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Thermal stability of polycarbonate-graphene nanocomposite foams

G. Gedler, M. Antunes, V. Realinho, J.I. Velasco*

Centre Català del Plàstic, Departament de Ciència dels Materials i Enginyeria Metal·lúrgica, Universitat Politècnica de Catalunya, BarcelonaTech. C/Colom 114, E-08222 Terrassa (Barcelona), Spain

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A thermogravimetric study in both nitrogen and air atmospheres has been carried out on unfilled and graphene-reinforced solid and foamed polycarbonate. Polycarbonate foams were prepared using a supercritical CO_2 dissolution one-step batch foaming process. Results showed that polycarbonate displayed a characteristic one-step decomposition under nitrogen, while three-step degradation was observed in air. In addition, as-received pristine graphene nanoplatelets displayed a three-step degradation in air, compared to a mild degradation under nitrogen. It was found that the thermal stability remarkably improved for the foamed composites, related to a combination of a heat transfer reduction promoted by the insulating cellular structure and the presence of the platelet-like graphene, which helped create a physical barrier effect, delaying the escape of volatile products generated during decomposition.

1. Introduction

Graphene-based polymer composites have been the subject of interest in recent years, mainly due to the combination of high thermal, mechanical and electrical properties of graphene, a monolayer of sp^2-hybridized carbon atoms arranged in a two-dimensional lattice [1]. Its incorporation into polymers may result in remarkable improvements of the host material [2–4]. The outstanding thermal stability of graphene makes it a very attractive material for the fabrication of polymer composites with improved thermal stabilities. Particularly, the thermal degradation of polymers such as PVA [5,6], PMMA [7], PS [8], polyaniline [9] or PP [10] using different types of graphene have been studied in the last few years, with important improvements in thermal stability being found for these composites. Another characteristic of graphene that could have an important effect in the thermal degradation is its particular flat-like morphology, which, depending on the dispersion and exfoliation degree of graphene nanoplatelets within the matrix, could promote a physical barrier effect to volatile gases generated during decomposition [11]. Hence, the dispersion of graphene in the polymer could have an important effect in the composites' decomposition mechanism. Several different techniques have been carried out in order to improve the dispersion of nano-sized fillers in composites. In situ polymerization [12,13], solution blending [14–17], or the combination of different melt-mixing techniques [13] have been used. However, these techniques limit the amount of produced composite. Currently, the trend is looking for mechanical, thermal and electrical improvements in composites with the smallest amounts of graphene using conventional industrial processing techniques such as extrusion.

Owing to its high mechanical properties and thermal stability, polycarbonate (PC) is one of the most used engineering plastics. Detailed investigations of the thermal degradation of PC have been successfully carried out. For instance, thermogravimetric analyses have been carried out in order to study the thermal behaviour of PC [18–22]. The thermal degradation pathways of PC in different atmospheres have been widely discussed [21,22]. Though studies of the thermal stability of PC composites with a silicate-layered nanoclay, montmorillonite, have been carried out [23,24], information regarding PC-graphene composites is still lacking.

The increasing interest in multifunctional materials and structures is driven by the need for the development of new materials that may combine structural functions with more functional characteristics, such as improved transport properties [25]. One possible strategy considers foaming of the base material and the control of its final cellular structure [26]. However, knowledge of the thermal stability of foams made from PC-graphene is still pretty scarce, mainly due to their multiphase complex nature. So far, only a few works have investigated the thermal degradation of graphene-based foamed composites, using silicone [27] and polystyrene [28] as polymer matrices.

In the present study, we conducted a thermogravimetric analysis on unfilled and graphene-reinforced solid and foamed

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* Corresponding author. Tel.: +34 937837022; fax: +34 937841827.
E-mail address: jose.ignacio.velasco@upc.edu (J.I. Velasco).

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polycarbonate composites that helped us to understand the effects of incorporating graphene nanoplatelets and foaming, as well as a combination of both, on the thermal stability of the prepared foams.

2. Experimental

2.1. Materials preparation

Composite preparation consisted in melt-compounding a pelletized polycarbonate (Lexan-123R-PC, supplied by Sabic, with a density of 1.2 g/cm^3 and MFI of 17.5 dg/min, measured at 300 °C and 1.2 kg) with 0.5 wt% of graphene nanoplatelets using a Brabender Plasticorder internal mixer at a constant temperature of 180 °C and screw speeds of 30, 60 and 120 rpm during a mixing time of 1, 2 and 3 min respectively.

The graphene nanoplatelets used in this study, with the commercial name of xGnP-M-15, so-called for now on GnP, were supplied by XG Sciences, Inc. These graphene nanoplatelets are 6–8 nm thick with a 15 μm average diameter, a typical surface area of 120–150 m^2/g and a density of 2.2 g/cm^3, as reported by the manufacturer.

