

Influence of the Expandable Graphite on the Thermal properties of a Rigid Polyurethane Foam for construction

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Abstract. In this paper, low-combustible composites were made by adding 0.8-25 wt% of expandable graphite to rigid polyurethane foams (PUF) to ensure effective and safe usage of building materials made of PUFs. Thermal gravimetric analysis (TGA) was used to study thermal properties and effectiveness of the resulting low-combustible composites in construction. The analysis of TGA curves of the studied composites can be interpreted as a two-stage process: acid-catalyzed degradation of PUF and formation of an intumescent char layer. A dense intumescent layer can provide an effective prevention of heat transfer. The paper showed that the addition of 25 wt% of expandable graphite to PUF composite improved the thermal stability by 8 °C, as compared to starting PUF, while the residue was 36.2 wt% at 600°C, which was higher by approximately 16 wt% than the residue of starting PUF. So, the sample with 25 % loading of expandable graphite in rigid PUF composite showed the best thermal characteristics.

1 Introduction

Nowadays, polyurethanes have been widely applied in paints, adhesives, elastomers, flexible and rigid foams, etc, and thus play an increasing important role in industry and daily life [1-3]. In the last thirty years, concerns about energy conservation have led to a worldwide use of thermal insulators. In particular rigid polyurethane foams (PUF) have been widely used for insulation in construction due to their superior mechanical properties and low thermal conductivity [4].

Rigid PUFs are usually made from branched hydroxyl terminated polyols and multifunctional isocyanates like methylene diphenyl diisocyanate (MDI) [5]. Foamed materials have a density within the range of from 16 to 48 kg/m³ and feature high mechanical strength for this density range [6], which is advantageous for construction applications.

The behavior of building materials during burning is the deciding factor that determines their safety. Like all organic materials, rigid PUFs degrade and burn when exposed to

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flame. Rigid PUFs are classified as combustible materials with medium flammability, which inhibits their wide application in construction. Meanwhile, the increasingly stringent requirements for fire safety of materials, especially those used in construction, have led to the approval of new regulations and wide applications of flame retarded materials [7-9].

The most common fireproofing method for PUFs is the incorporation of flame retardants during their production. The most common flame retardants are phospho-halogenated compounds.

Polymer materials containing conventional flame retardants generate highly toxic compounds during burning. For these reasons, there is a demand for materials which feature lower combustibility and low toxicity of combustion products. Intumescent compounds are promising materials to address those challenges.

Intumescent compounds are well known as new generation of flame retardants due to their merits, such as low emission of smoke and toxic gases produced during burning and anti-dripping properties [6]. Such an effective flame retardant is expandable graphite (EG).

EG is known to provide an effective protection for polymers. The layer structure of graphite makes it possible to insert other molecules between layers, for example, sulfuric or nitric acid. When subjected to heat, these inserted molecules degrade with the evolution of gas, the foaming occurs, and the layer thickness increases by 100 times. Typically, EG is used in combination with phosphorus compounds, antimony oxides, or metal hydroxides, which act as a substrate for the layer of expanded graphite [10-15].

Therefore, the relevant objective is to make low-combustible compositions by adding expandable graphite, as well as to study thermal properties of the resulting compositions to evaluate their combustibility in order to ensure effective and safe usage of building materials made of PUFs.

2 Materials and Methods

The main components of urethane mixture were polyol A (Izolan A 210-7) [16], isocyanate B (Vorotec SD 100) [16], expandable graphite (METOPAC EG 350-50 (80), GK Khimicheskieskie Systemy) [17]. The components were mixed manually in the following order: the expandable graphite was added to polyol A and mixed thoroughly for 5 minutes; isocyanate B was added to this mixture and mixed till the reaction of interaction started; the resulting mixture was poured into the pre-heated molding tool, the molding sides were closed, and it was held for 6 minutes. The samples were conditioned at the room temperature for 24 hours.

