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Flammability of Bio-Based Rigid Polyurethane Foam as Sustainable Thermal Insulation Material

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Abstract

One of the biggest disadvantages of rigid polyurethane foams is its low thermal resistance, high flammability, and high smoke production when burning. Greatest advantage of this thermal insulation material is its low thermal conductivity, which at 20–25 mW/(m·K) is superior to other commercially available insulation materials. In recent years polyurethane materials from renewable resources have been widely studied. But their use on industrial scale was limited due to inconstant performance and relatively high price of raw materials. Different bio-based raw materials, such as rapeseed oil and tall oil, could provide abundant feedstock for PU foam production. Decrease of flammability of PU materials conventionally is achieved by addition of flame retardants, halogen-containing compounds, and phosphates. It can be considered that halogenated fire retardants could have several health hazards, such as volatile compound emission from materials and toxic gas release during burning process. Expandable graphite could be an answer to this flammability problem. This chapter describes development of bio-based rigid polyurethane foams and their flammability reduction using sustainable flame retardants. Different expandable graphite intumescent flame retardants provided significant flammability reduction while maintaining low thermal conductivity of insulation materials.

Keywords: rigid polyurethane-polyisocyanurate foam thermal insulation, bio-based polyols, thermal insulation, flammability, intumescent flame retardants, expandable graphite

1. Introduction

1.1. Development of bio-based rigid polyurethane foams

Polyurethane (PU) materials have a broad range of applications such as flexible foams, rigid foams, thermoplastic elastomers, coatings, and adhesives. About 29% of the PU material industry is attributed to rigid PU and polyisocyanurate (PIR) foam production [1]. These materials are mainly used as heat-insulating materials in civil engineering and the refrigeration industry due to their low thermal conductivity (λ). The industry standard of λ for rigid PU/PIR foams is 0.020 ± 0.002 W/mK, which, compared to the case of other insulation materials such as extruded polystyrene (XPS), expanded polystyrene (EPS), glass, or mineral wool, is almost twice lower [2]. Low λ values of rigid PU/PIR foams allow their application of in fast-growing markets like the nearly zero energy building industry. An additional advantage over XPS/EPS foams is the sustainability of PU/PIR materials as they can be obtained from renewable resources.

Sustainable solutions have been studied across a whole range of polymer materials [3–6]. Emphasis has been placed on PU materials because at least one component of a polymer material can be obtained from renewable resources [3–13]. Unfortunately, the majority of PU materials are produced from petroleum-based feedstocks. In recent years, the prices of crude oil and petroleum-based feedstocks have fluctuated significantly. Although the current prices of crude oil are the lowest in the recent decade [14], it is important to find a suitable substitute to petrochemical raw materials as they will run out eventually. Also the use of renewable resources in polymer materials decreases the global warming potential of the material and can sequester a large amount of CO₂ from the atmosphere while improving the impact the material has on the environment [15]. This has led to an increasing need and interest in developing alternate polyols (e.g., BASF castor oil-based Balance™, Cargill soybean-based BiOH™, and Dow soybean-based Renuva™) based on raw materials from renewable resources that offer reduced prices with a more favorable environmental footprint compared to the current petroleum-derived polyols [16–18].

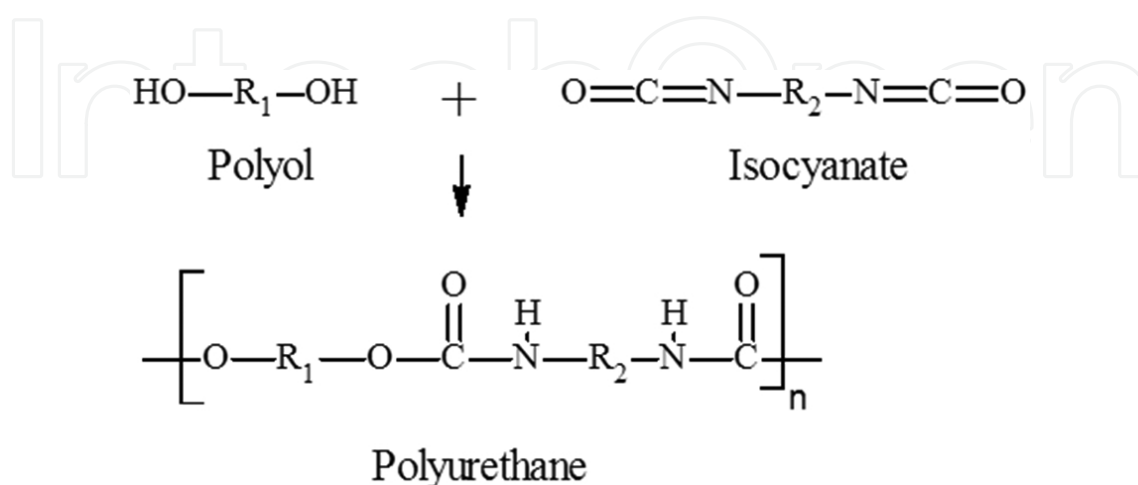


Figure 1. Generic scheme of PU material synthesis.

PU materials are obtained in the chemical reaction of hydroxyl derivatives—polyols and isocyanates as shown in **Figure 1**. For rigid PU foam synthesis, usually polyols with higher functionality ($f_n = 2.5\text{--}5.0$) and polymeric diphenylmethane diisocyanate (pMDI) are used.

Renewable materials are usually introduced into the PU polymer matrix as a polyol—a hydroxyl derivative of vegetable and other natural oils. Bio-based polyols have been investigated for some time, and studies in this field are currently continued. Good quality polyols have been obtained from different vegetable oils such as rapeseed oil (RO), castor oil, palm oil, and especially soybean oil [3–13]. Most of these oils are already used to produce a PU material feedstock on an industrial level [16–18] and can be potential replacements for petrochemical polyols in the synthesis of rigid PU foams.

Industry uses renewable raw materials not only because of the sustainability and marketing aspect of products. These materials provide a competitive and commercially viable alternative to petrochemical resources [19]. Vegetable oil polyols also provide additional positive properties of a PU material, such as higher hydrophobicity [11].

Vegetable oils are triglycerides of three different fatty acids that are joined together by the glycerol backbone as can be seen from **Figure 2**. Most of common natural oil triglycerides contain fatty acid chains that vary from 14 to 22 carbons in length, with 0–3 double bonds per fatty acid [3, 8, 10].

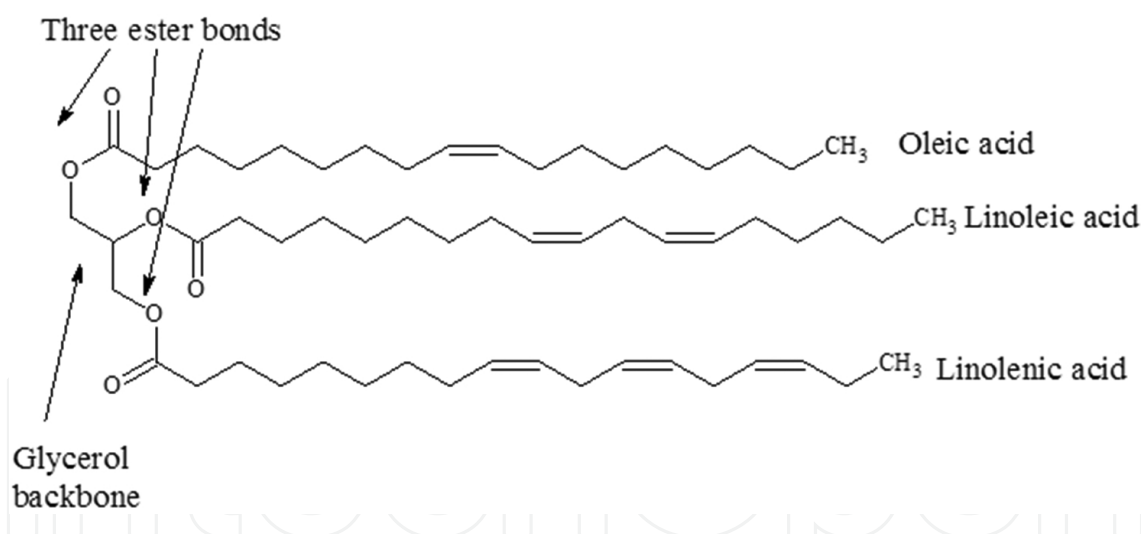


Figure 2. Generic structure of vegetable oil containing oleic, linoleic, and linolenic acid chains [11].

Before being applied in PUR systems, hydroxyl groups have to be introduced into structure of vegetable oil [6]. A number of methods to synthesize natural oil-based polyols are known, e.g., transesterification with polyfunctional alcohols, hydroformylation and hydrogenation, epoxidation followed by oxirane ring opening, microbial conversion, thermal polymerization followed by transesterification, ozonolysis and hydrogenation, or halogen addition and nucleophilic substitution [20, 21]. This chapter will describe polyols and rigid PU/PIR foams obtained from TO and RO using transesterification with polyfunctional alcohols [9, 10] and epoxidation followed by oxirane ring opening [10–13].

Unfortunately, most of the mentioned vegetable oils can be classified as first-generation bio-based raw materials [22, 23]. This means that the production of these polyols is competing with the production of food. TO can tackle this question because it is a by-product of cellulose production—a product of forest biomass processing and not an agricultural product. TO is a mixture of fatty and rosin acids, the generic structures of which can be seen from **Figure 3** [24–27]. TO, also like RO, should be chemically modified by introducing two or more hydroxyl groups in order to use it as a raw material for PU production.

