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RIGID POLYURETHANE FOAM THERMAL INSULATION PROTECTED WITH MINERAL INTUMESCENT MAT

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Abstract:

One of the biggest disadvantages of rigid polyurethane (PU) foams is its low thermal resistance, high flammability and high smoke production. Greatest advantage of this thermal insulation material is its low thermal conductivity (λ), which at 18–28 mW/(m•K) is superior to other materials. To lower the flammability of PU foams, different flame retardants (FR) are used. Usually, industrially viable are halogenated liquid FRs but recent trends in EU regulations show that they are not desirable any more. Main concern is toxicity of smoke and health hazard form volatiles in PU foam materials. Development of intumescent passive fire protection for foam materials would answer problems with flammability without using halogenated FRs. It is possible to add expandable graphite (EG) into PU foam structure but this increases the thermal conductivity greatly. Thus, the main advantage of PU foam is lost. To decrease the flammability of PU foams, three different contents 3%; 9% and 15% of EG were added to PU foam formulation. Sample with 15% of EG increased λ of PU foam from 24.0 to 30.0 mW/(m•K). This paper describes the study where PU foam developed from renewable resources is protected with thermally expandable intumescent mat from Technical Fibre Products Ltd. (TFP) as an alternative to EG added into PU material. TFP produces range of mineral fibre mats with EG that produce passive fire barrier. Two type mats were used to develop sandwich-type PU foams. Also, synergy effect of non-halogenated FR, dimethyl propyl phosphate and EG was studied. Flammability of developed materials was assessed using Cone Calorimeter equipment. Density, thermal conductivity, compression strength and modulus of elasticity were tested for developed PU foams. PU foam morphology was assessed from scanning electron microscopy images.

Keywords:

Polyurethane foam; intumescent textile; flammability; thermal conductivity, sustainable materials.

1. Introduction

Rigid *polyurethane* (PU) foams that are an interesting family of polymers, with excellent thermal insulation, chemical resistance and toughness combined with good flexibility at low temperatures. They are extensively used as thermal insulation in construction industry, in domestic appliances and refrigerators, as space filling material [1] as well as for transportation of liquefied natural gas and for insulation of cryogenic space launchers [2]. PU foams have excellent properties such as closed-cell structure, low thermal conductivity, low water adsorption and moisture permeability, and relatively high compressive strength. Thermal conductivity of PUR is from about 18 up to 28 mW/(m K). The thermal conductivity factor of PU foams is two times lower than that of polystyrene, which is an alternative material for insulation purposes [3]. However, PU foams are highly flammable and susceptible to degradation upon exposure to elevated temperature during fire accident. This constitutes a serious concern and restricts its application [4]. The Oxygen Index of non-modified PU foams is in the range of 16–18 [5]. Highly porous lightweight combustible foams tend to have fast flame-spread and high thermal emission [6]. Increasing demand for PU foams is the reason why many studies are devoted to flame-retardancy [7].

One of the problems PU foams facing nowadays is their dependence on petroleum origin raw materials. The synthesis of polymers from renewable resources has been investigated by leading research teams from different countries [8-12]. These studies have been initiated by a search for alternative raw materials, replacing the petrochemical resources running short. Investigations in the field of PU are especially active. Interest in the use of renewable raw materials, in particular, vegetable oils for preparing PU foams, is increasing [13]. One of the research activities in this article is focused on the use of pulp mill by-product – tall oil (TO) as a renewable raw material for the production of PU foams.

Numerous studies have aimed at improving the fire behaviour and thermal stability of (PU) foams obtained from renewable resources. For these reasons, studies to find effective conventional flame retardants (FR) have been carried out by many researchers in industry and universities over a long period of time, but so far there is a limited success [3]. PU foams can be rendered fireproof by introducing additive FR [14], reactive FR based on halogen and phosphorus polyols [15] or cyclo-trimerization of NCO- groups obtaining isocyanurate rings [16]. On the other hand, conventional FR containing halogens cause the development of very dense and toxic smokes [17].

In the new regulations [18], toxicity and density of the smokes are very important factors that should be considered in evaluating fire safety of materials, including PU foams as thermal insulating construction material, there is a real necessity for the industry to find a new type of FR [19]. Expandable graphite (EG) prepared from natural graphite by chemical treatment is a type of graphite intercalation compound. The excellent properties of EG kept most excellent characteristics of natural graphite, such as low price, electrical conductivity, increases of mechanical properties of polymers, high porosity and exchange surface, making it very useful as functional carbon materials that can be applied in various fields of polymer industry, but especially as FR [4]. Some studies implied that EG could produce good fire-retardant properties for some polymers, such as polyolefins [20], PU [4, 21-24], coatings [19], etc. There is one negative thing, if EG is introduced into PU matrix. For filled PU foams, an increase in thermal conductivity has been observed [19]. The thermal conductivity of PU is due to three modes of heat transfer: conduction of cell gas, conduction of solid polymer matrix and radiation between cell walls. Probably due to the presence of EG, which leads to an increase in the thermal conductivity of the solid polymer matrix.

To avoid the above-mentioned disadvantages, intumescent mat (IM – non-woven glass fibre filled with EG) is used as the FR. In this work for the development of TO-based PU, the well-known FR systems, such as phosphorus-containing additive FR and EG, are combined with IM and compared their fire behaviour. Particular attention has been put on heat release rate (HRR), obtained using Cone Calorimeter. It is known that the HRR peak value strongly influences the fire safety of materials as it is responsible for the ‘‘flashover’’ phenomena in a real fire situation: the lower the HRR peak value, the safer the materials in the case of fire [19, 25]. Recently, several research workers have investigated the fire behaviour foam/fabric combination [26, 27] using a cone calorimeter, but it is done only for flexible PU foams, with the idea to test the fire behaviour of mattresses, automotive and furniture cushions. The novelty of this study is improvement of flammability characteristics of thermal insulation material with IM.

2. Experimental

The goal of this study was to develop a rigid PU foam material that would have competitive flame resistance properties as well as low thermal conductivity. To meet EUs drive towards sustainable resource management, PU foams were developed using renewable materials. Also, synergy effect of non-halogenated FR; dimethyl propyl phosphate (DMPP) and EG was studied. Influence of three different EG contents 3%, 9% and 15% on PU foam fire behaviour was studied. PU foams filled with EG were compared with PU foams protected with two different IMs from Technical Fibre Products Ltd.

2.1. Materials

Rigid PU foams are obtained by mixing two liquid components; polyol component and isocyanate component. The basis of polyol component is polyol, which is a polyfunctional alcohol. Polyol for PU foams, used in this study, was obtained from TO. TO is a renewable raw material because it is the by-product of cellulose production. TO is a mixture of fatty and rosin acids, structures of which can be seen in **Figure 1,** and it is not usable for the production of PU materials without chemical modification.

