Grafting of Poly(acrylic acid) on Polyamide Yarn

JADWIGA BUCHEŃSKA

Technical University of Łódź, Man-Made Fibers Department, 90-543 Łódź, Żeromskiego 116, Poland

ABSTRACT: Graft copolymerization of acrylic acid onto PA6 yarn was examined in this study. Prior to the grafting process, the fibers were activated with a benzene solution of benzoyl peroxide. Next, the fibers were put into a bath containing acrylic acid, a dispersing agent, and the activator of reaction. The effects of the main process parameters and auxiliary additives on the degree of grafting, quantity of the homopolymer formed during grafting, effectiveness of grafting, extent of conversion, and grafting ratio were determined. Using calculation factors such as the reaction efficiency, the extent of reaction, and the ratio of grafting, the conditions of grafting were found that made possible the reduction or elimination of the by-product. Also determined were the influence of the degree of grafting on the moisture sorption and the swelling of modified fibers. In addition, the value of apparent activation energy was calculated (49.123 kJ/mol). © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 1914–1919, 2001

Key words: graft copolymerization; modified polyamide fibers; poly(acrylic acid); modification of fibers

INTRODUCTION

In recent years the scientific literature has revealed a growing interest in graft copolymerization on textiles as a method for allowing modification of the properties of textile fabrics without changing the manufacturing process. Many articles concerning this process have concentrated on the addition of carboxylic groups 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 or heat resistance.[1–7]

If a graft copolymerization of vinyl monomers on fibers is to be effective and suitable for practical use, it should be characterized by a minimal quantity of homopolymer formed during the process or its elimination, a grafting process lasting only a short time, and a technology that is wasteless and both environment- and work condition–friendly. Previous studies carried out in our laboratory[5,7–9] as well as in other research centers[10,11] failed to satisfy these requirements, first of all, because of the formation of considerable amounts of by-product (homopolymer). The presence of homopolymer in the grafting bath brings about an increase in its viscosity and makes the penetration of free vinyl monomer into fibers difficult, which decreases both the grafting degree on fibers and its utilization in the process. In addition, it is necessary to remove homopolymer from the modified fibers by means of prolonged extraction (often lasting for many hours). Thus, graft copolymerization of vinyl monomers has not as yet become a common modification process.

Therefore, a method has been developed for grafting vinyl monomers onto synthetic fibers that is different from conventional processes in two ways: the creation of active centers on fibers before the grafting process and the addition of a dispersing agent (NNO) and also in many cases

an activator in the form of diphenyl (DPh) to the grafting system.[12–17]

A previous article[18] reported the results of grafting poly(acrylic acid) on polyamide yarn with the use of the dispersing agent NNO as an additive in order to reduce the amount of homopolymer in the grafting system and to upgrade the process.

The present article presents the results of the same grafting process with the use of both NNO and DPh. Thus, the aim of this study was to develop such grafting conditions as to be able to eliminate homopolymer and to use the process without major problems, either on a larger laboratory scale or in an industrial setting. To do this, the study employed short grafting times and, because of environmental concerns, the use of reagents, including the combined use of both the NNO and DPh additives, in concentrations as low as possible while still being effective.

EXPERIMENTAL

Materials and methods

A polyamide monofilament yarn (PA6) produced by Stilon S.A.—Gorzów Wlkp. was used in the experiment. Fibers were prepared according to the method described in an earlier article.[21] For grafting and further modification the following reagents were used:

- Acrylic acid (AA) from FERAK (Berlin, Germany), pure grade, was stabilized with 0.05% hydroquinomethyl ether, bp 3125 K/10 mmHg n_D^{20} = 1.421; it was purified by distillation under vacuum and deoxygenated with nitrogen in the presence of metallic copper;
- Benzoyl peroxide (BP), of Argon Łódź, Poland), pure grade, was crystallized from a methanol–chloroform mixture and dried under vacuum over P_2O_5;
- Benzene, of POCh (Gliwice, Poland), pure grade;
- Dispersing agent NNO (a mixture of salts of multicore condensate aromatic sulfonic acids) of ZPO-Rokita (Zgierz);
- Diphenyl (DPh), of POCh-Gliwice, pure grade; and
- Nitrogen of Stilon S.A. (Gorzów Wlk.)

