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Enhancement of physical and reaction to fire properties of crude glycerol polyurethane foams filled with expanded graphite

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Abstract

The reaction to fire of polyurethane foams (PUFs) has been subject to an increasing relevance, so in this study the reaction to fire performance of PUFs derived from crude glycerol (CG) have been improved using expanded graphite (EG). The influence of different loadings of EG on the physical–mechanical properties of composite foams has been assessed and the results obtained show that it has significant impact. Moreover, the reaction to fire of the PUF and EG/PUF composites has been investigated and the results obtained showed that the fire behavior of composite foams containing as little as 5 wt% of EG are significantly improved. Indeed a dramatic reduction of the rate of heat release, mass loss rate, effective heat of combustion and specific extinction area, has been observed even for relative low EG amount. Likewise, the use of Infrared thermography as a function of time has proven that, when EG is used, the combustion stops suddenly and the temperature drops sharply compared with the behavior of the unfilled PUF sample, which suggest that EG acts like a flame extinguisher. The results obtained have proven the suitability of CG for the production of PUFs and that the addition of EG considerably improves the reaction to fire of composite foams.

Keywords: Polyurethane foams; Crude glycerol; Expanded graphite; Reaction to fire; Fire behavior

1. Introduction

Polyurethane foams (PUFs), like other polymers, rely on fossil feedstock's, because its two main reactants (the polyol and the isocyanate) derive from petroleum feedstock's. However, the increasing concern over environmental impact and scarcity of petroleum, has motivated the development of PUFs from bio and renewable raw materials.[1] In fact, extensive research has been concentrating on developing, bio-based polyols from renewable sources, such as biomass residues, vegetable oils or industrial by-products.[2–8] The resulting foams are mainly rigid due to the small chain length of the polyols, high cross linking density associated with high functionality and in some cases the presence of rigid groups such as aromatic rings. Therefore, this type of materials is generally used as structural and thermal insulation materials for construction.[9]

Rigid PUFs as well as most organic materials burn very easily. Despite of that, for many years the fire performances of PUFs were suitable, but nowadays materials have to meet ever more stringent requirements due to the greater attention paid to fire safety and improved fire performances are thus required.

During combustion, PUFs generate highly toxic smoke, especially CO and hydrogen cyanide. The inhalation of these gases causes severe health problems or even death. Moreover, during a fire, there is a dramatic increase of temperature which leads to the decomposition of PUFs releasing small molecules into the gaseous phase. The mixture of these small molecules with air forms a flammable mixture. In other words, when the concentration of this mixture and temperature cross the flammability limit, the material starts to burn.[10]

The behavior of a material with fire, can be classified by: (i) resistance to fire and (ii) reaction to fire. The fire resistance provides information about how well a building element, such as a wall, floor, door, etc, can maintain its properties when exposed to a fire. It is only related with what happens after flashover. The reaction to fire is related with the instant after the

beginning of a fire, its propensity to ignite or feed a fire. This behavior is assessed on the basis of standardized tests and described in a Euroclass classification.

As mentioned before, as a result of the increasing awareness of public opinion, the flammability properties of PUFs need be improved and this can be achieved by the incorporation of flame retardants.[10] The flame retardance mechanisms are physical and/or chemical thus, the use of different types of flame retardant can significantly change the flame retardant mechanisms.

Flame retardants can be used as additives or as reactives in order to interfere with combustion during different stages such as heating, decomposition, ignition, or flame spread. Halogenated paraffins and phosphorus containing compounds are the most common additive type flame retardants. The former may not be very compatible with the PUFs and for that reason may jeopardize the mechanical properties of the materials besides releasing irritant acids. The latter, being a reactive type flame retardant can react with functional groups of PUFs. They act as char-forming agents, reducing the generation of flammable gases.[10] Reactive type flame retardants have the advantages of (i) increasing compatibility between polymer, (ii) not degrading the mechanical properties of the PU, (iii) possessing better compatibility as the flame retardant group is a part of the binder and (iv) using small amount or low concentration for the enhancement of fire-retardancy.[10]

A very distinct type of flame retardants are inorganic fillers. These materials produce a stable organic–inorganic interface, which reduces the concentration of decomposition gases and increases the diffusion path barrier of the volatiles produced during the degradation process.[10] Nowadays EG is widely used as flame retardant in PUFs. Recently, A. Lorenzetti *et. al.* [11] reported the effect of expansion volume and of intercalants on the flame retardancy of EG in PUF and concluded that the expansion volume of EG does not seem to have a major influence on the flammability of this type of materials. Yet, the nature of EG intercalants does affect the fire

retardancy properties of PUFs, being the sulfur based more efficient than the phosphorous based counterparts.

Polyols from renewable resources commonly used in the production of PUFs are obtained from different vegetable oils such as rapeseed oil, castor oil, palm oil or soybean oil (e.g., BASF castor oil-based Balance™, Cargill soybean-based BiOH™, and Dow soybean-based Renuva™).[12] Most of them are already used at industrial level but the production of these polyols is competing with the production of food. In that sense, crude glycerol (CG) which is a byproduct of the biodiesel production, has received considerable attention.[6,13–15] Aleksander Hejna *et. al* [16] reported the reaction to fire of PUFs derived from CG, however the CG was used as polymerization reactant, together with castor oil to produce a bio-based polyol and the synthesized bio-based polyol was used as partial substitution (0–70 wt.%) of petrochemical polyol in the production of PUFs. Hence, to the best of our knowledge, this is the first report of PUFs derived from the direct use of unrefined CG evaluating its reaction to fire and improving it via the addition of EG.

2. Experimental

2.1. Materials

The foams studied were produced from the reaction between CG with a polymeric isocyanate in the presence of a catalyst, a surfactant and a blowing agent. CG sample was kindly supplied by Biopordiesel and had a water content of 1.6 ± 0.01 , an acid value (AV) of 23.1 ± 0.2 $\text{mg}_{\text{KOH}} \cdot \text{g}^{-1}$ and an hydroxyl number (OH_{number}) of 399.0 ± 4.7 $\text{mg}_{\text{KOH}} \cdot \text{g}^{-1}$. The polymeric isocyanate Voranate M229 MDI with a NCO content of 31.1% and a functionality of 2.7 was kindly supplied by Dow Chemicals. Tegostab B8404, a polyether-modified polysiloxane was used as silicone surfactant and was supplied by Evonik. Polycat 34, a tertiary amine was used as catalyst and supplied by Air Products. As blowing agent, distilled water was used. EG (EG GHLPX 95) was supplied by LUH and had a thermal conductivity of 0.290 mW/mK (at room

temperature) and a density of 0.5436 g/cm^3 . A detailed characterization of the EG sample used has been provided in previous reports [3] including the evaluation of its reactivity towards the isocyanate using XPS analysis, Fourier transform Infrared (FTIR), FT-Raman spectroscopy, X-ray diffraction and thermogravimetric analysis (TGA).

