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Graft copolymerization of methacryloyloxyethyl trimethyl ammonium chloride monomer onto polyamide 66 fibres

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ABSTRACT

Graft copolymerisation of methacryloyloxyethyl trimethyl ammonium chloride monomer {$H_2C=C(CH_3)CO_2CH_2CH_2N(CH_3)_3Cl$} (METAC) onto polyamide knitted fabrics using sodium persulfate as initiator has been investigated. The contents of METAC (quaternary ammonium groups) on polyamide fabrics are extremely valuable for further surface modifications (dyeing, printing, etc.). The effect of factors that may affect the grafting yield, such as monomer concentration, initiator concentration, temperature, and reaction time, have been examined. Suitable conditions that give the highest graft yield are reported. The impact of graft modification on the fibres is evaluated by several techniques: elementary analysis, thermogravimetric analysis, FTIR spectroscopy and zeta potential measurements.

Keywords: polyamide 66 fibers, quaternary ammonium, thermal analysis, FTIR spectroscopy, zeta potential.

1. INTRODUCTION

Graft copolymerisation using several types of vinyl monomers has gained importance in incorporating desirable properties, and a lot of work has been done on such grafting. A variety of monomers have been used on polyamide fibres to improve hydrophilicity (El-Salmawi *et al.*, 1993), dyebility (Bogoeva *et al.*, 1993), flame-retardancy (Hubokawa *et al.*, 1999), heat resistance (Mukherjee *et al.*, 1983), etc. The scope of the current work was to graft the methacryloyloxyethyl trimethyl ammonium chloride monomer onto polyamide knitted fabric. The influence of the main parameters on grafting has been determined and reported. Moreover, the characterisation of the modified textiles by various techniques in order to confirm grafting is exposed.

2. EXPERIMENTAL

2.1 Materials

Polyamide 66 (PA 66) monofilaments fibres used throughout this work were kindly supplied by Nylstar. They were knitted on a flat machine (Shima Seiki, E7) for the needs for latter experiments (dyeing). The vinyl monomer used (Aldrich) was of pure grade and used without further treatments. This monomer is the methacryloyloxyethyl trimethyl ammonium chloride. The initiator employed in this study is sodium persulfate (Aldrich) (Zhao *et al.*, 1999). Polyamides knitted fabrics were used after Soxhlet extraction in petrol ether and dried at room temperature.

2.2 Grafting Procedure

Polyamide knitted fabrics (0.5 g) was introduced into a three necked flask containing a required amount of the monomer and a definite volume of bidistilled water. The solution was deaerated by passing pure nitrogen gas for 1 hour. The polymerization was initiated by the addition of a known quantity of initiator. The flask was immediately placed in a thermostated oil bath. The time of adding the initiator was taken as the starting time for the reaction. The contents were stirred occasionally. The grafted knitted fabrics obtained were purified by extraction of untreated monomers and homopolymers with boiled water. After extraction, the grafted fabrics were dried in an oven for 24 hours.

2.3 Elementary analysis

The monomer used 'METAC' for grafting contains chlorine (Cl), element absent from the structure of polyamide. That's why we made an elementary analysis of this element. The analysis was achieved in a CNRS laboratory (Vernaison) using a silver-potentiometry method.

2.4 Thermogravimetric analysis

The thermal behavior of the grafted samples was investigated by thermogravimetric analysis (TGA) using a TGA 2950 (TA Instrument). Experimentation was done from 25 to 1000°C under nitrogen atmosphere at a heating rate of 10°C/mn. In each case, the mass of sample used was fixed at 15 mg.

2.5 FTIR spectroscopy

The FTIR spectra were recorded for ungrafted and grafted polyamide 66 using a microscope connected to Nexus FTIR spectrometer (Nicolet).

2.6 Zeta potential measurements

To measure the electrokinetic properties of the modified fabrics, we used the Zetacad analyzer from CAD-Instruments which is a specially designed automated equipment for the determination of Zeta Potential using the streaming potential technique (Bismarck *et al*., 1999a ; 1999b). The streaming potential for polyamide fabrics was obtained at room temperature as a function of the applied pressure (0-500 mbar). The latter contains the fabric through which the electrolyte solution (KCl 10^{-3} M) is pumped. After the preparation of the fabric measuring cell with approximately 5 g of fabric material, the cell was connected to the analyzer and rinsed quickly with the KCl electrolyte solution, followed by the removal of all the included air before the measurement started.