Renewable polyol from TO was synthesized in Latvian State Institute of Wood Chemistry (IWC) by esterification method with triethanolamine (TEOA). TO with 20% rosin acid content from Forchem (Finland) was used as a raw material. After TO esterification with TEOA [13], as shown in **Figure 2,** polyol with OH value of 347 mgKOH/g; water content of 0.2% and acid value below 5 mgKOH/g were obtained and used as the base for PU foam formulation.

TO polyol has quite low average functionality to be purely used in rigid PU foam formulation, that is why ~10% of higher functionality crosslinkage reagent Lupranol 3422 (OH value 490 mgKOH/g) from BASF was used. Other additives in PU foam formulation are as follows: surfactant – NIAX Silicone L6915; reactive amine-based catalyst – PC CAT NP10 from Momentive Performance Materials and 7% DMPP – the non-halogenated conventional FR from Lanxess AG. Distilled water

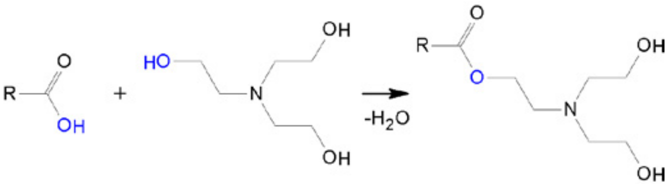


Figure 2. Reaction scheme of TO esterification with TEOA [13].

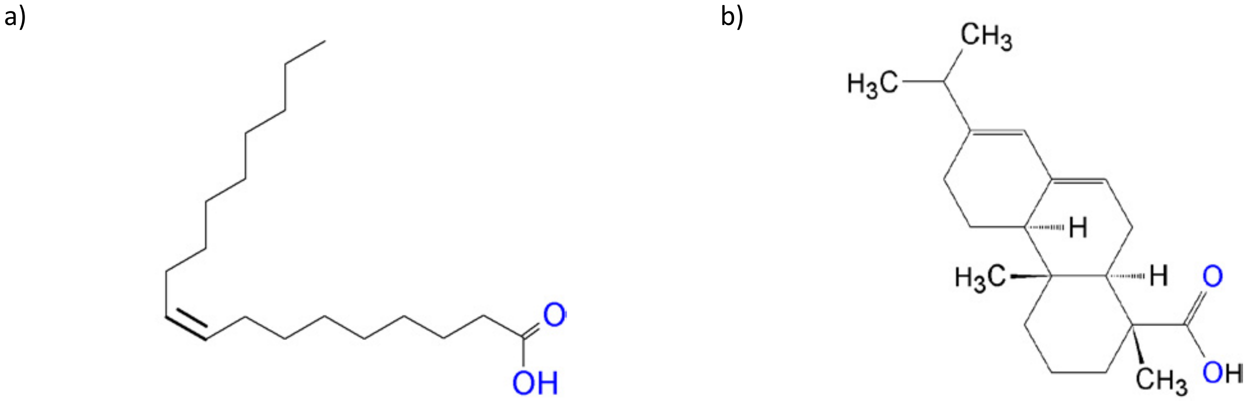


Figure 1. Basic structure of TO components: (a) fatty acid (oleic acid) and (b) rosin acid (abietic acid).

was used as the blowing reagent because of its relation with isocyanate, which results in emission of CO_2 gas. Polymeric diphenylmethane diisocyanate – IsoPMDI 92140 (pMDI) – from BASF was used as an isocyanate component (NCO = 31.5 wt%).

In this study, EG with trade mark EG 290 from Sinograf (Poland) was used. Carbon content in EG is 90%, particle dimensions 0.2–0.6 mm, expansion of EG 200–400 ml/g, moisture content ~1.5% and bulk density ~0.65 g/m^3.

Two types of IM from Technical Fibre Products Ltd were used. 60172A flexible, thermally expandable IM, which is graphite based, with mineral and glass fibres and aluminium trihydroxide. Activation temperature of this mat is >190°C at which the expansion ratio is 11:1 at 450°C. Thickness – 0.65 mm; typical density – 350 kg/m^3 and tensile strength – 35 N/15 mm. Other IM used in this study was 60152C flexible, thermally expandable IM, which is graphite based, with mineral and glass fibres. Activation temperature of this mat is >190°C and the expansion ratio is 9:1 at 450°C. Thickness is 2.00 mm; typical density is 220 kg/m^3 and tensile strength is 175 N/15 mm.

2.2. Methods

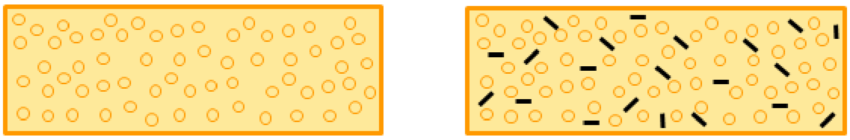
PU foam sample preparation: Polyol component was obtained by weighting all necessary components (polyol, crosslinkage reagent catalyst, blowing agent, surfactant, 7% conventional FR and EG) and stirring them for 1 min by mechanical stirrer at 2000 rpm. Afterwards, appropriate amount of MDI was added to obtain PU foams with isocyanate index 110 and both components stirred. The reacting mass of PU foam was poured into stainless steel closed type mould preheated at 50°C. For final curing of PU foams, the mould was placed in an oven at 50°C for 2 h. PU foams with two types of IM were obtained by placing the matt on the bottom of stainless steel mould and pouring PU reacting mass over it. In this way, one side of PU foam material becomes protected, and the other side was also tested in reaction to heat flux tests. **Figure 3** shows the four types of obtained PU foam samples: unmodified PU foam; PU foam filled with different amounts of EG (3%; 9% and 15%); PU foam protected with IM and PU foam with EG (3%; 9% and 15%) and IM.

PU foam characterization methods: Samples for different tests from prepared PU foam blocks were cut using band saw and afterwards they were conditioned for at least 24 h at room temperature. Bulk density of obtained PU foams was tested according to ISO 845 standard. Reaction to 35 kW/m^2 heat flux was tested using Cone Calorimeter from Fire Testing Technology Ltd. The peak HRR (pHRR, kW/m^2); time to pHRR (TTP, s); ignition time (IT, s); time to flame out (FOT, s); total smoke release (TSR, m^2/m^2) and maximum average rate of heat emission (MAHRE, kW/m^2) were determined by this equipment according to ISO 5660 standard. The thermal conductivity coefficient (λ, mW/m·K) was tested using Linseis Heat Flow Meter according to ISO 8301 standard. Compression strength and modulus of elasticity for PU foams parallel and perpendicular to foaming direction was tested according to ISO 844 standard with one offset of sample size; cylinders with a diameter of 20 mm and height of 22 mm were tested. Mechanical testing of PU foam was performed on testing machines Zwick/Roell 1000 N. Scanning electron microscopy (SEM) was applied to obtain images of PU foams and to determine material morphology. SEM microscope Tescan TS 5634 was used.