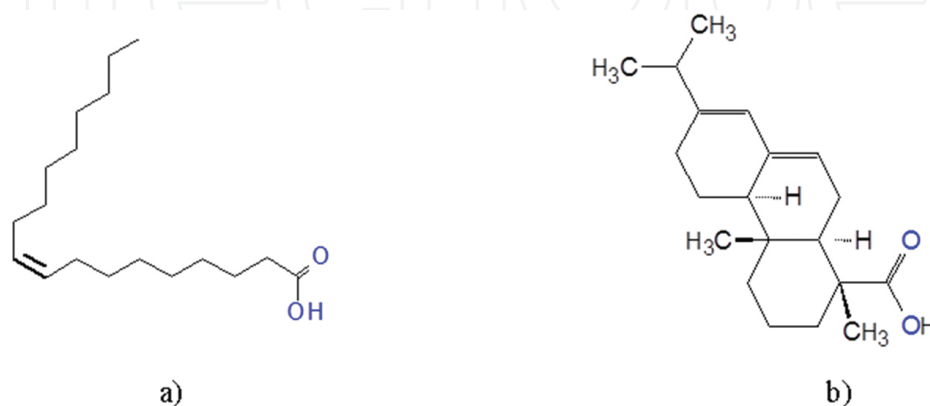


Figure 3. Basic structure of TO components: (a) fatty acid (oleic acid) and (b) rosin acid (abietic acid) [24, 25].

A renewable polyol from TO can be synthesized using a method developed at the Latvian State Institute of Wood Chemistry by the esterification of TO fatty and rosin acids with triethanolamine (TEOA). Distilled TO with a rosin acid content of 20% (Forchem, Finland) was used as a raw material for bio-based polyol development. **Figure 4** shows the TO esterification with TEOA [24, 25].

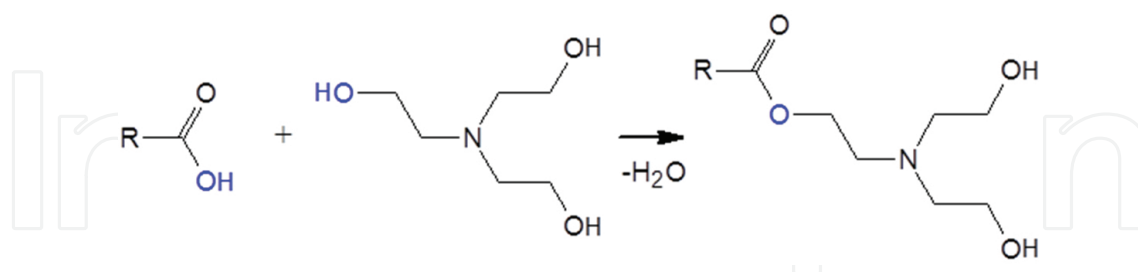


Figure 4. Reaction scheme of TO esterification with TEOA, where R is specific carboxylic acid radical [24, 25].

1.2. Flammability of rigid PU foams

One of the major disadvantages of rigid PU foams is their low thermal resistance, high flammability, and high smoke production when burning. PU foams based on petrochemical and bio-based polyols are ignitable and can be an additional fuel source in the case of a fire disaster. This is a serious concern and restricts the PU material application [28]. The limiting

oxygen index is the minimum concentration of oxygen in material surroundings that will support combustion of a polymer. It is measured by passing a mixture of oxygen and nitrogen over a burning specimen and reducing the oxygen level until a critical level is reached. The limiting oxygen index of non-modified PU foams is in the range of 16–18 [29]. Highly porous lightweight combustible foams tend to have a fast flame spread and a high heat emission. The increasing demand for PU foams is the reason why many studies are devoted to fire retardancy [30, 31].

An improvement in the thermal stability of PU foams may be achieved through the introduction of isocyanurate trimerization structures into the PU matrix [11], the so-called PIR foams. The trimerization reaction of isocyanate groups is shown in **Figure 5**. Isocyanurates, from a thermodynamic point of view, are more thermally stable than urethane bonds (urethane dissociates at approx. 200°C as opposed to 350°C for PIRs). The thermal stability of isocyanate-based polymers is provided in the following order: isocyanurate (350°C) > urea (250°C) > urethane (200°C) > biuret (135–140°C) > allophanate (106°C) [32, 33].

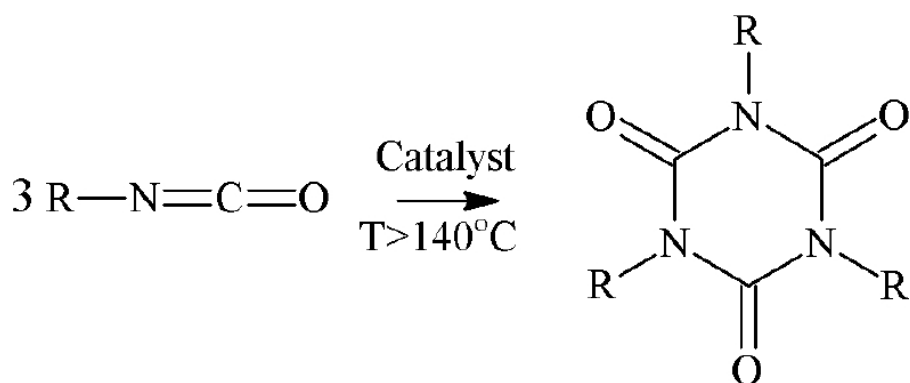


Figure 5. Trimerization reaction of three isocyanate groups.

PIR foams have higher fire retardancy but their broader use is limited due to price and technological difficulties. PIR foams are obtained in large excess of isocyanate (molar ratio of OH and isocyanate groups: 1/1.8–1/6), which means more complicated processing equipment as the volume ratios of components are not equal. Also the isocyanate trimerization reaction occurs only when the temperature of the reaction mixture is above 140°C. Thus, thermal insulation production via spray foaming in situ is difficult and rarely used commercially [33].

The decrease of flammability of PU/PIR materials is conventionally achieved by the addition of different flame retardants (FRs)—compounds, containing halogen, phosphorus, nitrogen, etc. Moreover, halogenated FR is the subject of considerable discussion in the industry and scientific community. It can be considered that halogenated FR could have several health hazards, such as volatile compound emission from materials and toxic and hazardous gas release during the burning process [34, 35].

Intumescent halogen-free FRs can be good substitutes for halogenated ones due to the formation of a protecting char layer that covers the surface of a material and limits the amount of heat reaching the polymer, slowing down the thermal degradation of the material. Also the

protective char layer decreases the transition of volatile compounds into the gas phase, thus reducing the amount of fuel in the gas phase and decreasing the emitted heat of the fire [36, 37]. Moreover, such an intumescent layer makes a thermal barrier, protecting the foam core from high temperature, and is used as a smoke suppressant [38, 39]. Expandable graphite (EG) can be used as a good substitute for halogenated liquid FR in rigid PU/PIR foams [40].

EG has a special graphite flake structure, i.e., stacked layers of hexagonal sp^2 -hybridized carbon structures. Intercalated EG with H_2SO_4 is shown in **Figure 6**. EG material can be treated with sulfuric acid, nitric acid, or acetic acid, which are intercalated into the graphite crystalline structure between carbon flakes. When heat is applied, the acid releases gas that expands or exfoliates the graphite particles.

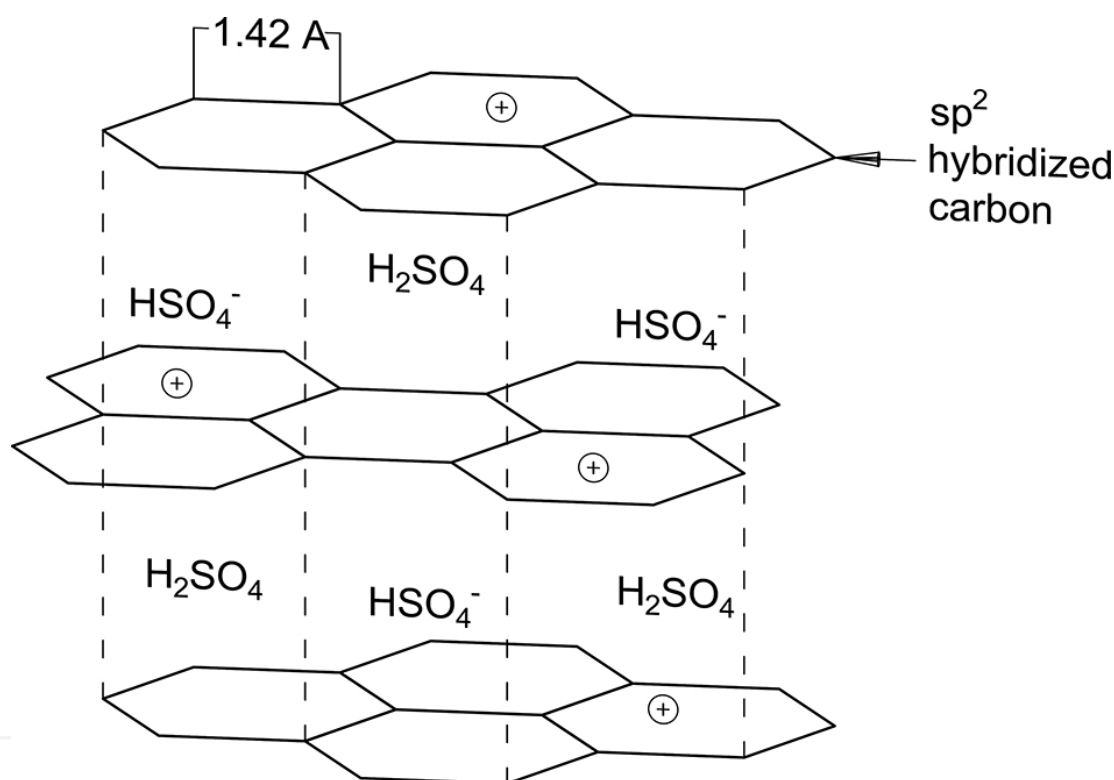
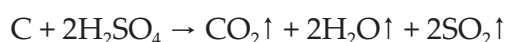


Figure 6. Generic structure of EG intercalated with H_2SO_4 [40].

High temperatures cause the oxidation of graphite in the following reaction with H_2SO_4 :



The released gases cause the expansion of graphite, which acts as a physical barrier for the heat and mass transfer from and into polymer material [41]. EG forms a stable char insulating layer structure on the surface of the material that prevents heat and volatile compound transfer. Volatile compound reduction in gas phase means less fuel for burning process. Also, limiting the heat transfer to material means longer degradation of polymer matrix, which in result limits the volatile compound release. Ultimately, the carbon char layer prevents the PU/PIR foams

from burning [42, 43]. Additional benefit of such FR is reduction of smoke as the protective char layer also stops particle escape into airflow.

