GRAPHENE-BASED DISPERSION AS FLAME RETARDANT COATING FOR POLYMERIC MATRICES

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Abstract
A novel graphene-based dispersion has been used as coating on different polymeric foams. This highly concentrated water-based pristine graphene dispersion has been developed and patented (patent pending) by Directa Plus, a company devoted to the large-scale production of graphene-based materials. The flame retardant behavior was investigated following standard procedures - ASTM D635, ASTM D3801, ISO 5660 - and the outstanding results obtained sustain the definition of a new class of non-toxic and highly efficient flame retardant materials.

1. Introduction
Graphene is defined as a two-dimensional carbon nanofiller with a one-atom-thick planar sheet of sp\textsuperscript{2} bonded carbon atoms that are densely packed in a honeycomb crystal lattice. It is regarded as the “thinnest material in the world” with tremendous application potential [1,2]. Since its first isolation [3], several graphene synthesis approaches have been proposed by the academic community, whereas the most promising methods could be identified with CVD as bottom-up strategy [4] and graphite exfoliation as top-down one [5]. CVD is able to produce high quality single layer graphene crystals, but the high cost associated with this technique together with its low yield still prevents its large scale adoption. On the other side, top-down approaches could provide graphene-based material on the ton scale, although the scalability of these methods and the quality of products are still under investigation. One common route pursued within top-down approaches consists in passing through graphite/graphene oxide preparation as intermediate material. This method involves harsh chemical treatments and results in an insulating highly defective product. Differently, Directa Plus has developed a production platform devoted to large-scale production of high quality pristine graphene nanoplatelets, whereas G+ grades, both in the form of dry powders or liquid dispersions, stem from different particles sizes and morphologies.
Polymer/graphene nanocomposites show superior mechanical, thermal, gas barrier, electrical and flame retardant properties compared to the neat polymer [6-8]. It was also reported that the improvements in mechanical and electrical properties of graphene-based polymer nanocomposites are much better in comparison to those of clay or other carbon filler-based polymer nanocomposites [8]. In this paper we investigate the flame retardant properties of polymeric foams coated with a dispersion containing colloidal graphene platelets.
2. Experimental activity

2.1 Graphene dispersion preparation and coating deposition

The present work is focused on the investigation of the flame retardant properties of LIQUID G+, a highly concentrated water-based graphene dispersion. The production of this dispersion consists of two main steps: the first being the thermal expansion of intercalated graphite (GIC) through a proprietary process [9], which is stable and continuous. The output is then confined in a liquid medium and energetically treated in order to push graphite exfoliation and to fine tune the flakes morphology, cutting down both lateral dimension and thickness.

An open-cell polyurethane foam and two closed-cell systems (polystyrene and polyethylene terephthalate-based) were treated with the graphene dispersion by either dip coating or direct painting procedures. Graphene dispersion is ready-to-use as produced: the low viscosity together with the high solid content allow to obtain a uniform coating without any specific and dedicated technique. After the foam coverage is completed, the specimens are dried under an hot air stream.

2.3 Flame retardant characterization

Flammability properties of the materials containing graphene were evaluated with UL-94 horizontal burning (ASTM D635) and Limit Oxygen Index (ASTM D3801). Combustion behavior was achieved with cone calorimeter test (ISO 5660) on 100x100x15mm samples with an heat flux of 35 kW/m².

3. Results and Discussion

In Table 1 the results of the flammability tests are reported and the combustion residues of PS foam and PS foam/G+ are compared in Figure 1. In terms of flammability the closed-cell systems coated with LIQUID G+ have had a dramatic improvement with a relevant increasing of the LOI value and no ignition in UL-94 test. The coating with G+, in fact, has created an uniform and resistant skin that preserve the polymeric foam to the fire. In the case of cone calorimeter test only in the case of PET foam there is an important decrease in the peak of HRR.

Electron microscopy was used in order to characterize the G+ coating (Figure 2), demonstrating that the heat developed during the burning test promotes its homogeneity.

<table>
<thead>
<tr>
<th>Sample</th>
<th>UL-94 test</th>
<th>LOI test</th>
<th>Cone test</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Burning time (s)</td>
<td>Burning rate (mm/s)</td>
<td>Dripping (%O₂)</td>
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<tr>
<td>PUR foam</td>
<td>70</td>
<td>3,8</td>
<td>Yes</td>
</tr>
<tr>
<td>PUR foam/G+</td>
<td>270</td>
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<tr>
<td>PS foam</td>
<td>11</td>
<td>-</td>
<td>Yes</td>
</tr>
<tr>
<td>PS foam/G+</td>
<td>-</td>
<td>-</td>
<td>No</td>
</tr>
<tr>
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<td>1,3</td>
<td>Yes</td>
</tr>
<tr>
<td>PET foam/G+</td>
<td>-</td>
<td>-</td>
<td>No</td>
</tr>
</tbody>
</table>

Table 1. Test results for the different materials
Figure 1. Combustion residues of PS foam (A) and PS foam/G+ (B).

Figure 2. Scanning electron microscopes images of PET foams. (C) Foam surface before coating treatment. (D) Foam surface coated with G+ dispersion before combustion. (E) Foam surface coated with G+ dispersion after combustion.
References