



Research paper

Sepiolite as replacement of short glass fibre in polyamide composites for injection moulding applications

Manuel Herrero^{a,*}, Karina Núñez^b, Raúl Gallego^b, Juan Carlos Merino^{a,b}, José María Pastor^{a,b}

^a Department of Condensed Matter Physics, Escuela de Ingenierías Industriales, University of Valladolid, Paseo del Cauce, 59, 47011 Valladolid, Spain

^b Foundation for Research and Development in Transport and Energy (CIDAUT), Parque Tecnológico de Boecillo, 47051 Valladolid, Spain

ARTICLE INFO

Keywords:

Sepiolite
Silane functionalization
Polyamide nanocomposites
Melt compounding
in-situ polymerization

ABSTRACT

Sepiolite polyamide 6 nanocomposites were prepared *via* melt compounding and *in situ* polymerization. The effects of the preparation approach, the amount of the clay and the surface clay modification were evaluated in order to check their influence on morphology, thermal, mechanical and flow behaviour of the final nanocomposites.

Regardless of the preparation method, all nanocomposites showed good dispersion of the sepiolite in the matrix and significant improvements in Young's modulus, tensile strength and heat-distortion temperature were achieved. However, the nanocomposites obtained in one-step by *in situ* polymerization presented slightly better mechanical properties, than the obtained by melt compounding, due to the greater dispersion of the nanoclay within polyamide matrix. Especially interesting were the materials reinforced with modified sepiolite, where the grafting of an aminosilane onto the sepiolite surface produced important increases in the elongation at break and impact values as consequence of the improved stress transfer between the sepiolite and polymer matrix.

Furthermore, nanocomposites with 10 wt% of sepiolite have been compared with higher loaded glass fibre polyamide. The nanocomposites presented similar or even better performances than commercial composites offering an important weight reduction for final applications.

1. Introduction

Ever since polyamide was discovered it has had great influence in the industry. The low cost, the good mechanical performance, its thermal properties, the low specific weight and the ability to be used in complex parts by injection moulding promotes high demand of this material (Kohan, 1995; Aharoni, 1997). Nowadays polyamide is used in several industrial sectors, such as automotive, aerospace, packaging, electrical and electronic and home equipment (DSM Markets, 2017).

To improve the properties and ensure competition with other materials, polyamides should be reinforced in many applications. In order to achieve increases in thermo-mechanical properties high amounts of glass fibre are used as reinforcement. Despite the improvements in some mechanical properties, the glass fibre produces a large loss in toughness, which means an important decrease of the deformation and impact test values. With the purpose of mitigating the adverse effects related to high loading, the newest road is the use of nanometric scale reinforcements, which can improve the polymeric matrix properties with low amounts (< 5 wt%) (Fernandez-Barranco et al., 2016; Nikolic et al., 2017).

Polyamide nanocomposites are usually obtained by melt compounding (Fornes et al., 2002; Fornes et al., 2004; García-López et al., 2005, 2010, 2013; Lin et al., 2016). In this approach at least two steps are needed: the first is the monomer polymerization, and the second, is the melt processing to mix the matrix and the nanoparticles. Another way to obtain polyamide nanocomposites is the *in situ* polymerization. This approach only needs one step because the nanoparticles are present in medium during the polymerization (Mittal, 2012). Ever since Fujiwara and Sakamoto (Fujiwara and Sakamoto, 1976), and then the Toyota researchers began to develop the *in situ* technique in the early nineties (Yanno et al., 1993; Kojima et al., 1993), their uses have been spreading for nanocomposites with different matrix and nanoparticles (nanoclays (Kornmann et al., 1998; Herrero et al., 2016), carbon nanotubes (Jia et al., 1999; Ryu and Han, 2014), layered double hydroxides (Peng et al., 2009; Martínez-Gallegos et al., 2009), graphene and graphene oxide (Chiu and Huang, 2012; O'Neill et al., 2014; Song et al., 2015), etc.).

Among the different fillers mentioned above, nanoclays have attracted most of the interest, due to their cost and their abundance as raw material. (Di Credico et al., 2018; Raji et al., 2018). Although

* Corresponding author.

E-mail address: manher@cidaut.es (M. Herrero).

historically the montmorillonite has been the most used, the needle-like shape clays have showed better performance in final properties of the nanocomposites (Xie et al., 2007; Bilotti et al., 2008, 2009; Herrero et al., 2016). In particular, sepiolite is a natural fibrous mineral clay with a molecular formula of $\text{Si}_{12}\text{O}_{30}\text{Mg}_8(\text{OH})_4(\text{H}_2\text{O})_4 \cdot 8\text{H}_2\text{O}$, structurally is composed by blocks of two tetrahedral silica sheets sandwiching an octahedral sheet of magnesium oxide hydroxide. The blocks are not sheets but ribbons, which are linked forming an open channel, allowing the penetration of small molecules. Due to the structure, a significant number of silanol groups (Si–OH) are present at the surface of the sepiolite (Grim, 1962; Tartaglione et al., 2008). These groups can be used to graft silanes with different functionalities affecting the compatibility and the dispersion of the sepiolite in the polymer matrix (Plueddemann, 1982; Xie et al., 2010; Siriwong et al., 2014).

The aim of this paper is to prepare sepiolite polyamide6 nanocomposites, capable of competing in properties but also in price with commercial glass fibre reinforced polyamides. The nanocomposites obtained in this study can spread the application field of these materials in different industrial sectors due to their great mechanical performance and good flow behaviour.