3. Results and discussion

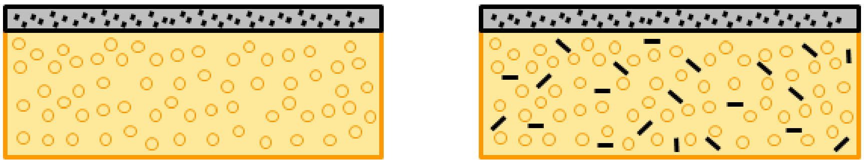
3.1. Characterization of obtained foams

Main characteristics of any thermal insulation foam are thermal conductivity and thermal resistance. **Figure 4** shows measured λ for all types of obtained PU foams. It can be seen that IM and PU foam composites are not worse thermal insulation materials than unmodified PU foam. λ of PU foam with no conventional FR is 24.44 mW/m·K, which is decent for the material that could be used in building construction. Unfortunately, the addition of conventional FR DMPP increased λ up to 28.74 mW/m·K, which is only marginally satisfactory, because at this value the developed PU foam thermal insulation properties are worse in



Rigid PU foam

Rigid PU foam filled with EG



Rigid PU foam protected with IM

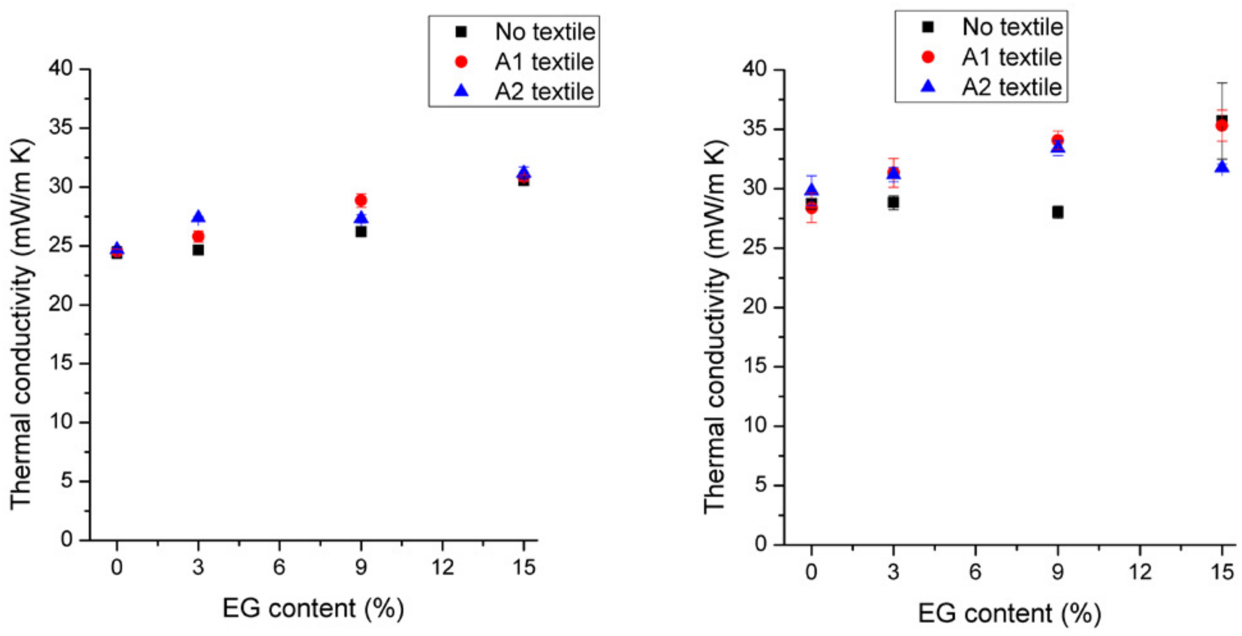
Rigid PU foam filled with EG
and protected with IM

Figure 3. Four types of PU foam samples studied.

the range of rigid PU foams. The increase in developed PU foam thermal conductivity can be explained with plasticization of PU polymer matrix. Most conventional additive liquid FRs decrease the glass transition temperature of PU polymer matrix [28]. They swell the network structure of PU matrix and dilute aromaticity. Due to the decrease of crosslinkage density, blowing agent can more easily defuse through PU foam cells even though developed PU foam has closed cell structure. Closed cell content of all developed PU foams was >90%. CO_2 or other gas (blowing agent) substitution with air in conventional PU foams is a slow process and takes years [29]. But even with λ 28.74 mW/m·K, developed PU foams are energy efficient thermal insulation material.

It can be seen that EG increases the λ, at 15% of EG in PU foam with conventional FR, λ increased from 28.74 to 35.72 mW/m·K. Carbon structure of EG is a good heat conductor; thus, the increase of λ. Best case scenario would be possible to obtain PU foam composite with low λ and high flame resistance properties. Further analysis of obtained PU foams will show that it is possible to find compromise between these characteristics using IM and EG as FR systems.

Other characteristics of developed PU foams are seen in **Table 1**. It can be seen that the addition of EG increased the bulk density of developed PU foams, but this did not improve the mechanical properties of PU foams. PU foams panels


a)

b)

Figure 4. Thermal conductivity of rigid PU foams protected with different IM: (a) with no conventional FR but with EG and (b) with DMPP as FR and EG.

Table 1. Bulk density, compression strength and Young's modulus for PU foams with no conventional FR but with EG and for PU foams with DMPP as FR and EG.

