

MECHANICAL PROPERTIES OF THREE-PHASE POLYAMIDE 6 NANOCOMPOSITES

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ABSTRACT

This work focus on the mechanical properties of three-phase nanocomposites using multiscale reinforcements. The influence of the nano-fillers content, as well as the temperature were studied. Polyamide-6 reinforced with short glass fibre 30 wt.% and with an addition of nanoclay (montmorillonite) and/or nanosilica (SiO₂) were tested in order to characterise their tensile properties at room temperature and at 65°C just above the polyamide 6 glass transition temperature. SEM analysis were conducted on the fracture surface of the tensile bars. SEM investigations showed the importance of the interaction matrix/filler for the material behaviour. Our study also shows that the increase of OMMT percentage in polyamide-6/glass fibre composite made the material more brittle and had a negative effect on the tensile properties. Further, for the silica-based nanocomposites, an optimum was found for a nanofillers content of 1wt.%.

Keywords: Three-Phase Nanocomposites, Polyamide-6, Impact.

1 INTRODUCTION

Nanomaterials are one of the promising technologies of this century. Layered silicates nanocomposites represent more than 50% of this annual consumption, and carbon nanotubes composites 21%. According to the Project on Emerging Nanotechnologies inventory, in March 2011, there were 1317 consumer products based on nanotechnology on market (PEN, 2011).

Nanocomposite materials are an attractive technology because using nano-fillers allows great improvements of the polymeric materials compare to micro-reinforcement, and suit to the goals of industries: produce lighter, thinner, stronger and cheaper structures (Njuguna *et al*, 2008). The nano-size of the fillers increases the area of contact between matrix and filler and so, reduces stress concentration around the filler. Also, the nano-size presents a very large surface area to volume ratio. For example, it augments the surface area to volume ratio up to 10³ times for a nanofiber compare to a microfiber (Njuguna *et al*, 2008). It is also significant to note that only 5 wt.% of nanofillers can significantly improve behaviour and properties of a neat polymer (Duval, 2008), compared to at least 20wt.% with glass fibre reinforcement, which allows a reduction of weight and cost.

Among all the properties enhanced thank to nanofillers, we can cite: strength, stiffness, heat-distortion temperature, scratch resistance, thermal, oxidative and dimensional stability, water and thermal permeability, corrosion resistance, surface hardness, barrier properties, flame retardancy and electrical conductivity (Schmidt *et al*, 2002; Garcés *et al*, 2000).

Some studies had focused their research on the influence of modified or unmodified clay on polymer nanocomposites' properties (Jimenez *et al*, 1997; Liu *et al*, 2003; Yu *et al*, 2004; Mishra *et al*, 2009; Zhao *et al*, 2010). For example, enhancement of mechanical properties of nanocomposites and three-phase nanocomposites are often confirmed. Mishra *et al*. (2009), had shown that Young modulus, tensile strength and elongation at break are increasing with the augmentation of organically modified montmorillonite (OMMT) content (until 3 wt.%) into a polyamide-66 matrix. Silva *et al*. (2012), reported an increase of 32% for the elongation at break for a 30wt.% glass fibre/polyamide-6 filled with 2wt.% of SiO₂ nanoparticles, compare to a classical polyamide-6/glass fibre. Wu *et al*. (2001) found that a polyamide-6/clay with 30wt.% of glass fibre had an enhanced tensile strength of 11% and a tensile modulus enhancement of 42% compared to polyamide-6/30wt.% glass fibre. Further, several parameters were demonstrated to have an influence on these mechanical properties (stiffness, modulus): interaction between the matrix and the fillers (Njuguna *et al*, 2011), fillers' size (Ng *et al*, 1999), fillers' volume fraction (Yang *et al*, 1998), and filler's shape (Garcés *et al*, 2000).

Others advantages are the cost which is low considering that only a small amount of filler is necessary, and the ease of manufacture without need to change the conventional processing conditions in order to manufacture new products (Njuguna *et al*, 2008).

2 MATERIALS AND METHOD

2.1 Materials and samples preparation

For this study, two types of three-phase nanocomposites were produced: polyamide-6 (Durethan B30) reinforced by 30% of glass fibre (ThermoFlow672) and particles of SiO₂ (Aerosil R 974), and polyamide-6 reinforced by 30 wt.% of glass fibre and montmorillonite (Dellite 43B, Laviosa Chemicals). In total, seven materials were manufactured with different content of nano-fillers (Table 1). The nano-materials were obtained by direct melting and extrusion in a twin-screw extruder at a maximum temperature of 280°C. The product was cooled in a water bath, pelletized and then dried. From granulates, test samples (crash cones, tensile bars and plates) were injected moulded according to the ISO 527 test standards.

