



# Barrier properties of polyamide 12/montmorillonite nanocomposites: Effect of clay structure and mixing conditions



N. Follain <sup>a,\*</sup>, B. Alexandre <sup>a</sup>, C. Chappey <sup>a</sup>, L. Colasse <sup>a</sup>, P. Médéric <sup>b</sup>, S. Marais <sup>a</sup>

<sup>a</sup> Normandie Univ, UNIROUEN, INSA Rouen, CNRS, PBS, 76000 Rouen, France

<sup>b</sup> IRDL – FRE CNRS 3744, Université de Bretagne Occidentale, F-29238 Brest Cedex 3, France

## ARTICLE INFO

### Article history:

Received 28 July 2016

Received in revised form

27 September 2016

Accepted 28 September 2016

Available online 29 September 2016

### Keywords:

Nanoclays

Nanocomposites

Polymers

Thermomechanical properties

Transport properties

## ABSTRACT

Hybrid films, composed of a PA12 polyamide matrix filled with 5 wt% of clays were melt processed under different mixing conditions to classically obtain montmorillonite-filled microcomposites and organo-modified montmorillonite-filled nanocomposites. The change in mixing shear rates allowed to notably modulating the fragmentation level for montmorillonite and the exfoliation level for modified montmorillonite. Barrier properties to nitrogen and water were altered with a reduction in PA12 chain mobility by confinement effect and geometrical constraints. Tortuosity effects induced by fillers were also highlighted. The water permeability and diffusivity were significantly decreased with exfoliated clays, while an increase was measured with an increased water solubility in presence of clay aggregates, both counterbalanced tortuosity effects. This trend was amplified when using low shear rates. According to filler used and mixing conditions, water sorption measurement has successfully demonstrated an increase in water solubility, due to filler affinity, which was surprisingly inconsistent with the change of water permeability. The occurrence of water plasticization phenomenon was also pointed out through the non-constant diffusivity, reflecting an increased free volume with water activity. Again, a decrease in water diffusivity was unexpectedly obtained, explained by tortuosity effects and ascribed to local water retention at the vicinity of clays, which creates water aggregates in films. These findings were also confirmed by a mathematical modeling approach of sorption process, discussing about the sorbed water access.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

As thoroughly stated by Sinha Ray and Okamoto [1] and Alexandre and Dubois [2], macroscopic properties of many polymer matrices were substantially improved by incorporating layered nanofillers. Widely used in injection-molding and extrusion processes, those are current industrial processes, polyamide 6 (PA6) [3–5], polyamide 11 (PA11) [5], and polyamide 12 (PA12) [5–7] are usually selected because offering good thermomechanical properties, ease of processing and industrial relevance. In the case of PA12, its low melting temperature reduces the risk of thermal degradation [8] of organo-modified silicate during the elaboration of PA12-based nanocomposites. The layered fillers classically used [9] are pristine montmorillonite, and organo-modified montmorillonite having, when properly dispersed and exfoliated, large surface-to-

volume ratios and a reduced hydrophilicity, provided to separate the clay layers, to facilitate the intercalation of polymer chains, and evenly to improve the polymer/clay affinity [1]. Depending on clays, microcomposite and nanocomposite films can alternatively be prepared using similar experimental processing conditions [2,10,11].

Improvement of properties [12–14], in terms of flame retardancy [15], thermo-mechanical [2,5], rheological [6,16], and barrier properties [10,11,17–20], has been notably obtained at very small nanofiller content, usually up to 5 wt% [14,21], which preserve the good processability of matrix but requiring to form a nanoscale filler structure. A fully exfoliated structure could offer the best enhanced performances, however, various mixed structures constituted of intercalated/exfoliated fillers are often encountered and few studies [20,22] have related a highly exfoliated clay structure formation within a polyamide matrix. The melt intercalation technique, indicated as environmentally friendly because without using organic solvent, is compatible with current industrial processes. The experimental principle is based on the melt mixing

\* Corresponding author.

E-mail address: [nadege.follain@univ-rouen.fr](mailto:nadege.follain@univ-rouen.fr) (N. Follain).

of a polymer and nanofillers, at a mixing temperature not too excessive to prevent the thermal degradation of clay modifier [8]. The compression-molding is usually thereafter applied for forming the hybrid films [23,24]. It emerges that processing conditions play a key role in the resulting structure (polymer crystallinity, clay dispersion and exfoliation levels) of the hybrid materials, and accordingly in its properties [25], in particular barrier properties [12]. More recently, a water-assisted extrusion process has been developed to exfoliate and to disperse clay structure [26–28], but some experimental conditions require to be controlled yet (content of liquid water to add, sticking of water-clay slurry on the metallic screw or throughput).

In the field of transport properties, the incorporation of nanofillers into the polymer matrix is an efficient way to make additional tortuosity to tortuosity mediated by polymer crystalline phase, resulting in a significant lowering of molecule transfer [29,30], which is as a function of filler uniform dispersion, exfoliation and orientation levels and the strong interfacial interactions between clays and polyamide chains. In the case of gases, only structural effects within nanocomposite films are highlighted. However, interactions between components of the nanocomposite films are not probed, requiring the use of polar diffusing species, such as water. Consequently, sorption, and permeation measurements are usually performed by using some species, differing in size and/or interaction capacity.