2.2.Characterization of CG

The acid value (*AV*), hydroxyl number (*OH number*) and the water content of the CG were determined according to the procedures described in appendix.

2.3.Production of PUFs

The polyol component and the corresponding amounts of catalyst (3 parts per polyol (w/w)), surfactant (4 parts per polyol (w/w)) and blowing agent (6 parts per polyol (w/w)), were placed in a polypropylene cup and homogenized using a mechanical stirrer for *ca.* 10 seconds at 700 rpm. Note that the amounts of water present in the polyols were subtracted to the amounts of blowing agent added. Next, different amounts of EG (PUFs were filled with EG up to 20% (w/w)) were added and the mixture blended again. Even though EG should not be considered a nanomaterial as all its dimensions are larger than 10 nm it is still a material of large surface area. Hence, in the present study, as the main objective was to achieve good reaction to fire performance, without jeopardizing the morphology of the ensuing PUF composites and subsequently the mechanical properties, the preparation of EG/PUF composite foams followed the same rationale as that associated with the preparation of nanocomposites, e.g. explore the large surface area of EG in terms of reaction to fire, and minimize the amount of filler used in order to avoid altering the mixture rheology to such point that the foaming process could be compromised as well as the extent of PU crosslinking. In view of this, and considering that loads between 5 and 10 w/w % relative to the matrix normally suffice to enhance the properties of nanocomposites, 5 w/w% was considered a good starting point to obtain a good reaction to

fire. In turn, as it will be discussed later, as the percentage of EG was increased, the morphology of the ensuing composite foams was rather disrupted (see SEM image of PUF-EG20 Figure 2 (e)) which indicated that the use of higher loads would compromise the composite foam's performance unless the formulation was changed which would limit direct comparison of results.

Finally, the appropriate amount of isocyanate to obtain a $R_{NCO/OH}=1.10$ (ratio between NCO groups of isocyanate and OH groups) was added and the mixture homogenized again. The $R_{NCO/OH}$ used in the PUFs production was determined using Eq. 1.

$$R_{NCO/OH} = (m_{ISO} \times \%NCO/M_{NCO}) / (m_{polyol} \times (OH_{number} + AV) / M_{KOH} + (m_{H_2O} + m_{BA}) \times Eq_{H_2O})$$

Eq. (1)

Where $R_{NCO/OH}$ is defined as the number of moles of NCO groups of the isocyanate per OH moles of each polyol and water, m_{iso} is the mass (g) of isocyanate, $\%NCO$ is the quantity of NCO groups in the isocyanate (31.1%) and M_{NCO} is the molecular weight of NCO group. m_{polyol} is the mass (g) of each polyol, OH_{number} and AV are the hydroxyl number and the acid value of each polyol respectively ($mg_{KOH} \cdot g^{-1}$). M_{KOH} is the molecular weight of KOH. m_{H_2O} is the mass of water present in each polyol, while m_{BA} is the mass of blowing agent (water) added. Finally, Eq_{H_2O} is the equivalent of OH groups present in the water.

The foams were obtained by free expansion in the cup mold at room temperature and the formulations are listed in Table 1.

Table 1 - Foam formulations

Sample code ^a	CG	Isocyanate (PHP)	Catalyst (PHP)	Surfactant (PHP)	Blowing Agent (PHP)	EG (wt/wt)
PUF-EG0	100	160	3	4	4.4	0
PUF-EG5	100	160	3	4	4.4	15
PUF-EG10	100	160	3	4	4.4	32
PUF-EG15	100	160	3	4	4.4	50
PUF-EG20	100	160	3	4	4.4	71

^a Sample Code (PUF-EGX): X - wt% of EG

2.4.Characterization of PUFs

Fourier Transform Infrared Spectroscopy (FTIR), density, Scanning Electron Microscopy (SEM), mechanical essays, Dynamic Mechanical Analyses (DMA) using the material pocket accessory and Thermogravimetric Analysis (TGA) were determined according to procedures described in appendix.

The thermal conductivity measurements were performed using the Gustafsson Probe method (or Hot Disk) with the Thermal Constant Analyser TPS 2500S.[17] This transient method uses an electrically conducting pattern (Nickel) element acting both as a temperature sensor and heat source, insulated with two thin layers of Kapton (70 μm). The TPS element is assembled between two samples of similar characteristics with both faces in contact with the sensor surface. For isotropic samples, the Hot Disk method allows the determination of the thermal conductivity, thermal diffusivity and specific heat. The Hot Disk method is an international standard for measuring thermal conductivity and thermal diffusivity with the designation ISO 22007-2.

Infrared Thermography was used to map dynamic heat transfer processes in real-time. The setup consists of a FLIR SC5650 camera with a Stirling cycle cooled Indium Antimonide detector, 25mK sensitivity, 640x512 resolution and was used at a 25 Hz windowed frame-rate.

The fire behavior was analyzed using a cone calorimeter apparatus according with ISO 5660 [18] at the Department of Applied Science and Technology (DISAT), Alessandria Section – Politecnico di Torino. The cone calorimeter apparatus exposes a small square horizontal test specimen (100x100x20 mm) to a preset heat flux (in our trials 50 kW/m^2), in the presence of an air flux (24 l/s) as in then ignited by electric spark. The fire effluent passes through a duct, containing a sensor which permits the determination of the rate of heat release (*RHR*) (by oxygen consumption) while CO and CO₂ production, expressed as kg of gas developed/kg of material combusted, is determined by infrared spectroscopic techniques. The test stops when the flame extinguishes. During the test several parameters can be measured, such as: *RHR* (kW/m^2); effective heat of combustion (*EHC*) (MJ/kg); mass loss (g/s); residual mass (%), carbon

monoxide and dioxide production (kg/kg) and specific extinction area (*SEA*) (m^2/kg). The parameters were recorded during time. After data elaboration, it is possible to obtain the peak and the mean value for each parameter during test (except for mass loss). Often, the value that is considered for analyzing fire behavior is the peak one, as it represents the worst situation in a real fire scenario.

3. Results and discussion

The use of renewable feedstocks for the production of thermal insulation PUFs have been widely reported.[4,6,14,15,19,20] Nonetheless, their reaction to fire have not received as much attention. Hence, in the present work, the reaction to fire of CG derived PUFs are improved by the addition of EG.

3.1. Monitoring of the reaction

FTIR spectrophotometry was used to monitor the formation of the urethane linkages, as a result of the reaction between the NCO groups of the isocyanate and OH groups of the CG as well as to monitor the extent of this reaction. All normalized FTIR spectra are presented in Figure 1.