To research with ^{1}H-NMR deuterated sulfuric acid (D_2SO_4) was used. As an internal standard,

4,4-dimethyl-4-silapentane sodium sulfonate was applied. The ^{1}H-NMR spectrum presented in this study was taken by means of a BS 487 NMR spectrometer from TESLA (Brno, Czechoslovakia) with a basic frequency range of 80 Mhz, provided with the recording and integrating devices. The ^{1}H-NMR spectrum was obtained at 297 K using the frequency 1.000 Hz.

The grafting of acrylic acid on PA yarn was realized according the method previously reported.[18] Grafting was carried under nitrogen at a temperature ranging from 343 to 358 K, reaction time ranging from 20 min to 60 min, and an acrylic acid concentration ranging from 2.5 wt % to 10.0 wt %. The quantity of dispersing agent NNO and diphenyl was constant (0.5 and 0.4 wt %, respectively). The degree of polymer grafting on PA yarn and the quantity of homopolymer formed during the process, grafting efficiency (E), extent of reaction (K), and grafting ratio (R) were calculated according to a method described in a previous article.[9]

The hydrophilic properties of the grafted fibers were examined by water sorption within 4 and 24 h by means of the desiccator method in 65% and 100% relative humidity, according to PN-71P-04635. The fibers were conditioned according to PN-P-04602, and their hygroscopicity was calculated, using the equation

$$H = \frac{m_F - m_0}{m_0} \cdot 100\% \text{ by wt} \qquad (1)$$

where m_o is the initial weight of dry fibers before moisture sorption or swelling, g; and m_F is the final weight of fibers after sorption or swelling and centrifugation, g.

Swelling of modified fibers in water was determined by the centrifugal method. The fibers were plunged into water and allowed to stand for 3 h. The fiber-to-bath ratio was 1:50, rotation speed was 4000 rpm, centrifugation time was 10 min, and the distance of samples from the centrifuge axis was 70 mm. The degree of swelling (S) was calculated using eq. (1).

RESULTS AND DISCUSSION

A high initiation rate of graft copolymerization with a low rate of side reactions can be obtained by using chemical initiators such as benzoyl peroxide. As can any covalent bond, the peroxide
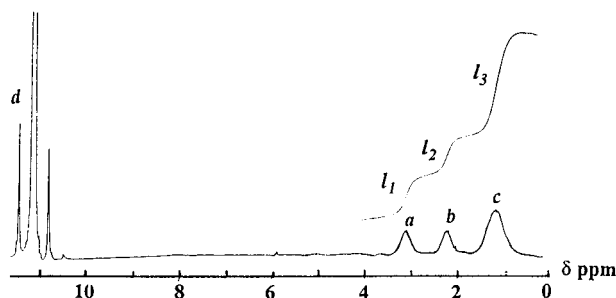
Figure 1 Spectral characteristic of PA yarn initiated with benzoyl peroxide, dissolved in D_2SO_4: (*a*) absorption band from the group $\overset{|}{N}$—CH_2—; (*b*) absorption band from the group —CH_2—$\overset{|}{C}O$—; (*c*) absorption band from the group —$(CH_2)_3$—; (*d*) absorption band from D_2SO_4; (l_1) integration curve for signal *a*; (l_2) integration curve for signal *b*; (l_3) integration curve for signal *c*.

bond can decompose to form two neutral radicals or two ions as a result of division. In both cases the cleavage of the covalent bond is an endothermic process. From the energetic point of view, the process of radical cleavage of a peroxide bond proceeds more easily if peroxide initiators containing a symmetric structure are used. Benzoyl peroxide is one such initiator, and therefore it was used in the present study.

The chemical initiation of a polymer consists in transferring the activity of the radical that resulted from the initiator decomposition onto the polymer chain. A radical or a growing macroradical can abstract an atom or a group of atoms from the polymer chain to form a new macroradical. This phenomena can be used to initiate the graft copolymerization. Thus, it is possible to create hydroperoxide groups in the polyamide macromolecule by means of heat in air as well as by using oxybenzoyl and phenyl radicals, which in addition can enhance the formation of new active centers capable of initiating graft copolymerization.

