THE 19TH INTERNATIONAL CONFERENCE ON COMPOSITE MATERIALS

EFFECT OF MICROSPHERE CONTENT ON FIRE PERFORMANCE AND THERMOMECHANICAL PROPERTIES OF PHENOLIC RESOLE SYNTACTIC FOAM COMPOSITES

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1 Introduction

In recent years, there has been a growing interest in the use of syntactic foam [1, 2] for many thermo-structural applications. They exploit several features typical of syntactic foams such as the good thermal insulation properties and the high specific mechanical properties. Syntactic foams are composite materials in which hollow microspheres are dispersed in a polymer binder. The hollow spheres may be made up of glass, metals, polymers or ceramics. The structure of a syntactic foam is entirely different from the conventional cellular foams like polyurethanes, PVC etc. In syntactic foams majority of voids are enclosed within rigid walls and therefore isolated from each other and hence are called “closed-cell foams”. Syntactic foams are essentially isotropic materials due to the randomness of the microstructure. Otherwise, there is an increased awareness for the need to improve fire standards in these areas where public safety is important. An approach to improving the fire performance of these composites is through the use of resins that are less susceptible to heat and flame. In this way, the use of phenolic syntactic foams seems to be a better compromise of mechanical strength, isolation and fire behaviour. The phenolic resins are a class of compounds that have superior fire and flammability properties compared to other thermoset resins such as the polyesters and epoxies. Because of their unique chemical structure which primarily comprises C-C bonds in aromatic rings, phenolic resins have intrinsic resistance to ignition, low generation of smoke and relatively low cost [3]. When phenolic resin based structures do burn, a porous carbon char is rapidly formed, as an effect of the thermal degradation reaction, which insulates and protects underlying material. Phenolic polymers, characterized by high aromatic ring content, decompose into aromatic fragments that fuse via condensation reactions to produce a high amount of char. It is known that 40-60% of the resin mass is transformed to char, resulting in a much lower yield of flammable volatiles compared to many other polymers (epoxy, polyesters). The char acts as a thermal insulation layer because the thermal conductivity of char can be lower than the conductivity of the virgin composite material [4]. For example, Fanucci [5] reports that the thermal conductivity of solid char at room temperature is 0.17 W.m⁻¹K⁻¹. Low density and highly porous chars tend to provide the best thermal insulation. The char layer reduces the conduction of heat to the underlying virgin material and thereby slows the decomposition reaction of the polymer matrix. An additional valuable property derived from the phenolic resin is the ability to retain its physical properties at high temperatures [4]. Due to their fire properties, it might appear reasonable to expect phenolic syntactic foam to show good structural performance in fire. Resole phenolic resins [3] are produced by a condensation reaction between phenol and formaldehyde. These resins are formed by reacting phenol with an excess of formaldehyde (molar ratio
P/F > 1) under alkaline conditions (Fig. 1). Typical ratios of formaldehyde to phenol used in the preparation of resole resins are between 1.5:1.0 and 3.0:1.0. The mechanisms of the reactions leading to the formation of resole phenolic resins have been the object of a number of studies. The formation of hydroxymethylphenols, the condensation reactions of hydroxymethylphenols to form resole precursors involving the loss of water, and the effect of pH and temperature on these reactions have received considerable attention. The chemistry is difficult to study as the result of the intractable nature of the cured resin. However, the evidence suggests that methylene linkages predominate (Fig. 1) although the cured resin may have a number of different crosslinks. The polymerization and the formation of a cross-linked network involve the use of heat and/or a catalyst.

This paper presents the material behaviour details of different systems of phenolic syntactic foams, all fabricated with glass microspheres as reinforcement but differing in their quantity. Blends of phenolic resins with different quantity of glass hollow microspheres, cured with acid hardener, were characterized, and specifically on their thermal and thermomechanical properties, thermal stability and fire behaviour. In particular, as mentioned previously, one of the roles of the char is to limit oxygen diffusion from the boundary layer to the bulk to prevent the exothermic degradation reactions of the polymeric matrix. Therefore, the mechanical characteristics and the physicochemical properties of the char are of fundamental importance to ensure good quality of an ablative material. Reinforcing microspheres may be therefore included in the ablative formulation to improve the char stability.