EG keeps most of natural graphite attributes, such as low price and high porosity, making it very useful as functional carbon material that can be applied in various fields of the polymer industry, but especially as FR [44]. EG addition with loads over 20% into rigid PU foams with an Apparent bulk density of 35 kg/m³ gives a significant improvement in the fire resistance of the materials [45]. The FR efficiency was enhanced when the apparent density of PU/PIR foams was increased at a fixed EG loads. Also with an increase in the EG content at a fixed apparent PU/PIR foam bulk density, the flammability was reduced [35, 39]. The size of EG particles also influences the FR efficiency. EG particles of a smaller size did not produce enough char to cover the whole surface of the burning sample, resulting in a poor fire-retardant property of rigid PU/PIR foams [46].

Although EG can replace halogenated FR and significantly decrease the flammability of polymer materials, there is a significant drawback regarding thermal insulation materials. Graphite is an excellent heat conductor, so with the addition of EG into PU/PIR foams, the thermal conductivity of the material rises, which is a highly undesired property for thermal insulation material [47]. To avoid the abovementioned disadvantages, IF (nonwoven glass fiber fabric filled with EG) can be used as a FR solution. Recently, several researchers have investigated the fire behavior of the foam/fabric combination [48, 49] using a cone calorimeter, but it was done only for flexible PU foams. The idea was to test the fire behavior of mattresses for automotive and furniture cushions; the results have shown that such fabric is a viable fire-retardant solution.

The goal of this study was to develop a thermal insulation material from renewable resources with competitive thermal insulation and fire retardancy properties and replace halogenated FR with more sustainable solutions. For this purpose, several bio-based polyols were used. TO, a by-product of cellulose production, was used to synthesize the raw material needed for PU/PIR foam development. TO was chosen as a cheap and available raw material, which is not competing with food production as other vegetable oils that are agricultural products. The bio-based polyol from TO was synthesized using the esterification reaction with polyfunctional amine-based alcohol—TEOA. RO was used as the second renewable material feedstock. Polyols for rigid PU/PIR foam production were obtained by two synthesis methods. The RO polyol was synthesized similarly to the TO polyol by transesterification of the triglyceride structure of RO with TEOA. The third type of the bio-based polyol was also obtained from RO, but double bonds in the RO chemical structure were targeted to introduce hydroxyl groups into the compound. The cumulative effect of the introduction of isocyanurate structures into the PU matrix and EG as additive FR is a prospective solution to decrease the flammability of rigid PU/PIR foams. The second approach to reduce the flammability of PU/PIR foams—protection of insulation materials with (IF), to keep excellent rigid PU/PIR foam insulation properties—was also investigated. Two different additive liquid FRs—tris(2-chloropropyl) phosphate (TCPP) and dimethyl-propyl-phosphate (DMPP)—were compared for their influence in the decrease of PU/PIR foam flammability.

2. Development of bio-based rigid PU foams

2.1. Bio-based polyols

The most significant properties of the polyols used in this study are presented in **Table 1**. TO polyol and RO polyols were synthesized at Institute of Wood Chemistry [10, 25, 26]. The epoxidized RO polyol was synthesized at the Cracow Technical University [11–13].

Polyol type	OH value, mgKOH/g	Viscosity at 25°C, mPa·s	Acid value, mgKOH/g	M _n , g/mol	f _n	Water content, %
TO polyol	342	280 ± 25	<5	391	2.39	0.24
RO polyol	301	190 ± 25	<5	474	2.55	0.05
RO Epoxy	276	2260 ± 50	<5	635	3.12	0.36

Table 1. Technical data of renewable polyols used for PU/PIR foam synthesis.

Gel permeation chromatography was used to determine the values of the number-average molecular weight (M_n) and number-average functionality (f_n) of the obtained polyols. The number-average functionalities of polyols were calculated based on hydroxyl values, and M_n was experimentally determined (Eq. (1)) [10]:

$$f_n = \frac{M_n \cdot OH_{val}}{56110} \quad (1)$$

where f_n is the number-average functionality, M_n is the number-average molecular weight, and OH_{val} is the hydroxyl value of polyol.

Viscosity of polyols was determined according to the DIN 53015 standard at 25°C using a falling ball viscometer KF 100 (RheoTec Messtechnik GmbH, Germany). Water content of polyols was determined according to the DIN 51777 standard.

The chemical structure of the used polyols was studied by Fourier transform infrared spectroscopy (FTIR) measurements. **Figure 7** presents FTIR spectra of polyols from renewable materials. Peaks at 3444–3385 cm⁻¹ indicated the presence of OH groups in the polyols chosen for this project. The TO polyol and the RO polyol showed double-bond stretching at 3008 cm⁻¹. In contrast, the RO Epoxy polyol did not have this peak as double bond was transformed in the epoxidation and ring-opening reaction. TO and RO polyol FTIR spectra were quite similar as expected, also because of the similarity of the chemical structure. Tertiary amine group vibrations are seen at 1043–1042 cm⁻¹. The RO Epoxy polyol differs from the TO and RO polyols with ether bond —C—O—C— symmetric stretching at 1103 cm⁻¹, which is present due to epoxy ring opening with diethylene glycol. The lack of epoxy ring vibration at the 928 cm⁻¹ peak confirms the ring-opening reaction. The addition of tertiary amine groups into the polyol could make it more catalytically active as most commercial PU catalysts are

amine based. This could be a beneficial property because catalysts are among the most expensive components in PU foam formulation. The TO polyol should contain aromatic structures because distilled TO with 20% of rosin acids was used to synthesize the TO polyol but no peaks associated with aromatic rings were noticed as the concentration of aromatic groups in the end product was too low. All natural oil polyols showed a C=O bond stretching peak at 1760–1665 cm^{-1} [10, 50, 51].

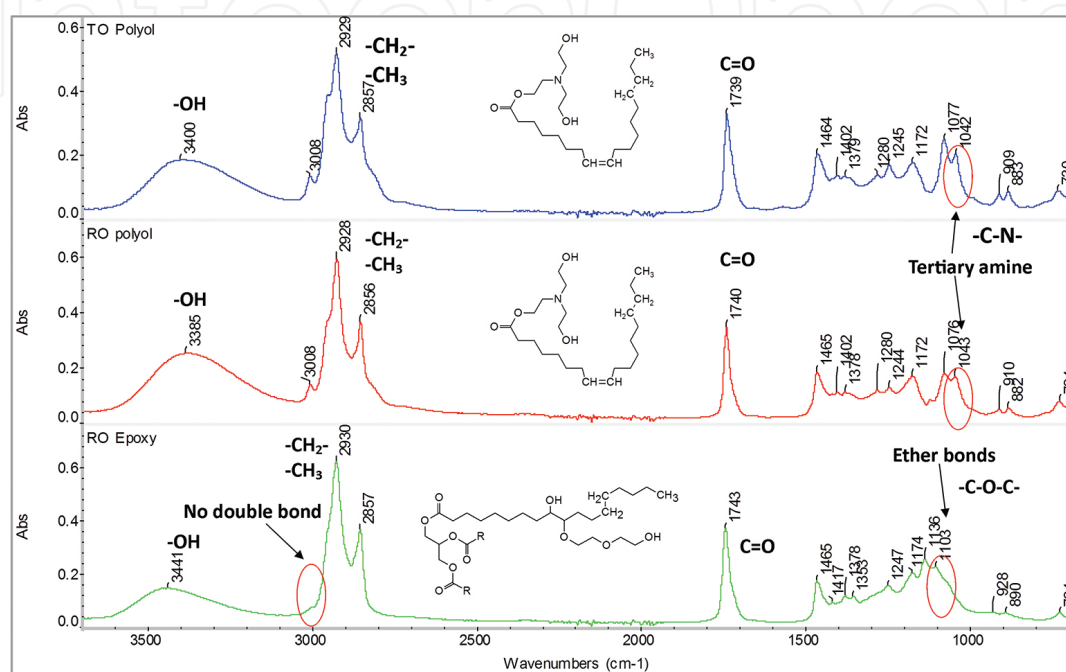


Figure 7. FTIR spectra for polyols from renewable raw materials.

2.2. Rigid PU/PIR foam sample preparation and materials used

2.2.1. Materials

Polyols from renewable resources were used as the base of the rigid PU/PIR foam polyol component. A higher functional polyether polyol based on sorbitol Lupranol 3422 (contains only secondary hydroxyl groups, OH value 490 mg KOH/g) from BASF was added to increase the cross-linkage density of the polymer matrix. An additive surfactant NIAX Silicone L6915 was used to obtain closed-cell PU/PIR foams. The reactive delayed action time amine-based catalyst NP-10 available from Momentive Performance Materials Inc was used. TCPP and DMPP from Lanxess Deutschland GmbH were used as additive liquid FRs. Distilled water was used as a chemical blowing agent. Polymeric diphenylmethane diisocyanate—IsoPMDI 92140 (pMDI) from BASF—was used as an isocyanate component (NCO = 31.5 wt%). EG with the trade mark EG 290 from Sinograft, Poland, was used as intumescent FR. Carbon content in EG was 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/m³.

IF from Technical Fibre Products Ltd. was used for the development of sandwich-type PU foam panels: flexible, thermally expandable IF (60152C) which is based on mineral and glass fibers with incorporated graphite particles. The activation temperature of this fabric is $>190^{\circ}\text{C}$, at which it starts to expand and reaches expansion ratio of 9:1 at 450°C . The thickness of non-expanded fabric is 2.00 mm; typical density 220 kg/m^3 and tensile strength 175 N/15 mm .