In order to check the presence and type of these radicals in the yarn initiated by the above-described method, ^{1}H-NMR analysis was performed. Figure 1 shows the spectral characteristics of polyamide yarn initiated with benzoyl peroxide. The spectrograms of yarns before and after thermal or radiation initiation have been shown in previous articles.[19,20]

From the spectrogram shown in Figure 1 it follows that the positions of signals a, b, c, and d

have hardly changed in relation to the signal positions of fibers initiated by thermal[19] or hydrothermal[20] methods, although the ^{1}H-NMR spectrograms of samples initiated with benzoyl peroxide have been repeated using a more precise (pulse) apparatus. There are no visible shift bands corresponding to phenyl and oxybenzoyl radicals that should appear at δ 7–8 ppm. Their absence in these ranges can be explained by their instability under the experimental conditions and by a very low concentration in the initiated fibers. On the other hand, some weak signals at δ 3.65 ppm and 5.87 ppm were observed, which may correspond to the positions of methine carbons in polyamide chains. However, they are not intense enough to be taken into account. The presence of the mentioned radicals can be confirmed in an indirect way, however—using this method of synthetic fiber initiation produces the best results in grafting vinyl monomers onto these fibers as compared to other initiation procedures. The spectral absence of the discussed radicals in fibers after initiation with benzoyl peroxide may also result from a portion of the benzoyl peroxide remaining on the fibers after initiation and decomposing not earlier than during grafting. Therefore, these radicals were not observed in the spectrogram of the initiated fibers.

The role of diphenyl and the dispersing agent NNO in the grafting bath is to increase the fiber swelling while simultaneously enhancing macroradical mobility and increasing the diffusion rate of the acrylic acid inside the fibers.

The dependence of the degree of grafting (*X*) and the amount of homopolymer (*Y*) on such grafting parameters as time, temperature, and monomer concentration are shown in Figures 2–4. Figures 2(a)–4(a) illustrate the effects of these parameters on the values of *E, K*, and *R*.

From these data it follows that the processes of grafting poly(acrylic acid) on polyamide yarn when using NNO and DPh show the highest efficiency at temperatures of 353–363 K with a concentration acrylic acid (C_{AA}) up to 7.5 wt % and with the reaction time dependent on the required degree of grafting and amount of homopolymer. In the case of monofilament polyamide yarns, the degree of grafting, *X,* should not exceed 35 wt % to prevent fibers from increasing rigidity, which arises with *X.*

Under accepted conditions a degree of grafting not exceeding this value is obtained when the grafting time (τ) is about 30 min. Under these conditions it is possible to obtain the highest
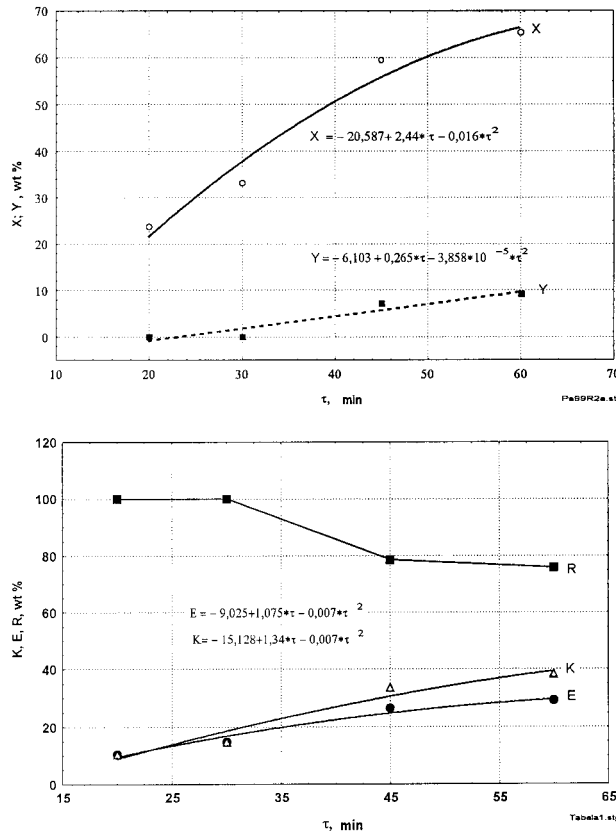
Figure 2 Dependence of degree of grafting of PAA on PA yarn (X, curve X) and homopolymer content (Y, curve Y) on time of grafting, τ ($T = 353$ K, $C_{AA} = 7.5\%$ by wt). (a) Effect of time of grafting on values of grafting efficiency (E), extent of reaction (K), and grafting ratio (R). Parameters of grafting as on Figure 2.