The undamaged materials were characterized in order to obtain experimental data on properties of phenolic syntactic foams and investigate the effect of change in glass hollow microsphere volume fraction. In order to determine their thermal and thermomechanical properties, an experimental programme including Thermo-Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Analysis (DMA) was conducted. A disadvantage in phenolic resins is that they are characterized by a complex process of polymerisation (cure) with generation of water, with consequent formation of voids [6]. The presence of water was revealed by all these techniques and had a great influence on properties of phenolic syntactic foams. These techniques allowed assessing their temperature capabilities, for all of these, their thermal stability and their temperature of degradation.

Finally, an experimental investigation into the structural performance of resole phenolic syntactic foam in fire was performed depending on the volume ratio of glass hollow microspheres. In this study, the chosen configuration is among the toughest: normal propane jet at high flow impacting the surface of phenolic materials. The formed char is susceptible to rapid removal or cracks by the mechanical forces produced as an effect of the elevated re-entry speeds, which results in reduction of the thermal insulation.

Fig. 1. The phenolic-resole type resin preparation, showing an indicative structure.

2 Experimental Procedures

2.1 Fabrication of Syntactic Foam Composites

Specimens for this research were produced by mechanical dispersion of glass hollow microspheres S38 from 3M Company, in resole phenolic resins.
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<table>
<thead>
<tr>
<th>Composition</th>
<th>Microsphere distribution (µm, by volume at different percentiles)</th>
<th>Effective top size (µm)</th>
<th>Target fractional survival (%)</th>
<th>Average true particle density (kg/m³)</th>
<th>Thermal conductivity (W/mK) at 21°C</th>
<th>Softening point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soda-lime (SiO₂-CaO-Na₂O)</td>
<td>15 40 75 85</td>
<td></td>
<td>90</td>
<td>380</td>
<td>0.127</td>
<td>600</td>
</tr>
<tr>
<td>Borosilicate (SiO₂-B₂O₃)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Table 1. The properties of S38 glass hollow microspheres as provided by the manufacturer 3M.

The properties of the microspheres are given in Table 1. They were processed by varying the volume fraction of microspheres: 0% (Phenolic matrix), 30% (SF-30%) and 50% (SF-50%). The phenolic based systems were cured at ambient temperature in wood rectangular moulds covered with silicon paper of dimension 345 mm x 315 mm through the careful addition of acid catalyst, p-toluene sulfonic acid PTSA. Four plates of 3 mm of thickness were made for each system. Of these, three were subjected to fire test with the remainder used to establish undamaged specimen properties.

The measured densities of the fabricated foam samples and the corresponding volume fractions of the constituents are presented in Table 2.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Id. No.</th>
<th>Theoretical density (g/cm³)</th>
<th>Measured density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Phenolic matrix</td>
<td>1.25-1.30</td>
<td>1.234</td>
</tr>
<tr>
<td>2</td>
<td>SF-30%</td>
<td>0.978</td>
<td>0.901</td>
</tr>
<tr>
<td>3</td>
<td>SF-50%</td>
<td>0.768</td>
<td>0.807</td>
</tr>
</tbody>
</table>

Table 2. The density of the unreinforced material and of the syntactic foams.

Water is produced as a by-product of the condensation cure reaction which causes micropores to develop in the phenolic matrix [3, 6], in addition to air bubbles induced by mixing, as shown in Fig. 2. The pores range in size from about 1 to 10 µm. Water is initially present as a solvent (20.4% by weight) in the uncured resin and more is formed during polymerization. In ambient temperature cure, as used in the present work, a significant proportion of this water is present as liquid contained within the micropores.

### 2.2 Thermal and Thermomechanical Characterizations

#### 2.2.1 Thermogravimetric Analysis

A PERKIN ELMER Simultaneous Thermal Analyser 6000 was used to study the thermal stability of the materials. Thermogravimetry is a technique that measures the change in weight of a sample as it is heated, cooled or held at constant temperature in a defined atmosphere. Runs were carried out from room temperature to 950°C at a heating rate of 10°C/min under O₂ atmosphere (40 mL/min).