Foam characteristic	**PU foam with no conventional FR**			
EG content, %	0	3	9	15
Density, kg/m³	58.9 ± 1.5	59.9 ± 1.9	61.9 ± 3.3	65.5 ± 3.7
Compression strength Z, MPa	0.38 ± 0.04	0.36 ± 0.03	0.35 ± 0.02	0.29 ± 0.03
Young's modulus Z, MPa	9.4 ± 1.5	8.7 ± 1.6	8.7 ± 0.8	7.1 ± 1.2
Compression strength X, MPa	0.22 ± 0.03	0.24 ± 0.02	0.21 ± 0.02	0.22 ± 0.02
Young's modulus X, MPa	4.2 ± 1.0	4.4 ± 0.7	4.1 ± 0.5	4.6 ± 0.6
	PU foams with DMPP			
Density, kg/m³	67.9 ± 2.3	70.0 ± 2.1	73.1 ± 3.4	68.6 ± 2.4
Compression strength Z, MPa	0.35 ± 0.03	0.45 ± 0.03	0.32 ± 0.03	0.32 ± 0.02
Young's modulus Z, MPa	7.4 ± 1.0	11.5 ± 1.6	7.0 ± 1.3	8.4 ± 0.6
Compression strength X, MPa	0.26 ± 0.01	0.35 ± 0.02	0.24 ± 0.01	0.17 ± 0.01
Young's modulus X, MPa	4.2 ± 0.3	6.8 ± 0.7	4.3 ± 0.3	2.5 ± 0.4

with bulk density ~60 kg/m^3 are used as thermal insulation in floor panels. Also, the increase in the bulk density correlates with the increase in thermal conductivity. EG does not have reinforcement effect. Even at 15%, EG in PU foam particles is too far spread out. From SEM images, it can be seen that although particles have good phase incorporation in PU matrix, they disrupt cell morphology. This is the reason behind the decrease in mechanical properties.

SEM images of developed PU foams are seen in **Figure 5.** It is clear that EG is evenly distributed across PU foam and it is located in walls and in cell cross points. Closer look on EG particle shows that there is no phase separation between PU matrix and EG. It is seen that PU foam with EG has much more uneven cell structure, which results in lower mechanical properties.

3.2. Flame protection of rigid PU foams

Main objective of this study was to obtain rigid PU foams with increased fire protection without losing superior thermal insulation properties. This was done by protecting one side of PU foam material with IM, which is seen in **Figure 6.** Because the thickness of the IM A1 (0.65 mm) is much smaller that of IM A2 (2.00 mm) PU foam, material has fully soaked through it, developing excellent adhesion of IM to PU foam. In case of IM, A2 PU foam has soaked only partially into IM. It is seen that PU matrix adhesion to glass fibre is excellent and there are even cells of PU foam blown into IM. Good phase adhesion of PU foam and IM means that this fire protection would be easy to up-scale, for example, in the production of PU panels. IM could replace paper roll that is used in PU panel production conveyor belts. This technique would introduce IM without using any adhesives that increased production costs.

Cone Calorimeter test give broad information about fire behaviour of developed materials. One of main the characteristics of material flammability is pHRR. As seen in **Figure 7**, the addition of EG into PU foams decreased it from 327 kW/m^2 in the case of unmodified material to 61 kW/m^2 for PU foam with 15% of EG, which was protected with A2 IM. In general, addition of EG decreases pHRR in PU foams with conventional FR as well as in foams without it. Incorporation of IM boosts this effect even more.

Similar results are seen for data of MAHRE as for data of pHRR. IM textile provided increased fire protection where comparable MAHRE value for unprotected PU foam could be reached only at higher than 9% content of EG. This is not viable, because 9% of EG and above increases the λ beyond point, where it is competitive with polystyrene foam. MAHRE data of PU foams are seen in **Figure 8.**

Conventional FR DMPP increased smoke release from burring material [17]. Fire retardancy mechanism of DMPP is the production of protective char layer over burning material as for most phosphorous FRs [30]. Development of char residue promotes production of solid particles in smoke thus increasing the smoke release rate. Nevertheless, PU foams protected with IM showed smaller amount of released smoke than unmodified PU foams as shown in **Figure 9.**

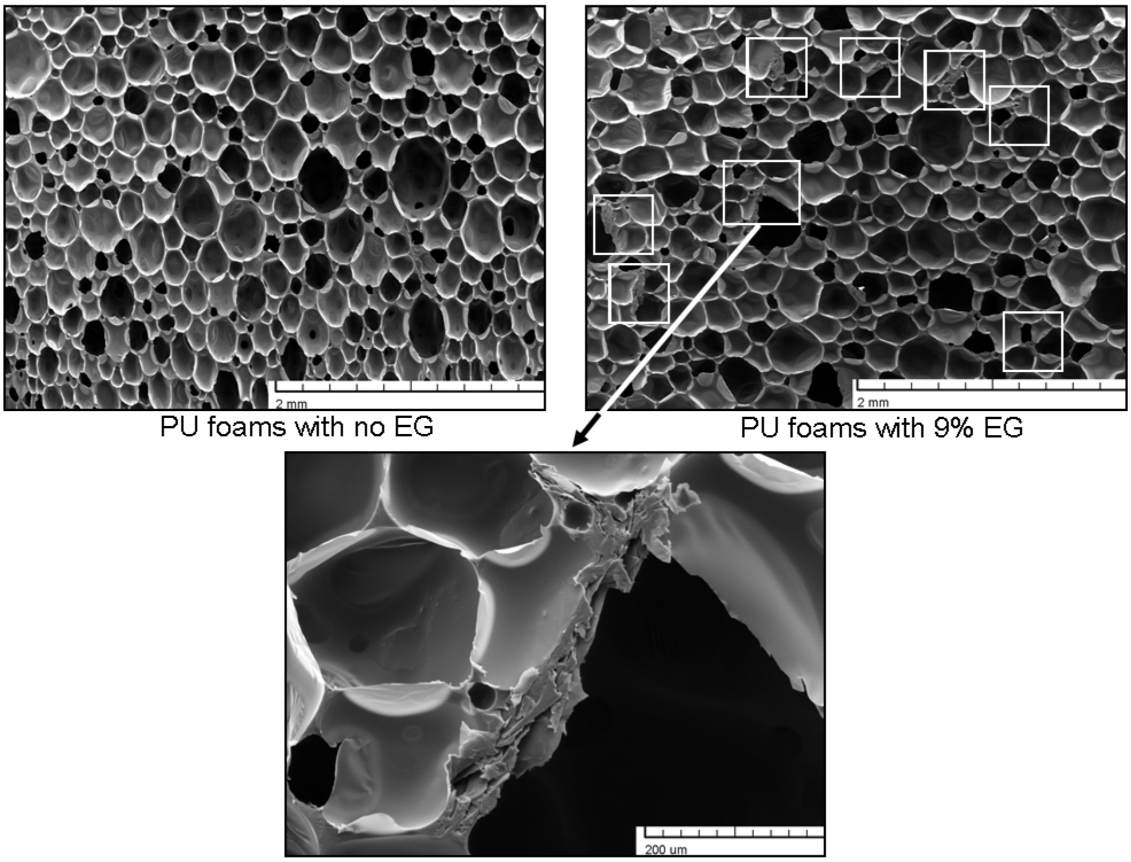


Figure 5. SEM images of PU foams with no conventional FR and 9% EG.