grafting ratio (R) and the lowest extent of reaction (K). The values of K and R depend on the amount of homopolymer formed during the grafting process—R should be as high and K as low as possible because homopolymer is not formed when the additives NNO and DPh are added in amounts of 0.5% and 0.4%, respectively.

From an analysis of the values of $E, K,$ and R it follows that the conditions developed for grafting poly(acrylic acid) on polyamide yarn have met the expected requirements concerning degree of grafting, amount of homopolymer (or its elimination), and shortening of grafting time to the minimum.

Activation Energy of Grafting Poly(acrylic acid) on Polyamide Yarn

The dependence of the grafting rate constant logarithm on the grafting temperature reciprocal

was determined (Table I, Fig. 5) in order to check whether the reaction under discussion applies to Arrhenius's equation or if it is possible to calculate the activation energy. These data were used to calculate the activation energy of grafting poly(acrylic acid) on polyamide yarn. The values in Table I should be considered approximate because the grafting process takes place in a heterogeneous system. The calculated apparent activation energy is 49.123 kJ/mol.

Moisture Absorption and Swelling of Modified Fibers

As is well known from the literature, the addition of another polymer in the form of a side branch into the main polymer chain of a synthetic fiber may result in modification of such fiber properties as strength, moisture absorption, and swelling. Given this possibility, the moisture absorption and swelling of grafted polyamide fibers were examined, and the results are given in Table II.
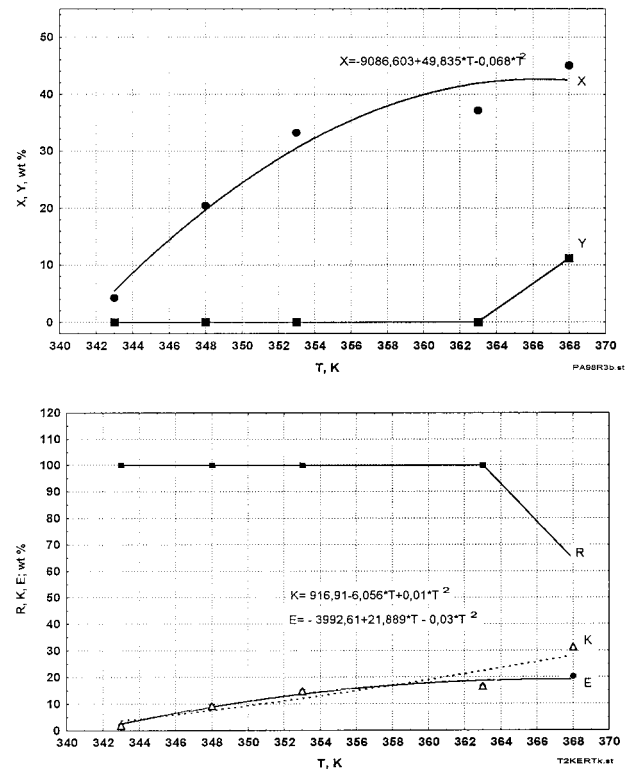