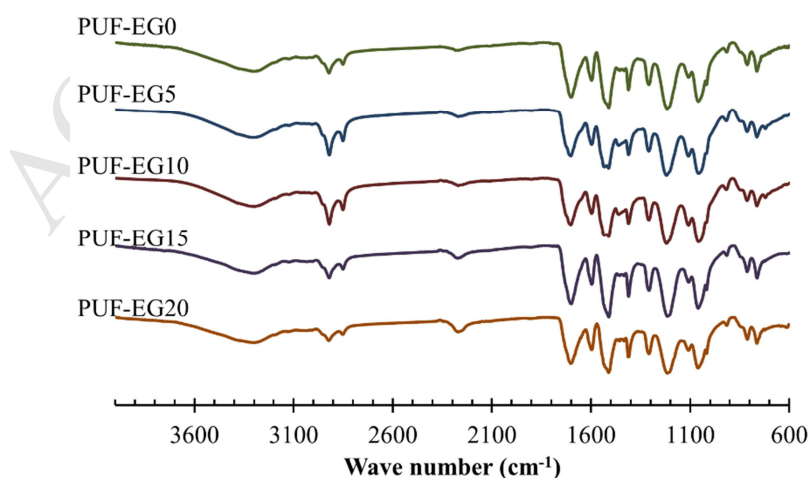


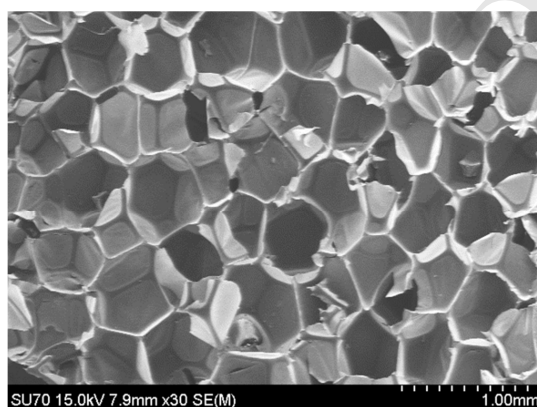
Figure 1 - Normalized FTIR spectra of PUF and PUF-EG composites

The normalized FTIR spectra of all samples present very similar profiles. In the two typical spectral regions of the urethane groups, a peak at 1710 cm^{-1} due to the stretching vibrations of the C=O of the urethane and ester groups of the polyol is present. Since isocyanate used reacts with water which was used as blowing agent, the peak at 1650 cm^{-1} typical of urea groups is also detected. The following region is associated with the nearly overlapped bands between 1540 and 1517 cm^{-1} , attributed to the free N-H absorption and to N-H groups which are hydrogen-bonded with carbonyl groups, respectively. Worthy of notice is the fact that with the increase of the EG amount, the small peak around 2270 cm^{-1} , typical of the stretching vibration of residual NCO groups, becomes more evident. This may be attributed to at least two possibilities: (i) the hydroxyl groups on the surface of EG can alter the isocyanate index ($R_{NCO/OH}$) defined as the number of moles of NCO groups of the isocyanate per OH mole of the polyol (which has been corrected for the presence of water but not for the presence of fillers) thus affecting the consumption of NCO groups. In previous reports [3] it was studied in detail the reaction between the EG and MDI. First, the elemental analysis of the EG used revealed the presence of 25.1% oxygen suggesting the presence of hydroxyl groups, which was further proven by FTIR analysis. Afterwards, EG was reacted with MDI and the resulting mixture was repeated washed and analyzed by different techniques. The FTIR spectra of EG-MDI mixture presented the $3200\text{--}3450\text{ cm}^{-1}$ region attributed to the symmetric and asymmetric stretching vibrations of the N-H, as well as the bands between 1540 and 1517 cm^{-1} which are attributed to the stretching and bending vibrations of the C-N and N-H of the urethane moieties, suggesting that urethane segments were formed by the reaction of EG with MDI. Moreover, by XPS analyses it was observed the N 1s peak in EG-MDI mixture which is ascribed to the N-H bonds and another peak at 402.0 eV which is ascribed to the N-C=O bonds. These results had confirmed the presence of urethane groups on the surface of EG after reacted with MDI. Finally, the EG-MDI mixture was analyzed by TGA and it was observed a two main decompositions steps: one around

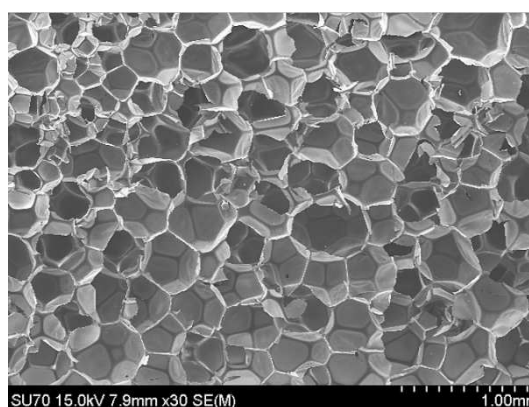
200 °C, related to the thermal decomposition of the aromatic segments of MDI and a second, around 470 °C related to the sublimation of the carbon backbone of EG, similar to the degradation profile of PUF-EG composites. Nevertheless, (ii) the interference of the EG on the rate of the polymerization namely associated with changes in the rheological behavior of the reaction mixture and/or coupling of EG surface groups with either the isocyanate, the polyol and/or the water used as blowing agent.[21]

3.2.Morphology

SEM analysis is an important and versatile tool to inspect the foam structure. During mixing, air bubbles are usually introduced in the reaction mixture and act as nucleation sites for the blowing gas generated from the reaction between isocyanate and blowing agent. The bubbles grow resulting in a closely packed network of bubbles responsible for the typical cellular structure of PUFs.[22] The cell structures of PUF-EG composites are presented in Figure 2.



(a)



(b)