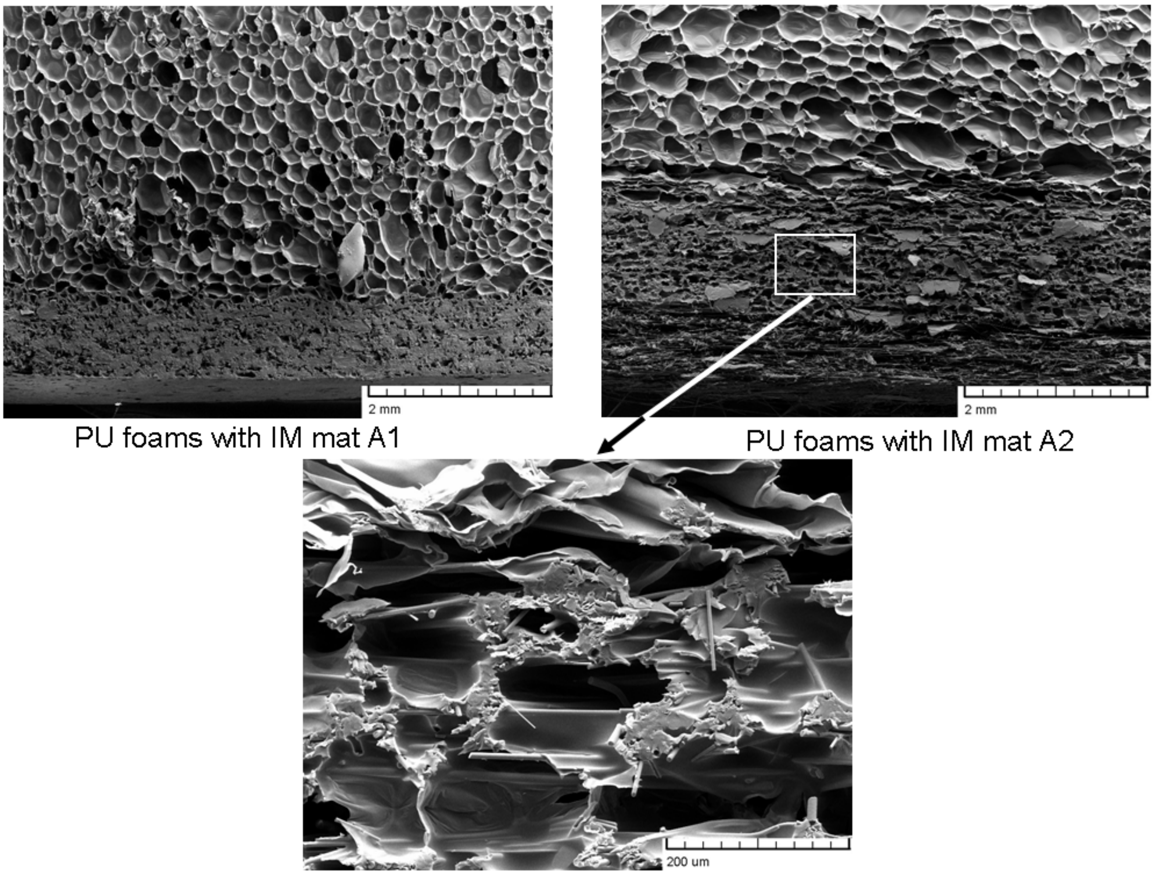


Figure 6. SEM images of PU foams with two types of IM.

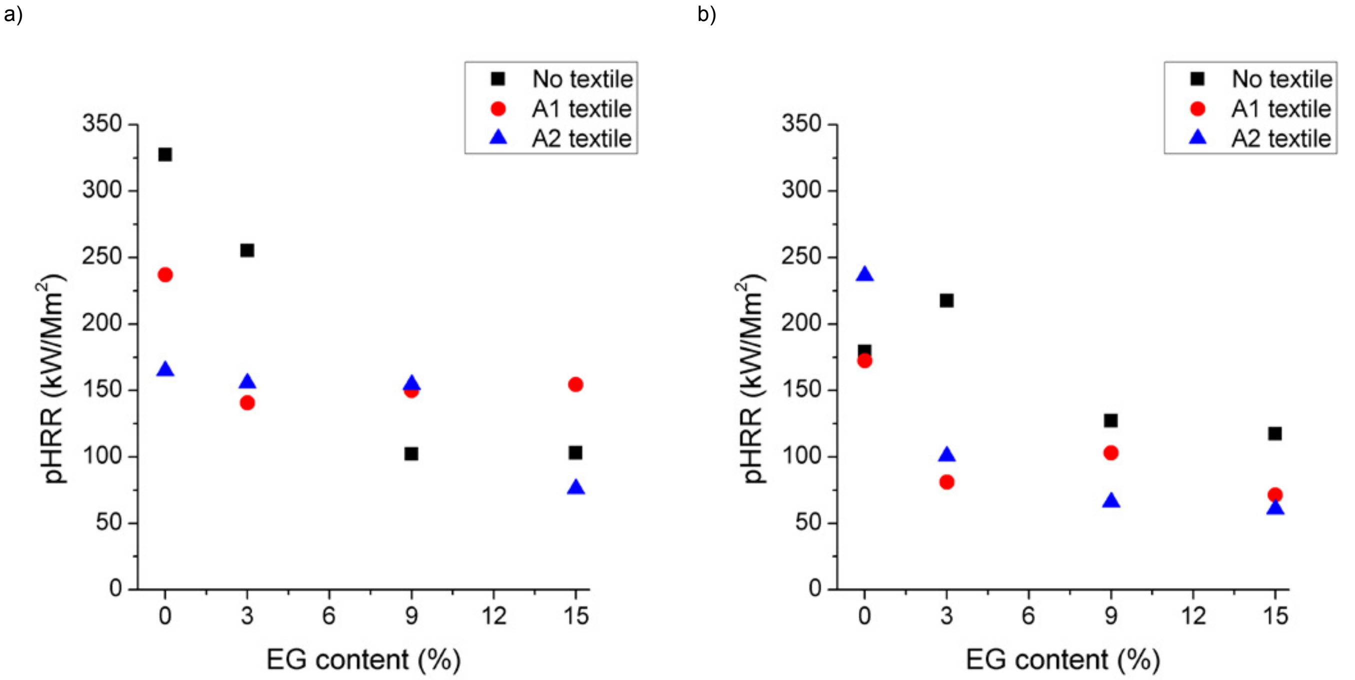


Figure 7. Peak heat release rate of rigid PU foams (a) with no conventional FR and (b) with DMPP as FR.