![Fig. 2. The scanning electron micrograph of the phenolic matrix for the unreinforced material showing the microporous structure that contains water.](image)

#### 2.2.2 Dynamic Mechanical Analysis

DMA test is widely used to investigate the structures and the viscoelastic behaviour of polymeric and composite materials for determining relative stiffness and damping characteristics. The dynamic mechanical measurements were conducted on DMA db50N from METRAVIB. The specimens were tested in tension/compression mode at 0.1 Hz frequency and 5 µm amplitude. The specimen sizes
were 12.5 mm long x 5 mm wide and 4 mm thick. Two consecutive thermal runs were made. A temperature ramp of 1°C per minute was maintained during the analysis from room temperature to 150°C for the 1st run and from room temperature to 250°C for the 2nd run before decomposition temperature. The viscoelastic parameter such as the storage modulus $E'/E'_\text{initial}$ and the damping factor $\tan \delta$ were plotted with temperature. These values change with temperature and different relaxations can be seen especially the relaxation $\alpha$ associated with glass transition.

### 2.2.3 Differential Scanning Calorimetry
The technique DSC, a METTLER TOLEDO DSC 1 STARe System, was carried from -50°C to 250°C before decomposition temperature at a heating of 10°C/min in inert atmosphere, twice for the same material. In the case of thermosets, it is used to measure characteristic temperatures as glass transition, endotherms and exotherms associated with post-curing, evaporation of volatiles and degradation and other processes that involve heat flow.

### 2.3 Fire Test
Fire tests were performed in order to: (i) determine the fire properties (fire reaction and fire resistance) of the material (ii) assess the improvements on those fire properties when using the different systems. Three tests for each sample of dimension 300 mm x 240 mm x 30 mm were carried out using a propane flame as a combustive, under high pressure, 4 bars, for the effect of ablation in order to examine in a first phase the cohesion of the char. Hot combustion gases (> 1000°C) were directed along the normal to the specimen. Fig. 3. shows the propane flame test apparatus. For each sample, the test consisted in following the variations in temperature on the back of the specimen using a type K thermocouple and its distribution over the entire surface covered by a steel plate (3 mm in thickness) using an IR camera FLIR SC7600 MWIR. This plate was coating in black to enhance the emissivity of the surface. In addition, observations were taken regarding the behaviour of the specimens including visible smoking, ignition, and charring. The structural performance of the materials in fire was quantified by the time-to-failure. In other words, time-to-failure is the period the material can support an applied force during a fire event before failing.

After fire test, the collected sample surface subjected to fire and the cross section were studied by binocular microscope on OLYMPUS SZ61 and the structure of porous carbonaceous residues were analysed by Scanning Electron Microscope (SEM) on Philips XL 20. It allowed to evaluate the bulk degradation of materials by erosion caused by the impact of the jet on the surface and the state surface (delamination, cracks, failure...). The char was also analysed by FTIR (ATR mode) and Raman spectroscopies, respectively on PERKIN ELMER Spectrum One and HORIBA XploRA, and X-ray Diffraction on MOXTEK MXP-D1 in order to measure the microstructural and chemical changes during a fire exposure.

![Fig. 3. Schematic of fire test.](image-url)
Furthermore, the catalyst employed was p-toluene sulfonic acid PTSA 65% wt in aqueous solution. The boiling temperature of the PTSA, formaldehyde and phenol are respectively 140°C, 98°C and 182°C. During this stage, the polymer network remained largely intact. Above ~ 300°C the second stage began, which mainly involved scission reactions along the chain, with elimination of some volatile by-products [4, 7]. The structure of gaseous products released and of degradation residues depended on the degradation atmosphere, temperature. In this study, the thermal decomposition of the phenolic material in an oxidizing atmosphere led to the total and rapid destruction of the phenolic networks. As confirmed in published data, the degradation mechanism of the phenolic network leads primarily to the formation of CH₄, CO, CO₂ and H₂O, with the absence of cyclic compounds [7]. As the amount of resin was different between systems, mass losses were more or less important and associated temperatures were shifted. The shape of the curves shows that the phenomena occurred in lower temperatures for the system with more filler. For the neat phenolic resin the curve presents a sudden decrease in the mass at 500°C. Indeed, at 350 °C, the matrix began to degrade progressively but at 500 °C, a sharp drop in its mass occurred. Because of the lack or the insufficient quantity of reinforcing fillers, this material did not resist at gas flow due to the vaporization of volatiles and pyrolysis gas. Thus, during the test, it exploded with the high internal pressures generated by these gaseous products. The chamber test was then polluted by the explosion of this material. This first approach showed the lower structural performance of this system without fillers. For the phenolic syntactic foams at 30% and 50% by volume of glass hollow microspheres, the different stages appeared in the degradative process, the material structure was not affected by the evaporation of the volatile due to the high volume percentage level of glass fillers. Once the decomposition was finished, an inorganic solid, about 13% by weight for SF-30% and 20% by weight for SF-50%, remained. It was 35% and 53% by volume of glass hollow microsphere according its density. It showed that high reinforced foam composites improved thermal stability compared to the unreinforced ones.