Table 1: Composition of the different studied nanocomposites.

	Type of Matrix	wt.% of PA6	Type of Glass Fibre	wt.% of GF	Type of filler	wt.% of filler
HZ12-01	Durethan B30	65	ThermoFlow 672	30	Dellite 43B	5
HZ12-02	Durethan B30	62.5	ThermoFlow 672	30	Dellite 43B	7.5
HZ12-03	Durethan B30	60	ThermoFlow 672	30	Dellite 43B	10
HZ12-04	Durethan B30	69	ThermoFlow 672	30	Aerosil R 974	1
HZ12-05	Durethan B30	69.5	ThermoFlow 672	30	Aerosil R974	0.5
HZ12-06	Durethan B30	68.5	ThermoFlow 672	30	Aerosil R 974	1.5
HZ12-07	Durethan B31	67	ThermoFlow 673	30	Aerosil R 974	3

2.2 Mechanical testing

Tensile tests, according to the ISO 527 standard were performed in the INSTRON 5500R electro-mechanical tensile-compression machine. Five specimens (flat dumb-bell type A), by materials and temperature, were tested at a speed of 1mm/min. The load was measured with a 100kN load cell and the longitudinal displacement with a laser extensometer. An environmental chamber was used in order to carry out the test at 65°C.

2.3 Scanning Electron Microscopy

The fracture surface of the tensile bars, tested at room temperature and at 65 °C, was analysed with a scanning electron microscope (FEI XL 30) in order to understand the failure mechanism and the relation between the matrix and the filler. The samples were previously coated with gold and palladium.

3 RESULTS AND DISCUSSION

3.1 Tensile properties

Effect of the filler's type

In this work, tensile properties of polyamide-6/glass fibre nanocomposites were investigated. Figure 1 represents the tensile stress vs tensile strain curves for the OMMT-based nanocomposites (graph on the left), and for the silica-nanocomposites (graph on the right). For both filler types, the materials showed a behaviour corresponding to a brittle material without yield point. However, we clearly see that the choice of the filler integrated to the polyamide-6/glass fibre composite, is an important factor. The polyamide-6/glass fibre/OMMT deformed less, the stress vs strain curves report a brittle behaviour with only elastic deformation. Whereas, the SiO₂-nanocomposites were less brittle, the curves present a beginning of plastic deformation before breaking. It is also important to note that OMMT-based composites is stiffer than the silica-based ones. However, the SiO₂-nanocomposites present an ultimate strength and strain at break significantly higher than the MMT-nanocomposites.

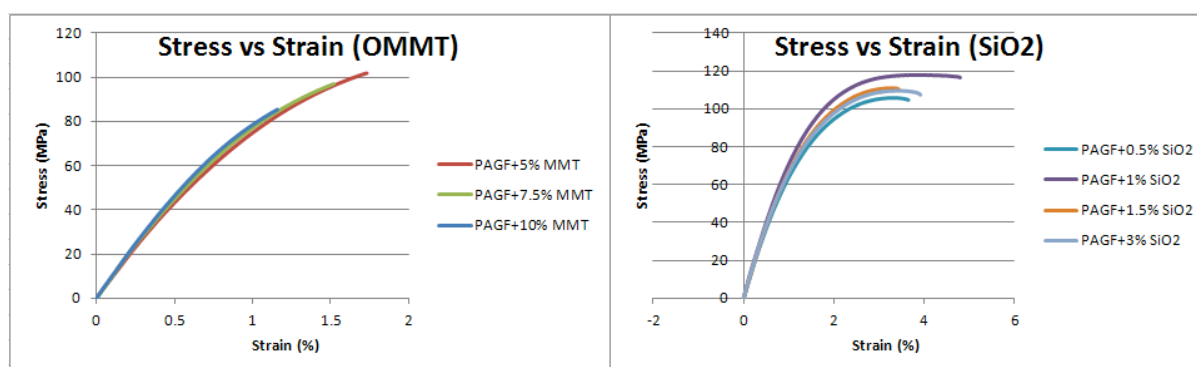


Figure 1: Tensile stress vs tensile strain curves for polyamide-6/glass fibre/OMMT and Polyamide-6/Glass Fibre/SiO₂ at different contents.

Effect of the fillers' content

The main results of the tensile tests for OMMT-nanocomposites are listed in Table 2. At room temperature, with increasing OMMT concentration the Young's Modulus was improved. But, at the same time, the material was less able to resist high load and consequently deformed. Further, it broke at lower stress and strain values as the material became more brittle. These results can be explained by the high content of nanofillers. Akkapeddi (2000), found that above 7 wt.% of nanoclay, polyamide-6 nanocomposites tend to present more fillers aggregates, and he suggested to use a nano-content inferior at 5 wt.% in order to avoid these agglomerates. This can as well give a suitable explanation for the big difference found for the tensile strain at break between a nanocomposite filled with 2 wt.% of nanoclay and the ones filled with a percentage superior to 5wt.%.

