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Erasure of the processing effects in polyamide 6 based cast films by the introduction of montmorillonite: Effect on water and oxygen transport properties

Mathieu Sabard [a,b,c], Fabrice Gouanvé [a,b,c,*], Eliane Espuche [a,b,c,**], René Fulchiron [a,b,c], Louise-Anne Fillot [d], Lise Trouillet-Fonti [d]

[a] Université de Lyon, F-69003 Lyon, France
[b] Université Lyon 1, F-69622 Villeurbanne, France
[c] CNRS, UMR5223, Ingénierie des Matériaux Polymères, Villeurbanne, France
[d] Laboratoire des Polymères et Matériaux Avancés, UMR5268 CNRS/Solvay 69192 Saint-Fons, France

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ABSTRACT

In this paper the influence of montmorillonite layers and of the processing conditions on the morphology and transport properties of polyamide 6 based films was investigated. Films were prepared by cast extrusion keeping all the extrusion parameters constant except the chill-roll temperature. Two chill-roll temperatures were used: 50 °C and 125 °C. The nanoclay amount contained in the different systems was low and varied from 0 to 1 wt%. The state of dispersion of the nanoclays and the structure of the matrix crystalline phase were investigated as a function of the film processing conditions. The water sorption properties and the oxygen and water permeation were determined and a detailed analysis of the transport mechanism was proposed. For the neat PA6 films, a great dependency of the processing conditions on the morphology and the transport properties was observed. A significant improvement of barrier properties was obtained for the film elaborated with the high chill-roll temperature. For the nanocomposites, independently of the nanoclay amount and the processing conditions, the polymer matrix morphology and the barrier properties were close to each other. Moreover they were similar to those observed for the neat matrix elaborated with the high chill-roll temperature. From this result, the nanoclay can be considered as an efficient additive to make PA6 films properties much less processing dependent.

1. Introduction

In recent years, the use of lamellar nanoclays like montmorillonites to enhance the mechanical, barrier and thermal stability properties of polymers attracted much attention from industrial research and academic community [1–11]. For example, significant improvement of barrier properties is often observed not only because of a tortuosity effect directly related to the shape, dispersion, and orientation of the nanofillers but also because of the strong interaction between the polymer chains and the nanofillers [12–14]. The structure of nanocomposites is known to play a major role in the enhancement of these properties. Depending on the process conditions and on the polymer/nanoclay affinity, intercalated and/or exfoliated structures are classically encountered [15–17]. Intercalated structures show regularly alternating layered silicates and polymer chains compared to exfoliated structures in which the nanoclay layers are completely separated and the individual layers are fully dispersed in the polymer matrix. Best performances are commonly observed with the exfoliated structures mainly due to the large aspect ratio and interfacial area of the nanoclay particles [16,18–20]. The methods used to prepare nanocomposites are also very important in terms of structural organization. Three techniques are mainly used: polymer intercalation from solution, in situ polymerization and direct melt intercalation [5,21]. Intercalation of polymer from solution is obtained from a soluble polymer and swelling nanoclays. The in situ polymerization technique involves the swelling of nanoclays within the monomer solution followed by the polymer formation between the intercalated layers. The melt process

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[*] Corresponding author at: *CNRS, UMR5223, Ingénierie des Matériaux Polymères, Villeurbanne, France.*
Tel.: +33 4 72 43 12 10.

[**] Corresponding author at:*CNRS, UMR5223, Ingénierie des Matériaux Polymères, Villeurbanne, France.*
Tel.: +33 4 72 43 27 01.

E-mail addresses: fabrice.gouanve@univ-lyon1.fr (F. Gouanvé), eliane.espuche@univ-lyon1.fr (E. Espuche).