![Fig. 4. The thermogravimetric curves of the three systems at a heating rate of 10°C/min under oxygen atmosphere.](image)

### 3.1.2 Dynamic Mechanical Analysis

For the first run, the plots of the storage modulus (E/E'initial) and the damping factor tan δ, versus temperature for the three systems are shown in Fig. 5. The magnitude of E’ began to decrease from about 60°C, which is related to a primary relaxation associated to the glass transition. However, this variation was not complete because of the appearance of two phenomena. Once the material was heated through this transition, the post-curing and the loss of volatiles (water, formaldehyde) occurred which led to the stabilization and/or the increase of the storage modulus. Upon post-curing, phenolic materials continued to crosslink due to the presence of active sites available even after they were cured at ambient temperature. Thus, the decrease in the storage modulus in the transition region associated with glass transition was shifted to a higher temperature, about 120°C. This decrease occurred within a large temperature range, because it was disturbed by different phenomena, such as the polymerization, departure of the plasticizer solvent (water, formaldehyde). Indeed, plasticizers work by embedding themselves between the chains of polymers, spacing them apart, significantly lowering the primary relaxation α temperature associated with the glass transition. The reduction in modulus with increasing temperature was much lower with increasing hollow glass microsphere volume fraction. It was explained by the difference in the amount of the matrix phase compared to unreinforced resin as glass microspheres do not undergo any transition in this temperature range. For the second run, the plots of the storage modulus (E/E'initial) and the damping factor tan δ, versus
temperature for the three systems are shown in Fig. 6. The decrease in the modulus linked to the primary relaxation \( \alpha \) region was shifted to higher temperatures, about 150°C. Moreover, the amplitude of the storage modulus loss associated with this transition was lower than in previous case because of higher crosslinking rate even in the case of neat matrix. Therefore, these materials exhibited enough high modulus at high temperature, especially for reinforced systems due to the presence of glass fillers as mentioned previously [8].

![Figure 5](image1.png)

**Fig. 5.** The DMA curves of the three systems at a heating rate of 1°C/min for the 1\(^{st}\) run.

![Figure 6](image2.png)

**Fig. 6.** The DMA curves of the three systems at a heating rate of 1°C/min for the 2\(^{nd}\) run.

### 3.1.3 Differential Scanning Calorimetry

All cured materials were analysed by DSC using two consecutive thermal runs, representing by run (1) and run (2) in Fig. 7. For each cured material, the following phenomena were noted for the 1\(^{st}\) run:
- In the range of -15 to 5°C, there was an endotherm except in the case of the system SF-50%. It could have resulted from the melting of residual water and the catalyst PTSA.
- Two phenomena were present from about 20 to 150°C, range changing more or less depending on system: a large endotherm followed and superimposed with an exotherm. The endotherm was related to a considerable vaporization of water and loss of other volatiles as residual formaldehyde and the catalyst PTSA. The large exotherm occurring at the same time with the release of water endotherm was linked to the residual polymerisation [9].
- No glass transitions were observed. For each cured material, the following phenomena were noted for the 2\(^{nd}\) run:
  - The endotherms and exotherms of the 1\(^{st}\) run disappeared in the 2\(^{nd}\) run, meaning that the resin was totally cross-linked and the material was completely dried.
  - Also, no glass transitions were observed. It is be noted that the glass transition is difficult to identify by DSC.

These results were consistent with DMA analyses.

![Figure 7](image3.png)

**Fig. 7.** The DSC curves of the three systems at a heating rate of 10°C/min.

### 3.2 Fire Test

#### 3.2.1 Fire behaviour

Depending on the amount of microspheres, the fire behaviour was very different. This test showed the importance of incorporating glass hollow microspheres for good structural performance in fire. Under a high velocity fluid stream, the unreinforced phenolic material did not have time to form a protective char. Its surface was continuously ablated leading to a complete perforation through the thickness after five minutes of exposure to the flame as shown in Fig. 8. Due to the absence of reinforcement, the neat matrix showed no mechanical resistance to the high gas flux, causing to the loss and the consumption of the material itself.
After five minutes there was a formation of a hole and the temperature on the back of the specimen was the temperature of the propane flame (Fig. 9). Before the failure, no temperature rise was observed.

