



Substrate effects on the surface properties of nylon 6



Qi Zhou^{a,*}, Jianghua Fang^a, Haoqi Gao^a, Leslie S. Loo^b

^a Department of Chemical Engineering, Ningbo University of Technology, Ningbo 315016, PR China

^b Department of Chemical and Biomedical Engineering, Nanyang Technological University, 637459 Singapore

ARTICLE INFO

Article history:

Received 18 March 2013

Received in revised form 9 May 2013

Accepted 13 May 2013

Available online 2 June 2013

Keywords:

Nylon 6

Surface structure and properties

Spin coating

Substrates

FTIR trichroic analysis

ABSTRACT

Thin nylon 6 films spin coated onto different substrates were characterized by wide-angle X-ray scattering (WAXS), Fourier transformation infrared (FTIR) spectroscopy, FTIR trichroic analysis and water contact angle (CA) measurements. The morphology and hydrophilicity of the nylon 6 surface were found to be greatly influenced by the nature of the substrate. The film surface contained primarily α -form crystals when it was prepared using hydrophobic substrates. This film was more hydrophobic. However, for hydrophilic substrates, the film surface comprised mainly γ -form crystals and demonstrated greater hydrophilicity. FTIR trichroic analysis of the N–H stretching vibration mode revealed that the presence of a hydrophilic substrate caused the N–H stretching bonds on the film surface to align preferentially in the direction perpendicular to the surface. Such effects were attributed to molecular interactions between the N–H bonds of the polymer and Si–O bonds of the hydrophilic substrate.

Crown Copyright © 2013 Published by Elsevier B.V. All rights reserved.

1. Introduction

The structure and morphology of nylon 6 have been extensively investigated to obtain high performance materials, such as nanocomposites, films and blends throughout the years. In some cases, it had been reported that the crystalline morphology on the surfaces showed different conformations relative to the bulk [1,2]. Surface characterization was of great importance for the understanding of polymer adsorption in terms of chain orientation and conformation. At the same time, it served to provide an overall view of the polymer properties from surface level to bulk material [3].

Recently, the migration phenomenon of nylon 6 nanocomposites during the formation of nanocomposites had been reported. The resulting nanocomposites showed enhanced surface mechanical and physical properties, such as better friction, wear and hydrophilicity [4–6]. Misra et al. [7] used atomic force microscopy (AFM), and transmission electron microscopy coupled with energy dispersive X-ray spectroscopy (TEM/EDAX) to study the crystalline morphology of the surface of nylon 6/polyhedral oligomeric silsesquioxane (POSS) nanocomposites. They observed that POSS molecules migrated to the surface resulting in an increase in stiffness and hardness. In our latest study [8], we investigated the effect of nanofillers such as POSS and layered silicates on the surface properties of spin coated nylon 6 films. Our studies also indicated it was necessary to understand the fundamental influence of the most

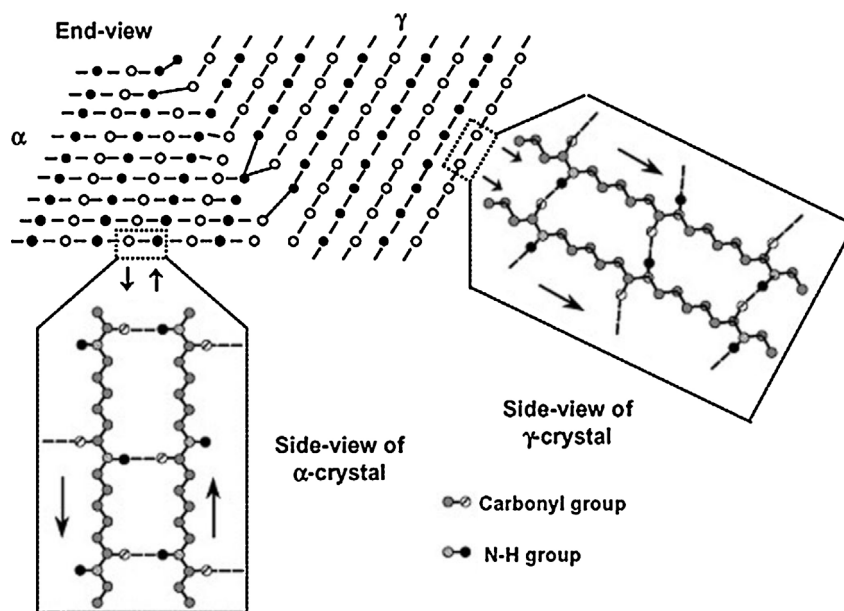
basic parameters (substrate materials) on the condensed state of nylon 6. More specifically, the resulting morphology and properties of nylon 6 crystal structure would depend on the nature of the substrate materials. Understanding such a relationship would provide insights in improving the surface properties and the migration of nanoparticles. Currently, the effect of substrate materials on nanocomposite formation was seldom investigated.

