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Graft copolymerization of acrylic acid onto polyamide fibers

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Abstract

The grafting of acrylic acid (AA) monomer ($CH_2{=}CH{-}COOH$) on polyamide 6.6 monofilaments (PA 6.6) using benzoyl peroxide (BPO) as initiator was carried out in order to enhance the hydrophilic nature of fibers. The grafting rate depends on the AA concentration, the BPO concentration, the time and the temperature of reaction.

The best conditions for optimum rate of grafting were obtained with a AA concentration of 0.5 M, a BPO concentration of 0.03 M, a reaction temperature of $T = 85$ °C and a reaction time of 120 mn.

The fiber surface has been investigated by many experimental techniques of characterization such as Fourier transform infrared spectroscopy (FTIR), calorimetric analysis (DSC), scanning electron microscopy (SEM), and contact angle measurements.

The effect of grafting of acrylic acid onto PA 6.6 fibers on their moisture and mechanical resistances was analyzed from water sorption and elongation at break measurements.

The analysis of the experimental data shows clearly the efficiency of the grafting reaction used, leading to a significant increase of the hydrophilic character of the PA 6.6 surface.

Keywords: Graft copolymerization; Polyamide 6.6 fibers; Fourier transform infrared spectroscopy; Thermal analysis; Scanning electron microscopy; Moisture regain; Elongation at break; Contact angle measurements

1. Introduction

The modification of polymers has received much attention recently. Among all the methods of modification, grafting is one of the promising methods. In principle, graft copolymerization is an attractive method to impart a variety of functional groups to a polymer [1].

Grafting reaction involves the copolymerization of a monomer onto the polymer backbone. The formation of copolymers of various synthetic and natural polymers via graft copolymerization has been extensively studied [2–4].

Several monomers such as vinyl and acrylic monomers were used in order to improve surface properties of fibers. Indeed, these monomers are known to polymerize with great facility in the presence of a wide variety of initiators. Methyl acrylate (MA) and methyl methacrylate (MMA) have been graft copolymerized with numerous polymeric backbones using various initiating systems. Radiation induced graft copolymerization of 4-vinyl pyridine onto polyamide fibers [5] and water soluble monomers such as acrylamide and acrylic acid (AA) onto polyamide fibers has been investigated by the preirradiation method and the grafting rate was reported to increase with increasing dose and monomer concentrations [3]. Many investigations concerning the grafting process have concentrated on the addition of carboxylic groups of some vinyl and acrylic monomers into fibers either to improve their hydrophilic properties or to prepare the fibers for further modification, resulting in new properties such as antistatic and antibacterial characteristics [6]. Surface of polyamide 6 yarn was modified by grafting of the acrylic acid (AA) with the use of the dispersing agent NNO (a mixture of salts of multicore condensate aromatic sulfonic acids) as an additive in order to reduce the amount of homopolymer in the grafting system [7]. In another study, the

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same grafting process was examined with the use of both NNO and diphenyl (DPh) [8].

In the present paper, we investigated the effect of grafting acrylic acid (AA) onto polyamide 6.6 fibers (PA 6.6) using benzoyl peroxide (BPO) as initiator. The free-radical polymerization method was used for grafting. The initiator was produced by the thermal cleavage of benzoyl peroxide [9].

The rather hydrophobic nature of the semi-crystalline PA 6.6 fibers, due to the low presence of carboxylic groups, lead to have a poor tinctorial affinity to the basic dyes. One of the most common ways used to improve these undesirable features is grafting vinyl and acrylic monomers onto it. Thus, in our case, grafting of acrylic acid will increase the carboxylic groups onto the PA 6.6 fibers able to improve their hydrophilic properties and their ability to be dyed with basic dyes.

In this work, the effect of monomer and initiator concentrations, the effect of temperature of the reaction and time of polymerization on the grafting rate were analyzed by means of Fourier transform infrared spectroscopy (FTIR), calorimetric analysis (DSC), scanning electron microscopy (SEM), moisture regain, elongation at break and contact angle measurements.

The evaluation of the effect of grafting on the dyeability of PA 6.6 fibers will be explored in a forthcoming paper.

2. Experimental

2.1. Materials

- Polyamide 6.6 monofilament yarn (PA 6.6) produced by Dupont of Nemours was used in the experiment for grafting.
- The acrylic acid (AA) monomer from Fluka before use was purified by distillation under vacuum and deoxygenated with nitrogen in the presence of metallic copper [8].
- Benzoyl peroxide was obtained from Acros Chemical Co., employed as initiator, was purified by using chloroform as solvent and precipitated by adding twice its volume of methanol [8,10,11].

In order to achieve a better diffusion of the initiator and the monomer in the peripheric layer of polyamide 6.6 fibers during grafting, fibers must be first swollen at 50 °C for 2–3 h in a solvent/nonsolvent system consisting of dimethyl formamide/water (50/50, v/v) and then washed with boiling water [8].

2.2. Grafting procedure

Swollen polyamide fibers (0.5 g) were introduced into a three-necked flask containing 50 ml of mixture 70/30 water/hexane. The contents of the flask were degassed with a steady stream of nitrogen for 30 min.

A known quantity of initiator was added. The flask was immediately placed in a thermostated oil bath. Then, the monomer was added to the reaction medium. Copolymerization reaction was carried out for 2 h at 85 °C.

The contents were stirred occasionally. As soon as the copolymerization time was reached, the homopolymer present in the grafting reaction mixture was removed with a solution of 6 g NaCl and 1 g NaOH. After soxhlet extraction with this solution, the grafted fibers were dried in an oven at 60 °C until they reached a constant weight [4].

2.3. Evidence of grafting

The grafting rate was established gravimetrically. Finally, weight gain measurements were calculated applying the following formula [12,13]:

$$\text{grafting rate} = \frac{W - W_0}{W_0} \times 100 \qquad (1)$$

where W_0 denotes the weight of the polyamide 6.6 fibers before graft polymerization and W is the weight of the PA 6.6 fibers after graft polymerization.

3. Fiber characterization

3.1. ATR-IR spectroscopy

The attenuated total reflectance technique was employed (ATR-IR). A Nicolet 360 FTIR AVATAR spectrometer provided with a germanium crystal was used. The incident angle of the IR radiation was 45°. One hundred and twenty-eight scans were obtained and averaged at a resolution of 16 cm^{-1}. The ATR-IR spectra of PA 6.6 surfaces before and after grafting were obtained to evaluate the chemical changes produced.

Spectra were recorded from 500 to 4000 cm^{-1}.

3.2. Thermal analysis

The calorimetric measurements were made with a Perkin-Elmer DSC-7 differential scanning calorimeter in a dry nitrogen atmosphere.

Indium and tin standards were used for calibration. Samples of about 6 mg were placed in the DSC pan.

A heating rate of 10 °C/min was used and a dry nitrogen atmosphere was maintained at a flow rate of approximately 150 ml/min.

3.3. Scanning microscopy

The surface morphology of ungrafted and grafted fibers was investigated by scanning electron microscopy.

Detailed images of PA 6.6 fibers surfaces were obtained using SEM (JEOL marque CAMBRIDGE model STEREO SCAN S200 Scanning Electron Microscope). The SEM samples were gold-sputtered before observation.

3.4. Moisture regain

The moisture regain was determined with reference to the French standards NF G 08-001. In order to evaluate the moisture resistance of ungrafted and grafted PA 6.6 fibers, fibers were conditioned at 20.0 ± 2 °C in a medium having a