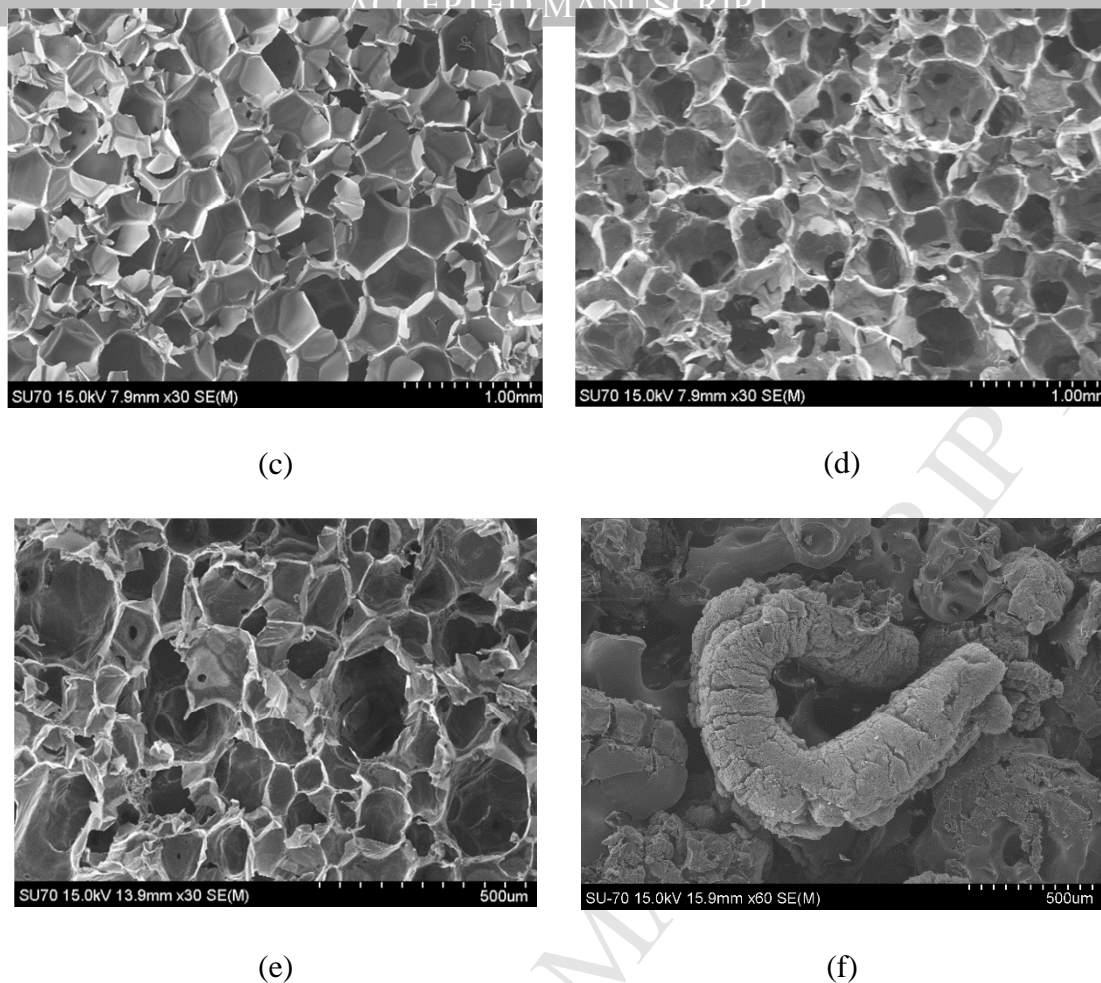


Figure 2 - SEM images of PUF-EG0 (a), PUF-EG5 (b), PUF-EG10 (c), PUF-EG15 (d), PUF-EG20 (e) and the “worm” like structure of the burnt EG (f)

From Figure 2 it is clear that the increase of the EG content results in poor homogeneity, especially for higher amounts of EG. The irregularity of the cellular structure is related to the fact that the EG content can affect the foaming process due to interactions between the polymer matrix and fillers during bubble nucleation, cell growth, and stabilization stages [23]. Furthermore, the aspect ratio of EG is also known to influence the shape of the cells and induce cell rupture. As the percentage of EG increases local stresses and/or irregular foam growth occur which is clearly observed in Figure 2 (e). Similar cases have been reported by others in the literature [24,25]. As the heterogeneity of the cells size increases it can be seen by the standard deviation of average cell size listed in Table 2. Since the morphology has a paramount importance on the properties of the foams, these observations are expected to have significant

effect on the properties of the foams. Table 2 summarizes the physical properties of PUF-EG composites prepared.

Table 2 - Physical properties of PUF/EG composites

PUF	Density (kg/m ³)	Average cell size (μm)	Young's modulus (kPa)	Toughness (J/m ³)	Compressive stress 10% (kPa)	Tg (°C)
PUF-EG0	44.5 ± 2.8	202.9 ± 8.7	620 ± 12	15629 ± 2716	46 ± 4	118.6
PUF-EG5	57.8 ± 3.1	195.7 ± 10.4	1858 ± 57	25467 ± 2715	128 ± 9	123.1
PUF-EG10	63.4 ± 3.6	186.4 ± 18.5	2270 ± 74	29883 ± 3010	140 ± 13	131.3
PUF-EG15	69.5 ± 4.0	178.8 ± 28.5	2581 ± 60	33857 ± 3678	149 ± 11	136.6
PUF-EG20	73.9 ± 4.3	152.6 ± 38.6	2864 ± 72	37283 ± 4318	163 ± 11	143.3

3.3. Density

The density of PUFs depends on the quantity of gas released during the blowing agent/isocyanate reaction and on the quantity and nature of the surfactant used, among others. However, the incorporation of fillers has a significant effect since addition of a more dense material to the foam can prevail over the other effects. Moreover, incorporation of fillers may also affect foam's density due to (i) the interference of the solid particles with the reaction between NCO groups with OH groups, and (ii) their influence on the foaming process, as referred above. The results obtained for the different samples prepared are summarized in Table 2 and confirm that the increase of EG load is associated with an increase in density. This is also in agreement with the results reported in the literature [24,26].

3.4. Mechanical properties

Compressive tests were performed to study the mechanical properties of PUFs and assess the effect that EG has on the stiffness of the foams. Figure 3 illustrates the compressive stress-strain plots of the PUFs prepared and in Table 2 the values determined for the Young's modulus, toughness and compressive stress are summarized.