3 RESULTS AND DISCUSSION

3.1 Evidence of grafting

The grafting percentage was calculated by using the formula:

$$G = (W_f - W_i) / W_i \quad (1)$$

where W_i and W_f are the weights of the polyamide knitted fabrics before and after graft polymerisation.

Grafting percentage depend upon a large number of variables (Shalaby *et al.*, 1984). Therefore, the effect of variables on percent grafting was investigated. During this study, one of the variables was varied while the other parameters were kept constant.

3.2 Variation of monomer concentration

The effect of METAC concentration on grafting percentage is presented in Fig.1. The results show that grafting percentage increases when the monomer concentration increased up to 1.8 mol/l then decreases. In fact, increasing monomer concentration increases the number of short chains and thus a better diffusion of the polymer into the fibre occurs. But at a higher concentration of monomer, the reactions that are competitive with the grafting like homopolymerisation probably take place in the solution. Homopolymerization is the combination of METAC macroradicals. The high homopolymer formation in the reaction increases the viscosity of the reaction medium, and then retards polymer diffusion in the fibre.

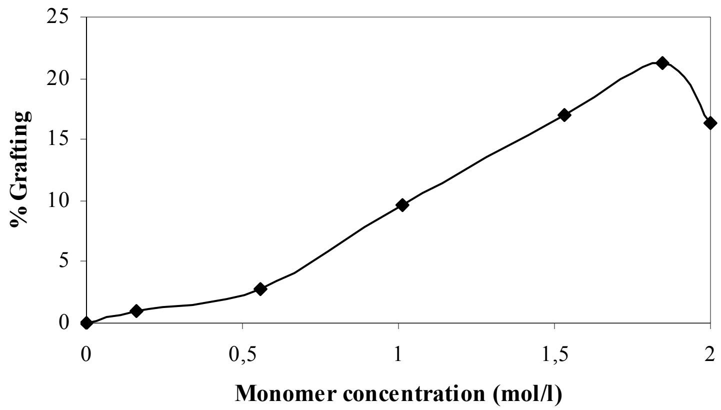

Fig.1 Variation of the grafting percentage versus METAC concentration ; [initiator]= $2*10^{-2}$ mole/l ; temperature 90°C ; time 2 hours.

3.3 Variation of initiator concentration

The effect of the initiator concentration on grafting percentage was investigated by changing the initiator concentration (Fig. 2). It is seen that increasing the sodium persulfate concentration up to 2.10^{-2} mol/l is accompanied by a significant enhancement in grafting percentage. Furthermore, the increase of the initiator concentration decreases grafting. Increase in initiator concentration acts as monomer concentration. At higher initiator concentration, a redundancy of free radicals is expected. As a result, participation of the free radicals in a termination process would be favoured over grafting, thus decreasing it.

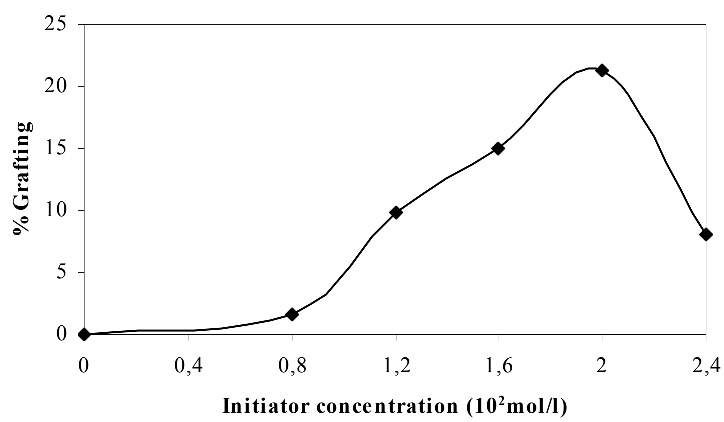

Fig.2 Variation of the grafting percentage versus initiator concentration ; [METAC]= 1.8 mole/l ; temperature 90°C ; time 2 hours.