Table 2: Tensile properties of the OMMT-nanocomposites at room temperature and 65°C.

	Percentage of Nanofillers	Young's Modulus (GPa)		Tensile Strength (MPa)		Tensile Strain at break (%)		Reference
		RT	65°C	RT	65°C	RT	65°C	
PA + GF + MMT	0%	6.92	-	116.2	-	5.2	-	Silva <i>et al.</i> 2012 Silva <i>et al.</i> 2012
	2%	7.61	-	109.7	-	5.1	-	
	5%	9.15	3.56	101.8	60.64	1.73	4.45	
	7.5%	9.69	3.82	96.9	56.83	1.52	4.08	
	10%	9.76	4.67	85.4	56.03	1.16	3.89	

The silica-nanocomposites were prepared at low content of nanofillers (between 0.5 and 3wt.%). Results of the tensile tests for SiO₂-nanocomposites are presented in Table 3. At room temperature, we could see that the material which has the best properties is the glass fibre filled polymer with 1 wt.% of nano-SiO₂. It was the only nanocomposite which shows an improvement in both the tensile strength and the modulus compared to glass fibre/polyamide-6, and it had the higher tensile strain at break. These results are in line with the findings of Zhou *et al.* (2008), for nano-silica/polypropylene composites. They reported an optimum between 0.4 and 0.8 vol.% of SiO₂, according to the treatment undergone by the filler.

Table 3: Tensile properties of the SiO₂-nanocomposites at room temperature and 65°C.

	Percentage of Nanofillers	Young's Modulus (GPa)		Tensile Strength (MPa)		Tensile Strain at break (%)		References
		RT	65°C	RT	65°C	RT	65°C	
PA + GF + SiO ₂	0%	6.92	-	116.2	-	5.2	-	Silva <i>et al.</i> 2012
	0.5%	7.78	-	105.7	-	3.65	-	
	1%	8.40	3	117.8	73.55	4.79	9.12	
	1.5%	7.95	4.46	110.9	67.83	3.43	7.54	
	3%	7.94	4.78	109.5	66.93	3.91	7.45	

Effect of the temperature

Figure 3 shows the difference between the tensile stress vs tensile strain curves at room temperature and at 65°C for the polyamide-6/glass fibre filled with 5 wt.% of OMMT and the one filled with 1.5wt.% of SiO₂. We can notice that the shape of the curve is similar for the OMMT-nanocomposites and the SiO₂-nanocomposites, even if the values are still lower for the OMMT one.

For OMMT-nanocomposites, the same trend concerning the nanofillers percentage (Table 2) can be noticed at 65°C than at room temperature. However, at this temperature, the material is more ductile than at room temperature which is a typical behaviour for a polymeric material especially when the temperature is above its glass transition. For a polyamide-6 matrix, the glass transition temperature was reported to be between 40°C and 50°C (Nielsen *et al.*, 1994). The modulus is almost halved, the tensile strength is lower, and its strain at break increases by a multiple of 2.5 or more.

The SiO₂-based nanocomposites also behave as a ductile material at 65°C. The tensile strength and strain at break follow the same trend than at room temperature and decrease when the nano-silica percentage increases. However, the modulus increases with the SiO₂ content.

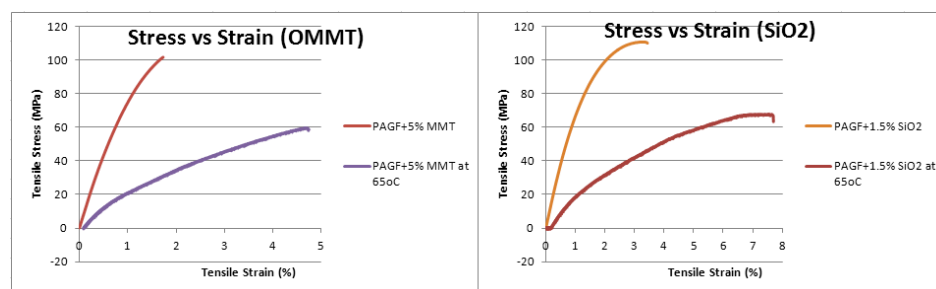


Figure 3: Tensile stress vs tensile strain curves for OMMT-nanocomposites (5 wt.%) and SiO₂-nanocomposites (1.5 wt.%) at room temperature and 65°C.