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implies a blend of a polymer with nanoparticles under shear above the softening point of the polymer. This last method is convenient for current industrial process, such as injection moulding and extrusion and is estimated to be more environmental friendly than the other methods since organic solvents are not used. However, it is generally recognized that the used processing conditions for melt process have a strong effect on the morphology of semi-crystalline polymer nanocomposites and thus may have significant influence on the barrier properties [1,22–24]. Indeed, like nanofillers, crystalline lamellae are considered to be impermeable to small molecules. Thus any change in the polymer crystalline phase due to the presence of the nanofillers or to the film process conditions can also lead to a modification of the barrier properties. Among the wide range of composite materials, polyamide 6 (PA6) films seem to be particularly concerned with this problem. Indeed, PA6 is usually selected for elaborating polymer nanocomposites because of the interesting properties associated with the possibility to extend the exfoliation [25–27]. PA6 is a semi-crystalline polymer which generally exhibits two major crystal forms: α phase and γ phase [28–30]. The α phase has a monoclinic structure, in which adjacent anti-parallel chains are joined by hydrogen bonds. It is the more stable crystalline form and it can be obtained by slowly cooling from the melt. The γ phase is also monoclinic or pseudohexagonal, in which pleated sheets of parallel chains are joined by hydrogen bonds. It is generally obtained by fast cooling. Another metastable pseudohexagonal β-form is described in the literature but it is rarely taken into account. It is not as well identified as the other crystalline structures and serious controversy about its characterization and existence still remains. This phase was first mentioned by Holmes et al. [31] and recently by Miri et al. [23] and Penel-Pierron et al. [32] as an intermediate structure between the α and the γ forms. In this phase, both hydrogen bonds between adjacent anti-parallel chains and between parallel chains are present [32,33]. The introduction of nanoclays within the PA6 matrix can lead to a modification of the crystalline structure of the polymer. No clear conclusion can be drawn concerning the crystalline index [25,28,34] but it is well recognized that the layered silicates can promote the growth of the γ phase. For Lincoln et al. [35] and VanderHart et al. [36], the γ phase is preferentially formed in the proximity of the silicate layers, whereas the α phase exists away from the polymer–clay interphase region. Despite the existence of an extensive work describing structural properties for PA6 nanocomposites [25,29,37–40], there is a lack of proper understanding to distinguish the part played by the impermeable nanoclays themselves on the barrier properties and their indirect effect by means of their role on the matrix crystalline phase. So, the aim of this work is to investigate the impact of the film processing conditions and of the presence of nanoclay on the morphology and transport properties of PA6 based films. Films were prepared by cast extrusion keeping all the extrusion parameters constant except the chill-roll temperature. The nanoclay amounts in the nanocomposite films were chosen to remain below 1 wt%. A detailed analysis of the crystalline structure was performed using different complementary techniques. Sorption properties were determined using water molecules and a detailed analysis of the sorption mechanism was proposed on the basis of thermodynamic modeling. Oxygen and water permeation properties were studied for the different films. Here again, a detailed analysis of the permeability coefficients was proposed.

2. Experimental

2.1. Materials

A commercial polyamide 6 (PA6) with an average molecular weight, M_w, close to 113,000 g mol^{-1}, was supplied by Solvay (Lyon). The used nanoclay is a commercial montmorillonite (Nanofil® SE 3010) provided by Süd Chemie. This is a natural montmorillonite (MMT) modified with dimethyl, di(hydrogenated tallow)alkyl ammonium. The surfactant amount is 43 wt%.

2.2. Film processing

Films were prepared from neat PA6 and nanocomposites at Solvay Research Center in Lyon. To avoid the presence of water during melt process, PA6 pellets and MMT were dried at 90 °C for at least 12 h before melt blending. Films were obtained using a cast-film line, consisting of a co-rotating screw extruder (Leistriz) with a screw diameter of 34 mm and a length-to-diameter ratio of 35 and a flat die of 400 µm of thickness. The feed rate was 8 kg h^{-1} and the temperature was maintained at 255 °C up to the extrusion die. After exiting the die outlet, the melt polymer was uniaxially drawn at a draw ratio of 7.4 and cooled using two different chill-roll temperatures (T_{CR}): either 50 °C or 125 °C. For the nanocomposite films, the MMT amount was equal to 0.5 or 1 wt%. The thickness of the films was estimated around 50 ± 10 µm. In the following part of the manuscript, the films will be named PA6/X/Y, where X and Y are the chill-roll temperature and the MMT weight per cent amount, respectively.

2.3. Transmission electron microscopy (TEM)

For TEM analysis, samples were microtomed at room temperature with a Leica EMFCS instrument equipped with a diamond knife to obtain ultrathin sections of 50 nm thick. The samples were imaged in a Philips CM120 transmission electron microscope with an accelerating voltage of 200 kV.

2.4. Differential scanning calorimetry (DSC)

DSC experiments were carried out with a Diamond Pyris DSC apparatus from Perkin-Elmer under nitrogen atmosphere. The weight of the samples used was approximately 10 mg. Heating ramp analyses were performed from 20 °C to 270 °C at a heating rate of 10 °C/min.

2.5. Wide-angle X-ray scattering in reflection mode (WAXS)

WAXS analyses in reflection mode were carried out at room temperature using a Cu tube ($\lambda = 1.54$ Å) and a Bruker D8 Advance diffractometer, where the K β line was removed with a nickel filter. The diffraction patterns were obtained in the range of 2θ between 1° and 30° by step of 0.02°. The films were deposited on neutral substrates with a thin transfer adhesive of no scattering response.

2.6. Wide-angle X-ray scattering in transmission mode (WAXS)

WAXS analyses in transmission mode were performed at the European Synchrotron Radiation Facility (ESRF, Grenoble, France) on the BM2 beam line. The data were collected with an incident photon energy of 16 keV ($\lambda = 0.77$ Å). A two-dimensional detector (CCD camera from Roper Scientific) located at about 15 cm from the sample was used. The contribution of the empty cell was subtracted from the scattering images of the studied samples. The data corrections included the calculation of a normalization coefficient due to an incident flux decrease, correction of the grid distortion of the detector, normalization to the detector response to homogeneous irradiation (flat field), and subtraction of the detector response without any beam. These corrections were performed with the software BM2IMG developed at the ESRF. The data were azimuthally averaged around the image centre