In HRR curves of developed PU foams, it is seen that EG decreases the peak heat release as well as total heat amount released. The burning process of PU foam samples is prolonged and occurs with less intensity. Rigid PU foam heat release curves for samples not protected with IM textile are seen in **Figure 10.** In **Figures 11** and **12**, heat release curves for PU foams protected with A1 and A2 IM textiles, respectively, are shown. Both IMs decrease heat release even if no FR is added into PU foam. Best results are obtained in sample, which was protected with A2 IM and 15% of EG, where there is a significant pHHR reduction. Different combinations of conventional FR DMPP and EG failed to significantly increase

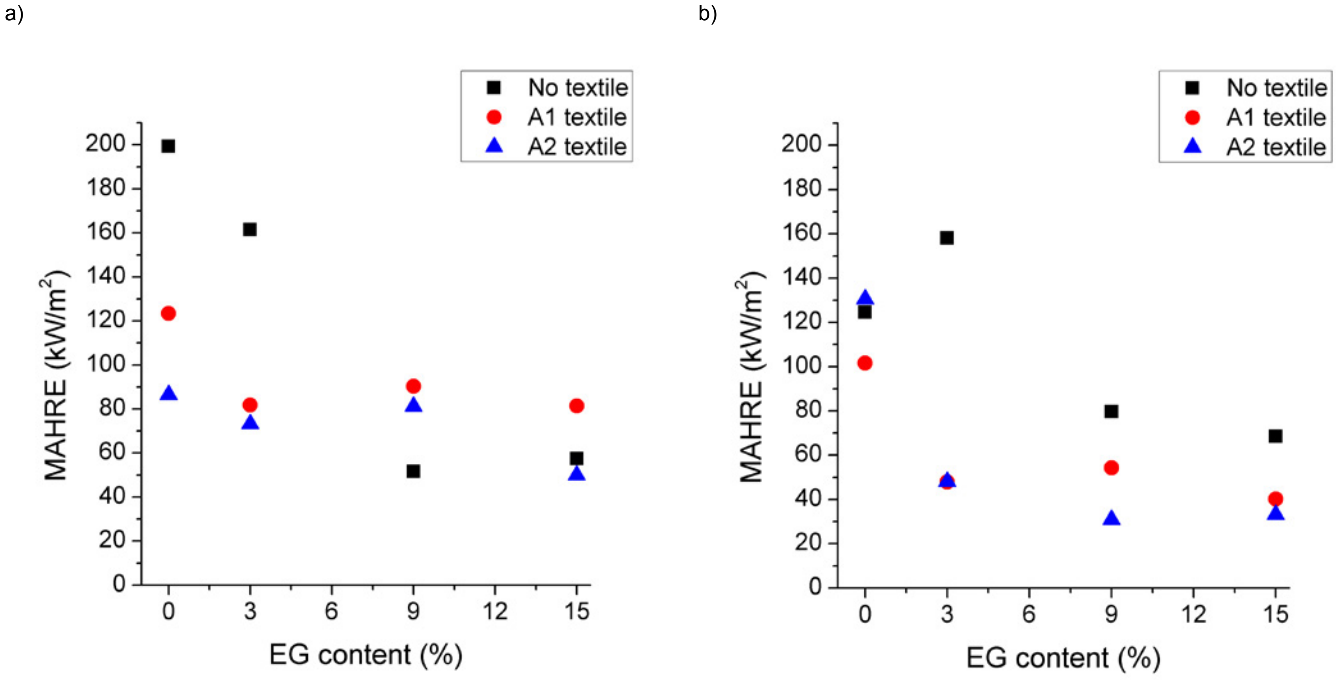


Figure 8. Maximum average rate of heat emission of rigid PU foams (a) with no conventional FR and (b) with DMPP as FR.

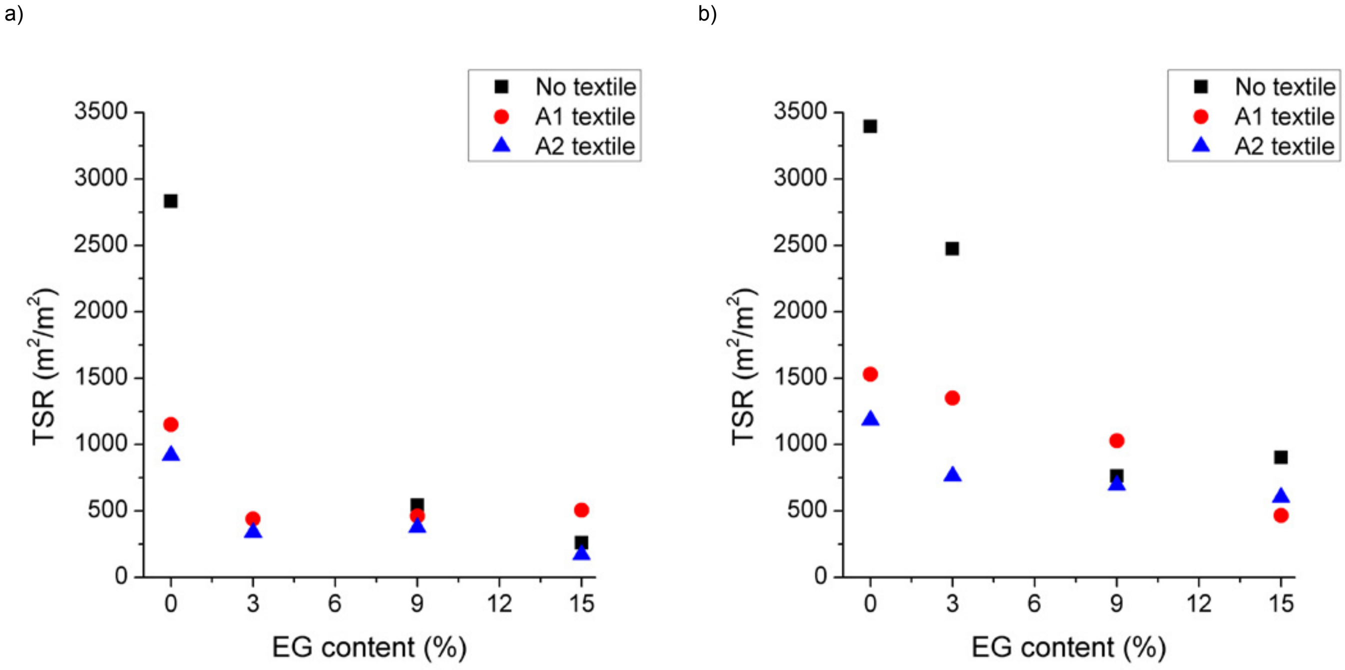


Figure 9. Total smoke release of rigid PU foams (a) with no conventional FR and (b) with DMPP as FR.