The aim of the present work is to investigate the influence of 5 wt% clay, in terms of polarity, within a polyamide 12 matrix on specifically barrier performances, correlated to structural and mechanical properties. In particular, the examination of water vapor sorption isotherms and data modeling (to evidence water-film interactions), which has never been reported, is an original work. The effects of structure and crystallinity, resulting to melt mixing conditions, on transport properties to nitrogen and water are evenly investigated. The transport properties are also thoroughly analyzed on the basis of thermodynamic and diffusivity parameters.

## 2. Experimental

### 2.1. Materials

Commercial polyamide 12 (PA12), referenced as Rilsan® AECHVO (Mw = 37 kg/mol, Mn = 20 kg/mol, Tm = 178 °C [10]), was provided by ARKEMA (Serquigny, France). Two additive clays supplied by Southern Clay Products (Rockwood Additives, Ltd.) were used: a natural unmodified montmorillonite, named Cloisite® Na<sup>+</sup> (noted as CNa), with a density of 2.86 g/cm<sup>3</sup> and an organo-modified montmorillonite, named Cloisite® 30B (noted as C30B), bearing a (tallow alkyl) methyl bis(2-hydroxyethyl) ammonium cation with a density of 1.98 g/cm<sup>3</sup>. The amount of ammonium cation in C30B (25 wt%) was measured by TGA analysis.

### 2.2. Preparation of composite films

Composites films were prepared by mixing PA12 with 5 wt% of filler in the molten state in Haake Rheocord internal mixer. The melt intercalation was performed during a residence time of 6 min at a temperature of 200 °C to minimize the thermal degradation of both PA12 and C30B [8,10]. Two blade rotational speeds, 32 and 100 rpm, were used to mix PA12 and fillers. Then, the films were processed by compression molding at 200 °C to get sample with thickness of 200–250 μm, by gradually applying pressure up to 250 bar during 10 min followed by a cooling step of 3 min. The PA12/CNa or the PA12/C30B films were indexed by 32 or 100 when preparing with a rotation speed of 32 and 100 rpm, respectively. Before characterization, the hybrid films were stored under vacuum

over P<sub>2</sub>O<sub>5</sub> powder at room temperature to remove residual water moisture.

### 2.3. Structural characterizations

The experimental mass fraction of clays incorporated into the polymer matrix were determined by thermal gravimetric analysis (TGA) using a TGA device (TGA-7, Perkin-Elmer) from 40 to 700 °C at 10 °C/min under nitrogen atmosphere.

The XRD measurements in reflection mode were performed on a X-ray diffraction D8 Advance diffractometer (Bruker AXS), with a Cobalt source ( $\lambda = 1.79 \text{ \AA}$  corresponding to the  $\alpha$  line of Co). Using Lorentzian equations, the fitting of diffraction peaks was performed to classically calculate the degree of crystallinity ( $\chi$ ) of the films according to:

$$\chi_{XRD} = \frac{A_c}{A_c + A_a} \quad (1)$$

where  $A_c$  and  $A_a$  are the area of the crystalline PA12 diffraction peak (at 20–25°) and of amorphous halo (at 20–23.5°), respectively.

For TEM observations, the hybrid films were directly embedded in Spurr resin before collecting ultrathin film sections using an ultracut UCT microtome (Leica, Austria) at room temperature. Sections were transferred on formvar carbon coated 100 mesh nickel grids. The TEM observations were obtained on a Tecnai 12 Biotwin microscope (FEI Company, Netherlands) operating at 80 kV, by means of image acquisition system (CCD Megaview II camera) controlled by Analysis software (Eloise, France).

Thermal behavior of film samples was analyzed by using differential scanning calorimeter Perkin-Elmer DSC-7 under nitrogen atmosphere. After a calibration step, samples of about 12 mg placed in aluminum pan were heated from 50 °C to 200 °C at a heating rate of 10 °C/min. The degree of crystallinity was determined according to:

$$\chi_{DSC} = 100 \times \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^0 \times (1 - \phi_w)} \quad (2)$$

where  $\Delta H_m$  is the melting enthalpy,  $\Delta H_{cc}$  is the cold crystallization enthalpy,  $\Delta H_m^0$  is the melting enthalpy of a PA12 supposed to be 100% crystalline (= 245 J/g [31]) and  $\phi_w$  is the weight fraction of clay. In the case of the cold crystallization phenomenon occurring in PA12 polymer, the corresponding enthalpy  $\Delta H_{cc}$  must be subtracted to the melting enthalpy for calculating the degree of crystallinity.

Mechanical tests were performed on an Instron model 5543 device with a load cell of 500 N in a climate-controlled room at 25 °C, at a cross-head speed of 5 mm/min and a strain gauge extensometer with a length of 30 mm. The films were transformed into plates according to the French standard NF EN ISO 527-3. The stiffness of films was evaluated using Young's modulus  $E$  (in MPa), ultimate tensile strength (in MPa) and elongation (in %). The tensile values were averaged from at least five specimens per film.

### 2.4. Nitrogen permeation measurement

Nitrogen permeation kinetic measurements were performed at 25 °C by means of a lab-built device using a barometric method based on the time-lag determination [10,11]. The permeability coefficient  $P$  was directly calculated according to:

$$P = \frac{J_{st}L}{\Delta p} \quad (3)$$

Download English Version:

<https://daneshyari.com/en/article/5022410>

Download Persian Version:

<https://daneshyari.com/article/5022410>

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