It is known that nylon 6 exhibits polymorphism, and that the polymorph depends on the crystallization condition. At room temperature nylon 6 shows two crystalline modifications, namely the α phase and the γ phase. Scheme 1 presents the two crystalline phase structure, including the direction of N–H bonds [9]. The principle differences between these two phases lie in the lattice parameters and the orientation of the hydrogen bonds between the N–H and C=O groups. The α phase has a monoclinic structure with $a=0.956$ nm, $b=1.724$ nm, $c=0.801$ nm, and $\beta=67.5^\circ$. The hydrogen bonds are formed between antiparallel chains in the α phase. The γ phase also has a monoclinic structure with $a=0.933$ nm, $b=1.688$ nm, $c=0.478$ nm, and $\beta=121^\circ$. But the twisted chains allow hydrogen bonds to be formed between parallel chains. The α phase is easily obtained by melt crystallization, while severe crystallization conditions are needed to obtain the γ phase. Moreover, the α phase can be transformed into the γ phase by treatment with aqueous potassium iodide–iodine solution. Furthermore, the α phase has been found to be the most stable structure of nylon 6 crystals [10–12].

In this paper, it was reported for the first time that different substrates can affect the crystalline morphology of nylon 6 films. The influence of the substrates on the crystalline state of nylon 6 films

* Corresponding author. Tel.: +86 57486066812.

E-mail address: zhouqi@nbut.cn (Q. Zhou).



Scheme 1. Schematic of the α and γ crystalline forms of nylon 6 as seen from end and side-view of each crystal. Closed and open circles represent chain axes projecting out of and into the page, respectively. Hydrogen bonds between polyamide chains are represented by dashed lines [9].

was studied using wide-angle X-ray scattering (WAXS), Fourier transform infrared (FTIR) trichroic analysis and water contact angle (CA) measurements.

2. Experimental

2.1. Materials

Pellets of nylon 6 were purchased from Nanocor, Inc. The solvent 2,2,2-trifluoroethanol was obtained from Sigma–Aldrich. The optical glasses were Pyrex Borosilicate Glass, purchased from SG scientific glass-blowing centre. The glass composition, as provided by the manufacturer, was 80.6% SiO₂, 13.0% B₂O₃, 4.0% Na₂O and 2.3% Al₂O₃. Polystyrene petri dish substrates were provided by Vacutest KIMA Company.

2.2. Nylon 6 thin film formation

Nylon 6 pellets were first dried in a vacuum oven for more than 24 h at room temperature and then stored in a desiccator. In order to make the thin films, the pellets were dissolved in 2,2,2-trifluoroethanol (about 5 wt%), and the solution was spin coated onto the optical glass and polystyrene substrates at five different spin rates: 1000 rpm, 2000 rpm, 4000 rpm, 6000 rpm and 8000 rpm. The films on the glass substrates were dried in vacuum between 70 and 80 °C for more than 12 h and cooled to room temperature. The films on the polystyrene substrates were dried in vacuum between 35 and 40 °C for more than 48 h and cooled to room temperature. Lastly, the films together with substrates were stored in desiccator prior to use.

2.3. Thickness measurement

Film thickness was measured using a Tencor Instruments Alpha Step 500 stylus profilometer and a Micro-Xam surface mapping microscope. Each film was measured 4 times. Finally, the average value of the film thickness was calculated.

2.4. WAXS

2θ scans were performed on a Rigaku Rint X-ray generator with Cu K α radiation at a voltage of 40 kV and a current of 40 mA. The X-ray beam irradiated at the samples was fixed at a constant grazing angle of 1.0°, while the detector counted the diffracted signals with 2θ ranging from 10° to 30°. Scan speed was 0.50°/min and scan step was 0.02°. The divergence, scatter and receiving slit were set at 1.00°, 1.00° and 0.30 mm respectively.

2.5. FTIR and FTIR trichroic analysis

FTIR spectroscopy was performed on a Nicolet Nexus spectrometer. The detector is a liquid nitrogen cooled mercury cadmium telluride (MCT) with a range of 650–4000 cm⁻¹. The resolution was 4 cm⁻¹. For trichroic (three-dimensional orientation) analysis of the film, infrared spectra in the thickness direction were obtained by the sample-tilting procedure described by Schmidt [13]. The beam spot size was set to 5.08 mm diameter at the sample with a total beam divergence of 1.9°. A custom-made device was used to rotate the films around a vertical axis. For normal transmission, the film surface was positioned perpendicular to the infrared beam. This was taken to be the reference angle, viz. 0°. Refractive index measurements were obtained from vertically polarized spectra of the films at angles of $\pm 45^\circ$. The spectra in the thickness direction were then calculated from horizontally polarized spectra of the films aligned at 0° and 45°. 64 scans were collected for each spectrum and zero-filled twice. A Pike wire grid infrared polarizer was used to obtain the polarized IR beam.

2.6. Water CA measurements

Contact angles were measured on a horizontal surface using a FTA200 Dynamic Contact Angle Analyzer, determined using a sessile droplet of ultrapure water (Milli-Q, Millipore Corp., 8.02 M Ω cm) having a volume of $\sim 50 \mu\text{l}$ at room temperature (about 23 °C), and determined at the triple point of air, water and nylon 6.

CA for the upside (the surface which was not in contact with the substrate) of the films was measured directly when the films

Download English Version:

<https://daneshyari.com/en/article/5359675>

Download Persian Version:

<https://daneshyari.com/article/5359675>

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