Original article

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Mechanical and flammability properties of a polyamide 6,6 nanocomposite for nonstructural marine engine components

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Abstract: The actual replacement of traditional metallic components with plastic-based materials in the marine sector is currently extremely limited, mainly due to mechanical requirements and flammability issues. In this work, a fiberglass-reinforced polyamide 6,6 matrix, loaded with innovative flame retardants based on nanosized organoclays has been evaluated as a replacement for aluminum in a marine engine cover. Experimental data were acquired to assess the mechanical performances and flammability properties of this novel polymer nanocomposite in comparison with those of a commercial sample based on the same polymeric matrix loaded with traditional flame retardants. The results showed that then use of nanoclays in place of standard flame retardants increased the mechanical properties of the polymer nanocomposite at all tested temperatures (22% of modulus increase at 20 °C, 93% at 110 °C), concomitantly meeting the minimum nonflammability requirements (self-extinguishing, without dropping of flammable material).

Keywords: flame retardance; mechanical properties; nanocomposites; polyamides.

1 Introduction

Nowadays, most of the components of endothermic engines are made of metal alloys. Nonetheless, aiming at cost and weight reduction, naval sector is looking for new, high-performance materials for nonstructural components of marine engines. Reinforced polymeric materials can be envisaged as a possible substitute for metal alloys. Currently, the use of plastic materials in the marine sector is extremely limited, mainly due to the severe operating conditions both in terms of environmental parameters (e.g., temperatures, contact with chemical agents) and in terms of mechanical forces involved. Moreover, the International Maritime Organization (IMO) denies the use of combustible materials in machinery areas *a priori*; thus, noncombustibility tests have to be carried out to verify materials behavior as regards to flammability according to Fire Test Procedure (FTP) code. Moreover, the provisions of the UL-94 standard for the flammability of plastic materials can also be considered [1–3]. Currently, the most used composites in marine applications are thermosetting-based materials for structural applications [4]. In the case of nonstructural components, the cost of high-performance thermosetting polymers is still too high to justify market penetration. On the other hand, thermoplastic composites reinforced with short discontinuous glass fiber can be processed by fast and cost-effective injection molding technology, allowing to produce cheaper components with good mechanical properties, corrosion resistance and lower weight with respect to metal-based components [5–7]. In this work, a real component for the marine sector (a marine engine cover, currently produced with aluminum) has been developed and characterized. A preliminary analysis of current rule framework and finite element simulations of a specific case (working condition of a cylinder head cover in a four-stroke marine engine) were carried out in our previous work [8]. Following these preliminary, computational-based results, we proceeded to acquire real experimental data under the same basic requirements for the cover material:

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flexural elastic limit >0.4 MPa; service temperature 50–80 °C (maximum working temperature 110 °C); nonflammability or self-extinguishing capacity (at least V0 or V1 according to UL-94 classification). A literature review in combination with CES Selector software and the Ashby method [9, 10] identified reinforced Polyamide 6,6 (PA66) as a suitable candidate. This compound meets all the requirements except for flammability, and appears to be the best compromise between strength-to-density ratio and price. Polyamide resins are extensively used in injection molded and extruded parts for engineering applications, thanks to their good mechanical properties [11–14]. PA66 can be successfully reinforced by glass fibers (GFs) and other inorganic additives. Short fiber composites are particularly appealing since they show better mechanical properties with respect to the unreinforced matrices, while being reshapeable, recyclable and easier to process than continuous, long fibers laminates [15]. Addition of GFs to a PA66 matrix results in a remarkable increase of flexural modulus E_F and flexural strength σ_F [9]. To comply with nonflammability requisite, flame retardants (FRs) have also to be added to the matrix. Regrettably, introducing FRs into PA66-GF composites negatively affects both their E_F and σ_F values, even if these quantities are still higher than those predicted for the unreinforced material [9]. As mentioned above, the limit of thermoplastic polymer composites is their low flame resistance; in fact, these materials typically burn easily and, as such, are classified as “high burning” in UL 94 tests. Nevertheless, there are several flame retardants additive that allows for important improvements in flame performance of polymer-based materials. The main limitation of these flame-retardant traditional additive, however, is the cost. Nano-engineered montmorillonites (MMTs) or “nanoclays” can be regarded as a valid alternative to traditional FRs in this situation. Layered silicates (known as “clays”) are commonly used as fillers to improve many materials properties [13, 16]. “Nanoclays” are defined as inorganic clay sheets with at least one dimension in the nanometer range [17–19], intercalated by organic chains [20]. In the late 80s’ – early 90s’ Toyota researchers were the first to develop polyamide-montmorillonite (PA-MMT) nanocomposites [21, 22]. As the interfacial area between the PA matrix and the nanoscaled dispersed particles was dramatically increased, these nanocomposites exhibited enhanced mechanical properties with respect to conventional polymer composites [12, 20, 23]. Notably, the flame-retardant characteristics of PA-MMT nanocomposites improved as well [20]. The degree of exfoliation of the nanoclays in the polymer matrix has a direct effect on the modulus and the strength of the resulting nanocomposite [12]. Early works reported on fabrication of these class of nanocomposites via in situ polymerization

