Available online at www.sciencedirect.com
SCIENCE DIRECT®
European Polymer Journal 41 (2005) 753–759
EUROPEAN POLYMER JOURNAL
www.elsevier.com/locate/europolj

FTIR spectroscopy study of the interaction between fibre of polyamide 6 and iodine

J. Maillo [a], P. Pages [b,*], E. Vallejo [a], T. Lacorte [b], J. Gacén [a]

[a] Departamento de Ingeniería Textil y Papelera, Technical University of Catalonia, Colom 11, 08222 Terrassa, Spain
[b] Departamento de Ciencia de Materiales e Ingeniería, Metalúrgica, Technical University of Catalonia, Colom 11, 08222 Terrassa, Spain

Received 29 June 2004; received in revised form 5 November 2004; accepted 5 November 2004
Available online 13 January 2005

Abstract

The IR spectra of several samples of polyamide 6 fibres treated with solutions of different concentrations of iodine and potassium iodide were studied. The IR spectra of their respective iodine desorptions, obtained by means of treatment with sodium thiosulphate, were also studied. The spectral changes observed are related to variations in the polymorphic crystalline α and γ forms of the polyamide, which demonstrate the formation of a complex between the triiodide ion and the polymer during the iodine sorption process and a structural change during desorption.

Keywords: Polyamide; Iodine; Crystallinity; Microstructure; FTIR

1. Introduction

The results of iodine sorption experiments performed on different polyamide 6 substrates seem to indicate that there are not only changes in the amorphous region, but that alterations are also being produced in the polymorphic forms of the crystalline regions. Therefore, sorption of iodine by the polyamide fibres in an aqueous medium is not only related to the free volume (as in the case of cellulosic materials and polyester) but also to the structural variations that are being produced in the crystalline regions. [1,2].

Polyamide 6 can crystallize into α and γ forms, although the α form is predominant. The two structures are interchangeable in such a way that the α form can be changed into the γ form by means of treatment in an aqueous iodine and potassium iodide solution and the γ form transformed into the α form through treatment with an aqueous phenol solution [3].

The objective of this work is to use FTIR spectrometry techniques [4] to study the changes that are produced in the polymorphic forms of the crystalline regions of polyamide 6 fibre when it is treated with iodine and potassium iodide solutions in an aqueous medium. As indicated in Ref. [5], these treatments cause a change from the crystalline α form to the crystalline γ form.

The greatest difference in the atomic packing of the α and γ polymorphic forms lies in the conformation of the C–N bond which is in the *trans* position in the α form and the *gauche* position in the γ form (see Fig. 1) [6].

In both forms the molecular chains are organized in parallel laminas with hydrogen bridges in just one

* Corresponding author. Tel.: +34 93 739 81 52; fax: +34 93 739 81 26.
E-mail address: pedro.pages@upc.es (P. Pages).

0014-3057/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.eurpolymj.2004.11.030

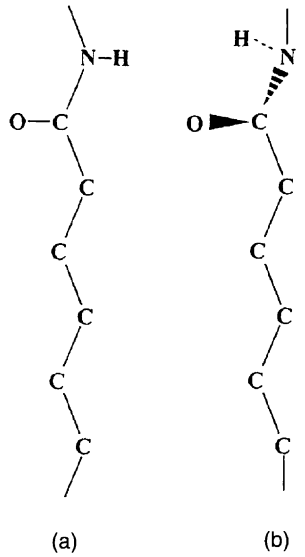

Fig. 1. (a) α form and (b) γ form packing in polyamide 6 crystals.

direction. The molecular conformations are different since in the α form the chains are totally extended, while in the γ form the methylene group next to the amide group has a twisted or bent conformation, similar to that which is found in proteins.

This difference is reflected in two of the structural parameters of the γ form which differ from those of the α form; the length of the repeated unit is shorter, and the amide group is at an angle about 60° with respect to the plane containing the chain segments of the methylene groups. Therefore, the direction of the hydrogen bridges is modified and a pseudohexagonal packing arrangement appears in the first form [7].

In order to change from the α form to the γ form, it is necessary to bend the CH_2 groups next to the CO–NH group.

This work focuses on researching the fibre of polyamide 6 FTIR spectrum bands associated with the crystalline α and γ forms together with the bands which correspond to chain segments that may vary as a consequence of crystalline transformations of the fibre.

In order to assess the effects of the treatments with iodine and potassium iodide solutions on polyamide 6 fibres, different concentrations are used and spectra are obtained for the iodized samples and for the same samples after they have been treated with sodium thiosulphate in order to remove the iodine.

The results of this research will demonstrate the differences that exist when the iodine sorption technique is applied to fibres of polyamide 6 as opposed to other fibres, due to the different fine structure that exists between them. In the polyamide fibres treatment with iodine not only affects the free volume, but it also causes changes or transformations in the crystalline regions.

2. Experimental method

2.1. Materials used

Continuous polyamide 6 thread (40 dtex/10 filaments).

2.2. Preparation of the material

The material is washed with a 1 g/l non-ionic detergent solution (bath ratio 1/60) at 40 °C for 30 min. It is then rinsed first with cold water, then warm water (5 min) and finally it is given one last rinse with cold water. It is then drained and dried at room temperature.

2.3. Iodine treatment

The iodine sorption technique is performed on the polyamide sample using a 0.03 N iodine solution for 20 min at 35 °C [2]. However, in order to study the effect of the iodine more closely, in the present work the following concentrations were used: 0.25, 0.5, 1 and 2 N.

The samples were treated with the different iodine solutions using a bath ratio of 1/100 for 4 h with the thermostat set to 35 °C. The substrates were then removed from the thermostat, washed and filtered in a vacuum tube with distilled water, until the water appeared to run totally clear. They were then drained and left to dry at room temperature.

2.4. Desorption treatment

Part of the iodized samples (following the treatment described above) were placed in a closed Erlenmeyer flask with a 0.1 N sodium thiosulphate solution and a bath ratio of 1/100 at room temperature. They were shaken every 30 min, until they had become totally white. They were then drained and left to dry at room temperature.

2.5. Preparing the samples for the FTIR study

A small amount of polyamide 6 (several mg) is first obtained by cutting the appropriate amount of the fibre using scissors which have been previously cleaned. The fibre is then sprinkled into a matrix of KBr, and it is ground in an agate mortar. When a homogeneous mixture has been obtained it is compressed by applying a pressure of 10 tonnes. In this way a compressed disk is obtained which can be used to allow the corresponding spectrum which is the object of study.