For both syntactic foams, burning is more progressive because of their easily and quasi-instantaneous charring when exposed to the flame. Thus, for several long minutes, no ablation of the surface occurred but its strength was compromised with the appearance of micro-cracks on the surface. During the test, the coalescence of these micro-cracks led to long cracks resulting in failure of the specimen. Fig. 10. shows the different macro-cracks of the two syntactic foams appearing during the fire test. For the specimen SF-30%, after 40 seconds, many cracks appeared on the edges of the plate, the spacing became larger during the test. This was due to pre-existing small cracks and micro-pores before the tests which were accentuated by the sudden drying. Indeed, the centre of the plate subjected by the flame did not present such cracks until after about 13 minutes. These cracks were decisive because after about 17 minutes, loud ‘bangs’ might be heard as sudden delamination between the char and the virgin material and departure of material occurred. The test was stopped before the formation of a hole but some explosion continued despite the absence of the flame leading a complete perforation due to a continuous release of volatile gases. Indeed, the delamination between the char layer/underlying undegraded composite occurred due to the difference in their thermal expansion coefficient. As explained below, the interface was also very brittle due to vertical and very close cracks of the char throughout its all thickness. These two phenomena could cause layers to fall off, thereby exposing uncharred material to fire. For the specimen SF-50%, no large cracks appeared until about 23 minutes causing the failure for the overall structure of the plate. During the tests, the time-of-failure became longer for syntactic foam with 50% by volume of microspheres. For both syntactic foams, other specimen presented a shorter time-of-failure with 6 min for SF-30% and 16 min for SF-50%. Cracks appeared very quickly because the presence of initial macro-cracks occurred just after processing at the edge of the samples. Fig. 9. shows that for both composites, the failure caused a sudden increase of the temperature on the back of the specimen. However, the insulation property is highlighted with a low temperature rise up to 100°C maximum before the failure of the composites. Moreover, during the test, all syntactic foam samples showed a loss of water droplets. This phenomenon could have a ‘cooling’ effect on heat conduction.

The presence of fillers allowed maintaining the mechanical strength of the char. The formation of cracks led to failure of the specimen but the high amount of glass hollow microspheres could better delay the propagation of cracks because they were stabilized by the microspheres. On the other hand, with few microspheres, the matrix phase was more important and thus favouring the propagation of cracks which weakened the char. Moreover, the pre-existing cracks whatever the system can lead precociously to the fracture of syntactic foam.

Despite the phenolic syntactic foam having better thermal stability and fire reaction properties, the fire tests revealed that it is not sufficient for structural performance in fire. The macro and micro cracks
weaken the char and their reduction is necessary to improve the material resistance to high gas flux. Delamination between char layers/composite could be expected to have a significant effect on fire behaviour due to the formation of unbounded interfaces. The char must adhere strongly to the underlying composite; otherwise it can flake off and expose virgin material directly to the fire.

3.2.2 Morphology of the char

Fig. 10. The front face of the plate of the syntactic foams (a) with 30% by volume of microspheres SF-30% (b) with 50% by volume of microspheres SF-50%.

Stage IV: Contraction due to depletion of char and glass/char reactions

The stage II was illustrated on Fig. 12. The unreinforced phenolic material did not have time to form char. The top surface looked like the texture of an orange peel. Under the effect of heat, a high internal pressures, due to the formation of volatile gases and vaporization of water, led to the formation of polymer matrix ‘bubbles’ swelling. This phenomenon led to the formation of micro-cracks which by propagation joined and caused a wrenching of material hence this aspect of ‘orange peel’.

Therefore, the cracking was due to the internal pressure rise, thermally-induced strains caused by thermal expansion and contraction, adding that others imperfections such pre-existing cracks appearing during the cure. Thus a discontinuous char structure containing cracks provided a pathway for the escape of flammable volatiles into the flame, and thereby reduced the effectiveness of the char layer to provide fire protection.

Fig. 11. The binocular analyses of (a) the surface of the upper layer (b) the cross-section of the char, of the syntactic foam filled with 30% by volume of microspheres after fire test.