2.2.2. Rigid PU/PIR foam sample preparation

The polyol component was obtained by weighting all necessary components (polyol, cross-linkage reagent catalyst, blowing agent, surfactant, 7% of liquid FR, and different amounts of EG) and stirred for 1 min by a mechanical stirrer at 2000 rpm. Then, an appropriate amount of pMDI was added to obtain PU/PIR foams with respective isocyanate indices ($II=110, 150, 200$, and 250) and both components were stirred. Isocyanate index is the ratio of the equivalent amount of isocyanate used relative to the theoretical equivalent amount times 100. The reacting mass of PU foam was poured into a stainless steel closed-type mold, preheated to 50°C . For final curing of PU foams, the mold was placed into an oven at 50°C for 2 h. PU/PIR foams with IF were obtained by placing the fabric on the bottom of the stainless steel mold and pouring the PU/PIR reacting mass over it. In this way one side of the PU/PIR foam material became protected; this side was also tested in the reaction to heat flux tests. Four types of the obtained PU foam samples are unmodified PU/PIR foam, PU/PIR foam filled with different amounts of EG (3%, 6%, 9%, and 15%), PU/PIR foam protected with IF and PU/PIR foam with EG (3%, 9%, and 15%), and IFs that are shown in **Figure 8**.

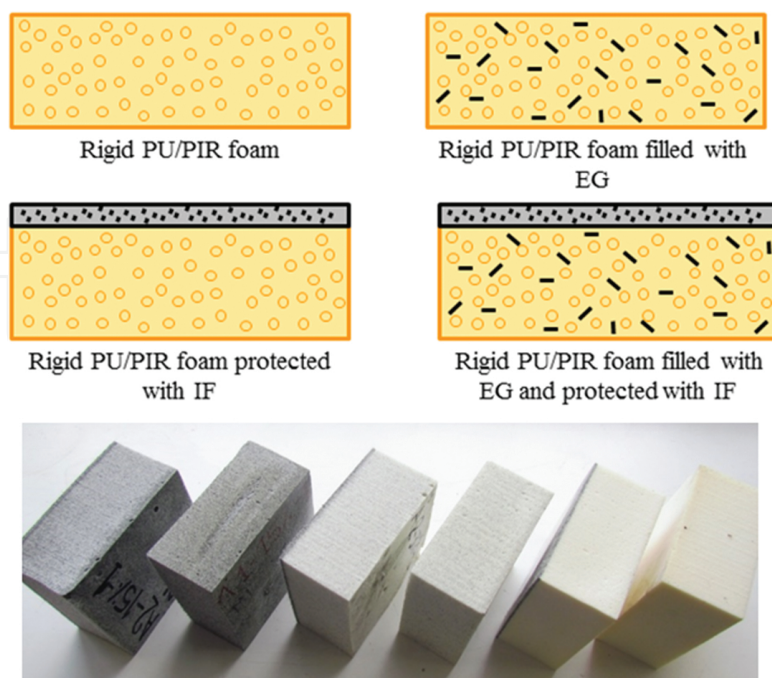


Figure 8. Four types of PU/PIR foam samples studied [47].

Samples for different tests from the prepared PU/PIR foam blocks were cut using a band saw and then conditioned for at least 24 h at room temperature. The apparent bulk density of the obtained PU/PIR foams was tested according to the ISO 845 standard. The reaction to the 35 kW/m² heat flux was tested using a FTT Dual Cone Calorimeter from Fire Testing Technology Ltd. The peak heat release rate (pHRR, kW/m²), time to pHRR (TTP, s), ignition time (IT, s), time to flame out (FOT, s), total smoke release (TSR, m²/m²), and maximum average rate of heat emission (MARHE, kW/m²) were determined by this equipment according to the ISO 5660 standard. The distance from the heater to the sample surface was set at 25 mm and the horizontal sample holder was used. The thermal conductivity coefficient (λ , mW/m·K) was tested using a Linseis Heat Flow Meter according to the ISO 8301 standard. Compression strength and modulus of elasticity for PU foams parallel and perpendicular to the foaming direction were tested according to the ISO 844 standard with one offset of the sample size; cylinders with a diameter of 20 mm and a height of 22 mm were tested. Mechanical testing of PU/PIR foam was performed on testing machines Zwick Roell 1000 N. Scanning electron microscopy (SEM) was applied to obtain images of PU/PIR foams and to determine the material morphology. SEM microscope, Tescan TS 5634, was used. The thermal stability was tested via thermogravimetric analysis (TGA) using a Mettler-Toledo TGA/SDTA 851e under a nitrogen flow and at a heating rate of 10°C/min from room temperature to 1000°C.

3. Properties of bio-based rigid PU foams

3.1. Thermal conductivity of the developed rigid PU/PIR foams

The main characteristics of any thermal insulation material are thermal conductivity and thermal resistance. **Figure 9** shows the measured λ for the rigid PU foam obtained from the TO polyol and filled with different amounts of EG particles. The isocyanate index of these samples was 110. **Figure 9(a)** is for the PU foam without DMPP liquid FR and the image (b) is for the PU foam with the addition of 7% of DMPP. λ values of samples with IF protection were also measured. It can be seen that IF has no effect on the λ of PU foams, but there is a clear increase of thermal conductivity with the addition of EG. The λ of the PU foam with no DMPP FR is 24.44 mW/m·K, which is decent for the material that could be used in building construction. Unfortunately, the addition of DMPP increased λ up to 28.74 mW/m·K which is only marginally satisfactory, because at this value the thermal insulation properties of the developed PU foam are in the range of XPS/EPS. Rigid PU foams cannot compete with XPS/EPS in terms of price even if they are produced from renewable resources. The increase of the developed PU foam thermal conductivity can be explained by the plasticization of the PU polymer matrix. Most of conventional additive liquid FRs decrease the glass transition temperature of the PU polymer matrix [52]. They swell the network structure of the PU matrix and dilute aromaticity. Due to the decrease of the cross-linkage density, blowing agent can diffuse more easily through the PU foam cells even though the developed PU foam has a closed-cell structure. The closed-cell content of all developed PU foams was >90%. The substitution of CO₂ or another gas (blowing agent) with air in conventional PU foams is a slow process and

takes years [53]. However, even with λ 28.74 mW/m·K, the developed PU foams are an energy-efficient thermal insulation material.

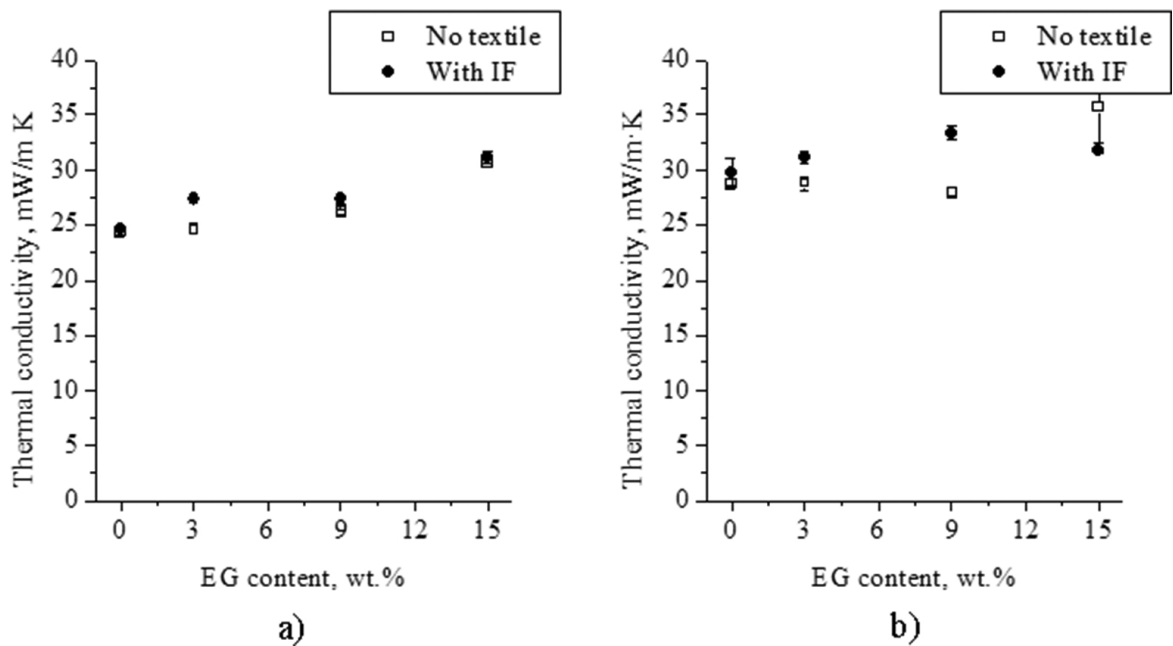


Figure 9. Thermal conductivity of rigid PU foams (II-110) protected with IF: (a) with no liquid FR but with EG and (b) with DMPP as FR and EG.

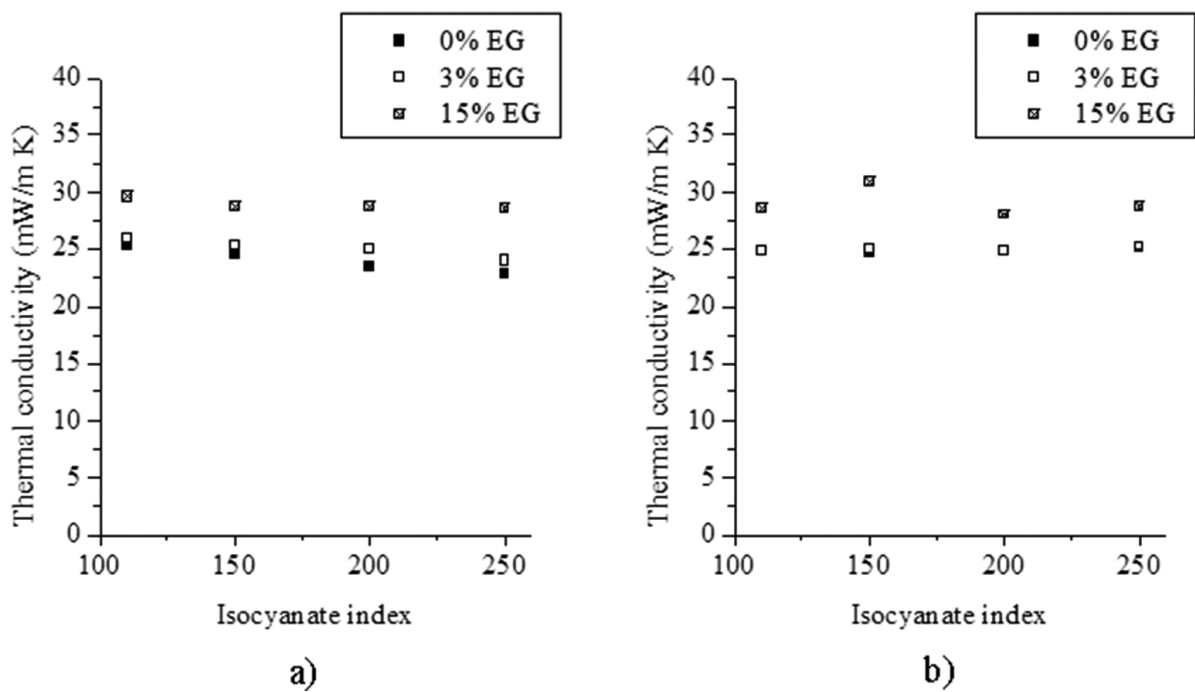


Figure 10. Thermal conductivity of rigid PU/PIR foams with different isocyanate indices and different EG content: (a) with no IF and (b) protected with different IF.