2. Experimental section

2.1. Materials

The nanoclays used for the preparation of the polyamide nanocomposites were a commercial sepiolite (Sep), fine powders without any surface modification, supplied by TOLSA S.A.. The fillers were dried under vacuum at 80 °C for 24 h before any treatment. The 3-aminopropyltriethoxysilane (APTS) used for surface modification was purchased from Sigma-Aldrich and used as received.

For polymerization reaction, the monomer (caprolactam) was purchased from Brueggermann Chemicals and the 6-aminohexanoic acid from Sigma-Aldrich, both were used as received. The commercial grades of polyamide6 (PA6) used in the study were two of the most widespread polyamides from DSM: the neat polyamide AKULON K222D and the reinforced with 20 wt% of glass fibre KGV4.

2.2. Surface modification of the sepiolite

The functionalization was performed with 100 g of Sep in a solution of ethanol-H₂O (95:5 v/v) and 25 ml of APTS. The suspended Sep in the solution was mechanically stirred for 1 h under dry nitrogen. Then, the APTS was added and stirred for 5 h, filtered and washed with methanol and water. The functionalized sepiolite (SepAPTS) was dried before use.

2.3. Melt compounding process

Polyamide K222D and Sep were dried under vacuum at 80 °C at least 24 h before processing. Once the materials were dried, nanocomposites were obtained using a co-rotating twin-screw extruder, model Leistritz 27 GL (L/D = 36), and different contents of Sep (ranging from 0 to 10 wt%). The extrusion temperature was selected at 260 °C and the materials were extruded at 150 rpm. The neat K222D was submitted same processing to secure the same thermal history. After that, the nanocomposites (MISep-PA6) were pelletized and dried before injection.

2.4. In situ polymerization process

In situ polymerization was carried out in a 21 reactor vessel equipped with a mechanical stirrer under argon atmosphere. Typical procedure involved 1000 g of caprolactam, 60 g of 6-aminohexanoic acid and 50 g of water. The polymerization process needs two steps; the first is the ring opening, which consisted in a water reflux for two hours at 150 °C. The second is the polymerization, which carried out at 260 °C

for 6 h, removing the condensation water by distilling. The *in situ* nanocomposites (Sep-PA6 and SepAPTS-PA6) were obtained using the same methodology but adding different amounts of Sep and SepAPTS during reactor loading (ranging from 0 to 10 wt%). After the 6 h, the melted nanocomposites were quenched in water and pelletized in a plastic crusher machine. The removal of unreacted monomer and oligomers was carried out by Soxhlet extraction using methanol (8 h), and washed three times with boiling water. Prior to the injection process all nanocomposites were dried for 24 h.

2.5. Injection moulding

The pelletized samples were injected using a Krauss Maffei KM 200 injection moulding machine to obtain the test specimens for each characterization. The temperature of the cylinders was 250 °C and the mould temperature was 60 °C.

2.6. Characterization

2.6.1. Fourier transform infrared (FTIR)

The chemical surface modification of the nanoclay was studied by attenuated total reflection FTIR. The spectra were recorded in a Bruker Tensor 27 using 2 cm⁻¹ as resolution spectra (16 scans) in the region from 500 to 4000 cm⁻¹.

2.6.2. Thermogravimetric analysis (TGA)

TGA was used to determine the Sep (and SepAPTS) content in the nanocomposites and glass fibre in KGV4. TGA was also used to determine the amount of APTS in SepAPTS. In both cases, thermogravimetric curves were obtained in nitrogen atmosphere at a heating rate of 10 °C min⁻¹ using a Mettler Toledo TGA851.

2.6.3. Differential scanning calorimetry (DSC)

The melt and crystallization temperatures, as well as the degree of crystallinity for each material were measured by DSC, with Mettler Toledo DSC 851e, in the temperature range from 25 to 300 °C at a heating rate of 20 °C min⁻¹ under nitrogen flow. For all specimens, the previous thermal story was removed by heating them to above their melting point. The heat of crystallization for 100% crystalline PA6 was as taken 190 J/g (García-López et al., 2010).

2.6.4. Electron microscopy

Transmission Electron Microscopy (TEM) measurements were carried out using a JEOL JEM-1011HRP Electron Microscope working at 100 kV of accelerating voltage. The nanocomposites samples (100 nm) were cut at room temperature with RMC PowerTome ultramicrotome, using a MicroSTAR Diamond knife.

2.6.5. Tensile tests

The Young's modulus and tensile strength were measured with an Instron Model 5500R60025 at a speed of 1 mm min⁻¹ and 50 mm min⁻¹ respectively, according to ISO 527-1. For each material, seven specimens were tested and mean values of the mechanical parameters were calculated.

2.6.6. Heat-distortion temperature (HDT)

Heat deflection temperature (HDT) was measured in a CEAST HDT-3-VICAT P/N 6911/000, using 1.8 MPa load, according to ISO 75. For each nanocomposite, three specimens were tested and mean values were calculated.

2.6.7. Charpy impact

The notched Charpy test values were measured in a Resil 6957 impact pendulum at room temperature according to ISO 179. For each nanocomposite, eight specimens were tested and mean values were calculated.

Download English Version:

<https://daneshyari.com/en/article/8045655>

Download Persian Version:

<https://daneshyari.com/article/8045655>

[Daneshyari.com](https://daneshyari.com)