[21, 22]; later efforts showed the possibility to produce such nanosystem by melt compounding [24, 25], which is a preferable method for commercial purposes. Our earlier computer-based results [8] showed that it is possible to save about 50% of a marine engine cover weight by replacing the currently adopted aluminum-based cover with one made of PA66 reinforced with glass fibers and nanoclays. To confirm these simulation findings, in this work we measured and compared the mechanical performances and flammability properties of PA66-based materials loaded with a fixed amount of GFs (30%) and with different FRs (i.e., no FR, a traditional FR, and a nanoclay-based FR). Furthermore, we used these materials to fabricate cover prototypes by injection molding as shown in Figure 1. Samples from these prototypes were finally employed to compare the performances of the commercial and the experimental nanocomposite in processed parts.

2 Materials and methods

2.1 Materials

Table 1 summarizes the materials analyzed in this work. Three different compounds were evaluated: two commercially available formulations from Vamptech (“Denyl-66” and “Vampamid-66”, Vamp Tech SpA, Busnago, Italy) and one compound modified with

Figure 1: Cover prototype.

nanosized organoclays (“Nanto-MMT”, Nanto Protective Coating, Trieste, Italy). Denyl-66 is composed of PA 66 with 30% GFs. Vampamid-66 is composed by PA66 with 30% GFs and halogen-based FRs. According to the relevant technical datasheet, this material is ranked “UL-94 V0” with respect to its flame-retardant ability. Nanto-MMT was obtained by melt compounding Denyl-66 (85%) with nanosized organoclays (5%) and phosphate-based FRs (10%). Nanoclays (average platelet size: 110 nm; cation exchange capacity: 140 meq/100 g) were obtained from high-grade bentonite (98% purity) functionalized with octadecylamine to enhance the degree of exfoliation and favor the proper orientation of the platelets inside the hosting polymeric matrix.

2.2 Sample preparation

Two different typologies of samples were prepared: test samples and prototype samples. Test material specimens (Denyl-66, Vampamid-66 and Nanto-MMT) were obtained directly in the final dimension required by mechanical testing (nominal thickness $h = 4$ mm; nominal width $w = 10$ mm, nominal length $l = 80$ mm) via injection molding. Prototype marine engine covers in real dimensions (Vampamid-66 and Nanto-MMT) were realized through injection molding with a BMB 1400 injection machine (BMB SpA, Italy). Melting temperature was set to 280 °C, while mold temperature was 80 °C. Prototype samples were then roughly cut directly from the prototype covers with a GMT12JL power tool (Robert Bosch GmbH, Germany) and then adjusted to final dimensions by an MS20 moto-saw (Dremel, USA). For the preparation of Nanto MMT materials, a preliminary step was required consisting of melt blending between nanoclays and glass-reinforced PA-66 in order to achieve a good nanofiller dispersion. This step was a key point to allow for proper interaction between the inorganic filler and the organic polymeric chains. Lab-scale material melt-blending was performed with Xplore 15 twin-screw corotating microextruder (DSM BV, the Netherlands) operating at 150 rpm, with a 260–275–285 °C temperature profile, whereas for the prototype material melt blending was performed with an APV MPX30 twin-screw counter-rotating extruder (Baker Perkins Ltd, UK) operating at 350 rpm, with a 270–260–250 °C temperature profile.