Table 1 shows the composition of the rigid PUF samples without and with expandable graphite.

Table 1. Composition of PUF samples.

Sample name	Polyol (weight parts)	Isocyanate (weight parts)	EG (weight parts)
RPUF	100	55	0
RPUF/EG0.8	100	55	0.5
RPUF/EG4	100	55	2.5
RPUF/EG8	100	55	5.0
RPUF/EG16	100	55	10.0
RPUF/EG25	100	55	15.0

The resulting samples were studied to determine the following parameters:

1. The thermal conductivity (λ) was determined by the procedure according to GOST 7076-99 [18]. The test equipment was the electronic thermal conductivity meter ITP-MG4.

2. The thermal gravimetric analysis was recorded using synchronous thermal analyzer TG 209 F1 [19]. For thermal degradation, the samples were heated from 30 °C to 600 °C at a rate of 10 °C/min in argon or air atmosphere according to GOST 29127 [20].

3 Results and discussion

A widespread use of rigid PUFs for thermal insulation in construction is driven by their low thermal conductivity. It is known that radiation, convection within the cells, and conduction through the polymer network are involved in heat transfer through PUF. In view of this, thermal conductivity is a function of not only gas composition, but also foam density and structure [6].

The results of thermal conductivity calculation are given in Table 2.

Table 2. Thermal conductivity of PUFs.

Parameter	RPUF	RPUF/ EG0.8	RPUF/ EG4	RPUF/ EG8	RPUF/ EG16	RPUF/ EG25
λ (W/(m * K))	0.061	0.062	0.066	0.055	0.058	0.056

Low thermal conductivity of RPUF sample ($\lambda=0.061$ W/(m*K)) is the reason why the temperature of its surface increases quickly when ignition occurs, which leads to a rapid flame propagation on the surface.

In this paper, expandable graphite was added to the formulation to slow down surface burning, which had an insignificant influence on the thermal conductivity of PUF. Thus, $\lambda = 0.056$ W/(m*K) with 25 wt% in PUF (sample RPUF/EG25). So, the addition of max. 4 wt% of EG to PUF has no impact on thermal conductivity, and 8-25 wt% of EG in PUF results in an insignificant decrease in this property as compared to the starting PUF.

Therefore, thermal conductivity of PUF composite with various EG loadings does not depend on their content as thermal conductivity is based on the void content in the material.

The burning behavior of a material depends on the ease of its thermal degradation. Thermal analysis provides sufficient information about the mechanism of material degradation, chemical transformations and other processes, which are followed by mass loss, endothermic and exothermic reactions. This method makes it possible to analyze thermal degradation of PUFs using the obtained data.

Thermal stability of PUF samples, including the starting sample and EG-filled samples, was studied using TGA in argon and air atmosphere.

Figure 1 shows the investigation of degradation process in the inert atmosphere (TGA curves), and Figure 2 shows DTG curves.

The thermograms of the studied PUF samples (Figures 1, 2) were used to determine the onset temperatures, temperatures at 5 % mass loss ($T_{5\%}$), the temperatures of maximum mass loss (T_{max}), residue char at 600 °C, maximum degradation rate at T_{max} , these parameters were summarized in Table 3.

TGA analysis in the inert atmosphere (Table 3, Figures 1, 2) showed that all the samples went through several stages of mass loss with various intensity. So, the degradation of the starting PUF sample had four stages.

Table 3. Data obtained from curves of TGA tests of RPUF and RPUF/EG composites under argon.