Figure 3 Dependence of degree of grafting of PAA on *PA* yarn (X, curve X) and homopolymer content (Y, curve Y) on temperature of grafting, T ($C_{AA} = 7.5$ % by wt, $\tau = 30$ min). (a) Effect of time of grafting on values $E, K,$ and R; parameters of grafting as on Figure 3.
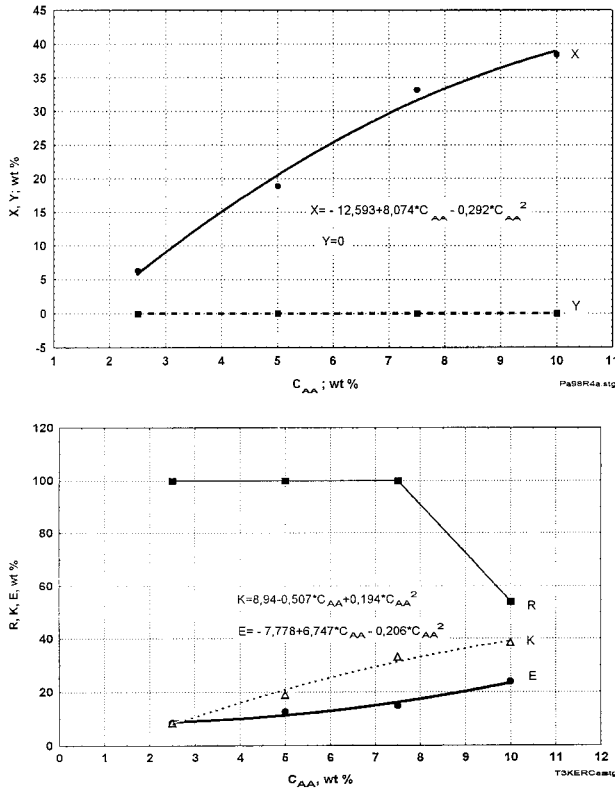
Figure 4 Dependence of degree of grafting of PAA on PA yarn (*X,* curve X) and homopolymer content (*Y,* curve Y) on concentration of acrylic acid in bath grafting, C_{AA} (*T* = 353 K, *τ* = 30 min). (a) Effect of concentration acrylic acid in bath grafting on values *E, K,* and *R*; parameters of grafting as on Figure 4.

As the data show, the moisture absorption and swelling in water of grafted fibers increase depending on the degree of grafting and therefore on the number of added carboxyl groups as well as on exposure time and relative humidity during the measuring.

The moisture absorption (*H*) or swelling (*S*) of the modified fibers at a specified relative humidity can be presented in the form of the following functions, using the least-squares method:
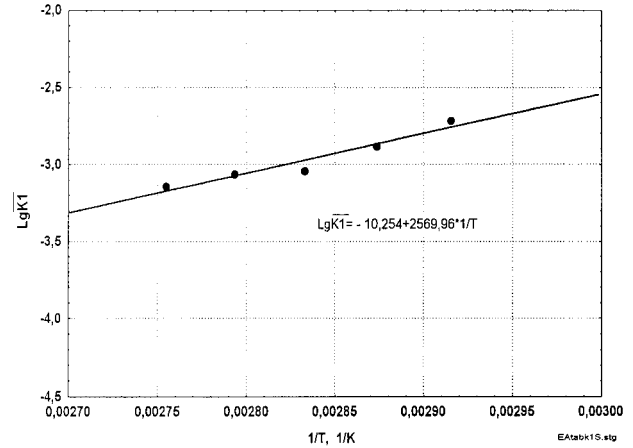

Figure 5 Dependence − log V = *f*(1/*T*) for PA yarn grafted with poly(acrylic acid).

$$H_{PA, 65} = 0.045X + 2.356 \tag{2}$$

$$H_{PA, 100} = 0.177X + 8.275 \tag{3}$$

Using the above method, the value of swelling of the grafted fibers may be given as follows:

$$S_{PA} = 0.520X + 13.627 \tag{4}$$

where $H_{PA,65}$ is the moisture absorption of modified PA fibers at 65% relative humidity (RH) after 4 h of storage under the mentioned RH (wt %); $H_{PA,100}$ is moisture absorption of the modified PA fibers at 100% RH under equilibrium (wt %); S_{PA} is the degree of swelling of modified PA fibers under specified conditions (wt %); and *X* is the degree of grafting (wt %).

The advantage of the above functions is that, with their course and the value of *X,* it allows the prediction of the values of moisture absorption and degree of swelling of the modified fibers or fabric for specified conditions of relative humidity.