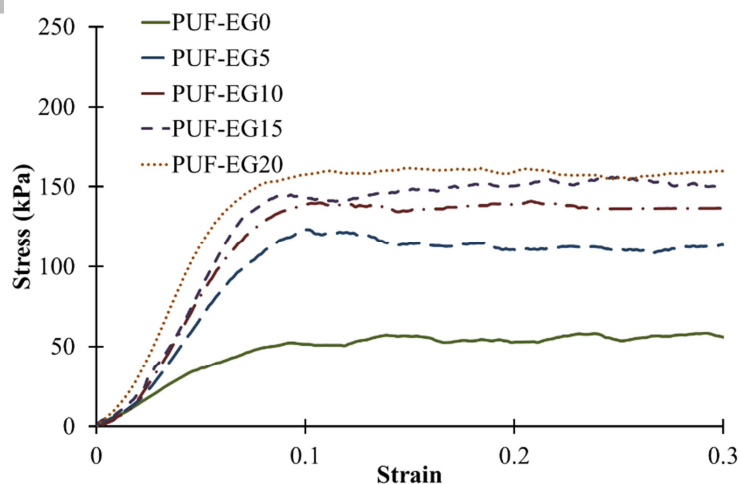


Figure 1 - Compressive stress-strain curves of PUFs

The mechanical properties of PUFs depend primarily on the cells' morphology with the strength being higher in the direction of foam expansion. Thus, alterations on the ratio of height to diameter of cells will have a major impact. From Figure 3, it can be seen that all the compressive stress-strain plots of PUFs are composed for: (i) a first linear region which corresponds to the elastic response of the material and (ii) second domain in which the curves presents a large plateau due to the material deformation, due to the plastic deformation and/or rupture of the cell walls whilst the stress is constant until the cells are crushed. Nevertheless, some differences can be observed between the samples. The addition of EG to PUFs is known to have variable effects depending on the percentage of loading, on the size of particles and, whether the fillers are partially incorporated in the cell walls, or between them.[26] Furthermore, as discussed previously, the reaction between the isocyanate and the functional groups on the EG surface and lead to a reduction of crosslinking density of the polymer matrix, which affects the mechanical properties of the ensuing composites. The results summarized in Figure 3 and Table 2 (Young's modulus (E), toughness and compressive stress ($\sigma_{10\%}$)) suggests that the filler-reinforcing effect of EG may be predominant, increasing the slope of the linear reagon as well as the maximum stress achived, in other words, enhancing the stiffness of the foams. Nonetheless, the mechanical properties of the foams are also dependent on their density, to exclude the effect of density variations, normalized values of the compressive Young's modulus

(specific modulus), toughness (specific toughness) and compressive stress $\sigma_{10\%}$ (specific stress) were determined and are presented in Table 3.

Table 3 - Young's modulus, compressive stress ($\sigma_{10\%}$) and toughness normalized for density

PUF	Specific modulus ($\text{m}^2 \cdot \text{s}^{-2}$)	Specific toughness ($\text{m}^2 \cdot \text{s}^{-2}$)	Specific compressive stress ($\text{m}^2 \cdot \text{s}^{-2}$)
PUF-EG0	13.9	351.2	1.0
PUF-EG5	32.1	440.6	2.2
PUF-EG10	35.8	471.3	2.2
PUF-EG15	37.1	487.2	2.1
PUF-EG20	38.8	504.5	2.2

Considering the data normalized for the density, it is clear that the increase of EG content has a direct effect on the mechanical properties of the foams, increasing the stiffness of the foams.

3.5. Dynamic Mechanical Analysis

DMA measurements were carried out in order to determine the glass transition (T_g) of composites foams. To be sure that the T_g values were not affected by possible heterogeneities of the samples, analyses of powdered samples were also carried out using the material pocket accessory of the DMA instrument. From Table 2 it is clear that the T_g values of PUFs increase with the increase of the filler content. The T_g values of composites have been widely investigated and different effects on the T_g have been reported. [25] As shown in Table 2, the PUFs filled with EG showed higher T_g than the pristine PUF, due to the rigid filler system which limited the mobility of the polymer chains. Similar results are reported in literature. [27]

3.6. Thermal conductivity and thermal diffusivity

Generally, the thermal conductivity (k) is related to the foams density, the ratio of open/closed cells and the thermal conductivity of the gas used as blowing agent. Whilst the

whole foam only contains a small fraction of PU, and the k value of the polymer is much higher than that of the blowing agent, higher density foams have higher thermal conductivity.[28] Yet, in the case of PUF/EG composites, as EG itself has a high thermal conductivity so its presence is expected to increase the PUFs thermal conductivity. In fact, the thermal conductivity of this type of composites is governed by the transport of phonons whose transport is favored by the larger grain and crystallite size of bigger graphite flakes as the interface is reduced [29]. Therefore, as higher percentages of EG are used, aggregates may become larger, facilitating the transport of phonons and consequently the thermal conductivity increases.

As regards the role of EG as a fire retardant, what actually is of interest is its thermal barrier effect, i.e. the thermal diffusivity. The thermal diffusivity is defined as the rate of heat that is transferred from the hot side to the cold side of a material and is calculated dividing the thermal conductivity by density and specific heat capacity.[30] Since the addition of EG increases the specific heat of the material and the density (see Table 2 and 3), the thermal diffusivity of the composites decreases. Therefore, the heat transfer rate from the hot side to the cold side drops when higher loadings of EG are used which helps to prevent combustion as will be discussed next.

Table 4 - Thermal properties of PUFs/EG composites

PUF	Thermal conductivity (W/m.K)	Thermal diffusivity (mm ² /s)	Specific heat (MJ/m ³ K)
PUF-EG0	0.039	0.428	0.097
PUF-EG5	0.047	0.336	0.148
PUF-EG10	0.049	0.321	0.154
PUF-EG15	0.053	0.309	0.171
PUF-EG20	0.081	0.214	0.380

3.7. Thermogravimetric analysis

As mentioned earlier, one of the limitations of polymeric materials is their poor thermal stability at high temperatures and EG is frequently used to minimize this and confer fire retardant

properties.[31] The thermal degradation of these composites was investigated by TGA under oxygen atmosphere and compared with the results obtained for EG and neat PUF.

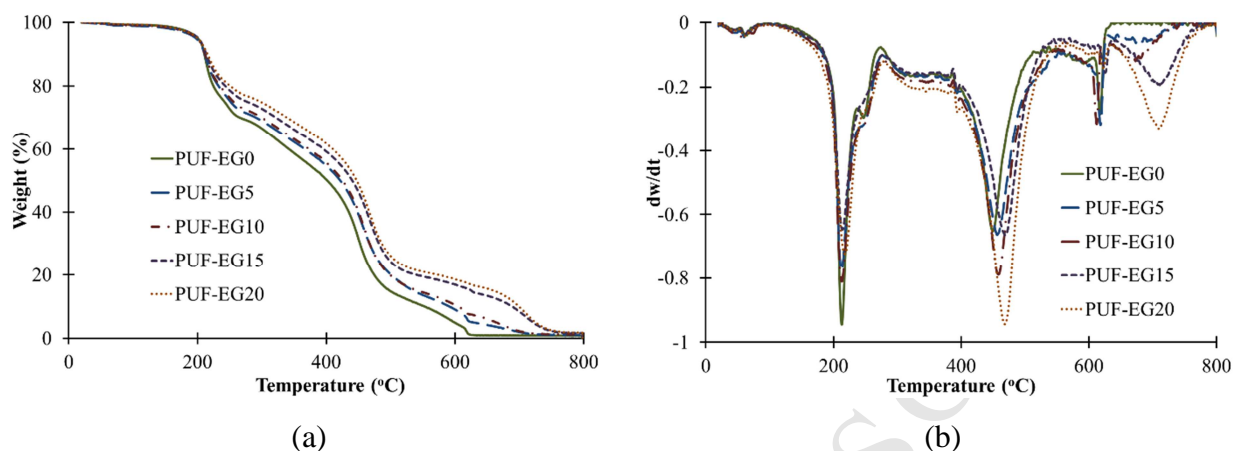
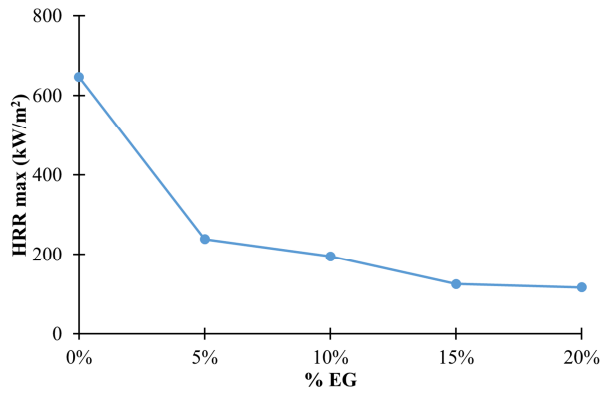


Figure 2 - Thermal degradation (a) and dw/dt (b) of PUFs.