3.2 Scanning Electron Microscopy

The SEM investigations explain the fracture behaviour of the studied nanocomposites. In the case of OMMT-nanocomposites, at room temperature, we can see a lot of pull-out of the fibre (Figure 4a). The matrix underwent only elastic deformation, and we can notice that the surface is typical from a brittle fracture. However, Figure 4b shows that, for silica-nanocomposites at room temperature, the matrix was plastically deformed. The matrix/fibre adhesion was very strong (Figure 4c), so the glass fibres had to break instead of just pulling-out of the matrix. This explains the higher strength of nano-silica reinforced polyamide.

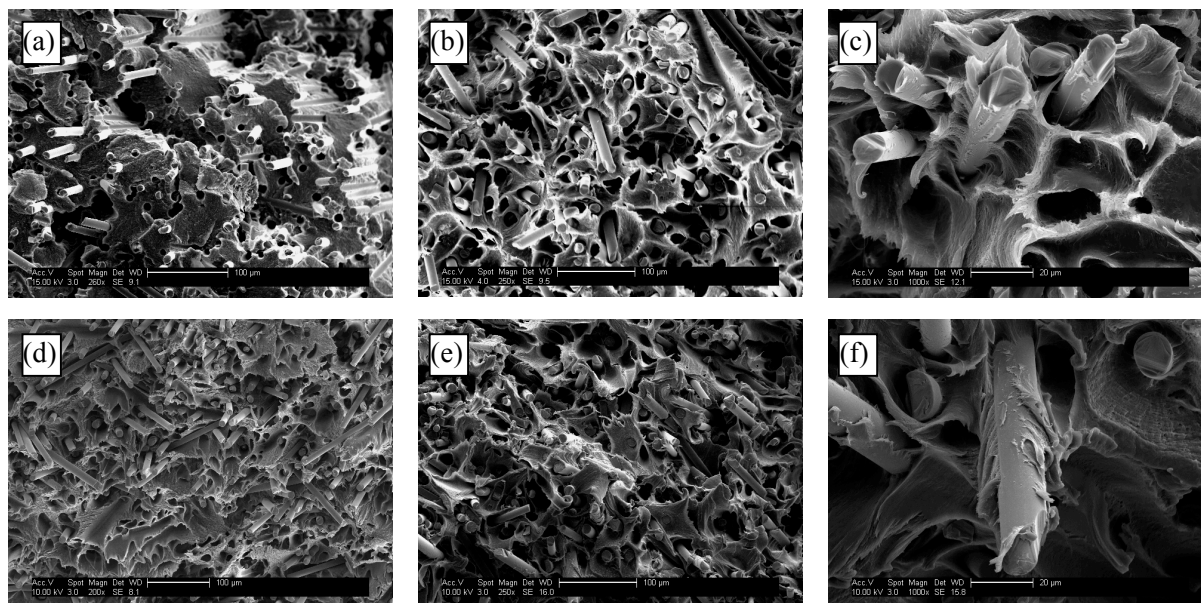


Figure 4: SEM pictures of the tensile fracture surface (a) OMMT-nanocomposite at room temperature, (b) silica-nanocomposite at room temperature, (d) OMMT-nanocomposites at 65°C, (e) silica-nanocomposite at 65°C, and zoom at the glass fibre for silica-nanocomposites (c) at room temperature, and (f) at 65°C.

The fracture surfaces of the tensile bars tested at 65°C for both OMMT and nano-silica composites correspond to a ductile fracture with plastic deformation and drawing of the matrix. We generally noticed more fibre breakage and only few fibre pull-out. However, even at 65°C the fibre/matrix interaction was weak for the OMMT-nanocomposites, as we found only clean fibres. For the nano-silica composites, a lot of matrix' traces were found stuck on the fibre (Figure 4f), which again can explain the higher strength for these materials compared to the composites with OMMT.

4 CONCLUSION

The aim of this study was to identify the effect of the nano-fillers (type and content) on mechanical properties as well as the influence of the temperature. It was shown that the increase of OMMT percentage in polyamide-6/glass fibre composite made the material more brittle and had a negative effect on the tensile properties. It could be explained by the weak interaction between the matrix and the fibres observed thanks to SEM pictures. The high content can as well create nanofillers aggregates and so make the material more brittle. For the nano-silica addition in polyamide-6/glass fibre, the nanocomposites with 1 wt.% of SiO₂ presented the best tensile properties. As for classic polymeric materials, increasing the temperature made all the nanocomposites more ductile. This is confirmed by the SEM pictures which show that for OMMT-nanocomposites, the fracture surface is brittle at room

temperature, and became ductile at 65°C. To general, it can be said that the integration of secondary nanofillers is a good way to enhance the mechanical properties of PA composites, however the percentage and type of filler play a crucial point.

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