MONTMORILLONITE-DOPED COMMINGLED COMPOSITES FOR IMPROVED FIRE PERFORMANCE

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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 combustion behavior. The preparation of the composite has involved several steps. Firstly the nanoclay was dispersed in the PA6 matrix. Then, the produced compound was spun in filaments and commingled with glass fibers. Finally, the laminate preform was consolidated. In order to evaluate the effect of the nanoclay on the combustion behavior of the GFCC, samples based on the neat PA6 were produced as well. The results show that the effect of the nanocomposite matrix was a significant improvement regarding heat release when a continuous external heat flux is applied (cone calorimeter), whereas in the presence of the glass fibers the positive effect is more pronounced in tests where a small flame is induced to ignite the vertically oriented sample (UL94 vertical burning test). This is connected to the different mechanisms by which the nanoclay affects the combustion behavior, whether in the presence of glass fibers or not.

1. Introduction

Due to their high specific strength and stiffness, fiber-reinforced polymer composites have been increasingly used over the last decades. While these properties have made composites very attractive for the aerospace and marine industry, to name a few, 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 attributed to the organic matrices that are utilized in composite materials. In particular, at elevated temperatures these organic resins soften, causing a considerable deterioration of mechanical properties whilst at higher temperatures they decompose and produce smoke and toxic or flammable products [1-3]. In addition, these products can also burn and release heat, which can lead to flame spread and fire exacerbation. Finally, depending on the heat flux and the loading conditions, a composite component can collapse in a matter of few minutes, which can have a detrimental effect on the overall structural capacity and performance [1-7]. Even though a large number of polymer resins are flammable and thus their respective composites, ways to improve their low inherent fire retardancy using clay fillers have been suggested and studied thoroughly in the literature [8-9]. Initially, fillers in the microscale had 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 to the mechanical properties. This can be overcome with the use of nanofillers, which provide a higher surface area and so require lower content to increase the fire retardancy of the base system.

Although the incorporation of nanoclays into the resin has been extensively studied, there is a shortage of studies where continuous fiber reinforcement is also involved. In such cases, issues relating to high viscosity and particle filtration have been reported [1,10]. This study describes the development and fire reaction of novel nanoparticle modified commingled fiber-reinforced composites [11]. In particular, the concept behind this work has been to initially obtain fire-optimised matrix formulations which would then be melt-spun into continuous fibers and eventually commingled with conventional glass fibers to produce composite preforms for consolidation (Fig. 1). 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, would provide an extremely even and efficient distribution of the fire-retarding additive throughout the composite part. Such a novel approach is regarded as a highly efficient means of dispersing fire retardant particles within a fiber-reinforced polymer composite, and can be clearly extended to every sub-micron filler to improve any other property. This fiber-level doping of the polymer, along with the use of commingling for mixing the fiber and resin, should overcome the existing practical difficulties of achieving high particle loadings with conventional composites, namely excessive resin viscosity and undesirable fiber filtration of the particles.

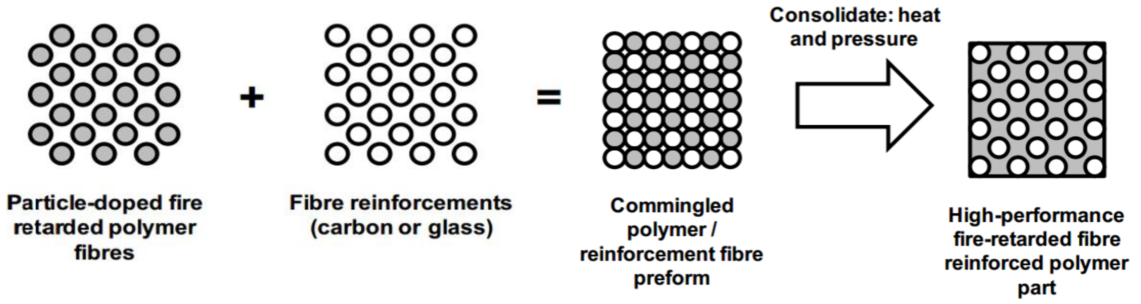


Figure 1. Schematic of the use of commingled fibers to provide a high performance fire-retarded fiber-reinforced polymer composite part [11].

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, which is a layered silicate, was selected. It was purchased by Rockwood Additives, which sold it under the trade name of Cloisite® 30B. Finally, for fiber reinforcement 3B Advantex® glass fibers (200tex) were used.