Table I   Values of the Grafting Rate Constant ($\overline{K_1}$), Log ($\overline{K1}$), Preexponental Constant (*A*) from Arhenius Equation, and Activation Energy (*E_a*) of the Grafting of PAA on PA Yarn

No.	*T* (°C)	*T* (K)	1/*T* (K⁻¹)	($\overline{K1}$)	LG ($\overline{K1}$)	*A*	($\overline{E_a}$) (kJ/mol)
1	70	343.0	0.0029155	0.0019100	−2.71897		
2	75	348.0	0.0028736	0.0013039	−2.88476		
3	80	353.0	0.0028329	0.0009094	−3.04125	2569.96	49.123
4	85	358.0	0.0027933	0.0008623	−3.06434		
5	90	363.0	0.0027548	0.0007193	−3.14309		

Table II   Swelling in Water and Moisture Sorption for PA6 Yarn Taken at an Equilibrium State at 65% and 100% Relative Humidity

| Sample (X wt %) | Hygroscopicity in % by Weight at | | | | Swelling of Silk (wt %) |
| | 65% RH | 100% RH | 65% RH | 100% RH | |
	After 4 h		Equilibrium State, After 24 h		
PA-untreated	1.50	4.75	3.37	8.12	15.00
PA-PAA (2.99)	2.36	4.78	3.43	9.06	16.50
(13.07)	3.06	5.48	3.79	10.33	18.10
(28.88)	3.82	5.96	3.92	13.01	29.90
(38.40)	3.92	6.90	3.97	15.32	33.32

CONCLUSIONS

- An effective process for the grafting of poly-(acrylic acid) on polyamide yarn has been developed, using the addition of a dispersing agent and an activator in the grafting bath.
- Using calculation factors such as the reaction efficiency, the extent of reaction and the ratio of grafting, the conditions of grafting have been found under which the by-product (homopolymer) can be reduced or eliminated, which provides a highly economical grafting process for fiber modification (T = 353–363 K, C_{AA} = 7.5 wt %, C_{NNO} = 0.5 wt %, and C_{DPh} = 0.4 wt %).
- The values of activation energy of the grafting process have been calculated to be 49.123 kJ/mol.
- The moisture absorption and swelling of the modified PA fibers have been examined and described with mathematical equations.

REFERENCES

1. Bucheńska, J. Pol. Pat. 174,681 (1998).
2. Bucheńska, J. Pol. Pat. 174,680 (1998).
3. Bucheńska, J. Pol Pat. Appl. 306,638 (1994).
4. Bucheńska, J.; Skwarski, T. Polimery (Warsaw) 1992, 37, 257; Chem Abstr 1993, 118, 170, 809.
5. Bucheńska, J.; Skwarski, T.; Sójka-Ledakowicz, J.; Okoniewski, M. Pol. Pat. 112,021 (1981).
6. Bucheńska, J. J Appl Polym Sci, 1995, 58, 1901.
7. Bucheńska, J.; Skwarski T.; Sójka-Ledakowicz, J.; Okoniewski, M. Pol. Pat. 111 985 (1981).
8. Bucheńska, J.; Skwarski, T. Polimery (Warsaw) 1991, 36, 23. Chem Abstr 1993, 118, 104 662n.
9. Bucheńska, J. J Appl Polym Sci 1995, 58, 1901.
10. Okoniewski, M.; Sójka-Ledakowicz, J.; Ledakowicz, S. J Appl Polym Sci 1988, 35, 1241.
11. Okoniewski, M.; Zawadzka, E. Pol. Pat. 106,188 (1980).
12. Bucheńska, J. Fibres & Textiles in Eastern Europe 1996, 4, 53.
13. Bucheńska, J. J Appl Polym Sci 1997, 65, 967.
14. Bucheńska, J. J Appl Polym Sci 1997, 65, 1955.
15. Bucheńska, J. Fibres & Textiles in Eastern Europe 1995, 3, 56.
16. Bucheńska, J. Słomkowski, S.; Tazbir, J.; Sobolewska, E. Pol. Pat. Appl. 333,082 (1999).
17. Bucheńska, J.; Słomkowski, S.; Tazbir, J.; Sobolewska, E. International Conference, MEDTEX '99—Textiles in Medicine, Łódź, May 10–11, 1999.
18. Bucheńska, J. J Appl Polym Sci 1996, 61, 567.
19. Bucheńska, J. J Appl Polym Sci 1966, 60, 519.
20. Bucheńska, J. Fibres & Textiles in Eastern Europe 1995, 3, 55.
21. Bucheńska, J.; Skwarski, T. Polimery 1990, 35, 447; Chem Abstr 1993, 118, 61400g.