value. The addition of EG leads to an increase in the Tmax₁ value and a decrease in the Tmax₂ value. This result indicates that changes in the properties of FPFs are observed as a result of the presence of filler in the tested foams. The results obtained in this study indicate that the best improvement in the thermal stability could be obtained as a result of EG addition. Moreover, replacing some portion of FPNX by EG made it possible to improve the thermal stability of FPF compared with that of FPF+FPNX.

3.2 Dynamic mechanical analysis

The storage modulus (SM) values of the tested materials were determined from SM curves. The glass transition temperatures (T_g) were determined from the loss tangent ($\tan \delta$) curves. These results are presented in Table 2.

Material	SM [MPa]	T_g [°C]
FPF	$2,43 \pm 0,18$	$-30,74 \pm 0,43$
FPF+FPNX	$2,89 \pm 0,01$	$-26,84 \pm 0,25$
FPF+EG	$3,18 \pm 0,02$	$-28,29 \pm 0,97$
FPF+FPNX+EG	$3,46 \pm 0,02$	$-27,93 \pm 0,56$

Table 2. Selected results obtained from DMA curves of the tested materials.

Modification of FPFs by the addition of FPNX or EG leads to an increase in the SM value. The SM describes the stiffness of the material and its ability to store energy [16]. The highest values were obtained for FPF+FPNX+EG. It can be assumed that this type of modification leads to changes in the mechanical properties of FPFs. Moreover, the addition of FPNX or EG leads to an increase in the T_g value. The best results were obtained for FPF+FPNX, but the T_g value for FPF+FPNX+EG was satisfactory.

3.3 Cone calorimeter

Cone calorimeter analysis is one of the most popular research techniques used to determine the fire-related properties of polymer materials [17]. The curves obtained from the cone calorimeter analyses are presented in Figure 3. It could be observed that the addition of EG or FPNX+EG leads to an increase in the foam's burning time. Moreover, it could be observed that the addition of EG and FPNX+EG causes a large change in the burning behaviour of FPF, especially in comparison with that of FPF or FPF+FPNX. The heat release rate (HRR) value is considered the most important parameter describing the fire properties of polymer materials [5]. The HRR curve for foam with FPNX+EG shows two peaks. It is most likely related to the formation of a char layer, which protects the material from burning for some time [18].

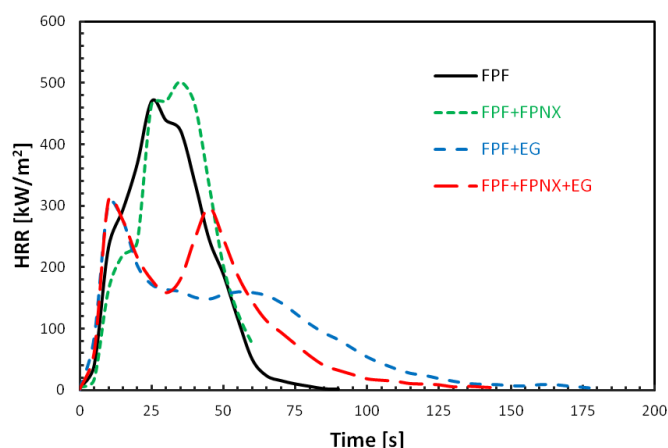


Figure 3. The results of the heat release rate of the tested materials.

Selected results determined during the cone calorimeter analyses are presented in Table 3. The addition of EG makes the PHRR value much lower than the PHRR value observed in FPF. Similar results was observed for FPF+FPNX+EG. However, the tPHRR values indicate that FPF+EG and FPF+FPNX+EG required less time to achieve the PHRR. Only the addition

of FPNX leads to an increase in the tPHRR value, and in this foam, the PHRR value was higher than that observed in FPF.

Material	PHRR [kW/m ²]	tPHRR [s]	EHC [MJ/kg]	CO/CO ₂ [kg/kg]
FPF	470,28	25	26,69	0,01
FPF+FPNX	501,79	35	22,36	0,07
FPF+EG	303,80	10	26,11	0,04
FPF+FPNX+EG	308,54	10	22,80	0,05

Table 3. Selected results of the tested materials obtained from CC testing.

The values of the effective heat of combustion (EHC) for foams with fillers are lower than those for unfilled foam. This result confirms that the fillers used in this work can be considered effective flame retardants for FPFs. The best results were obtained for FPF+FPNX and also to FPF+FPNX+EG. The results of the CO/CO₂ weight ratio show that the addition of any filler leads to an increase of this parameter. The highest value of the CO/CO₂ weight ratio was observed for FPF+FPNX. This means that the fillers used in these studies produce high levels of toxic fumes. These results could be caused by the high content of fillers used in these studies. Studies conducted by Modesti M. et al indicate that the addition of a large amount of EG (at 25 wt %) to polyisocyanurate-polyurethane foams leads to a significant increase in the CO/CO₂ weight ratio [19]. Therefore, it is possible that the amount of filler used in this work is high enough to increase this ratio in FPFs. However, to verify this assumption, further research is needed.

3.4 Linear flammability

The results obtained from the linear flammability tests are presented in Table 4.

Material	Linear flammability [mm/min]
FPF	111
FPF+FPNX	0
FPF+EG	47
FPF+FPNX+EG	20

Table 4. The results obtained from the linear flammability tests.

The addition of FPNX to FPF makes it possible to obtain non-flammable foam (the value of linear flammability was set as 0 mm/min). The addition of EG also reduces the value of the linear flammability. Significant changes were observed in the foam after the addition of both fillers. The addition of 5 wt % FPNX mixed with 10 wt % EG makes it possible to obtain foam with a large reduction of flammability. This level of linear flammability suggests that EG combined with FPNX may be an effective flame retardant.

4 Conclusions

The aim of this work was to assess the possibility of reducing the flammability of FPFs modified by phosphorous and expandable graphite fillers and to verify the possibility of replacing phosphorous additive with expandable graphite. The results of these studies indicate that phosphorous filler Fyrol PNX could be an effective flame retardant, but only the linear flammability test gave a positive result. The results obtained from the cone calorimeter suggest that this filler promotes the burning of FPF and produces higher amounts of toxic gases (PHRR and CO/CO₂). Moreover, this filler leads to a significant reduction in the thermal stability of FPF. Foam modified by the addition of EG achieved the best thermal stability from all of the tested foams. The results from the cone calorimeter showed that the

addition of EG produced the lowest value of PHRR. This means that this filler can be considered an effective flame retardant. The modification of FPF by the addition of a mixture of FPNX and EG leads to good results for the thermal stability and the fire retardancy. This was confirmed by CC analyses, TGA, DMA and linear flammability tests. Therefore, to summarise the results of these studies, it can be concluded that introducing a mixture of FPNX and EG may be an effective method for improving the thermal stability and the fire retardancy of FPF.

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