Modification of polyamide 6.6 dyeing properties by grafting with poly(acrylic acid)

Miranda, T, Santos, J, Soares, G. M. B.
2C2T – Centre for Textile Science and Technology; Department of Textile Engineering; Minho University, 4800-058 Guimarães, Portugal
gmbs@det.uminho.pt

Abstract

The wet chemical surface modification continues to be a growing area of research interest. This study describes preparation and characterization of poly (acrylic acid)-grafted polyamide 6.6 fabric. Poly (acrylic acid) has been grafted onto polyamide backbone using benzoyl peroxide (BPO) as catalyst in aqueous medium.

The benzoyl peroxide initiator optimum concentration was 0.03 M. The best conditions for optimum grafting reaction were reaction time 120 min, grafting temperature 85°C, monomer concentration 0.5 M and BPO concentration 0.03 M.

The grafting rate was evaluated gravimetrically. The maximum grafting percentage obtained was 13.3%.

All samples were characterized by Fourier–transform infrared spectroscopy with attenuated total reflectance (FTIR-ATR).

The influence of acrylic acid grafting onto polyamide 6.6 was studied in terms of dye uptake using a basic dye, Rouge Maxilon GRL. Mechanical properties were also analysed.

Keywords: Graft copolymerization, Polyamide 6.6 fabric, dyeing properties

1. Introduction

The modification of polymers continues to receive a lot of attention from the scientific community. Its popularity is due to the fact that it allows obtaining materials with new functionalities without requiring specialized equipment[1]. Among all the methods of modification, grafting is one of the most promising processes. Graft copolymerization is mainly an attractive method to impart a variety of functional groups on polymers[2].

Grafting reaction involves the copolymerization of a monomer onto the polymer backbone. The formation of copolymers from several natural and synthetic polymers by graft copolymerization has been widely studied[3-5].

This work describes the preparation and characterization of poly (acrylic acid)-grafted polyamide 6.6 fibers. The acrylic acid (AA) has been grafted onto polyamide 6.6 (PA 6.6) backbone using benzoyl peroxide (BPO) as initiator in aqueous medium[4].

The hydrophobic nature of the semi – crystalline polyamide 6.6 fibers with low presence of carboxylic groups, results on a poor dyeability with basic dyes. The grafting rate depends on AA concentration, BPO concentration, time and temperature of the reaction. Makhlouf and collaborators studied the best conditions for same grafting reaction and they found out that those were 0.5 M of AA, 0.03 M of BPO, reaction time of 120 min and grafting temperature of 85°C[4].

Previous studies showed that the acrylic acid grafting increased the carboxyl groups on the polyamide 6.6 fibers, which improves their hydrophilic properties and ability to be dyed with Red Astrazon 5BL basic dye[6].

In the present study, the modified polyamide 6.6 samples were characterized by the use of FTIR-ATR techniques and they were comparatively analyzed in terms of dye uptake and mechanical properties.

2. Experimental

2.1 Materials

The acrylic acid (AA) monomer (VHR International) and a Rouge Maxilon GRL dye (Huntsman, Portugal) were used without previous purification.

Polyamide 6.6 fabric was purchased from Lameirinho, Portugal.

2.2 Methods

In order to achieve a better initiator and monomer’s diffusion in polyamide 6.6 surface during grafting reaction, samples must be previously swollen at 50ºC for 2 hours in dimethyl formamide/water (50/50, v/v) and followed by boiling water washing [4].

2.3 Grafting reaction procedure

Swollen polyamide fabrics (0,5g) were put in a flask that contains 50 mL of water/hexane (70/30) mixture. Then, they were bubbled with N_2 during 30 minutes.

A known amount of initiator and monomer was added to the grafting reaction that was carried out for 2 hours at 85ºC under stirring.

The grafted fabrics were put in a 100mL aqueous solution with NaCl (6g) and NaOH (1g) to remove any formed homopolymer and they were dried at 45º C during 1 hour and 24 hours in a vacuum oven[4]. The grafting percentage was calculated using the following equation in which W_0 and W are respectively the fabric weights before and after graft copolymerization:

$$\text{Grafting percentage} = (W - W_0)/ W_0 \times 100$$

2.4 Fourier–transform infrared spectroscopy (FTIR) spectroscopy analysis

IR analysis was performed using a Nicolet-Avatar 360 Fourier–Transform Infrared spectrophotometer (Portugal). FTIR spectra of polyamide 6.6 samples were obtained by attenuated total reflectance technique (ATR) with zinc selenide as the ATR crystal material. The ATR correction was made with OMNIC 5.2 software (Nicolet, Izasa, Portugal). The FTIR spectra of polyamide and grafted polyamide samples were recorded with 4 cm^{-1} resolution, 32 scans and wavenumber ranged between 400 and 4000 cm^{-1}.

