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Fire reaction of nanoclay-doped PA6 composites reinforced with continuous glass fibers and produced by commingling technique

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ABSTRACT

In this paper, we report the development of a glass fiber commingled composite (GFCC) based on a nanoclay-doped polyamide 6 (PA6) and the evaluation of its fire reaction. The preparation of the composite comprised several steps. Firstly, the nanoclay was dispersed in the PA6 matrix. Then, the produced compound was spun in filaments and commingled with continuous glass fibers. Finally, the laminate preform was consolidated. Reference samples based on the neat PA6 were produced as well. As a results, although it is well known that, in the presence of a relevant amount of continuous fibers, the behavior of the material is mainly driven by the fibers themselves (e.g. mechanical, thermal, conductive, and so on), the effect of the clay was interesting, especially in flammability test (UL94 vertical burning test), where the total burning time passes from 227 s to 146 s.

1. Introduction

Due to their high specific strength and stiffness in relation to weight, fiber-reinforced polymer composites have been increasingly used over the last decades. While these properties have made composites very attractive for the transport industry (aerospace, rail, automotive and marine sectors), composites pose some drawbacks, which prevent them from fully replacing traditional materials in primary applications. One of these is the poor fire performance, which is mainly limited by the intrinsic properties of the organic matrices that are utilized in composite materials. Moreover, while glass fibers role is the mechanical reinforcement of the polymer, they may negatively affect composite fire reaction [1,2]. However, even though a large number of polymer resins are flammable and thus their respective composites, different ways to improve their low inherent fire retardancy using inorganic fillers have been suggested and studied thoroughly in the literature [3–5]. Initially, fillers in the micro-scale have been added to polymers to increase the fire performance. However, high filler loadings are generally required to improve the fire retardancy and this has significant implications on the mechanical properties and technical difficulties in processing of fiber composites. These limitations can be overcome with the use of nano-sized fillers, which provide a higher surface area and thus require lower content to increase the fire retardancy of the polymer-based composite [6,7].

Although the incorporation of nanoclays into the polymers has been extensively studied, a few studies are reported for the inclusion of nanoclays in continuous fiber reinforced matrices for fire retardancy, likely owing to issues relating to high viscosity and particle filtration during manufacturing [8,9]. Nguyen et al. reported on the effect of nanoclay on the fire performance of epoxy/glass fiber composites, showing delays in HRR rise, reduction in heat release rate and lower smoke production for glass fibre/nanoclay combinations [10]. More recently, the same authors reported an extensive DoE study to determine the effects of organophilic clay, loading levels and dispersion degrees into three types

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of glass reinforced thermosetting resins (polyester, vinyl ester and epoxy) by vacuum infusion [11].

The combination of nanoclay and continuous glass fiber was also explored in laminates. Shen et al. [12] reported on Polyamide 6 glass fiber laminates the inclusion of clays induced delays in both ignition time and time to peak heat release, despite the value of the peak heat release rate was not significantly affected. Successful examples of the use of nanoclay as synergist in flame retarded glass fiber reinforced thermoplastics were also reported [13,14]. These studies describe the development and the assessment of reaction-to-fire properties of novel nanoparticle modified commingled fiber reinforced composites, which preparation technique was previously reported (see for example [15]). In particular, the concept behind this work has been to obtain fire-optimized matrix formulations, which are melt-spun into continuous fibers and eventually commingled with conventional glass fibers to produce composite preforms for consolidation. During consolidation, the very short polymer flow lengths, which are characteristic of commingled fiber composite systems, along with the use of sub-micron-scale particulate fillers that are unlikely to be filtered-out by the fiber reinforcements during processing, provide an extremely even and efficient distribution of the nanoclays throughout the composite part. This novel approach is a highly efficient means of dispersing fire retardant particles within a fiber-reinforced polymer composite, and can clearly be extended to any sub-micron filler to improve also other properties. Fiber-level doping of the polymer, along with the use of commingling for mixing the fiber and polymer matrix, may overcome the existing practical difficulties of achieving high particle loadings with conventional composites, i.e. excessive polymer viscosity and undesirable fiber filtration of the particles.