Samples	$T_{5\%}$ (°C)	T_{max1} (°C)	Mass loss rate at T_{max1} (wt%/min)	T_{max2} (°C)	Mass loss rate at T_{max2} (wt%/min)	Char residue (%)
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RPUF	247	329	6.5	361	5.9	20.3
RPUF/EG0.8	240	334	5.3	367	5.4	20.7
RPUF/EG4	254	324	5.8	373	5.1	23.8
RPUF/EG8	214	308	6.5	-	-	26.4
RPUF/EG16	188	310	6.9	-	-	28.4
RPUF/EG25	255	321	6.2	-	-	36.2

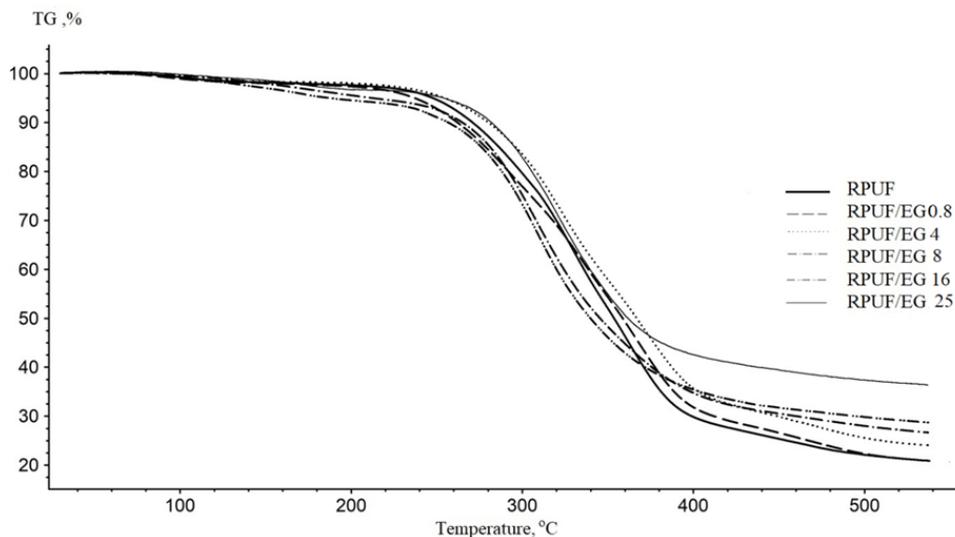


Fig. 1. TGA curves of RPUF and RPUF/EG composites under argon.

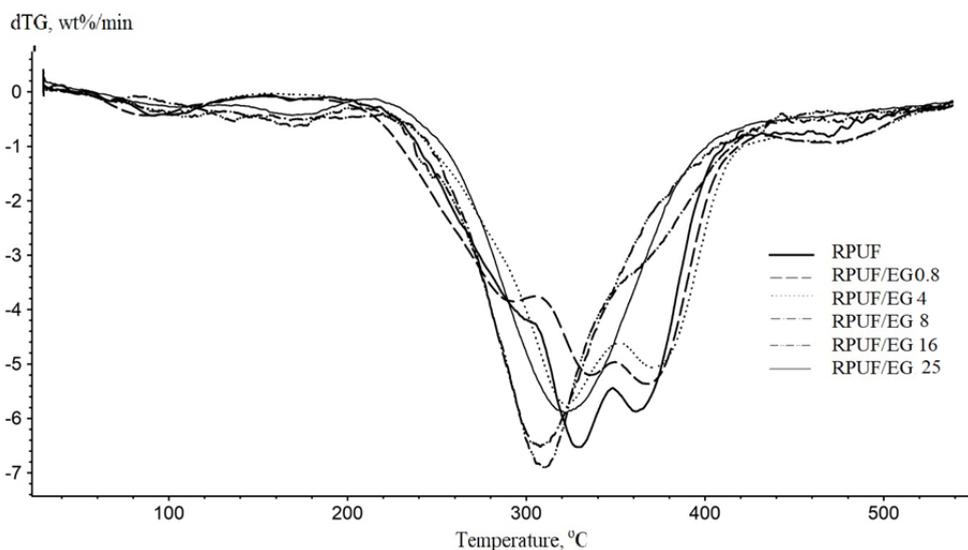


Fig. 2. DTG curves of RPUF and RPUF/EG composites under argon.