2.3 Mechanical characterization

Flexural properties were determined on test samples according to ISO 178 using an AGS-X dynamometer (Shimadzu Corporation, Japan) equipped with a temperature-controlled chamber. All test samples were subjected to three-point bending at a crosshead speed of

2 mm/min, with a span $L = 16$ h. Furthermore, test samples of Denyl-66 were mechanically tested at 20 and 110 °C, while the mechanical behavior of Vampamid-66 and Nanto-MMT was investigated at 20, 50, 65, 80 and 110 °C to fully assess their performances at different temperatures. Prototype samples were tested at room temperature only. Flexural modulus E_F was determined from the slope of the initial linear portion of the stress-strain ($\sigma - \epsilon$) curve. Flexural strength σ_F was determined as: (a) the σ value at conventional deflection or (b) the σ value at the breaking point (when the sample broke before reaching the conventional deflection). According to ISO 178, conventional deflection as the deflection equal to 1.5 h. With $L = 16$ h, this corresponds to a flexural strain $\epsilon = 3.5\%$. Impact properties were determined at room temperature according to ISO 179-1 with a Charpy CEAST 6540 (Instron, USA - hammer energy: 15 J; un-notched sample; flatwise direction), on five samples for each composition (test samples: Denyl-66, Vampamid-66 and Nanto-MMT; prototype samples: Vampamid-66 and Nanto-MMT).

2.4 Flammability tests

Flammability tests were performed on five samples for each composition (nominal dimension $125 \times 12 \times 3.2$ mm) according to UL-94 standard. Briefly, a flame (Versaflame Butane Torch, Dremel, USA) was applied to the sample edge for 10 s (flame was applied once for horizontal tests, twice for vertical tests); after flame removal, the burning time and flame speed was recorded and the material therefore categorized. According to the UL-94 standard, materials were ranked “HB” (slow Horizontal Burning) if the burning rate was less than 3"/min or stopped burning before the 5" mark; “V2” or “V1” (Vertical burning 2 or 1) if burning stopped within 60 s, with flaming drips allowed (V2) or flaming drips not allowed (V1). The “V0” ranking (Vertical burning 0) required burning stop within 10 s, with flaming drips not allowed.

3 Results

3.1 Mechanical properties

Stress-strain curves of Denyl-66 and Vampamid-66 test samples at room temperature and 110 °C are shown in Figure 2, from which the typical stress–strain curves of reinforced materials characterized by high strength levels and low deformation capabilities can be observed. The corresponding flexural properties (E_F , σ_F and ϵ_F) for these two test samples are gathered in Table 2. At room temperature, these materials show values of E_F and σ_F in line with those predicted for PA66 reinforced with GFs ($E_F = 6.4\text{--}7.6$ GPa; $\sigma_F = 180\text{--}290$ MPa) and PA66 reinforced with GFs and traditional FRs ($E_F = 4.2\text{--}5.1$ GPa; $\sigma_F = 75\text{--}124$ MPa), respectively [9]. As expected, both at room temperature and at 110 °C Vampamid-66 has lower E_F and σ_F with respect to Denyl-66. The typical stress–strain curves for Vampamid-66 and Nanto-MMT test samples are shown in Figure 3, while the relevant flexural properties of the same

Table 1: The three different PA6,6-based composites analyzed in this work.

Material (trade name)	Characteristics
Vamptech Denyl-66 3010 T	PA 66, 30% glass fibers reinforced
Vamptech Vampamid-66 3026 V0 40 MF	PA 66, 30% glass fibers reinforced, halogen flame retardant
Nanto MMT	Realized by melt compounding 85% Denyl-66 with 5% nano-sized organoclays and 10% phosphate-based flame retardants

test samples at different test temperatures are reported in Table 3 and Figure 4. As seen from Table 3, the registered values of E_F and σ_F decrease with increasing testing temperature for all samples; nevertheless, Nanto-MMT additives grant better performances at all tested temperatures. The comparison of flexural properties for test vs. prototype Vampamid-66 and Nanto-MMT samples at room temperature is reported in Table 4. It is possible to notice that there is no difference in the average value for Vampamid-66: only a slight decrease in the value of E_F for prototype samples can be recorded, while the standard deviation for prototype samples is higher. Conversely, for the Nanto-MMT prototype samples, both E_F and σ_F average values decrease considerably with respect to test samples values, and standard deviation rises substantially. This points out an influence of the processing step conditions used for the preparation of test samples compared with prototype ones. It is well demonstrated in literature [20–22, 26] that the performance of nanocomposites is strictly related to their processing conditions and to the nanofiller dispersion level achieved during the blend melting. Thus, according to the results shown in Table 4, it can be assumed that during the preparation of Nanto-MMT materials using the lab scale extruder the proper control of processing conditions was obtained. On the other hand, as scaling up the production of Nanto-MMT at a pilot plant level required a modification in processing conditions and parameters, the same level of control could not be completely attained. It can be reasonably concluded that the higher and fine control of the processing conditions and parameter in the microextruder allowed to achieve a better dispersion of nanoclays in the polymeric matrix in comparison to that obtained at the pilot scale. A less homogeneous dispersion of the nanoclays in the Nanto-MMT prototype caused a higher standard deviation in the experimental results in relation to the position of the cut on the prototype cover. The impact strength of Denyl-66, Vampamid-66 and Nanto-MMT are reported in Table 5. For test samples, it can be observed that toughness