2.2. Composite manufacturing

Nanocomposite production. The PA6-2wt%C30B nanocomposite compound was 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.

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 multihole spinneret.

Fiber Commingling. A four-axis Waltritsch & Wachter filament winding machine was utilised for the fiber commingling. Initially, the PA6 and PA6+2%wt Cloisite along with 3B Advantex® Glass fibers (200tex) were fed into the filament winding machine. The fibers were then drawn over a steel plate (100×100×3 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 were drawn perpendicular to the 0° direction.

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.

2.3. Characterization

Glass fiber content. ISO 3451 and ASTM D2584 tests were performed to determine the volume fraction of the glass reinforcement. Samples of PA6- and PA6+2%wt Cloisite comingled composite laminates, were weighed and placed into dried and pre-weighed porcelain crucibles. The porcelain crucibles were then heated in an oven at 565°C in air atmosphere for 5 hours and they were finally weighed after having been cooled down. The nominal densities for the PA6 and glass fibers were 1.130 g/cm^3 and 2.260 g/cm^3 respectively.

Optical microscopy. To investigate the microstructure of the glass fiber reinforced PA6 and PA6+2%C30B laminates, optical microscopy was performed on a Nikon Eclipse LV150N optical microscope and images were acquired by a Nikon DS-Fi2 camera. For the microscopic inspection, numerous specimens acquired from G/PA6 and G/PA6+2%wt Cloisite laminates were ground and polished up to 1 μm grit size (diamond suspension) in a Struers Rotopol 1® polishing machine.

Cone Calorimetry. Cone calorimeter (CC), IS0 5660, is a bench-scale test which measures reaction-to-fire properties of combustible materials in a well-ventilated environment. This method is versatile and widely used in fire safety and provides a series of fire reaction properties, including heat release rate (HRR), time-to-ignition (TTI), smoke density, and yields of CO_2 and CO, to name a few. Cone calorimetry was conducted for both unreinforced and glass fiber-reinforced PA6 and PA6+2%wt Cloisite laminates, using 100×100×3 mm specimens (three per material system) at 50 KW/m^2.

UL-94 Vertical burning test. UL-94 vertical burning tests were performed in an enclosed laboratory hood, free of induced or forced draft during test, according to ASTM D3801. Five specimens for every material were tested, as recommended by the standard. The test consists in applying a small flame to the vertically mounted sample for 10 seconds twice, and measuring the burning time. The other parameters which are recorded for every test are: the mass of the sample before and after the test, whether the flame reaches the top of the sample and whether the cotton is ignited by burning particle drops. Based on the aforementioned data, a material can be classified as VO, V1, V2 and NC where V0 signify the best performance and NC - non classified - to the worst (i.e. highest burning time, cotton ignited, flame up to the top).

IR Spectroscopy. Mid infrared (MIR) spectroscopy was conducted in reflection mode (ATR) on the burnt surfaces of the studied materials.

3. Results and discussion

Table 1 reports the glass fiber content of the studied materials, whereas figure 2 shows the optical micrographs of their cross sectional area. As it is possible to observe, a good glass fiber content was obtained, with the presence of just few voids.