Only the samples with graphite loading of up to 4 wt% (samples RPUF/EG0.8, RPUF/EG4) has TG and DTG curves (Figures 1, 2) of the nature similar to starting PUF.

The first degradation stage of starting PUF and samples with a loading of 0.8 wt% (RPUF/EG0.8) and 4 wt% (RPUF/EG4) features a region between 70 °C and 200 °C with 2.5% mass loss. This stage can be associated with evaporation of small molecules of unreacted isocyanate starting components [21]. The second and third degradation stages occur at temperatures of 210-340 °C and 350-450 °C respectively, and it is primarily due to the formation of starting polyurethane components (isocyanates and polyols) as a result of breaking of urethane bonds in hard segments [21]. Hence, PUF has a bimodal structure and features two peak degradation temperatures T_{max1} and T_{max2} (Figure 2, Table 3). The first and second peak degradation temperatures correspond to the hard and soft segments of polyurethane, respectively. The material degradation ends at a temperature of above 450 °C.

The analysis of TG curves (Figure 1) showed that the thermal stability of RPUF/EG4 sample with 4 wt% loading increased by 7 °C as compared to the starting PUF ($T_{5\%}=247$ °C), and $T_{5\%}$ is 254 °C.

The mass loss rate decreases depending on the graphite loading (Table 3). The reason is that the intumescent layer forms at the initial degradation stage, and the volatile combustible fragments could have diffused slowly as a result of thermal degradation, so the mass loss rate decreased. At the same time, the content of residue also increases with increasing loading of graphite at 600 °C: from 20.3 wt% for starting PUF to 23.8 wt% for RPUF/EG4 sample with 4 % loading, which indicates that the char layer has formed.

Therefore, as the amount of graphite increases up to 4 wt% in PUF composite denser intumescent particles form, which results in lower mass loss rate and higher thermal stability.

The studied PUF samples with 8-25 wt% of graphite loading go through three degradation stages (Figure 2). RPUF/EG8, RPUF/EG16, RPUF/EG25 samples show the following stages:

-70-200 °C: removal of highly volatile components and unreacted starting components;

-210-450 °C: activation of thermal oxidative processes and resolution of polyurethane into starting products (isocyanate and polyatomic alcohol), which is followed by significant heat production;

->450 °C: completion of the material degradation.

PUF composites with 8 and 16% of graphite loading have lower temperature characteristics as compared to the starting PUF. Residual acid inside the EG layers can contribute to lower degradation temperatures of PUF polymer matrix [22]. For example, onset temperature of $T_{5\%}=214$ °C and $T_{max}=308$ °C is typical for the sample with 8 % loading of graphite (RPUF/EG8 sample, Table 3), and $T_{5\%}=188$ °C, $T_{max}=310$ °C - for the sample with 16 % loading of graphite (RPUF/EG16, Table 3), and the residue is 26.4 wt% and 28.4 wt%, respectively, at 600 °C, this value exceeds the value of starting PUF material by 6.1 wt% and 8.1 wt%, respectively.

Therefore, 8 and 16 wt% of EG in PUF composite accelerated the initial degradation stage significantly. It resulted in the formation of a dense intumescent layer on the sample surface, which led to a slower degradation process in PUF and slow diffusion of volatile combustible fragments.

A higher amount of EG in PUF composite (25 wt%) improves the thermal stability by 8 °C, as compared to starting PUF, and RPUF/EG25 sample features $T_{5\%}=255$ °C, $T_{max}=321$ °C, while the residue is 36.2 wt% at 600 °C. Higher temperature characteristics of the initial degradation stage can be attributed to a higher expansion rate of graphite, i.e., a high EG loading (25 wt%) of PUF results in larger particles of the intumescent layer in the composite, which slows down the degradation process of polymer matrix after acid decomposition.