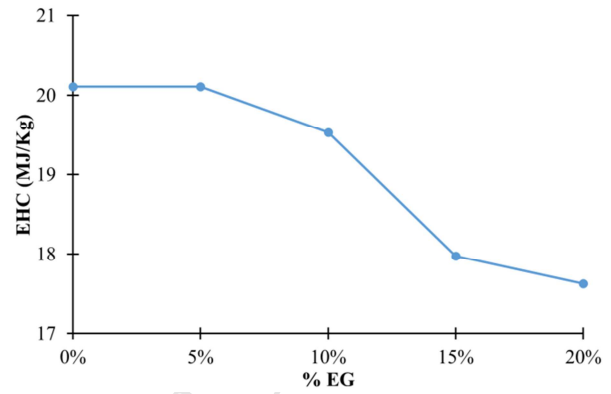
As expected the decomposition profiles observed are typical of PUFs which are characterized by two main decompositions steps: one around 180 °C, related to the thermal decomposition of the hard segments (e.g. urethane groups) and gases released by EG, and a second around 460 °C related to the soft segments. [32–34] From TGA, it was observed that the presence of EG reduced the weight loss of PUFs in the initial stage of degradation. At 215 °C, the weight loss of the neat foam was 13.9%, while the weight loss of PUF-EG20 was only 9.8%. This behavior can be attributed to a barrier effect provided by EG which reduces both the heat and oxygen fluxes toward the polymer surface, which limits the weight loss rate. The reduction of weight loss is in accordance with the increase of the residual mass results of the cone calorimetric tests, as will be discussed later. Moreover, Figure 4 (a) reveals small differences in the second decomposition step associated with the soft segments. The slight differences detected regarding the rate of decomposition of the soft segments for the different loads of EG, can be ascribed to the poor dispersion of the fillers and changes of the crosslinking density, as previously mentioned.[10]

3.8. Reaction to fire

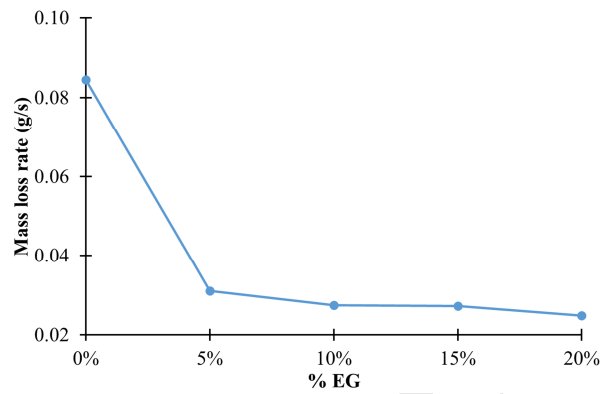
The reaction to fire of the foams were evaluated by means of cone calorimeter analysis and the obtained results are presented in Figure 5 and Figure 6.



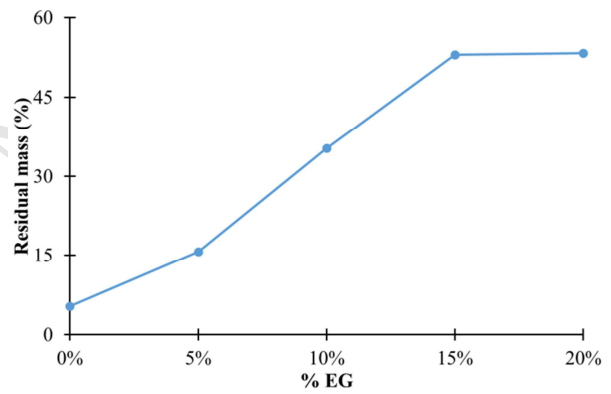
(a)



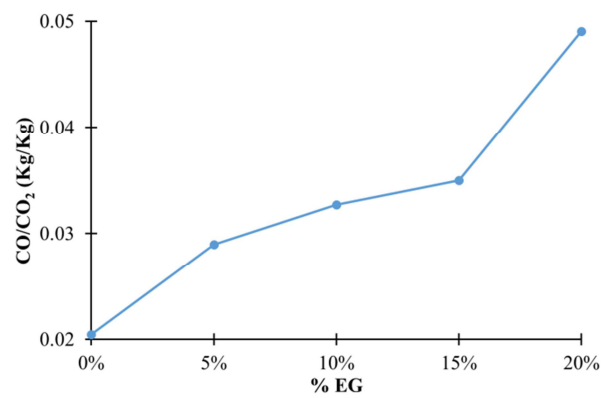
(b)



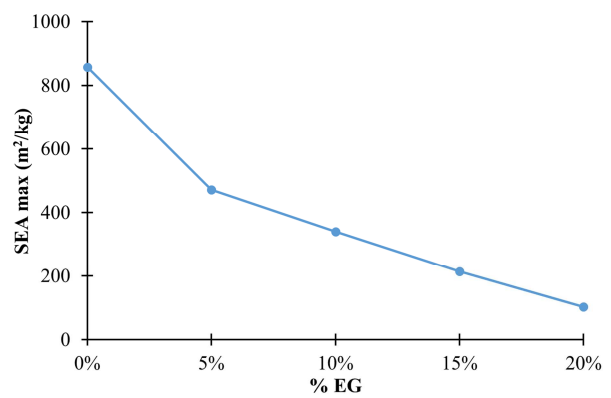
(c)



(d)



(e)



(f)

Figure 5 - HRR max (a), EHC (b), mass loss rate (c), residual mass (d), CO/CO₂ ratio (e) and SEA max (f)