3.4 Variation of reaction temperature

The graft copolymerisation was carried out at 5 different temperatures ranging from 75 to 95 °C keeping the others conditions constant (Fig. 3). By increasing the temperature, we suppose that the mobility of reactive species and the swellability of polyamide fibres will be higher. In fact, increasing the temperature of the medium up to 90°C causes an increase in the grafting percentage. However, beyond this value, we notice a decrease. These results indicate that at a higher temperature than the appropriate one the homopolymerization of METAC takes place.

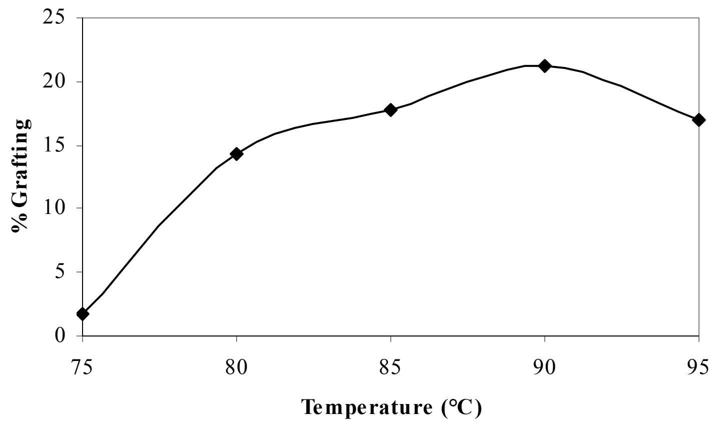

Fig.3 Variation of the grafting percentage versus temperature reaction ; [METAC]= 1.8 mole/l ; [initiator]= 2* 10^{-2} ; time 2 hours.

3.5 Variation of reaction time

We notice that not only temperature but also time affects the grafting percentage (Fig. 4). In fact, 2 hours are sufficient to obtain the maximum grafting percentage (21.3%).

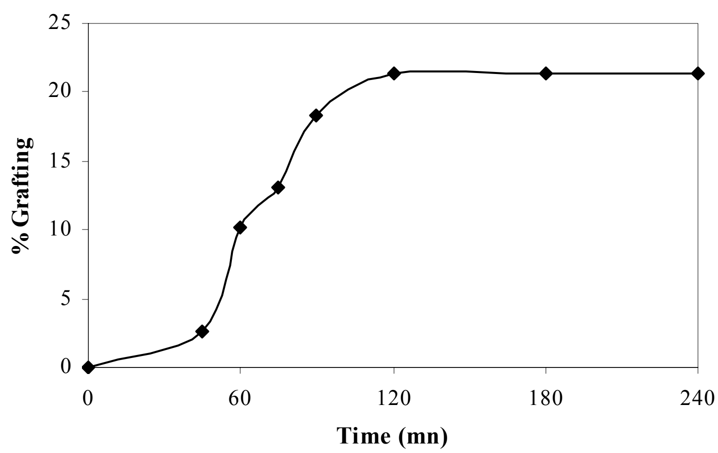

Fig.4 Variation of the grafting percentage versus time reaction ; [METAC]= 1.8 mole/l ; [initiator]= 2* 10^{-2} ; temperature 90°C.

3.6 Elementary analysis

We notice that chlorine is present in the treated knitted fabrics which confirms that the grafting took place. The quantity of chlorine increases since the grafting percentage increases (Table.1). As it was foreseeable, we obtain a linear relation between the percentage of chlorine and the grafting percentage.

%G	% Cl (*)
9.72	2.57
14.94	3.56
21.3	6.58

* : gram for 100 gram of grafted fiber (elementary analysis)

Table.1 Ratio of chlorine on polyamide fibers at different grafting percentage

3.7 Thermogravimetric analysis

The TG curves (Fig. 5) of the ungrafted polyamide and the grafted polyamide knitted fabrics and of the METAC show one, two or multiple significant changes in the slopes, which prove that the degradation are one-, two- or mutiple-step processes. In the case of the grafted polyamide knitted fabrics, the first step may be assigned to the degradation of METAC. The second step corresponds to the decomposition of polyamide. Thanks to these curves of thermogravimetric analysis, we can also check the grafting percentage. Indeed, the masse lost before the second decomposition (397°C) corresponds to the mass of graft incorporated during grafting (the grafting percentage is of 21.3 %, the value of lost mass is of 20 %).