With a higher graphite loading, the char residue increases at 600 °C and peaks at 36.2 wt% for RPUF/EG25 sample, the resulting intumescent layer acts as a heat insulation barrier to prevent PUF from further degradation.

Therefore, the thermal studies of PUF composites showed that EG loading of 0.8-25 wt% led to the formation of an intumescent layer during heating for all the samples, and RPUF/EG25 sample with 25 % loading had the best thermal characteristics, its char residue was 36.2 wt% at 600 °C.

The thermal studies in air showed that the introduction of 0.8 wt% of EG did not change the main PUF degradation characteristics.

Figure 3 shows the investigation of the degradation process for the filled PUF samples under oxidizing atmosphere (TGA curves), and Figure 4 shows DTG curves. The analysis results for thermograms are shown in Table 4.

The addition of 4 wt% of EG to PUF composite results in higher thermal stability under oxidizing atmosphere, such parameters as $T_{5\%}$ and T_{max} increase. For example, $T_{5\%}$ increases by 16 °C and is equal to 238 °C, and $T_{max}=306$ °C, while the mass loss rate decreases down to 8.5 wt%/min.

The addition of 8 wt% of graphite to PUF leads to a significant decrease in such parameters as $T_{5\%}$ (approximately by 70 °C) and T_{max} (approximately by 8 °C), the mass loss rate at T_{max} also decreases from 10.7 to 7.9 wt%/min. Lower values of $T_{5\%}$ and T_{max} were attributed to the influence of residual acid inside the EG layers, which accelerated the degradation in PUF.

EG loading of minimum 25 wt% is most effective for PUF composite. $T_{5\%}$, T_{max} are insignificantly lower in RPUF/EG25 sample than those in starting PUF, the mass loss rate at T_{max} is lowest (7.3 wt%/min) and the char amount is highest among all the other studied samples. So, the earlier degradation encouraged the formation of stable substances which inhibited the degradation rate and increased the char yield in the range of higher temperatures. So, the addition of EG of minimum 25 wt% to PUF leads to lower combustibility of the composite.

Table 4. Data obtained from curves of TGA tests of RPUF/EG composites under air.

Samples	$T_{5\%}$ (°C)	T_{max} (°C)	Mass loss rate at T_{max} (wt%/min)
RPUF	222	302	10.7
RPUF/EG0.8	223	302	10.2
RPUF/EG4	238	306	8.5
RPUF/EG8	150	294	7.9
RPUF/EG25	218	300	7.3

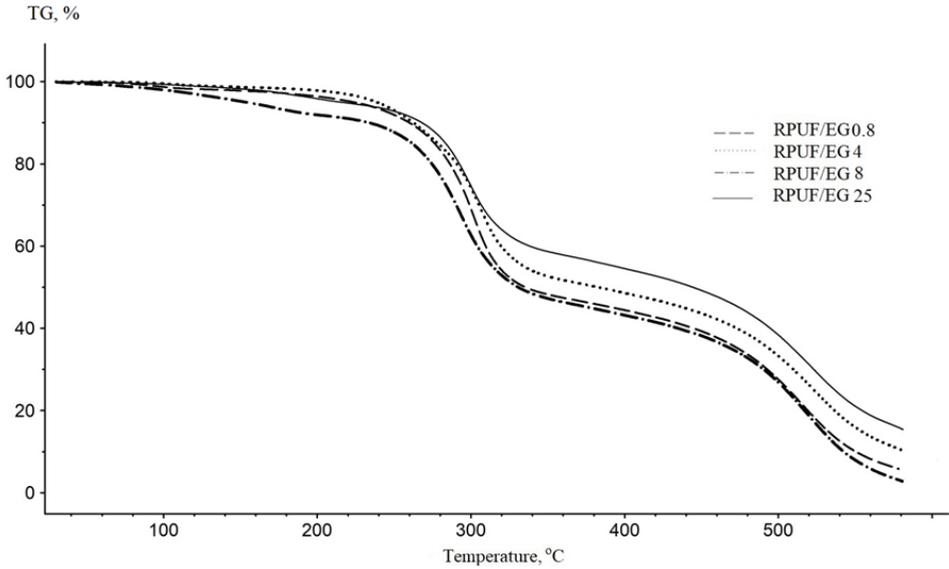


Fig. 3. GA curves of RPUF/EG composites under air.