Figure 10 shows λ values of rigid PU/PIR foam with different isocyanate indices and different EG content. Also in the case of different isocyanate indices, IF had little influence on the thermal conductivity of the developed materials, and λ values increased with increasing EG content. The lowest value of λ was 22.80 mW/m·K in the case of rigid PIR foam with the highest isocyanate index (250). Due to cyclotrimerization, shown in **Figure 5**, the cross-linkage density of the polymer matrix and aromaticity increased. This helps reduce the CO₂ diffusion through cell walls. The λ value of 22.80 mW/m·K can be considered up to industrial quality standards of a rigid PU/PIR foam thermal insulation material.

Also for rigid PU/PIR foams obtained from RO bio-based polyols, the EG increased the λ value. Similarly to the TO polyol, the PU/PIR foam with a higher isocyanate index had a lower λ value, and the PU/PIR foam based on the RO Epoxy polyol showed the best insulation properties with λ value of 22.79 mW/(m·K) (**Figure 11**).

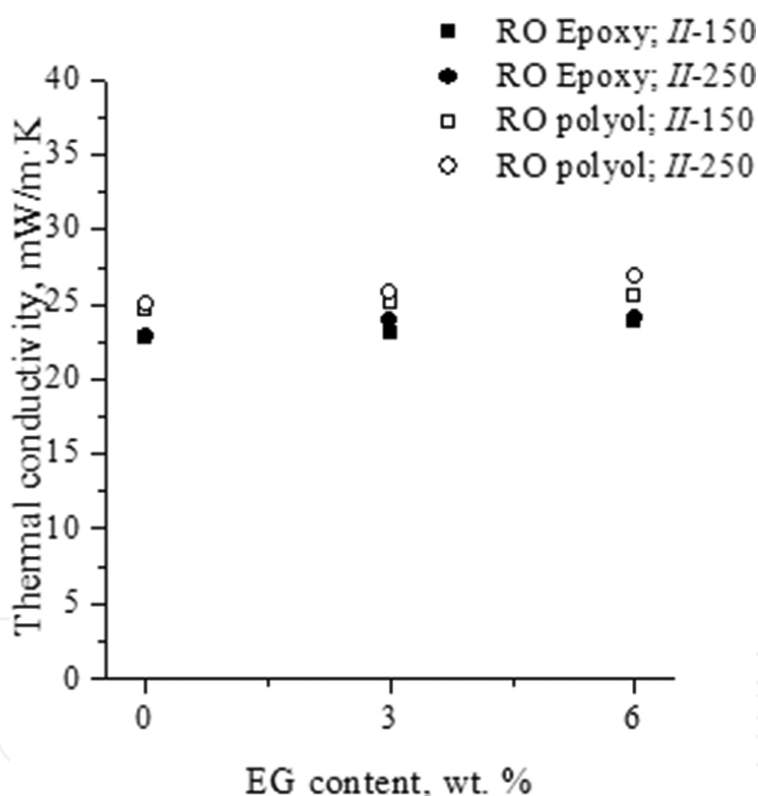


Figure 11. EG influence on the thermal conductivity of rigid PU/PIR foams based on different RO polyols.

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

3.2. Mechanical and morphological properties of the developed rigid PU/PIR foams

Other characteristics of the developed TO polyol-based PU foams with different amounts of EG are listed in **Table 2**. It can be seen that the addition of EG increased the apparent bulk density of the developed PU foams, but this did not improve the mechanical properties of PU foams. PU foam panels with the apparent bulk density $\sim 60 \text{ kg/m}^3$ are used as thermal insulation in floor panels. The increase of apparent bulk density also correlates with the increase of λ . EG does not have a reinforcement effect. Even at 15% of EG in PU foam, the particles are too far spread out. SEM images show that, although the particles have good phase incorporation into the PU matrix, they disrupt the cell morphology. This is the reason for the decrease of mechanical properties.

Foam characteristic				
Rigid PU/PIR foams based on TO polyol with no liquid FR				
EG content, %	0	3	9	15
Apparent bulk density, kg/m^3	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
Rigid PU foams based on TO polyol with DMPP				
Apparent bulk density, kg/m^3	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
Z-measurements of compression strength parallel to foaming direction				
X-measurements of compression strength perpendicular to foaming direction				

Table 2. Bulk density, compression strength, and Young's modulus for PU foams with no liquid FR but with EG and for PU foams with DMPP as FR and EG.

The compression strength and Young's modulus of rigid PU/PIR foams with different isocyanate indices and different EG content can be seen from **Figure 12**. The increase of isocyanate index also improved the mechanical properties of the developed insulation materials. The highest values of compression strength and Young's modulus (0.49 and 10.34 MPa, respectively) were achieved for rigid PU/PIR foams with an isocyanate index of 200. The improvement of mechanical properties can be attributed to the increase of the cross-linkage density and aromaticity of the developed PIR foams. At an isocyanate index of 250, a drop in mechanical properties was noticed, which can be explained by the insufficient

technological conditions during the foaming and PIR foam curing process, such as temperature.

SEM images of the developed PU foams are shown in **Figure 13**. It is clear that EG is evenly distributed across the PU foam and it is located in walls and cell cross points. A closer look at the EG particle shows that there is no phase separation between the PU matrix and EG. It can be seen that the PU foam with EG has a much more uneven cell structure, which results in lower mechanical properties.

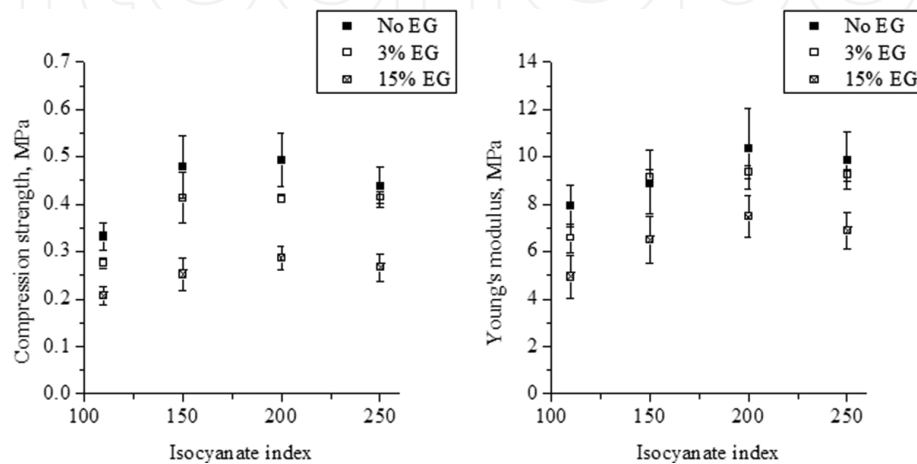


Figure 12. Compression strength and Young's modulus of rigid PU/PIR foams with different isocyanate indices and different EG content.

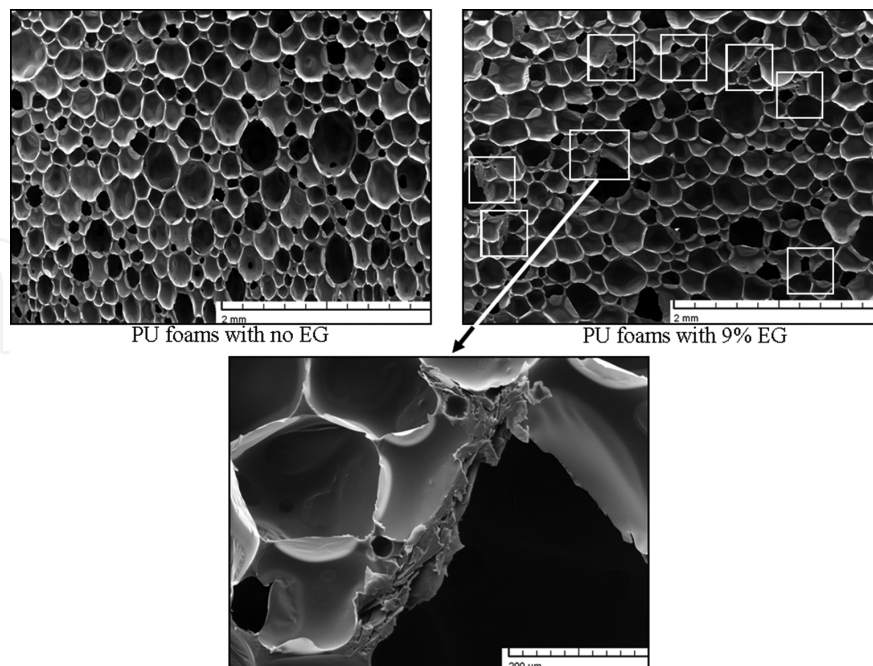


Figure 13. SEM images of PU foams with no conventional FR and 9% EG.