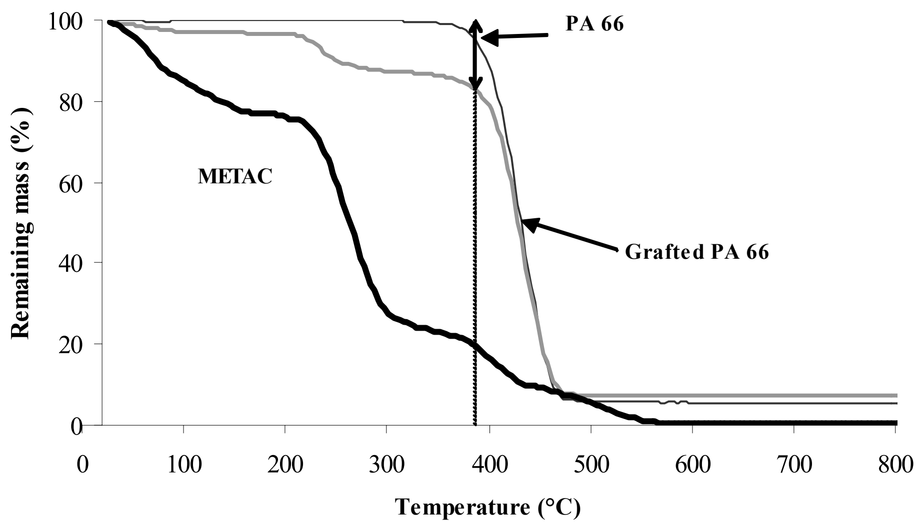

Fig. 5 TG curves of polyamide knitted fabric, grafted polyamide knitted fabric and METAC

3.8 FTIR spectroscopy

The FTIR spectra of ungrafted and grafted polyamide 66 are given in Fig. 6. The peak of interest is 1730 cm^{-1} characteristic of the stretching vibration of the COOR group present in METAC polymer. This fact confirms the chemical grafting of METAC onto the polyamide 66 fibre.

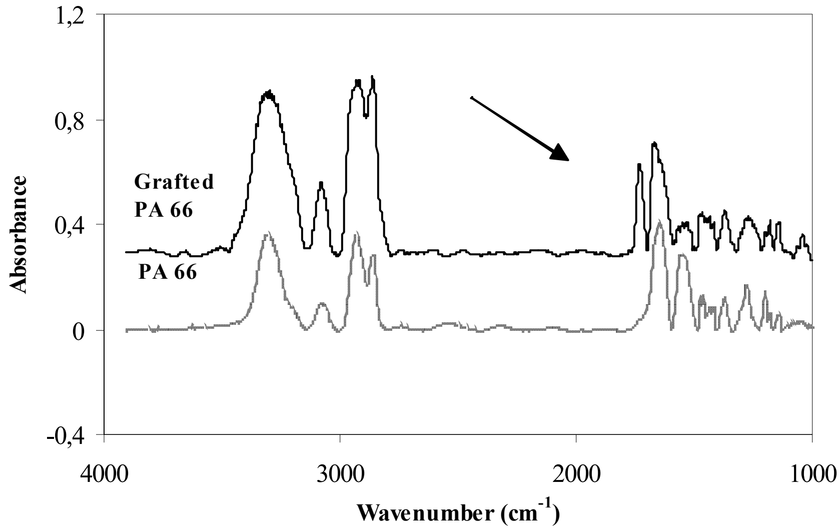

Fig. 6 IR spectra of the original fabric and the grafted fabric

3.9 Zeta potential measurements

Knowing the streaming potential and the pressure in the cell, the zeta potential is calculated by using this equation (Ribitsch *et al.*, 1998):

$$\xi = \frac{E}{\Delta P} * 10000 * 13.55 * C * \lambda \qquad (2)$$

($C = 16.32 - 0.35197 * T + 0.00351 * T^2$)
where:

ξ : zeta potential (mV) ; E : tension (mV) ; ΔP : pressure (mBar) ; λ : conductivity ($S.cm^{-1}$)

The streaming potential as a function of the pressure was recorded for untreated and treated fabrics at different grafting percentage keeping the pH value of the medium constant. From the zeta potential values obtained for each fabric, we can get information about the degree of interaction between the fabric and the ions of the electrolyte solution (KCl). We obtain a negative zeta potential for untreated and a positive one for treated fabric (Fig. 7, Fig. 8)