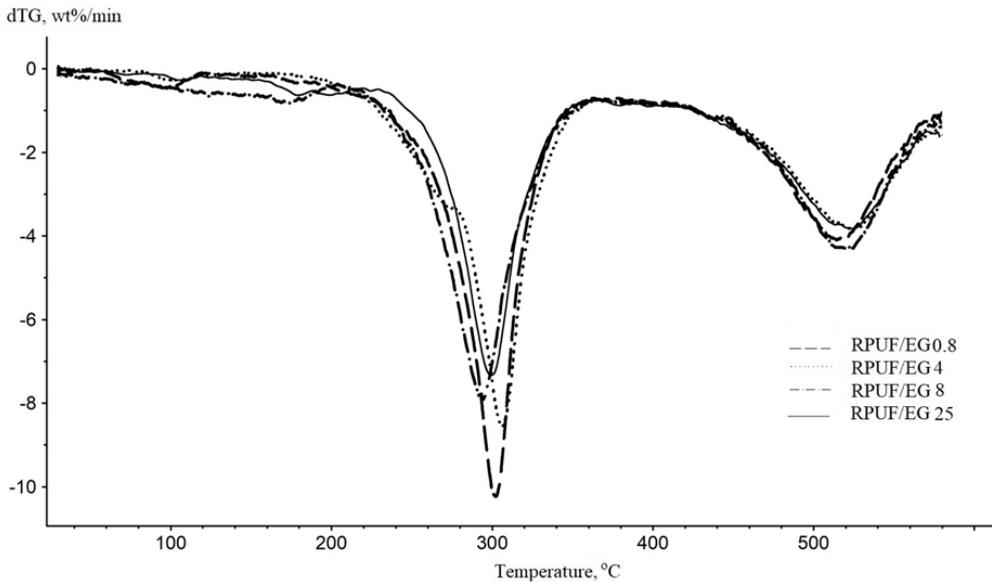


Fig. 4. DTG curves of RPUF/EG composites under air.

4 Conclusions

The thermal studies of PUF composites showed that EG loading of 4-25 wt% led to the formation of an intumescent layer during heating for all the samples. RPUF/EG25 sample with 25 % loading showed the best thermal characteristics. The addition of 25 wt% of EG to PUF composite improves the thermal stability by 8 °C, as compared to starting PUF, and RPUF/EG25 sample features $T_{5\%}=255$ °C, $T_{max}=321$ °C, while the residue is 36.2 wt% at 600 °C, which is 16 wt% higher than in starting PUF. Higher temperature characteristics of

the initial degradation stage can be attributed to a higher expansion rate of graphite, i.e., a high EG loading (25 wt%) of PUF results in larger particles of the intumescent layer in the composite, which slows down the degradation process of polymer matrix after acid decomposition.

When 8 and 16 wt% of EG were added in PUF, the composites accelerated the initial degradation stage significantly. It resulted in the formation of a dense intumescent layer on the sample surface, which led to a slower degradation process in PUF and slow diffusion of volatile combustible fragments. For example, onset temperature of $T_{5\%}=214$ °C and $T_{\max}=308$ °C is typical for the sample with 8 % loading of graphite, and $T_{5\%}=188$ °C, $T_{\max}=310$ °C - for the sample with 16 % loading of graphite, and the residue is 26.4 wt% and 28.4 wt%, respectively, at 600 °C, this value exceeds the value of starting PUF material by 6.1 wt% and 8.1 wt%, respectively.

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