The main objective of this study was to obtain rigid PU/PIR foams with decreased flammability without losing superior thermal insulation properties. This was done by protecting one side of the PU foam material with IF, as shown in **Figure 14**. It is seen that the PU matrix adhesion to glass fiber is excellent and there are even cells of PU foam blown into IF. The good-phase adhesion of the PU foam and IF means that this fire protection would be easy to upscale, for example, in the production of PU/PIR sandwich-type panels. IF could replace paper roll that is used in PU/PIR sandwich-type panel production conveyor belts. This technique would introduce IF without using any adhesives that increase the production costs.

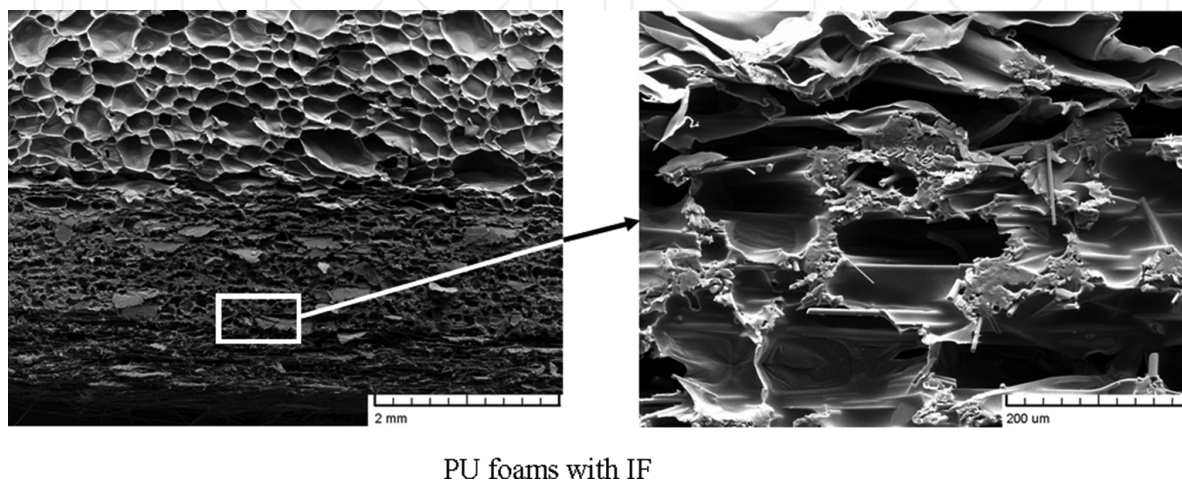


Figure 14. SEM images of PU foams with IF.

3.3. Flammability of rigid PU/PIR foams

3.3.1. EG influence on heat release of PU/PIR foams in the cone calorimeter test

The cone calorimeter test gives a significant amount of information about the flammability of the tested materials and their reaction to the heat flux. This test is a useful technique to compare different materials and gain the initial idea how a material will react in a case of fire. In the cone calorimeter test, the material is subjected to the radiant heat flux $q_{\text{ext}} = 0\text{--}100 \text{ kW/m}^2$, where the flux of 35 or 50 kW/m^2 is commonly used. The small sample size of $100 \text{ mm} \times 100 \text{ mm} \times 50 \text{ mm}$ makes this technique very useful to compare and optimize materials as for the single burning item test where much bigger samples are required. The cone calorimeter test gives the initial idea how a material will behave in an open-fire scenario. Usual parameters that are obtained after this test are HRR curves in time, time to ignition (TTI), total heat release (THR), pHRR, TSR, and MARHE.

pHRR can be used to compare materials provided that the test setup conditions are kept the same for all tested samples (sample thickness, sample holder, distance from the heater, heat flux, airflow). **Figure 15** shows a comparison of rigid PU foams from the TO polyol filled with different amounts of EG and two different liquid additive FRs (TCPP and DMPP). The addition of EG into PU foams decreased pHRR from 327.4 to 102.9 kW/m^2 when no other FR was used.

There was no synergistic effect between EG and DMPP or TCPP because the pHRR of PU foam samples with 15% of EG and 7% of liquid FR did not decrease below 102.9 kW/m². Although the sample with only DMPP showed the lowest values of pHRR and THR of 179.1 and 28.2 kW/m², respectively, in comparison with the sample with no FR-327.4 and 55.3 kW/m², its application could be limited due to increase of λ mentioned in **Figure 9**. DMPP works as plasticizer and promotes easier diffusion of gas from PU/PIR foam cells. The blowing agent in PU/PIR foam cells is replaced with air and λ is increased from 24.44 to 28.74 mW/m·K.

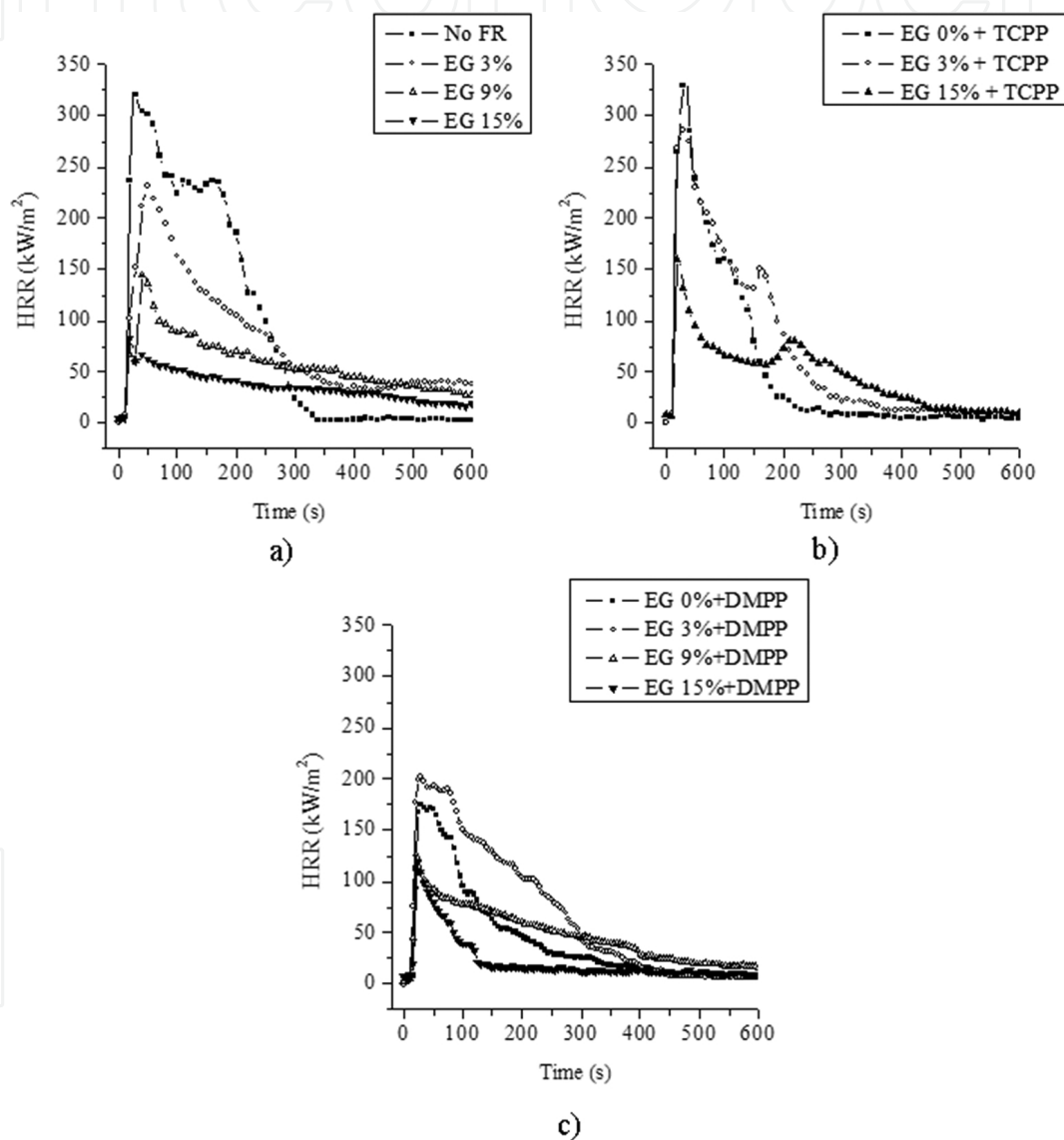


Figure 15. HRR curves of PU foam based on TO polyol with II-110, different amount of EG, and (a) no liquid FR, (b) 7% TCPP, and (c) 7% DMPP.

The addition of trimerization products of isocyanate groups into the polymer matrix increases its thermal stability and decreases flammability, which can be seen in **Figure 16(a)**. The increase of the isocyanate index from 110 to 250 decreased pHRR from 354.5 to 304.8 kW/m². The

increase of the isocyanate index prolonged the burning of PU/PIR foam but the material burned with less intensity. **Figure 16(b)** shows HRR curves of PU/PIR foams protected with IF. There was no heat release detected because the material did not ignite during the whole test time. The fabric did what it was designed to do and formed a protective char layer on top of the PU/PIR foam.