2. Experimental

2.1. Materials

The thermoplastic polymer used in this study is the Polyamide 6 (PA6) Ultramid B27E, kindly supplied by BASF, having a reported density of 1.12–1.15 cm^3/g (ISO 1183). As a nanofiller, an organically-modified montmorillonite, Cloisite® 30B (C30B) which is a layered silicate (supplied by Rockwood Additives) was selected. Finally, for fiber reinforcement 3B Advantex® glass fibers (200 tex) were used. Note that the unreinforced neat and C30B-doped samples for the characterizations were produced with an Arburg 50 injection molding machine.

2.2. Composite manufacturing

Commingling is a technique for the production of thermoplastic composites reinforced with continuous fibers. The use of continuous fibers can guarantee higher mechanical properties if compared to short fiber composites. The production of the commingled composite consists in several steps, which are described in the following paragraphs. Fig. 1 illustrates the scheme of the processing phases.

2.2.1. Nanocomposite production

The nanocomposite compounds were produced with a co-rotating twin-screw extruder (Leistritz 27). The polymer was introduced through the main feeder, while the filler was introduced through the side feeder, in the percentage of 2 wt%. Both the polymer and the nanoclay were dried before compounding.

2.2.2. Fiber spinning

The neat PA6 and the nanocomposite were spun in fibers with a melt spinning line with in-line solid state drawing supplied by Extrusion Systems Limited, equipped with a multi-hole spinneret [16].

2.2.3. Fiber commingling

A four-axis Waltritsch & Wachter filament winding machine was utilised for the fiber commingling. Initially, the PA6 or PA6+2% C30B along with the glass fibers were fed into the filament winding machine. The fibers were then drawn over a steel plate (260 × 260 mm) acting like a spindle along one direction (nominally 0° direction) for 20 rounds. Finally, in order to prevent the preform from swelling during consolidation, a few fibers (1 round) were drawn perpendicular to the 0° direction. In essence the laminate had a $[90/0_{10}]s$ layup, while the thickness for the G/PA6 was 3.06 ± 0.15 mm and 3.18 ± 0.18 mm for the G/PA6-2%C30B.

2.2.4. Consolidation

The preforms obtained by the fiber commingling were subsequently taken to an 80-ton Talent mould carrier for consolidation. The preforms were consolidated at 280 °C using 35-ton pressure (6.48 MPa).

2.3. Characterization

2.3.1. Morphological characterization of the nanocomposite

The dispersion of the nanoclay in the PA6 matrix was evaluated by both SEM analysis (SEM Leo 1450 VP) and X-Ray diffraction (Philips X'Pert MPD $\lambda(CuK\alpha) = 1.540562$ Å, in configuration θ/θ).

2.3.2. Glass fiber volume fraction and density measurements

ISO 3451 standard tests were performed to determine the volume fraction of the glass reinforcement. The nominal densities for the PA6 and glass fibers were 1.13 g/cm^3 and 2.62 g/cm^3 respectively. To obtain the density of the composite laminates, a Micromeritics AccuPyc 1330 pycnometer was utilised. Such an apparatus uses an aluminum chamber with a known volume of 40.7 cm^3 where the pre-weighed sample is placed and the average density reading is provided based on three iterations.

2.3.3. Optical microscopy

In order to investigate the microstructure of the PA6 and PA6+2%C30B commingled composite laminates, optical

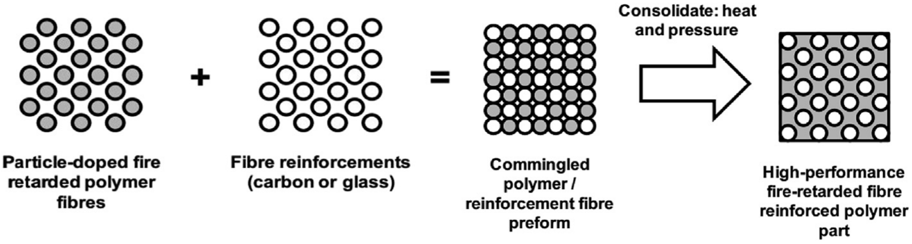

Fig. 1. Schematic sketch of the processing phases of commingled laminates.