decreases remarkably from Denyl-66 (PA-66 30%GFs) to Vampamid-66 (PA-66 30%GFs + FRs) samples, suggesting that commercial FRs cause an embrittlement of the nanocomposite. Nanto-MMT test samples, on the other hand, show impact strength values higher than Vampamid-66, prompting for a less pronounced effect of Nanto FRs on embrittlement with respect to commercial FR-based compounds. Nevertheless, by carefully comparing test and prototype samples, only a slight decrease of impact strength value for Vampamid-66 can be observed, while the values of the same quantity recorded for Nanto-MMT prototype samples is roughly halved with respect to the relevant test samples. This is in line with the results previously achieved in flexural tests and can be ascribed to the same reasons discussed above, *i.e.*, the influence of the processing step conditions used for the preparation of test samples respect to prototype samples, and nanoinclusion dispersion level achieved during blend melting [20–22, 26].

3.2 Flammability

The flammability classification of all examined materials is reported in Table 6. Accordingly, Denyl-66 is ranked as UL-94 HB and, as expected, does not comply with non-combustibility requirements. Vampamid-66, thanks to the added commercial FRs, complies with noncombustibility requirements (UL-94 V0). Interestingly, although Nanto MMT features a longer burning time after flame removal, it can be still self-extinguishing without dropping flammable material (UL-94 V1).

4 Discussion

The experimental findings reported above clearly show the advantage of using nanoengineered montmorillonites (nanoclays) in the place of commercial halogen-based

Figure 2: Stress-strain curves of Denyl-66 and Vampamid-66 (test samples) at (a) room temperature; (b) 110 °C.

Table 2: Flexural properties of Denyl-66 and Vampamid-66 test samples.

Flexural properties (test samples)						
T (°C)	Denyl 66			Vampamid 66		
	E_F (GPa)	σ_F (MPa)	ε_F (%)	E_F (GPa)	σ_F (MPa)	ε_F (%)
20	7.5 ± 0.3	196.2 ± 0.1	3.1 ± 0.1	5.0 ± 0.1	81.2 ± 0.9	2.5 ± 0.1
110	3.5 ± 0.1	90.2 ± 1.1	5.9 ± 0.5	1.8 ± 0.1	29.3 ± 0.9	–

Figure 3: Stress-strain curves of test samples: Vampamid-66 (a) and Nanto-MMT (b) at different temperatures.

Table 3: Flexural Vampamid-66 and Nanto-MMT (test samples) at different temperatures (T).

T (°C)	Flexural properties (test samples)			
	Vampamid 66		Nanto MMT	
	E_F (GPa)	σ_F (MPa)	E_F (GPa)	σ_F (MPa)
20	5.0 ± 0.1	81.2 ± 0.9	6.1 ± 0.2	121.6 ± 3.6
50	2.7 ± 0.1	51.1 ± 0.5	4.6 ± 0.1	82.6 ± 0.4
65	2.3 ± 0.1	43.1 ± 0.6	3.7 ± 0.1	63.2 ± 1.7
80	1.8 ± 0.1	35.5 ± 0.8	3.6 ± 0.1	60.6 ± 0.4
110	1.8 ± 0.1	29.3 ± 0.9	3.1 ± 0.1	43.2 ± 1.4

flame-retardants in glass-fiber reinforced PA66. Indeed, for Nanto-MMT not only the minimum noncombustibility requirements were met but also the relevant mechanical

properties increased with respect to the alternative commercial FR-based compounds. It is known that both stiffness and strength of PA-66 increase with nanoclays loading [16, 25–27]. Properly dispersed nanoclays are very effective in enhancing the mechanical behavior of the corresponding polymer-based nanocomposites: e.g., with respect to glass-fibers, the same increase in mechanical moduli requires—by weight—approximately one third of nanofillers content [16]. It is reported that the addition of nanoclays leads to an increase in flammability time; this is attributed to the stacking effects of the platelets, which creates a physical barrier on the material surface and within the bulk material itself [28, 29]. Here, it was further shown that these properties were obtained by means of melt compounding a commercial PA-66 30%GF with long-chain amine-functionalized nanoclays. The mechanical