Stage I: Linear thermal expansion
Stage II: Expansion due to pyrolysis, volatiles and vaporization of water
Stage III: Contraction due to sudden drying and char formation

Fig. 12. The scanning electron micrograph of the top surface of the unreinforced phenolic material.
Fig. 13. shows the surface of the upper layer of the syntactic foam filled with 30% by volume of microspheres before and after fire test. The undamaged syntactic foam presents some micropores due to the presence of the water. The pores ranged in size from about 1 to 10 µm. After fire test, two changes were observed on a microscopic scale. First, the degraded matrix that was the char was very porous. The pores formed evacuation pathway of pyrolysis gases. They could also cause structural damage by producing weak and brittle char with formation of cracks. During the heating of the material, the pores initiated, grew and coalesced under the high internal pressures exerted by decomposition gases. The density of the char showed a lightweight character with 0.629 and 0.581 g/cm³ for respectively the systems SF-30% and SF-50%. Secondly, despite the fact that some microspheres were broken or removed, the microspheres were well held in the impact of the flame. They were also deformed under the effect of heat. According to the supplier 3M, the softening point of glass microspheres is 600°C. Also, Fig. 14. presents the aspect of the char at the vertical crack, of the syntactic foam filled with 50% by volume of microspheres after fire test. Most microspheres were present and were not damaged. The structural integrity of this carbonaceous layer seemed to be maintained by the contribution of the microspheres.

Fig. 15. presents a through-thickness of phenolic syntactic foams exposed to one-sided heating in a fire after test. Four different layers were observed. Indeed, the thermal gradient which is established in the thickness induced a transformation sequence, represented by different layers, whose boundaries changed very rapidly [4, 11]. Four formed zones could be highlighted:

(i) The porous char layer represents the thermomechanical degradation of the phenolic matrix in porous carbonaceous material
(ii) The decomposition zone is the region where the polymer matrix was heated to above the decomposition reaction temperature but below the char formation temperature. In this region the matrix was partially degraded, usually by scission of the chains into high molecular weight fragments that were too heavy to vaporize. However, the decomposition process was not complete and therefore the matrix had not been reduced to char and combustion gases.
(iii) The drying-out and post-cured layer was formed by the removal of water initially present and water released by the end of the polycondensation of the resin.
(iv) The virgin material was not affected by the fire because the temperature was too low to cause any softening or decomposition of the matrix. The maximum temperature of the lower side of the plates during the test before failure was about 100°C. However, slight post-curing likely took place.
Finally, the processes that occurred when a phenolic syntactic foam is exposed to high heat flux are summarized in Table 3.

<table>
<thead>
<tr>
<th>Process</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anisotropic heat conduction through virgin material and char</td>
<td></td>
</tr>
<tr>
<td>Thermal expansion/contraction</td>
<td></td>
</tr>
<tr>
<td>Decomposition of polymer matrix</td>
<td></td>
</tr>
<tr>
<td>Pressure rise due to formation of combustion gases and vaporization of moisture</td>
<td></td>
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<tr>
<td>Flow of gases from the reaction zone through the char zone</td>
<td></td>
</tr>
<tr>
<td>Flow of gases into the virgin composite</td>
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<tr>
<td>Thermally-induced strains</td>
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<tr>
<td>Formation of micro- and macro-cracks in the char</td>
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<td>Formation of delamination between layers char/underlying degraded composite</td>
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<tr>
<td>Softening of hollow glass microspheres</td>
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</tr>
<tr>
<td>Ablation</td>
<td></td>
</tr>
</tbody>
</table>

Table 3. Summary of the main processes when a phenolic syntactic foam is exposed to fire

3.2.2 ATR Spectral Analysis

ATR spectra of the chars from syntactic foams and glass hollow microspheres shown in Fig. 16, are broadly similar one another. They showed three peaks, typical of the composition of the soda-lime-borosilicate microspheres: very intense band at 1050 cm\(^{-1}\) due to asymmetric stretching of the Si-O-Si chain, weaker symmetric band at 820 cm\(^{-1}\) corresponding of the Si-O-Si chain, and weak broad absorption at 1400 cm\(^{-1}\) for the stretching vibration of the B-O linkages [12]. For chars, no bands of cured resole phenolic resins were observed, for instance OH stretching of phenolic ring and methyol group at 3375 cm\(^{-1}\) or C-O stretching of dimethylene ether bridge at 1220 cm\(^{-1}\) [3], as shown in the spectrum relative to the matrix without glass microspheres.