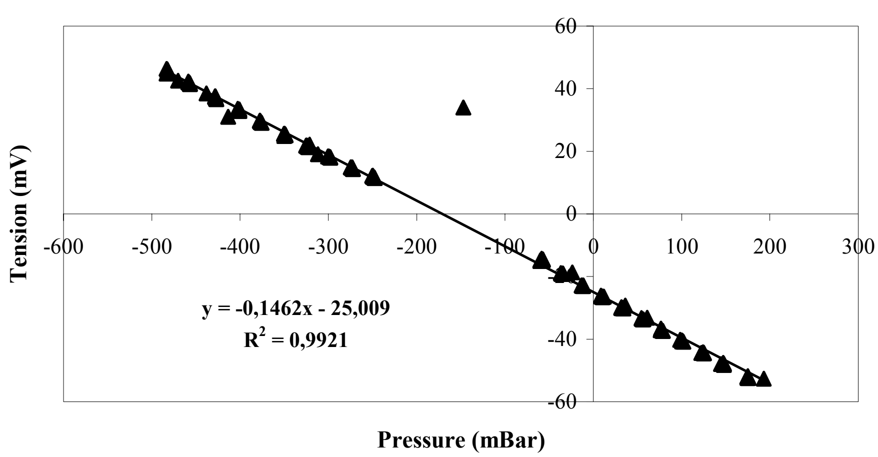

Fig.7 Tension as a function of pressure for the original polyamide fabric

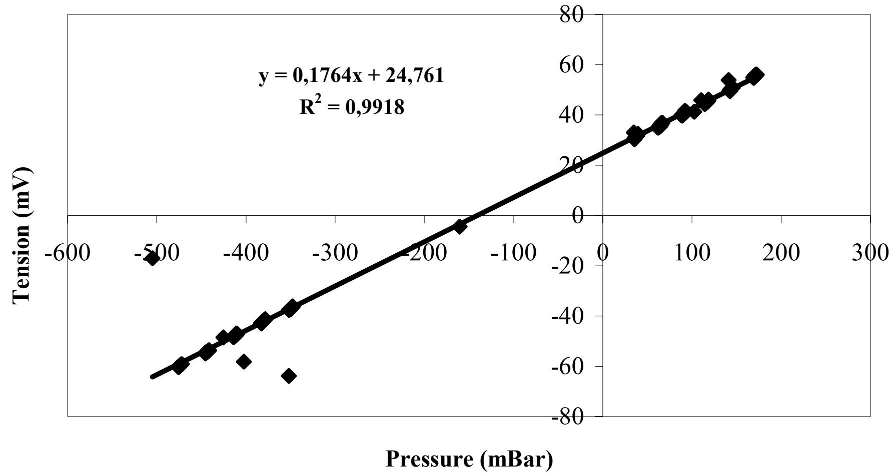

Fig.8 Tension as a function of pressure for the grafted fabric (% G = 17.41)

In table 1 is shown the relationship between zeta potential of PAM fabrics and grafting percentage. We notice the increase in zeta potential when the percentage grafting increases. Change of the sign of the zeta potential can be explained by the presence of quaternary ammonium groups (charged positively).

% Grafting	Zeta potential (mV)
0	- 33
5.65	+ 6
8.92	+ 24
14.94	+ 26
17.41	+ 54

Table.2 Zeta potential as a function of grafting percentage

4. CONCLUSIONS

In this study, grafting of polyamide 66 fabrics with methacryloyloxyethyl trimethyl ammonium chloride monomer (METAC) using sodium persulfate was performed. By looking for the optimum conditions (1.8 mol/l monomer concentration, $2*10^{-2}$ mol/l initiator concentration, 90°C and 2 hours reaction time), we found a grafting process which allows us to prepare a kintted fabric with a high degree of METAC grafting. The maximum grafting percentage was 21.3 %. With the use of infrared spectroscopy, thermogravimetric and elementary analyses, we have confirmed the incorporation of METAC into polyamide knitted fabrics. From the observation of the zeta potential measurements, we confirm the presence of positive charges on knitted fabrics caused by grafting. These positive charges will improve the dyeing ability of polyamide.

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