Figure 4: Flexural elastic modulus (a) and flexural strength (b) of Vampamid-66 and Nanto-MMT (test samples) as a function of temperature.

Table 4: Flexural Vampamid-66 and Nanto-MMT at room temperature: comparison between test samples and prototype samples.

	Flexural properties (test vs prototype samples)			
	Vampamid 66		Nanto MMT	
	E_F (GPa)	σ_F (MPa)	E_F (GPa)	σ_F (MPa)
Test samples	5.0 ± 0.1	81.2 ± 0.9	6.1 ± 0.2	121.6 ± 3.6
Prototype samples	4.6 ± 0.4	80.1 ± 4.8	5.0 ± 0.1	100.4 ± 23.5

Table 5: Impact strength of Denyl-66, Vampamid-66 and Nanto-MMT.

	Impact strength (kJ/m ²)		
	Denyl 66	Vampamid 66	Nanto MMT
Test samples	41.0 ± 2.2	15.9 ± 0.5	23.9 ± 0.7
Prototype samples	–	13.2 ± 1.8	11.4 ± 0.5

Table 6: UL-94 flammability tests results for all materials considered.

Material	Flammability classification (according to UL-94)
Denyl-66	HB – slow burning
Vampamid-66	V0 – after flame burning time <10 s, no flaming drops
Nanto-MMT	V1 – after flame burning time <30 s, no flaming drops

properties of Nanto-MMT test samples are superior to those of Vampamid-66 test samples in terms of E_F , σ_F and impact strength. The comparison between Nanto-MMT test samples and prototype samples pointed out a decrease in performance of the latter, while the properties of Vampamid-66 prototype samples remained in the same range of test samples. This is mainly related to the optimal processing conditions reached with the lab scale micro-extruder compared with the pilot scale one. Nevertheless, it is expected that, during the scaling up to industrial extruder, an optimization of the screw profile and processing condition could compensate and adjust the loss of performance, obtaining a proper dispersion of the platelets inside the polymer matrix. It is known from the literature [16, 23] that modified nanoclays can act as flame retardant agents working in synergy with traditional FRs. Under this assumption, small amounts of nanoclays together with reduced amounts of traditional FR (e.g., less than 15% w/w phosphate-based FR) can achieve the same flammability properties of a higher amount of traditional flame retardant (generally halogen-based flame retardants used in an

amount $\geq 30\%$ w/w). The present work clearly demonstrates that, for PA-66 30%GF composites, a 5% w/w nanoclay loading synergistically interact with the 10% of phosphate-based added FR to obtain V1 flammability behavior. It is expected that a V0 level can be reached considering one of the following options: (1) optimizing the dispersion of the nanoclays and the phosphate-based fire retardant in the polymer during blending, and (2) changing the phosphate-based FR using the same amount of a melamine-based FR.

5 Conclusions

In this work, the mechanical and flammability properties of commercial PA-66 30% GF samples containing traditional flame retardants were compared with those of a PA-66 30% GF compounded with a nano-engineered FR based on montmorillonites. Experimental data showed that the use of nanoclays instead of traditional FRs led to increased flexural modulus (from 22% at 20 °C to 93% at 110 °C) and flexural strength (from 50 to 70%) of the corresponding PA66-GF reinforced plastics in a wide range of temperature, while preserving the minimum non-combustibility requirements (self-extinguishing, without dropping of flammable material). Remarkably, besides being more environmentally compatible, the use of nanoclays is also cost-effective; indeed, traditional FRs are very expensive and generally used in high amount in order to achieve the required flammability resistance. This study clearly demonstrated the possibility to partially substitute traditional expensive FRs with innovative and cheaper nanoclays, with a positive effect also on mechanical performance.

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