3.2.3 XRD Analysis

Fig. 17. shows the XRD patterns of the phenolic matrix, glass hollow microspheres S38 (3M) and the char from the two syntactic foams (SF-30%, SF-50%) in order to study the morphology of the char formed during fire tests. First, the cured resin presented a broad maximum peak at \(2\Theta \approx 20.5^\circ\), which was due to adjacent chains of linear polymer. This peak disappeared completely for the char with high heat exposure. The diffraction pattern of glass microspheres confirms that the Soda-lime-Borosilicate glass beads are fully amorphous and contain no crystalline silica (cristobalite, quartz), with a broad maximum peak at \(2\Theta \approx 13^\circ\). For both chars, the XRD patterns revealed the formation of graphitic carbon, which is confirmed by the appearance of two sharp peaks at \(2\Theta = 21.5^\circ\) and \(2\Theta = 24^\circ\) [13]. This reflection is superimposed on a broad band, which denotes the presence of a fraction of amorphous carbon and the presence of hollow glass microspheres. The phenomena of carbonization and graphitization occurred during fire exposure.
3.2.4 Raman Spectra Analysis

Fig. 18. shows the Raman spectra of the phenolic matrix, glass hollow microspheres S38 (3M) and the char from the two syntactic foams (SF-30%, SF-50%). These spectra showed the chemical changes occurring during the degradation of the phenolic matrix of both syntactic foam represented by the char, after fire tests. First, the phenolic matrix showed broad bands, characteristics of the polymeric structure of a cured phenolic resin. For the hollow glass microspheres, four narrow peaks could be distinguished associated with oxide glass (Table. 1: Soda-lime and borosilicate glass): the 2500 and 460 cm$^{-1}$ strong bands and the 1540 and 1470 cm$^{-1}$ weak bands. In particular, the 460 cm$^{-1}$ band was the basic band in glass with B$_2$O$_3$, due to symmetrical stretching and partially deformation vibrations of Si-O-Si bridges. At the surface of the char for both syntactic foams after fire tests, the original cured resin structures disappeared completely, showing the total carbonization of the phenolic matrix. The bands associated to glass microspheres were present, because of the presence of the microspheres in the char after fire tests, as explained above. It can be observed that the spectrum of each char shows two strong wide peaks centred around 1355 and 1600 cm$^{-1}$, characteristics of a carbonaceous structure. The peak located to 1355 cm$^{-1}$ call D band was due to a disordered (amorphous) structure in the carbon whereas the peak at 1600 cm$^{-1}$ called G band was due to a graphitic structure. The differences in the bands between ordered and disordered carbon-carbon structures show the carbonization and graphitization of the phenolic matrix [13, 14].

Conclusion

Unreinforced phenolic materials and phenolic syntactic foams were ‘living’ materials with increasing temperature, with the combination of two phenomena: vaporization of water and other volatiles, and post-curing. They were not completely cured. High reinforced foam composites improved thermal stability compared to the unreinforced ones. Moreover, these materials exhibited enough high modulus at high temperature, especially for reinforced systems due to the presence of glass microspheres.

Syntactic foams presented a mechanical advantage compared to unreinforced material under the impact of a high flux of flame. The formation of the char could help retain the structural integrity of a fire-damaged composite by holding the microspheres in place after the polymer matrix has been degraded. The neat phenolic matrix underwent only wrenching of material. However, the presence of pre-existing cracks and the cracks weaken the char leading precociously to the fracture of the syntactic foam. They could also lead to a delamination between char layers/underlying undegraded composite. Due to this phenomenon, the char could flake off and exposed virgin material directly to the fire. The presence of water can be both an advantage and a disadvantage for the structural integrity of composites. It can be expected to have a ‘cooling’ effect on heat conduction but under the effect of heat, a high internal pressure, due to the vaporization of water, led to the formation of micropores and cracks.
Thus, despite the phenolic syntactic foam having better thermal stability and fire reaction properties, these defects reduced the high structural performance of syntactic foam in fire.

Finally, char is a highly porous material that can consist of crystalline (ie. graphitic) and amorphous regions. At high temperature (≥ 1000°C), the carbonization and the graphitization of the phenolic matrix occurred.

Post-fire mechanical properties could be investigated.

References