time to ignition where highest IT value of 12 s was for sample with 15% of EG. Addition of IM substantially increased IT from 7 to 40 s in case of PU foams with A2 IM and 15% EG. Also noticeable increase of time when heat release peak occurs was seen for PU samples, which were protected with IMs. Most significant data of Cone Calorimeter test are seen in **Tables 2** and **3.**

4. Conclusions

This study showed novel method of passive fire protection of rigid PU foams using flexible, thermally expandable IM. This fire resistance improvement method would be easily up-scalable in production of PU foam panels. Synergy between two types of additive FRs and IM was investigated. Conventional FR as well as EG decreased thermal conductivity of developed PU foams, which gives advantage to IM, where no worsening in

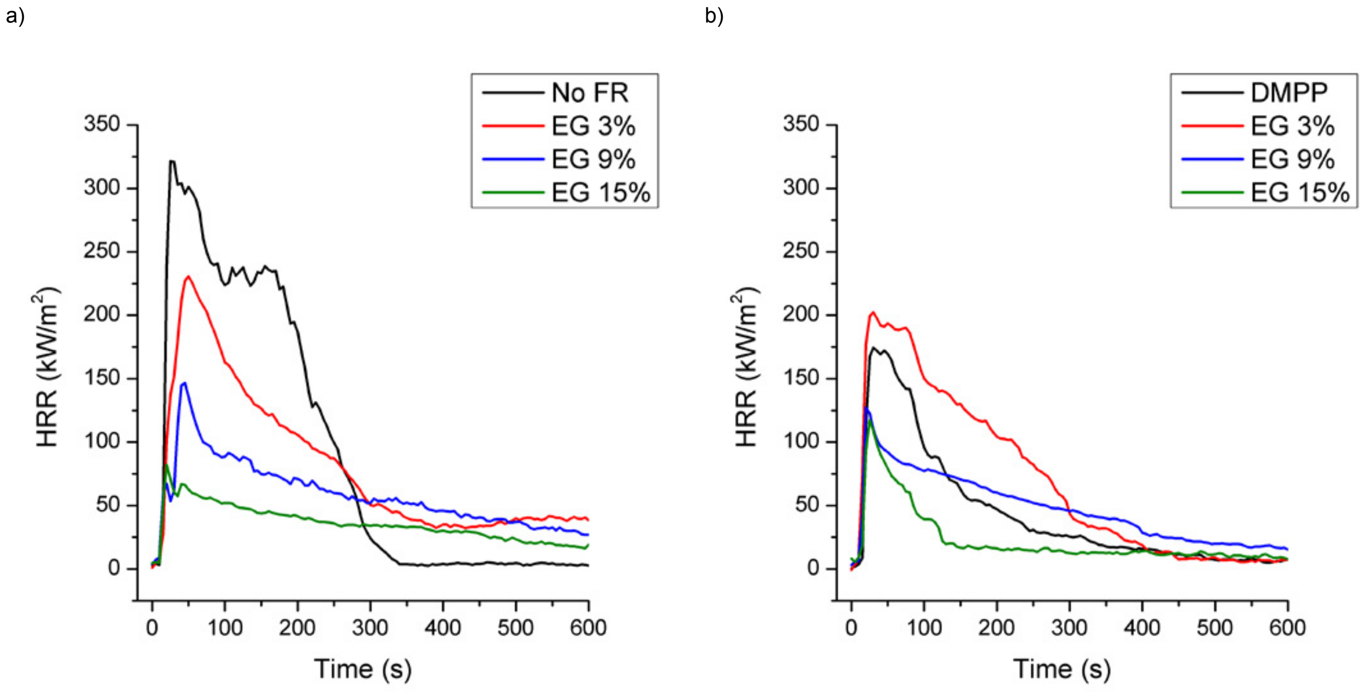


Figure 10. Heat release rate of rigid PU foams (a) with no conventional FR but with EG and (b) with DMPP as FR and EG.

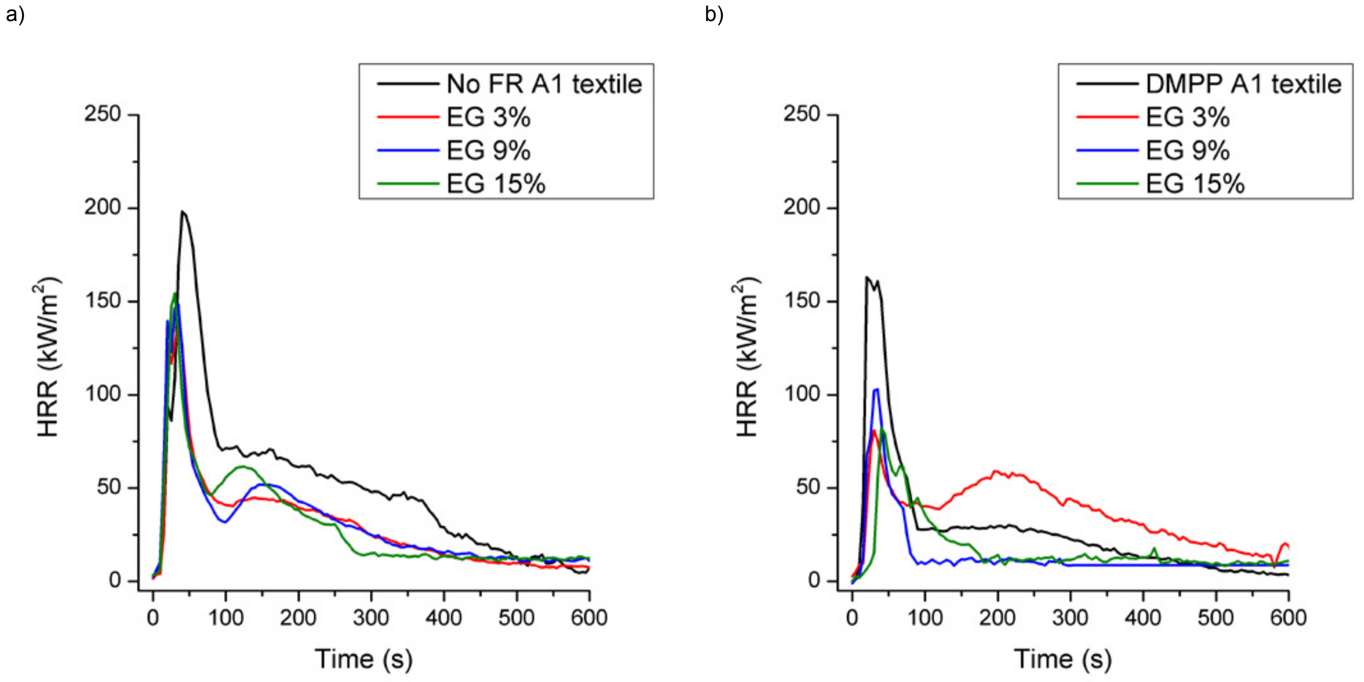


Figure 11. Heat release rate of rigid PU foams protected with A1 textile (a) with no conventional FR but with EG and (b) with DMPP as FR and EG.