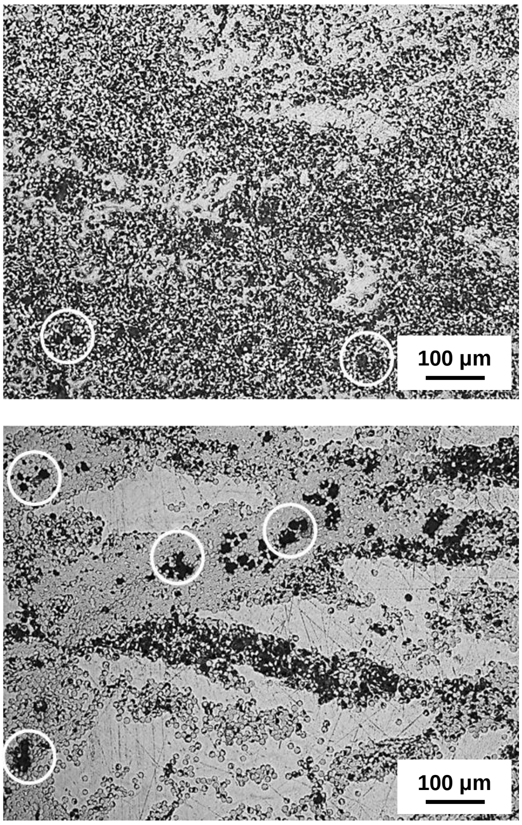


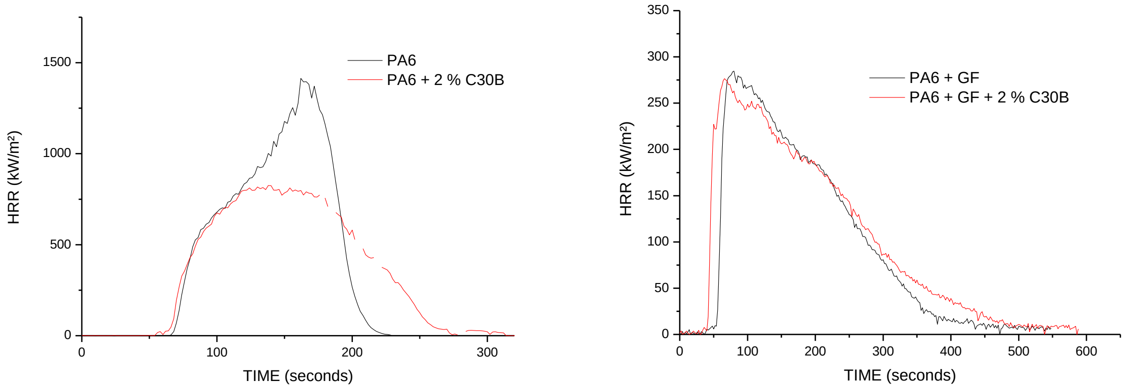
Figure 2. Typical optical micrographs of the microstructure in G/PA6 (top) and G/PA6+2%wt Cloisite (bottom) laminates from Batch 1 (×10). White circles indicate areas with voids.

Material/Method	ISO 3451	ASTM D2584
PA6-GF	53.9%	53.7%
PA6-GF-C30B	50.9%	51.2%

Table 1. Glass fiber volume fraction results.

Figure 3 reports the HRR curves of all the studied materials. Figure 3a shows the results of the unreinforced systems, whereas figure 3b reports the curves of the glass fiber reinforced ones. It is clear in the case of the unreinforced systems that the effect of nanoclay is very significant, with a reduction of about 50% of the HRR peak for the nanoclays doped material. However, the same effect is not visible in the tests with the reinforced systems, where the peak HRR is similar for the two materials.

It is to be noticed that the shape of HRR curve of PA6 is modified by the presence of the clay (Figure 3a), from “intermediate thick non charring” behavior to “thick charring” that is typical of polymers which on burning produce a thermally stable protective surface due to accumulation of thermally stable combustion residues [12]. In the case of PA6-clay, the stable residue is the clay surface layer left by polymer combustion. In the case of the glass fiber PA6 composite the “thick charring” behavior is displayed due to the protective glass fiber layer produced by polymer combustion which overrides the effect of the clay (Figure 3b).



(a) **(b)**

Figure 3. HRR curves for the studied materials. (a) unreinforced and (b) glass fiber renforced PA6 and PA6-doped.

Table 2 reports the results of UL94 vertical burning test. It can be seen from the decrease of the total combustion time and of burnt material, and on the lower number of totally burnt samples, that clay improves fire retardant performance significantly for both PA6 and GF-PA6

Material	Total burning time (t1+t2) (s)	Residual mass (%)	Afterflame up to the holding clamp	Cotton indicator ignited by flaming particles or drops	UL-94 Classification
PA6	256 ± 177	38 ± 41	2/5 samples	5/5 samples	NC
PA6+C30B	35 ± 13	87 ± 5	0/5 samples	5/5 samples	NC
PA6+GF	227 ± 20	80 ± 2	5/5 samples	0/5 samples	NC
PA6+GF+C30B	146 ± 40	92 ± 7	2/5 samples	0/5 samples	NC

Table 2. UL94 results.

There is thus a significant difference in the effect of the nanoclay on the fire behavior depending on the presence or not of glass fibers, in a test in which the sample is continuously subjected to an external heat source (cone calorimeter) and in a test in which the fire is just induced at the beginning and it is then self-fed (UL94).

