Journal of Membrane Science 450 (2014) 487–498

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Influence of montmorillonite and film processing conditions on the morphology of polyamide 6: Effect on ethanol and toluene barrier properties

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ARTICLE INFO

Article history:
Received 6 June 2013
Received in revised form
6 September 2013
Accepted 14 September 2013
Available online 21 September 2013

Keywords:
Microstructure
Structure–properties relations
Pervaporation
Sorption
Polyamide

ABSTRACT

Nanocomposite films were prepared by cast extrusion using two chill-roll temperatures from polyamide 6 and an organo-modified montmorillonite. The impact of the nanoclay amount in the range from 0 to 1 wt%, as well as the processing conditions on the morphology and transport properties were investigated. The microstructure of the polymer highly depended on the films processing and the presence of the nanoclays. A detailed analysis of ethanol/toluene pervaporation properties was proposed for the all range of ethanol/toluene composition on the basis of thermodynamic and kinetic point of view. The transport mechanism was complex and resulted from a combination of different contributions involving the polymer–permeant and permeant–permeant interactions, the free-volume holes and the amount of γ phase in the crystalline part of the polymer. This study underlined the potentiality of using molecules differing in their interaction as an original way to probe the architecture of these systems.

1. Introduction

Due to the increasing demand for energy and strict air pollution regulations, numerous studies have been focused on the development of alternative fuels to replace gasoline [1,2]. Ethanol/gasoline mixture is one of the widely employed renewable alternative fuels because of its low cost, high efficiency and low air pollution [3,4]. Previous studies have assessed the feasibility of employing ethanol as an additive in automobile engine fuel due to its high octane value [5,6] and the ability of ethanol to increase the octane value of gasoline [7]. Another important property of ethanol is the high oxygen content in its chemical structure, which promotes complete combustion of fuels within engine cylinders and reduces the emission of most air pollutants [8]. In addition to good mechanical properties, gasoline tanks have to combine high barrier properties to non-polar solvents and polar solvents to avoid the emission of volatile organic components. Historically the materials used for this application were made of metal. However metal fuel tanks cannot be used to contain ethanol, because they are susceptible to corrosion. In contrast, polymer materials will be a better choice. In the polymeric materials family, polyolefins, such as polyethylene (PE) is probably the most prevailing and suitable materials, because it is recognized as a light weight, easy design and processing, low cost and anticorrosion material and displays also good permeation resistance to polar solvents [9,10]. However, PE is notorious for its poor barrier properties to non-polar solvents [11]. In order to improve this specific property, many routes have been applied [12,13]. These technologies include surface treatment of PE by fluorination or sulfonation [14,15], coextrusion of laminates of two or more polymers [16,17]. However, some of these techniques represent expensive manufacturing costs. So, the polymer blending concept can be an alternative and a promising option for this application. In contrast to polyolefins, polar polymers like polyamide 6 (PA6) are known for their excellent barrier properties to non-polar solvents. In consequence of that, blends of PE and PA6 have been the topic of many research efforts [17,18]. It is generally recognized that the barrier properties of PE/PA6 blends depend greatly on the resulting morphology going from dispersed PA6 phase in a PE matrix to dispersed PE nodules in a PA continuous phase. However, one must keep in mind that the barrier properties of PA6 itself are key factors in determining the barrier properties of PE/PA6 blends. PA6 is a semi-crystalline polymer which generally exhibits two major crystal forms: α phase and γ phase [19–21]. The α phase has a monoclinic structure, in which adjacent anti-parallel

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http://dx.doi.org/10.1016/j.memsci.2013.09.023

chains are joined by hydrogen bonds. It is the more stable crystalline form and 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 there remains serious controversy about its characterization and existence. This phase was firstly mentioned by Holmes et al. [22] and recently by Miri et al. [23] and Penel-Pierron et al. [24] 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 [23–25]. It is generally recognized that the barrier properties of a semi-crystalline polymer like PA6 depend greatly on the morphology. Thus, any change in the polymer crystalline phase in particular due to the film processing can lead to a modification of the barrier properties. Numerous studies have repeatedly shown that polyamide is particularly concerned with this problematic [26–29]. A previous work performed in our laboratory has shown that a high γ phase proportion in the crystalline phase as well as a low amount of the free-volume holes particularly at the crystalline–amorphous phase interface could significantly enhance water and ethanol barrier properties of neat polyamide 6 films [30]. Furthermore, many studies reveal the effect of lamellar nanofillers such as nanoclay for the reinforcement of PA6 barrier properties [31,32]. This barrier effect is generally attributed on one hand to a direct effect assigned to the tortuosity phenomenon corresponding to an increase of the diffusion path through the matrix which is usually related to the shape, the dispersion, the amount of the nanoclay platelets [33,34]. On the other hand, the presence of nanoclay can also lead to a variation of the crystalline phase of the matrix which can be at the origin of a variation of the transport properties [26]. Indeed, like nanoclays, crystalline lamella is considered to be impermeable to small molecules. Nevertheless, it is often difficult to distinguish the part played by the matrix crystalline phase from the direct effect of the nanoclays in the barrier properties. Despite the existence of an extensive work describing structural properties and water barrier properties for PA6 nanocomposites [30,32,35,36], there is a lack of proper understanding of the transport properties of these films to polar and non-polar solvents and mixture of both. So, the aim of this work is to investigate the impact of the film processing conditions and the presence of nanoclay on the morphology and the ethanol and toluene transport properties of polyamide 6 based films. The films were prepared by cast extrusion using two different chill-roll temperatures and the nanoclay amount were chosen to remain below 1 wt%. A detailed analysis of the crystalline structure and of the molecular mobility in the amorphous phase was performed using different complementary techniques. To have a good understanding of the transport phenomenon, sorption and pervaporation measurements were performed using pure ethanol and pure toluene solvents. Moreover, pervaporation experiments were performed for different ethanol/toluene mixtures varying by their composition. An analysis of the mechanism was proposed on the basis of thermodynamic and kinetic point of view. Due to their different interaction capacities, ethanol and toluene could be sensitive to different parameters. These two molecules could then also be used as complementary probes allowing an original and detailed study of the neat polyamide 6 matrices and related nanocomposites architectures.

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 Rhodia (Lyon). The nanoclay used 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 inorganic amount is 57 wt%. The ethanol (99.8%) and toluene (99%) were purchased from Sigma Aldrich and were used as received. The characteristics of the solvents are listed in Table 1.

Table 1
Characteristics of the permeant molecules.

	Molar volume (cm^3 mol^{-1})	Boiling point (°C)	Hansen solubility parameters		
			δ_d	δ_p	δ_h
Ethanol	58	78	15.8	8.8	19.4
Toluene	111	106	18	1.8	2

2.2. Film processing

Films were prepared from neat PA6 and nanocomposites at Rhodia Research Center in Lyon (CRTL). To avoid the presence of water during melt process, PA6 pellets and MMT were dried in oven 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, L/D 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 at 50 °C or at 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 this article, the films will be named PA6/X/Y, where X and Y being the chill-roll temperature and the MMT weight 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 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 $K\beta$ 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)