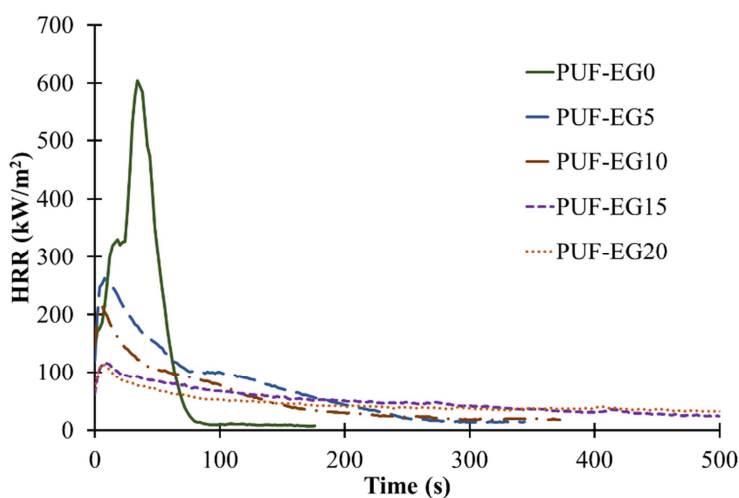


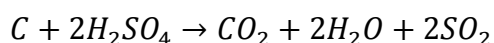
Figure 6 - HRR curves of PUFs

One of the most important reaction to fire parameters is the heat release rate (HRR). It represents a quantity of heat generated per unit area and time, and is related with the flashover phenomena in a real fire situation [35]. From the results presented in Figure 5 (a) and Figure 6, it can be seen that this parameter dropped significantly with the presence of the flame retardant. In fact, the HRR value of PUF-EG5 is 63% lower when compared with the pristine foam. When a sample is ignited, heat is generated so HRR is an index of the extent of fire [36] and the results presented in Figure 5 (a) are in agreement with the videos presented in supporting information. From the videos, it can be seen that when EG is used, the flame stops from the moment the ignition source is removed, preventing the complete combustion of the foams. In other words, even though the exterior of the material is burned, the interior remains intact (see Figure A.4). The same observations were reported by A. Lorenzetti *et. al.* [11] From the study of the effect of expansion volume and intercalants on the flame retardancy of EG in PUFs, it was reported that the decrease of the HRR is associated with the heat shield formed by the expansion of the EG due to: (i) the gases which are released from the redox reaction (explained below) of EG dilute the

flammable gases, suffocating the flame; and (ii) the decomposition, being an endothermic process, absorbs the heat released during combustion.

The effective heat of combustion (*EHC*), which is the ratio of *HRR* to mass loss rate, discloses the degree of burning of volatile gases in gas-phase flame during combustion [37]. *EHC* provides an insight of the mechanism of flame retardants and as it can be seen in Figure 5 (b), the presence of EG is associated with a reduction of the *EHC* value, even though the mass loss also decreases with the presence of EG (see TGA results). This means that the presence of EG prevents the combustion and the release of heat when the matrix is decomposed into the gas products. Jarosinski *et. al.*, have attributed this to the fact that some products released by the flame retardant could quench radicals derived from the matrix and prevent the combustion of original ignitable components.[38]

The char layer produced from the EG, being a thermal barrier as well as an oxygen barrier, prevents further decomposition of the materials. Therefore, due to this protection effect, increasing the amount of EG leads to a reduction of the rate of mass loss (Figure 5 (c)), and subsequently the residual mass of the PUFs after burned increased (Figure 5 (d)). These results are in agreement with the studies by TGA (Figure 4 (a)) as well as the thermal diffusivity data presented in Table 4: lower thermal diffusivity and higher percentage of residues were registered for higher loads of EG. Nevertheless, the role of EG as flame retardant is also associated with its ability to expand forming the so called “worm” like structure (see Figure 2 (f), Figure A.3 and videos in supporting information). The expansion of this filler suffocates the flame and the compact char layer formed limits the heat and mass transfer from the polymer to the heat source. According to M. Modesti *et. al* [39], this expansion is due to a redox process between H_2SO_4 (present within the graphite layers) and the inner graphite surface that generates gases according to the reaction:



In fact, the gases released can increase the volume of the materials by about 100 times.

This structure modification was confirmed by FT-Raman and XRD analyses (see Figure A.1 and Figure A.2).

The CO/CO₂ weight ratio can be taken as an index of combustion completeness, as well as of smoke toxicity as it is well known that compounds deriving by incomplete combustion are more toxic than those deriving by complete one [24]. In Figure 5 (e) the variation of CO/CO₂ weight ratio as a function of EG loading indicates that the higher the percentage of EG the higher the toxicity of the smoke. This is due to the physical barrier effect of the char layer formed which thwarts the oxygen diffusion and favors the development of products of incomplete combustion, like CO. Nevertheless, the CO/CO₂ values obtained for the neat and PUF-EG05 foams, are lower than PUFs produced from petroleum feedstock, tested under the same conditions.[24]

The specific extinction area (*SEA*) is a measure of smoke density and its value should be as low as possible so that people can more easily escape from a fire situation [35]. From the results presented in the Figure 5 (f), it can be seen that the presence of the flame retardant, significantly decreased the values of this parameter, meaning that it has an important role in the condensed phase.

Finally, from Figure 6, it can be seen that the HRR curves have more than one peak, which is due to the combustion process of intermediary decomposition products, intermediary char or even due to the release and combustion of volatiles.[11,40]

Considering the distinct effect that EG loadings have on the different reaction to fire parameters, within the range studied, 5 wt% was considered the best compromise. This percentage of filler ensures a significant reduction of the maximum heat released and of mass loss when compared to the unfilled PUF and the lowest toxicity of smoke when compared to higher loading tested. Moreover, the use of 5 wt% EG already has a good impact on the mechanical properties of the ensuing composite PUF and minimal impact on the cellular structure.

3.9. Thermographic analysis of combustion

The combustion of all samples was monitored using Infrared thermography as a function of time. Samples used were cut as cubes with 1 cm edge approximately. The samples were ignited from the bottom. Representative snapshots of the combustion of samples PUF-EG0 (a) and PUF-EG5 (b) are presented in Figures 7 and 8. The color palette in the vertical scale spans the temperature range from 500 up to 1000°C.

The combustion of sample PUF-EG0 (a) proceeds in a steady way, from bottom to top, and the temperature of the burning front (regions above 500°C) is typically in the range 600°C, with rare regions attaining maximum temperature of about 750°C. The temperature of the sample decreases steadily over more than 10 s, which is the time of the complete combustion of the PU.

The combustion of the composite samples (in the Figure represented by sample PUF-EG5 (b)) proceeds in a much more inhomogeneous way. A maximum temperature of about 1000°C is quickly attained and concentrated in the “worm” like structure that is developed at the surface of the sample (described before). Then the combustion is seen to stop very suddenly at about 4.0 s. Within about 0.5 s no points observed exceed 450°C. The behavior of the other filled samples is similar, forming the worm like structure, burning at about the same temperature (1000°C) and stopping suddenly after a few seconds.