In order to understand why, a thorough study was planned, based on different techniques. First, two thermocouples were placed on top and bottom of the cone specimen during the test, in order to monitor the surfaces temperatures. The top thermocouple was fixed in a way that the hot junction is kept in contact with the sample, until the sample thickness is reduced by the burning process. The typical output is shown in figure 4 for pristine PA6, clearly showing melting, thermal decomposition and ignition processes [13], matching the Heat Release Rate Curve. Figure 5 reports the results obtained for the unreinforced system (figure 5a) and glass fiber reinforced system (figure 5b). In Figure 5b, it can be seen that in the presence of glass fibers, the increase in temperature due to the ignition is not as abrupt as in the case of the unreinforced systems. However, in both unreinforced and GF reinforced systems, no significant difference in time to ignition is visible between the nanoclay-doped and neat matrix.

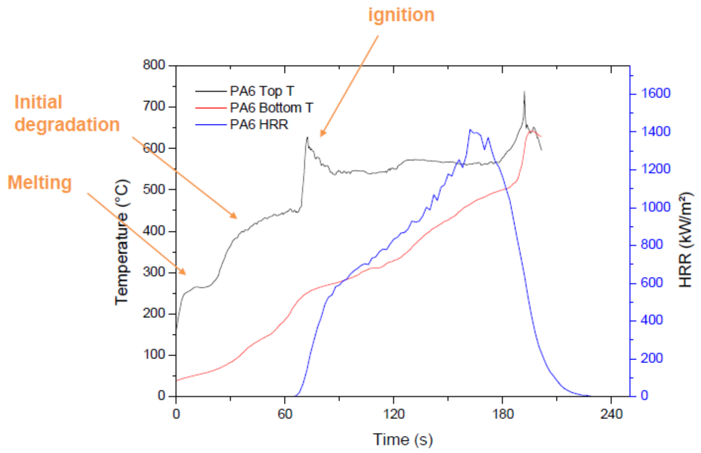


Figure 4. HRR and temperature curves superposition for PA6.

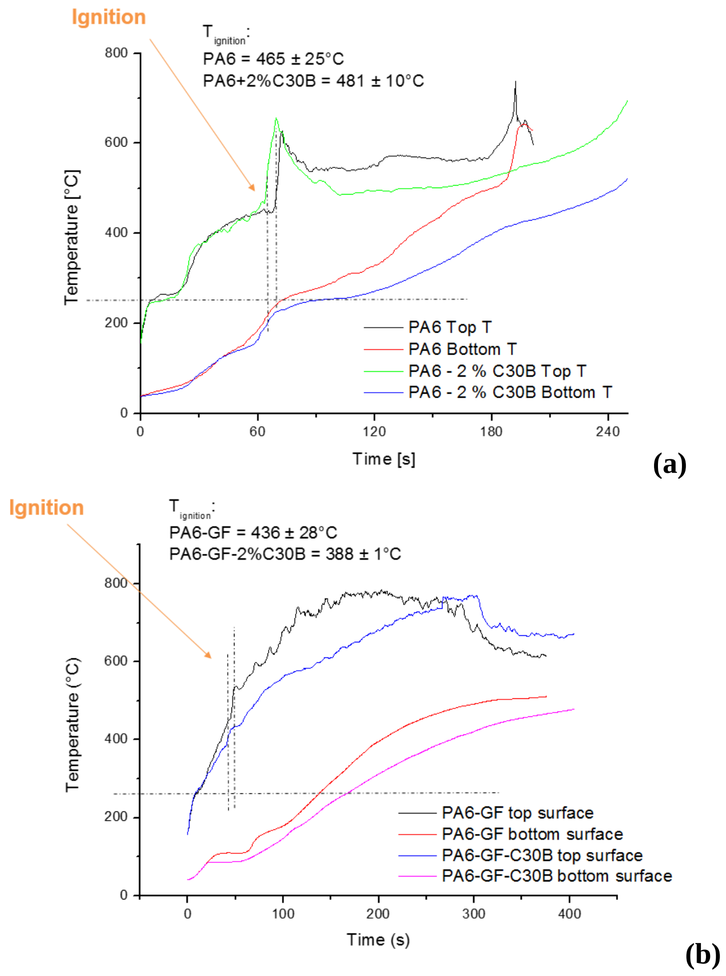


Figure 5. Temperature curves for the studied materials. (a) unreinforced and (b) glass fiber renforced PA6 and PA6-doped.