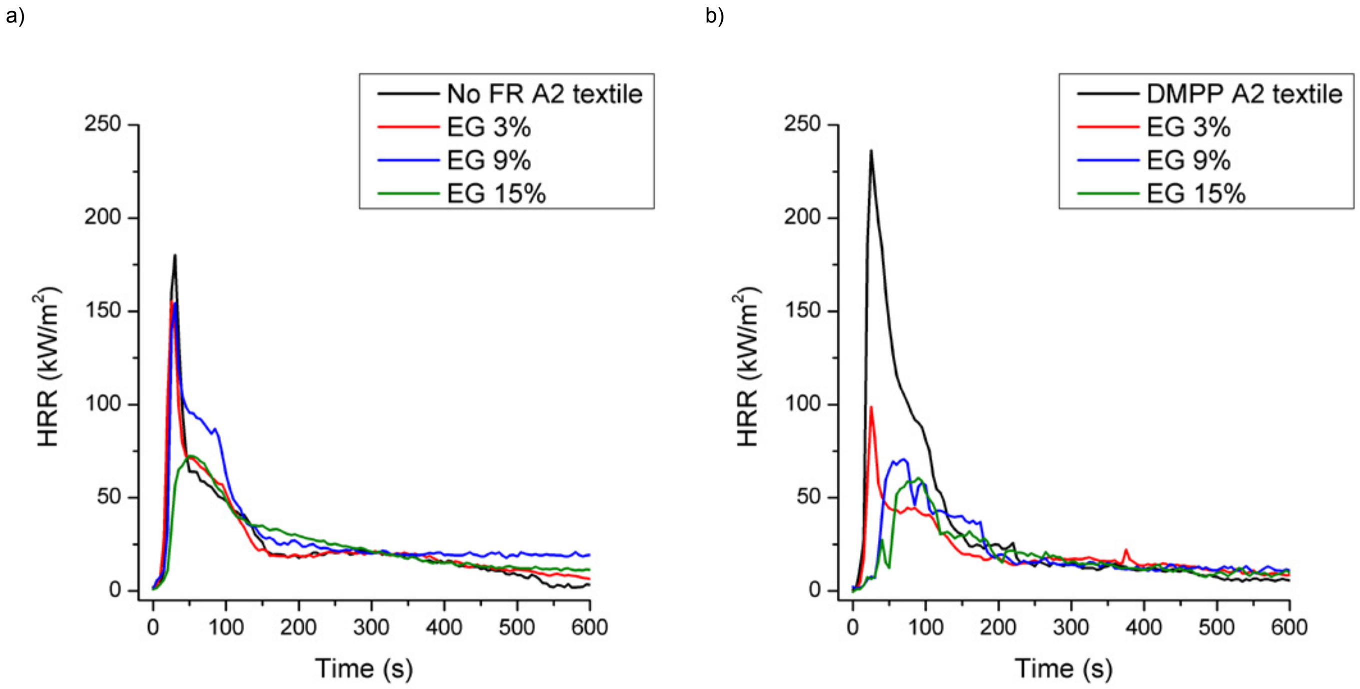


Figure 12. Heat release rate of rigid PU foams protected with A2 textile (a) with no conventional FR but with EG and (b) with DMPP as FR and EG.

Table 2. Peak heat release rate (pHRR); time to peak of heat release (TTP); ignition time (IT); flame out time (FOT); total smoke released (TSR) and maximum average rate of heat emission (MAHRE) for rigid PU foam with different amount of EG and IMs

PU foam	**EG content (%)**	**pHRR (kW/m²)**	**TTP (s)**	**IT (s)**	**FOT (s)**	**TSR (m²/m²)**	**MAHRE (kW/m²)**
No FR	**0**	327	28	6	335	2832	199
No FR	**3**	255	42	4	620	4156	162
No FR	**9**	102	23	3	792	543	52
No FR	**15**	103	28	12	651	261	58
No FR A1	**0**	237	43	3	543	2409	123
No FR A1	**3**	141	30	4	571	2055	82
No FR A1	**9**	150	33	7	344	2328	90
No FR A1	**15**	154	30	4	384	1150	81
No FR A2	**0**	165	63	5	428	440	87
No FR A2	**3**	156	27	4	440	461	73
No FR A2	**9**	154	30	4	266	506	81
No FR A2	**15**	76	50	6	419	919	50

Table 3. Peak of heat release rate (pHRR); time to peak of heat release (TTP); ignition time (IT); flame out time (FOT); total smoke released (TSR) and maximum average rate of heat emission (MAHRE) for rigid PU foam with different amount of EG, IMs and conventional FR DMPP.

PU foam FR	EG content (%)	pHRR (kW/m^2)	TTP (s)	IT (s)	FOT (s)	TSR (m^2/m^2)	MAHRE (kW/m^2)
DMPP	**0**	179	36	6	397	3396	125
DMPP	**3**	218	48	5	393	2473	158
DMPP	**9**	127	20	5	589	762	80
DMPP	**15**	117	25	8	135	902	69
DMPP A1	**0**	172	22	6	188	1529	102
DMPP A1	**3**	81	64	6	204	1350	48
DMPP A1	**9**	103	46	6	98	1029	54
DMPP A1	**15**	71	47	33	153	467	40
DMPP A2	**0**	236	28	7	197	1185	131
DMPP A2	**3**	101	27	8	308	762	48
DMPP A2	**9**	66	53	25	112	693	31
DMPP A2	**15**	61	98	40	271	604	33

thermal conductivity was noticed. Also, additive FRs decreased physical–mechanical properties and morphology of PU foams. Nevertheless, best fire performance for PU foam protected with 2.00-mm thick IM and filled with 15% of expandable graphite with conventional DMPP FR was determined. IM provided lowest peak of heat release in cone calorimeter test of 61 kW/m^2 with significant delay of peak of 70 s when compared with unmodified foam.

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