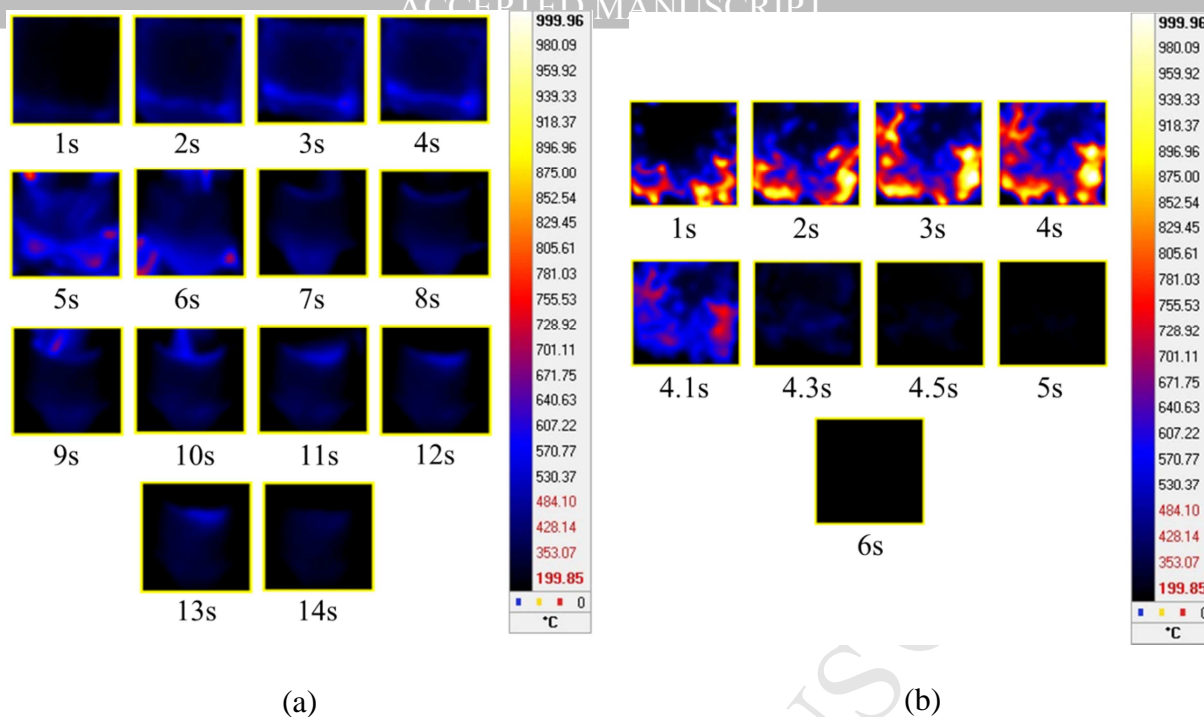


Figure 7 - Thermographic images during the combustion of PUF-EG0 (a) and PUF-EG5 (b)

Figure 8 presents the time variation of the maximum temperature points of all the samples during combustion. The higher temperature and time-limited combustion of the composite PUFs is clearly demonstrated. The sharp stop of combustion is also similar, the maximum temperature dropping from about 1000 to near 400°C within 0.5s for all EG filled samples, in clear contrast with the slow decay observed in the neat PUF. These results suggest that EG is not only a fire retardant but can also be seen as a flame extinguisher.

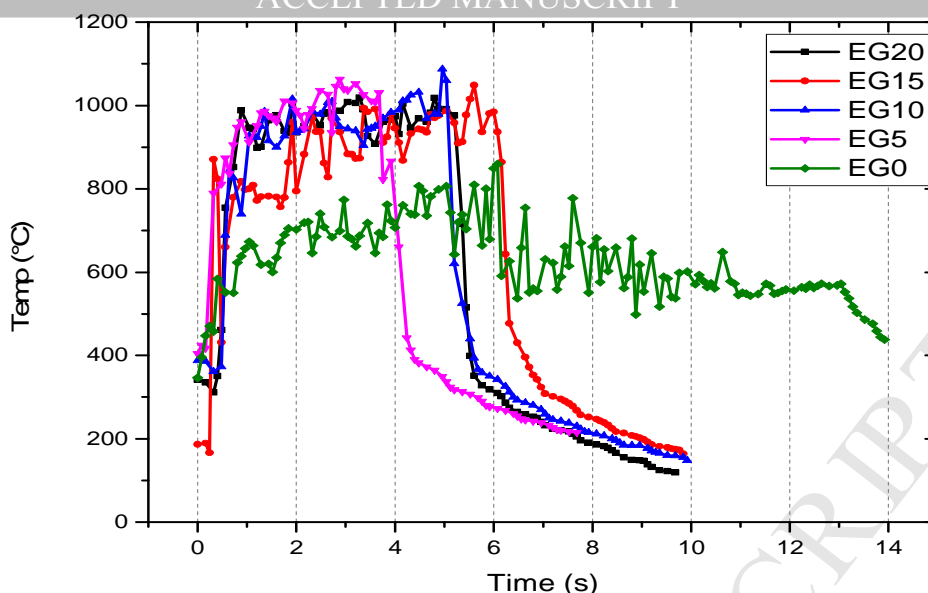


Figure 8 - Time dependence of the maximum temperature of all the samples during combustion.

Conclusion

In the present study, CG was used to produce ecofriendly PUFs and their reaction to fire were improved by the addition of EG. The presence of EG, proved to have a significant effect on the cellular structure and on the properties of the foams. Whilst it can disrupt the foam structure, increase its density and its thermal conductivity and it can also increase its stiffness, acting as mechanical reinforcement. Furthermore, the presence of EG, has an important effect on the reaction to fire of the materials: increased the CO/CO_2 ratio of the smoke released and the residual mass of the foams after burned. Due to the physical barrier effect of EG, the *HRR*, the *EHC*, the mass loss ratio and the *SEA* decreased. Nevertheless, the presence of 5 wt % of EG, did not present a significant disruption of the cellular structure nor did it affect adversely the properties of PUFs, whilst having a significant effect on the heat and smoke released, and more importantly acted like a flame extinguisher.

Appendix

More details regarding the the effect of the burning process on the structure of EG, EG and PUF-EG5 which were burned and characterized by FT-Raman and X-ray diffraction (XRD) can be found in the supporting information.

Acknowledgements

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- Crude glycerol was successfully used to produce ecofriendly PUFs
- The fire response of composite PUFs derived from crude glycerol and the effect of using expanded graphite as flame retardant was evaluated;
- Addition of EG to crude glycerol PUFs enhanced the mechanical properties of the ensuing composites;
- The fire response of composite PUFs using as little as 5 wt% of EG was significantly improved;
- Infrared thermography has proven that when EG is used the combustion stops suddenly suggesting that EG acts like a flame extinguisher;