In order to understand what happens inside the material during cone calorimeter test, from the moment of heat application to ignition, a series of cone calorimeter tests were conducted on the studied materials stopping them just after the ignition. Infrared analysis was performed on the residues. The results are reported in figure 6. In particular, the study was focused on the Si-O-Si stretching vibration, which is present both in the nanoclay and in the glass fibers. As it is possible to observe, in the case of PA6 (figure 6a) there is a clear increase of this peak, which can be related to the accumulation of nanoclay on the surface before ignition. Thus, in the molten polymer, clay lamellas tend to migrate towards the surface for thermodynamic incompatibility with the polymer matrix since the organic modifier is decomposed at this stage. During combustion, clay will further accumulate on the surface owing to polymer ablation due to thermal degradation.

From figure 6b, we can see that, in the case of GF reinforced PA6, the increase of the peak is still present (although less pronounced). Nonetheless, the same increase was observed even in the GF-neat PA6 samples (not shown here). This can be taken as an evidence that the protection supplied by glass fibers residual from combustion is effective and that clay added to the polymer matrix either cannot migrate to the surface because of the glass fibers barrier or that the contribution to protection from the clay is insignificant.

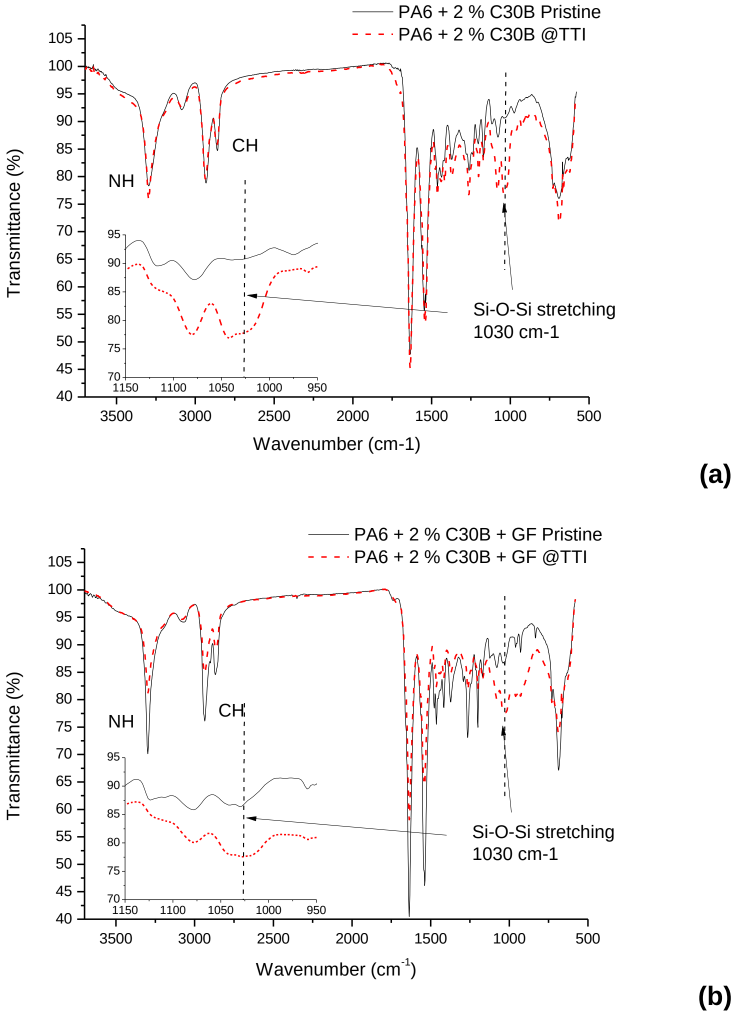


Figure 6. IR spectra of the studied materials before and after the cone induced ignition. (a) unreinforced and (b) glass fiber renforced PA6 and PA6-doped.

Conclusions

The obtained results can be summarized as follows. The most important contribution of the nanoclay in improving the fire performance of the PA6 is in the formation of a protective surface layer in front of the heat source. In the case of the fiber reinforced PA6, it is proposed that the protection is provided by the glass fibers themselves and it is seen that the effect of the clay is insignificant in cone calorimeter tests at 50 kW/m^2 heat flux. In the case of vertical burning test (UL-94), when the flame is self-fed, the clay can still act as a flame propagation inhibitor.

Acknowledgement

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