2.5 Dyeing procedure

The untreated and grafted polyamide samples were dyed with Rouge Maxilon GRL (0.5% w.o.f), using a 25:1 liquor ratio. Fig. 1 shows the dyeing process profile for Rouge Maxilon GRL basic dye.

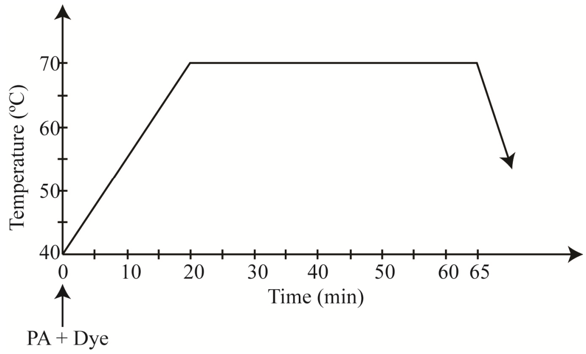

Fig. 1 - Dyeing process profile for the basic dye Rouge Maxilon GRL

2.6 Fabric strength tests

To establish the influence of the grafting on the strength properties of samples, elongation tests were performed according to ISO 13934-1 (Hounsfield Tester). For each sample were performed an average of 5 strength tests in warp and weft direction.

3. Results and discussion

The reaction mechanism of acrylic acid grafting onto polyamide 6.6 fabric using BPO as initiator is evidenced in Fig. 2.

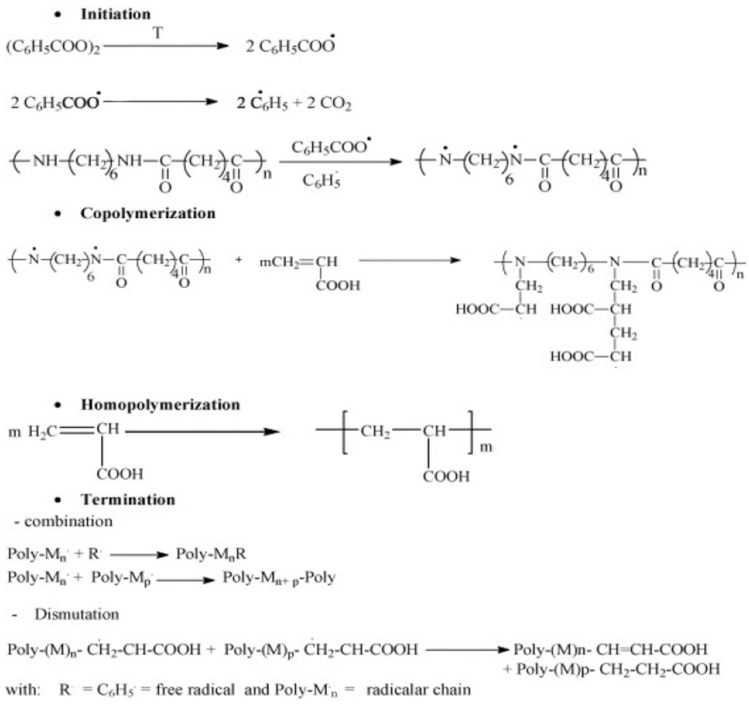

Fig. 2– The reaction mechanism of acrylic acid grafting onto polyamide 6.6 fabric using BPO as initiator

The grafting rate depends on a great number of variables such as monomer and initiator concentrations, reaction time and temperature. Makhlouf and collaborators[4] already investigated the influence of these parameters. Based in the best conditions reported, the effect of initiator on the grafting rate was analyzed.

4.1 Variation of BPO concentration

The initiator concentration effect on grafting rate was studied for different BPO concentrations. These results are shown in Table 1.

Table 1 - Study of initiator concentration effect on grafting rate for different BPO concentrations.
[AA] = 0.5 M, temperature 85 ºC, time 120min.

Grafting rate (%)	[BPO] (M)
8.18	0.02
13.2	0.03
9.67	0.04

Based on these results, the increasing of BPO concentration up to 0.03 M leads to a significant enhancement in grafting percentage, reaching 13.2 %. However, higher BPO concentration decreases the grafting percentage. Similar results were reported by another researchers[4,7].