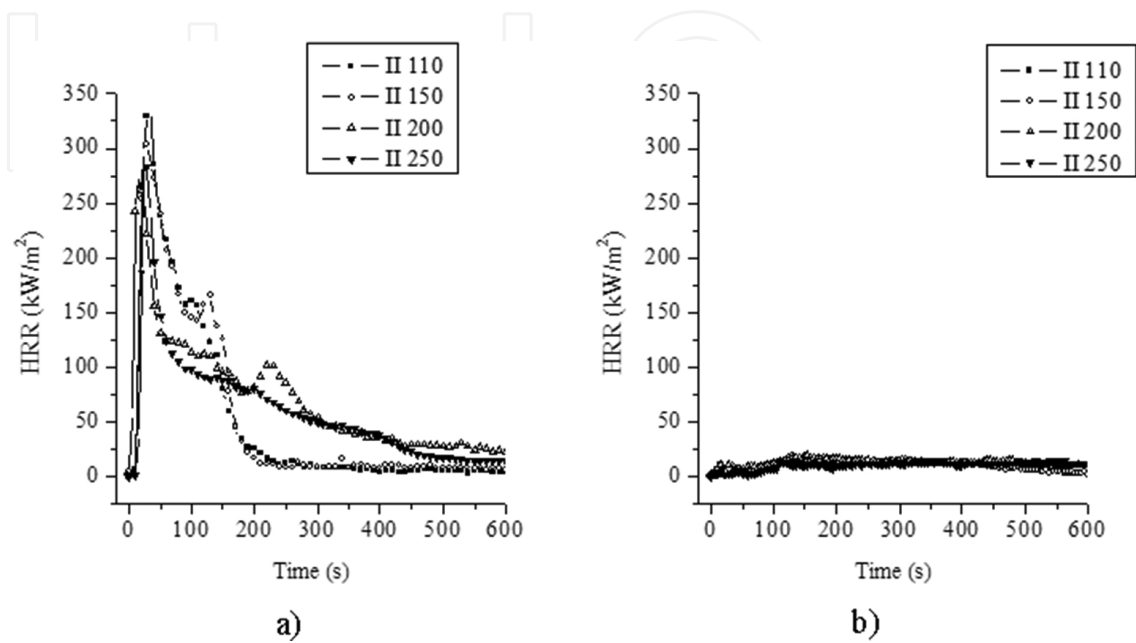


Figure 16. Rigid PU/PIR foam HRR curves: (a) foams with different isocyanate index and (b) PU/PIR foams with IF protection.

Figure 17 demonstrates the images of PU/PIR foams during the cone calorimeter test. The IF formed a thick char layer on top of the PU/PIR foam that stopped the degradation of the PU/PIR polymer matrix. IF gives excellent fire protection while keeping low thermal conductivity values as seen in **Figures 8** and **9**.

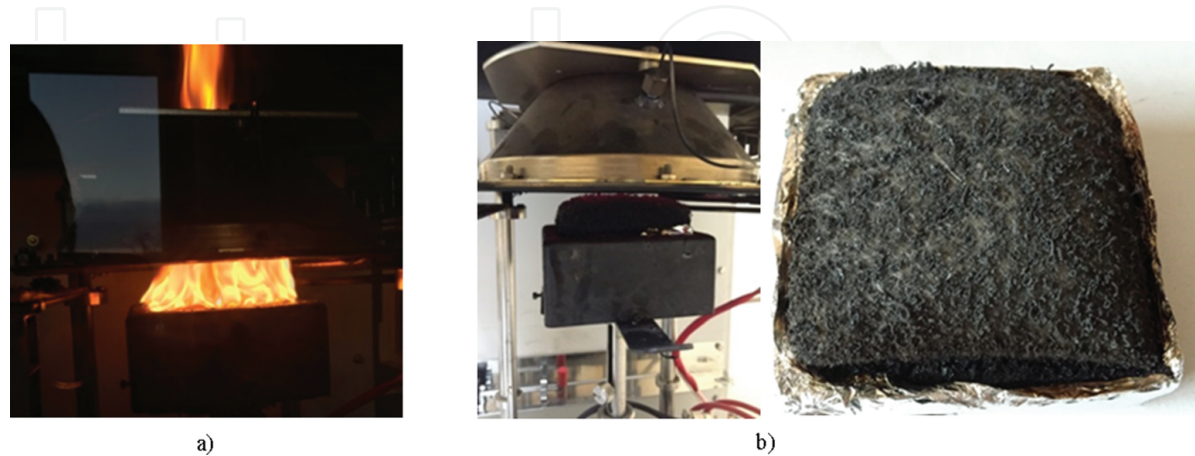


Figure 17. Rigid PU/PIR during the cone calorimeter test: (a) foams with no IF and (b) PU/PIR foams with IF protection.

Most significant flammability data after the cone calorimeter test of TO polyol-based PU foam with the isocyanate index 110 and different amounts of EG are summarized in **Figure 18**. The liquid FR TCPP showed the smallest effect on PU foam flammability when compared to DMPP at low loads of EG. However, there was a synergistic effect of TCPP together with EG, where at 9 and 15% of EG, pHRR and TSR showed lower values than the PU foam with DMPP and with no FR. A simplified interpretation of the cone calorimeter data can be done using the MARHE coefficient. This index is deduced from the maximum of HRR, which is often considered to be one of the most important fire hazards. However, this coefficient can be used to compare the materials tested under the same conditions. It can be seen that the most significant reduction of MARHE is for samples with 9 and 15% loads of EG and that only DMPP decreases MARHE for samples with no EG. In summary, the EGs significantly decrease the flammability of PU foams.

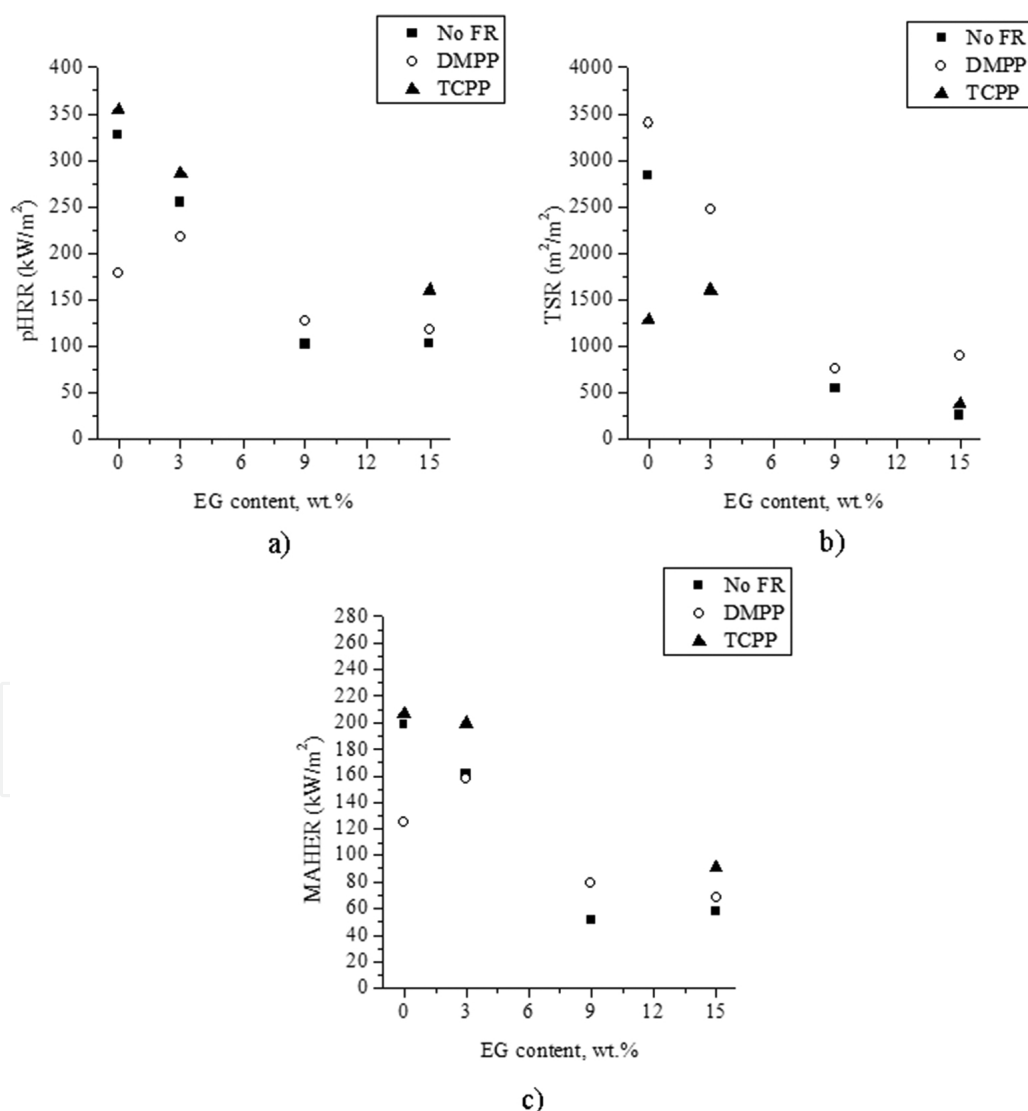


Figure 18. (a) pHRR, (b) TSR, and (c) MARHE of PU foam with different loads of EG and two different liquid FRs.

Figure 19 shows the pHRR and MARHE coefficients of rigid PU/PIR foams with different isocyanate indices and with and without IF fire protection. As mentioned, the samples with IF did not ignite, so the flammability characteristics are very low. For samples with no IF, the pHRR decreased with the increase of the isocyanate index, which correlates with the statement that cyclotrimerization groups are more thermally stable. Similarly to the case of the PU foam with an isocyanate index of 110, the addition of EG decreased PHRR and MARHE.