After removing from the mixer, the graphene-reinforced PC composite was placed in a 3.5 mm-thick circular mould and compression-moulded at 220 °C and 45 bar using a hot-plate press *IQAP-LAP PL-15*. Once cooled under pressure at 45 bar using a water cooling system, the solid discs were removed from the mould and used as foaming precursors. These solid foaming precursors were later saturated with CO_2 and foamed using a one-step batch foaming process according to the procedure explained in one of our previous works [29].

2.2. Testing procedure

Thermogravimetric analysis was performed in a TGA/DSC 1 Mettler Toledo Star System analyser by heating samples of around 10.0 mg from 30 to 1000 °C at a heating rate of 10 °C/min under both nitrogen (constant 30 ml/min N_2 flow) and air atmospheres (constant 60 ml/min air flow). The temperatures corresponding to mass losses of 1, 5 and 50%, as well as the mass of the final residue obtained at 1000 °C, were reported for the unfoamed and foamed unfilled and graphene-reinforced polycarbonate composites.

X-ray diffraction (XRD) was carried out using a Panalytical diffractometer operating with CuKα radiation ($\lambda = 0.154$ nm) at 40 kV and 40 mA. Scans were taken from 2 to 60° with a scan step size of 0.02°.

In order to observe the stacks of graphene platelets distributed within the cell struts of the foamed composites and have an idea of their main dimensions, a JEOL JSM-5610 scanning electron microscope was used, with a voltage of 15 kV and a working distance of 30 mm. Samples were previously prepared by fracturing at room temperature and depositing a thin layer of gold at their surface using a BAL-TEC SCD005 Sputter Coater in argon atmosphere.

3. Results and discussion

3.1. Thermogravimetric analysis

The TGA and respective DTG thermograms of the solid and foamed unfilled polycarbonate (respectively called PC and PC-f), as well as the solid and foamed graphene-reinforced composites (respectively, PCg and PCg-f), were obtained under both nitrogen and air atmospheres. A characteristic one-step decomposition was observed under nitrogen atmosphere, while three-step degradation was observed in air. Additional thermogravimetric analysis was carried out under both atmospheres on the original powder-like graphene nanoplatelets. The results are depicted in Tables 1 and 2 and discussed as follows.

3.1.1. Thermogravimetric analysis under nitrogen atmosphere

3.1.1.1. Unfilled polycarbonate. The TGA and respective DTG thermograms of the unfilled solid polycarbonate (PC), presented in Fig. 1a, showed a characteristic one-step decomposition with an onset temperature at 1 wt% loss of 388 °C and a T_{max}, defined as the temperature at maximum mass loss rate in the DTG curve, of 430 °C. It is well known that the main degradation pathways of polycarbonate can be classified into two categories [21]: chain scission of isopropylidene bonds and hydrolysis/alcoholysis of carbonate bonds, including rearrangements of some carbonate bonds like decarboxylation or cross-linking upon heating, ultimately resulting in CO_2, H_2O and char.

The corresponding DTG thermogram suggested that two events could be occurring at a different rate due to the shoulder observed in Fig. 1a, related on one side to a smaller quantity of material undergoing the degradation at that temperature, and on the other to the two peaks observed in the heat flow curve (Fig. 1b), indicating that two different exothermic processes were taking place. The first peak was attributed to the chain scission of isopropylidene bonds (stage I), starting the degradation in accordance with the bond dissociation energies [21], while the second one was related to the hydrolysis and alcoholysis of carbonate bonds as well as the rearrangements of some carbonate bonds with continuing the chain scission (stage II). A wider and also intense peak was observed during this second process, related to a more exothermic decomposition. After this decomposition, there was a temperature range where the process slowed down due to the amount of material remaining.

Though the unfilled foamed polycarbonate (PC-f) showed a similar one-step decomposition, there was a delay corresponding to the beginning of the process for a 1 wt% loss of about 34 °C and of 55 °C for a 5 wt% loss when compared to the solid material. The DTG curve showed how the degradation occurred faster than for the solid PC, though with a T_{max} about 70 °C higher (see Fig. 1a). The delay during the beginning of the degradation was attributed to the material's cellular structure, which acted as an improved thermal insulator, inhibiting heat transfer at the beginning of the thermal decomposition. The high mass loss rate can be explained as follows: the cellular structure of the material is filled with air, as well as some remaining CO_2 from the foaming. As a result of the presence of the aforementioned gases, in addition to the start of the external degradation of the material, a simultaneous internal degradation

Table 1
TGA and DTG data under nitrogen atmosphere obtained at 10 °C/min.

Material code	Temperature (°C)				Residue at 1000 °C (wt%)	Relative density
	1 wt% loss	5 wt% loss	50 wt% loss	Max. mass loss rate		
PC	388	407	465	430	16	1.00
PC-f	422	449	500	500	20	0.43
	421	452	512	512	23	0.38
	417	451	510	510	22	0.46
	420	442	497	497	21	0.46
PCg	422	462	503	493	21	1.00
PCg-f	450	477	517	515	24	0.49
	431	462	513	512	23	0.47
	444	474	516	515	22	0.79
	436	467	510	507	22	0.59
	436	469	515	513	23	0.38
	461	484	519	517	25	0.35