The enhancement of grafting rate by increasing the BPO concentration to a certain limit, implies that the primary free–radical species $C_6H_5COO^{\cdot}$ and/or the secondary free radical species $C_6H_5^{\cdot}$ formed by dissociation of BPO in the polymer chains, participate directly in the initiation of grafting. Thus, it is suggested that the formation of PA 6.6 macroradicals at the fabric's surface capable of initiating grafting increases until 0.03 M of BPO. At higher BPO concentration, it is expected a larger number of free radicals. Therefore, the phenoxo and phenyl free radicals participation in termination process decreases the grafting yield[4].

4. 2 FTIR - ATR spectra

The FTIR spectra of original and grafted polyamide (Fig. 3) clearly reveal the graft copolymerization with the appearance of a new peak at ~ 1700 cm^{-1} assigned to the stretching vibration of carbonyl group of carboxylic group of acrylic acid[8].

Furthermore, spectra of Fig. 3, shows also a growing of the carbonyl group peak intensity as a grafting percentage function.

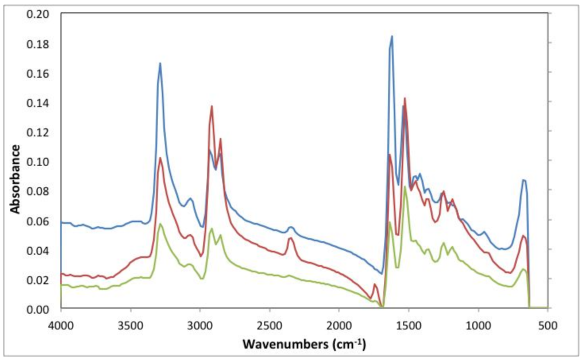

Fig 3- FTIR-ATR spectra (——) grafted PA with 0.03M BPO; (——) grafted PA with 0.02M BPO and (——) untreated PA.

4.3 K/S values of dyed samples

The influence of acrylic acid grafting on polyamide 6.6 dyeing properties was studied using a basic dye, Rouge Maxilon GRL.

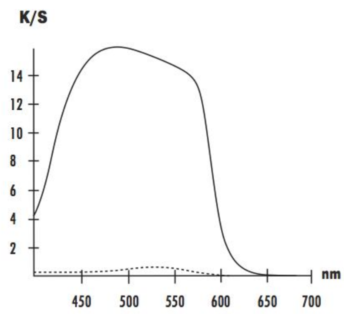

Fig. 4- K/S values presented by the different samples dyed with Rouge Maxilon GRL: (.….) Standard PA and (——) treated PA with 0.03M BPO.

Dye uptake can be deduced by the analysis of K/S values presented by the different dyed samples. Fig. 4 shows the obtained results by PA and grafted PA. If we compare K/S results of modified sample and the untreated sample, it can be concluded that the dye uptake increase in the modified sample.

(a) (b)

Fig. 5 - Grafting effect on dyeing polyamide 6.6 with Rouge Maxilon GRL; (a) Polyamide with acrylic acid with 13.2% of grafting; (b) Polyamide 6.6 untreated

The Fig. 5 shows that the chemical modification of PA 6.6 with AA improved the dyeability.

4.4 Mechanical properties of polyamide

Table 2 presents the experimental results obtained by mechanical tests made on the untreated and grafted polyamide 6.6 fabrics. The elongation (at break) results increase with the grafting percentage (46.55% for 13.30% of grafting). Indeed, the new polymerized molecules grafting, in the polyamide 6.6 amorphous regions, increase the mechanical resistance of yarns[4].

Table 2 – Elongation at break (%) of untreated and treated PA 6.6 (warp direction) with 13,3% of grafting.

Elongation at break (%)	Grafting (%)
40.72	0
46.55	13,3

5. Conclusions

The results obtained demonstrated that the grafting of acrylic acid monomer onto polyamide 6.6 fabrics was carried out by free-radical polymerization owing to thermal cleavage of the benzoyl peroxide. The maximum grafting percentage obtained was 13.3%. The work described allows us to conclude that the initiator optimum concentration was 0.03 M.

The chemical modification with acrylic acid onto PA 6.6 fabric improved the dyeing ability of the materials.

The experimental results about mechanical properties have shown an increase of elongation at break with an increase of graft yield.

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