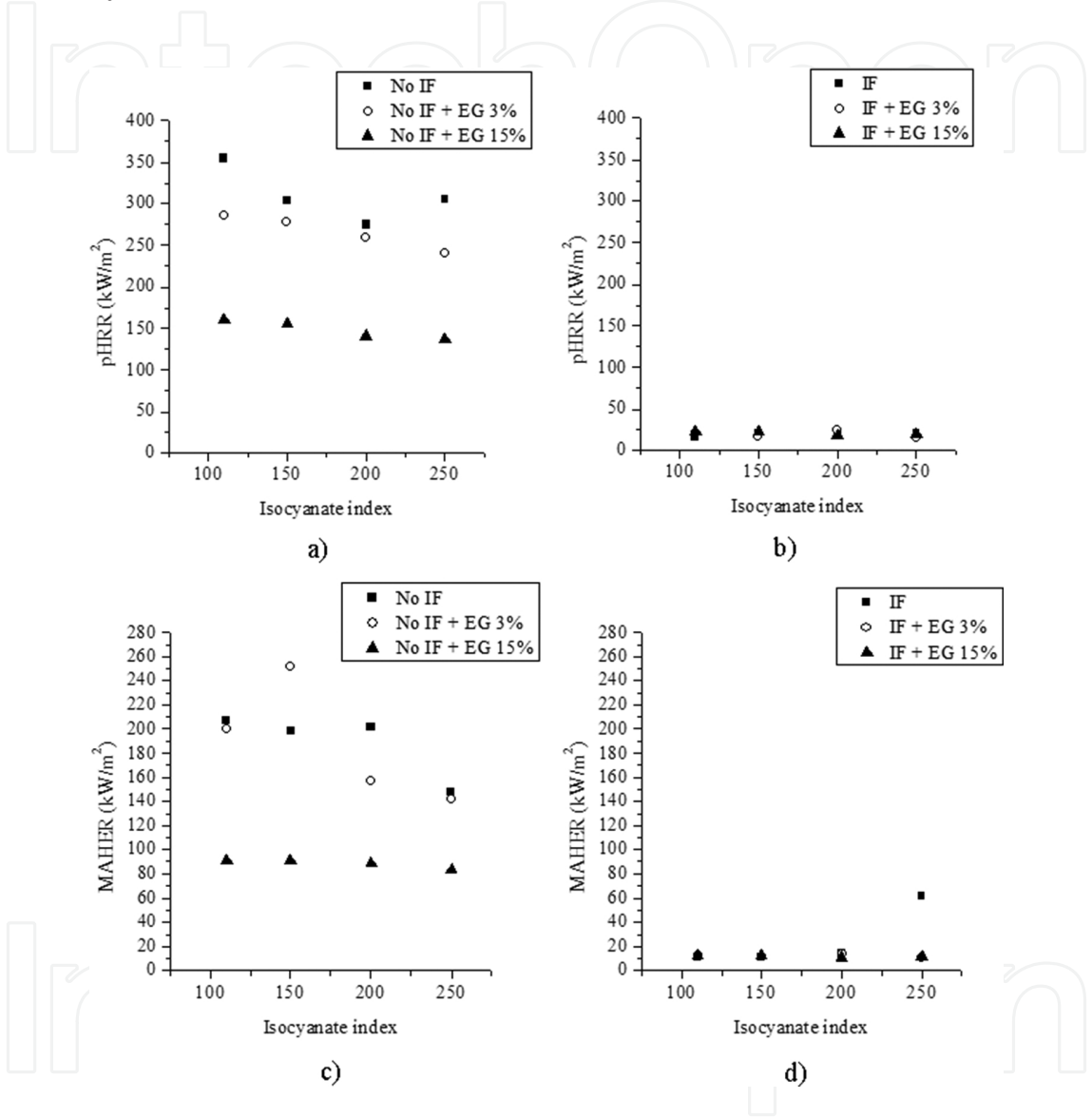


Figure 19. pHRR for rigid PU/PIR foams: (a) with no IF, (b) with IF; and MARHE: (c) with no IF, and (d) with IF.

Smoke is very important fire hazard as the majority of human victims in a fire disaster are due to poisoning with toxic gases. The cone calorimeter gives very little information about the chemical consistency of smoke. The data obtained is the solid particle amount in the smoke produced while burning the sample. **Figure 20** shows graphs with TSR data of rigid PU/PIR foams with different isocyanate indices and different EG amount. It can be seen that the addition of EG and the increase of the isocyanate index significantly decrease the amount of the produced smoke.

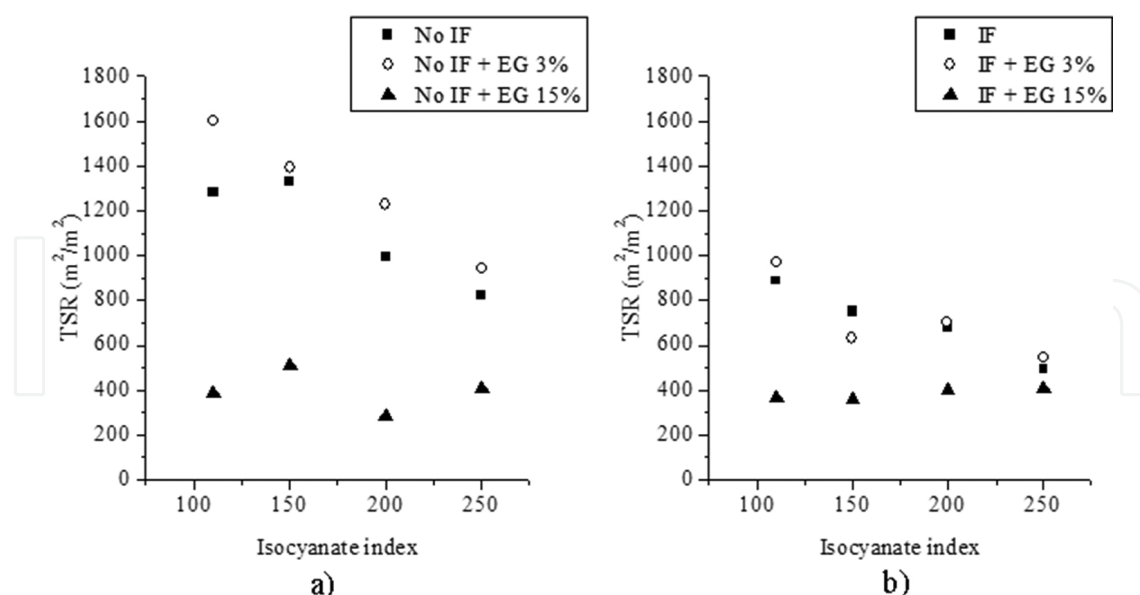


Figure 20. Total smoke released of rigid PU/PIR foams: (a) with no IF and (b) with IF.

TGA data for the developed rigid PU and PIR foams are presented in **Figure 21**. The first initial step of mass loss at 200–220°C can be attributed to the release of the additive liquid FR, unreacted isocyanate/polyols, water moisture, and other small volatiles. The next stage of degradation with the mass loss at 270°C is related to the degradation of PU soft segments in the case of the PU foam with the isocyanate index 110, as well as decoupling and pyrolysis of fatty acid dangling chains [37, 38]. At 327–351°C, breaking of isocyanate structures is observed for PU and PIR foams. Then, at 380–454°C, decomposition of aromatics and char products is seen. The rigid PIR foams with the isocyanate index of 250 produced more char residue than PU foams, namely, 20.6% and 12.3%, respectively. The TGA confirms the previous statement that PIR foams are a more thermally stable polymer material.

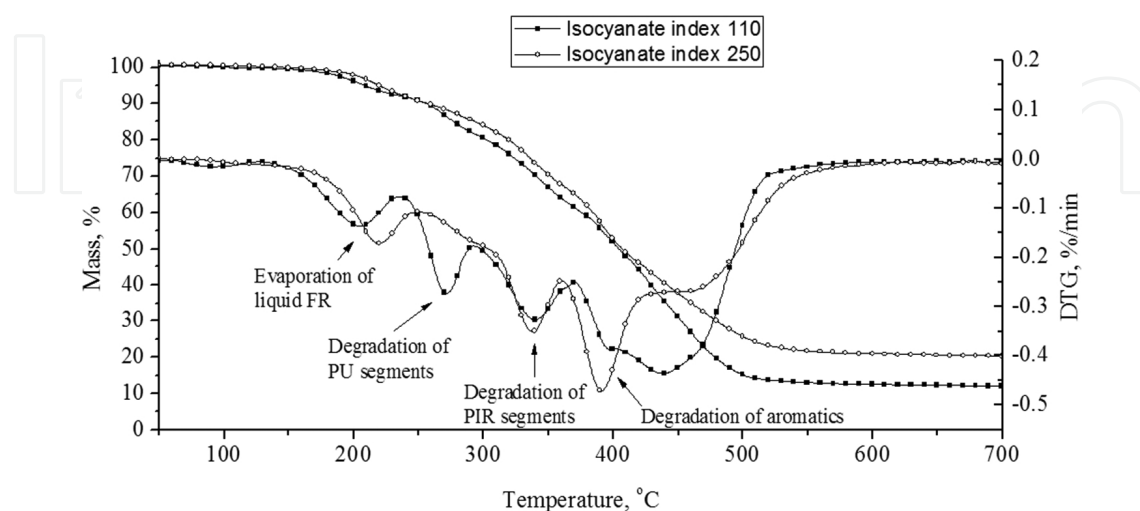


Figure 21. TGA curves for rigid PU and PIR foams obtained from TO polyol.

4. Summary

This study showed the properties of rigid PU/PIR foams obtained from different renewable raw materials—bio-based polyols synthesized from RO and TO. Bio-based polyols are a suitable substitution for petrochemical materials, as the main characteristic of a thermal insulation material—thermal conductivity—was at 22.0 mW/m·K, which is considered the industry standard for this type of material.

This study also showed a novel method of replacing liquid halogenated FR with intumescent fire protection of rigid PU/PIR foams using flexible, thermally expandable IF and EG. The addition of IF into rigid PU/PIR foams would be easily upscalable in the production of sandwich-type panels. The study of SEM images showed that no additional adhesive is needed as IF is incorporated into the PU/PIR foam structure. The synergy between two types of liquid FR (TCPP and DMPP) and additive EG was investigated but no significant improvement in fire retardancy was detected. At lower loads of EG, only DMPP showed the reduction of the heat release of PU foams. The conventional FR as well as EG increased the thermal conductivity of the developed PU/PIR foams, which gives preference to IF, where no reduction of thermal insulation properties was noticed. Also additive FR decreased the physical-mechanical properties and disrupted the morphology of PU foams. Nevertheless, one of the best fire performances of PU foam filled with 15% of EG with 7% of the conventional DMPP FR was determined. EG provided the lowest peak of heat release in the cone calorimeter test of 102.9 kW/m². Although EG provided excellent fire retardancy properties, the increase in thermal conductivity from 22.80 to 35.72 mW/m·K would not be acceptable for commercial use of this material. Therefore, IF is the best option as it not only stopped the material from igniting in the cone calorimeter test but also did not influence the thermal conductivity of the developed PU/PIR foams.

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