

Polypropylene Fibers Grafted with Poly(acrylic Acid)

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ABSTRACT: An effective method for the grafting of poly(acrylic acid) on polypropylene fibers has been developed, using diphenyl and a dispersing agent (NNO) in the grafting bath as additives to facilitate the grafting process. The method makes it possible to obtain high grafting degrees of poly(acrylic acid) on polypropylene fibers with a minimal quantity of homopolymer as a side product. The effect of grafting degree on the moisture absorption and swelling of the modified fibers has been examined and described with mathematical equations. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2295–2299, 2002

Key words: poly(propylene); modification; graft copolymers

INTRODUCTION

Polypropylene belongs to the group of polymers with the largest versatility of uses, including its dominating position as a raw material for fibers and fabrics. An important role of polypropylene fibers is played in medical applications.

Among blood-compatible materials, grafted copolymers have become of interest due to their athrombogenic properties. They depend on the biopolymer microstructure resulting from the fact that there is a proper quantitative proportion between the hydrophobic polymer being a matrix and the hydrophilic polymer added to the matrix. The athrombogenic properties are also affected by negative chains of the hydrophilic polymer such as poly(acrylic acid) incorporated into the biopolymer as a side branch of the polypropylene chain.

The presence of a hydrogen atom at the tertiary carbon atom in the polypropylene macromolecule makes it possible to prepare grafted copolymers by the methods of chain transfer or by using peroxide or hydroperoxide groups introduced into the polypropylene macromolecules by

fibers oxidation^{1–5} or irradiation with high- or low-energy particles.^{6–10} The cited studies have dealt with the effect of the grafted polymers on the properties of the modified fibers, especially moisture absorption and dyeability.^{11,12} These grafting processes were characterized by a prolonged time of grafting, sometimes lasting up to several dozen hours,⁵ which may be due to the inhibiting effect of antioxidants present in fibers, as well as by a considerable quantities of homopolymer that made the fibers penetration by the free vinyl monomer difficult.

Due to these difficulties, grafting on polypropylene fibers was not dealt with for some period of time until the appearance of the issue of biocide fibers designed for medical purposes when these fibers became of interest probably due to their chemical passivity, taking into account that their modification (e.g., sulphonation after grafting) resulted in a lower strength loss than that in the case of polyester fibers.¹³ Polypropylene fibers grafted with polystyrene, sulphonated, and then treated with an antibiotic or anesthetic, have been used as surgical threads among patients with a reduced immunity in oncological hospitals in the area of the former Soviet Union.¹⁴

The aim of the present study was to modify polypropylene fibers by grafting poly(acrylic acid) and to examine the effect of the reaction param-

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eters on the degree of grafting and the amount of side products (homopolymer). It was also intended to examine physical and chemical properties of the grafted fibers such as moisture absorption and swelling.

EXPERIMENTAL

Materials and Methods

Multifilament polypropylene PP fibers were used in our studies. The fibers were prepared according to the method described earlier.¹⁵ Before modification, the parent fibers were cleaned from a spin finish by heating at 333 K in aqueous soap solution ($2 \text{ g} \cdot \text{dm}^{-3}$) for 1 h, followed with extraction of methanol soluble components in Soxhlet's apparatus for 2 h. Then fibers were dried at 323 K to a constant weight in presence of P_2O_5 . The following reagents were also used:

1. Acrylic acid (AA) from FERAK (Berlin, Germany) stabilized with 0.05% hydroquinone monomethyl ether, b.p. 312.5 K/10 mmHg, $n_D^{20} = 1.421$, was purified by distillation under low pressure, deoxygenated with nitrogen in the presence of metallic copper;
2. Benzoyl peroxide (BP), pure grade, of Argon (Łódz, Poland) was crystallized from methanol-chloroform mixture and dried under vacuum over P_2O_5 ;
3. Toluene, of POCh (Gliwice, Poland); pure grade;
4. Dispersing agent NNO (a mixture of salts of multicore condensat aromatic sulphoacids) from ZPO-Rokita (Zgierz), without further purification;
5. Diphenyl (DPh), of POCh-Gliwice, pure grade;
6. Nitrogene of NYLSTAR (a joint venture of Rhodia and Snia) (Gorzów Wlk.).

The grafting of acrylic acid on PP fibers was realized according ref. 16. Shortly, active centers on the PP fibers were formed by treatment with BP. A $2.0 \text{ g} \pm 0.1 \text{ mg}$ sample of PP fibers were kept in 40 cm^3 of 5% wt/v toluene solution for 0.5 h at 323 K. Then, the excess off the BP solution was squeezed out and traces of toluene were removed by evaporation for 15 min at 368 K. The pretreated fibers were placed into a 250 cm^3 reactor equipped with mechanical stirrer, a thermometer, a reflux condenser, and nitrogen sup-

ply. Grafting was carried out in AA solution (concentration varied from 2.5 to 15.0 wt %/v), DPh and NNO (0.4 wt % each). The fibers-to-grafting bath ratio was 1 : 50 in all the experiments. The grafting was carried out under nitrogen at temperatures varied from 343 to 373 K. The grafting time was carried from 15 to 60 min. The unbound poly(acrylic acid), (PAA), homopolymer was removed by extraction with boiling water for 1 h. The amount of PAA grafted onto PP fibers was determined gravimetrically (samples were dried at 323 K to a constant weight). The modified PP fibers samples with 9.43 to 70.34 wt % of PAA were received.

The degree of polymer grafting on PP fibers and the quantity of homopolymer formed during the process were calculated as done previously.¹⁷

The hydrophilic properties of the grafted fibers were examined by water sorption within 4 and 24 h by means of the exsiccator 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:

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

where m_0 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 (S) in water was determined by the centrifugal method. The fibers were plunged into water and allowed to stand for 3 h. The fibers-to-bath ratio was 1 : 50, rotation speed 4 000 rpm, centrifugation time 10 min, and the distance of samples from the centrifuge axis -70 mm. The degree of swelling (S) was calculated by means of eq. (1).

RESULTS AND DISCUSSION

Prior to the grafting process, polypropylene fibers were activated by the formation of peroxides and hydroperoxides on them through their treatment with a toluene solution of benzoyl peroxide at elevated temperature (323 K), followed by pressing off the excess solution of peroxide and drying the fibers for several minutes at elevated temperature (368 K) to evaporate the solvent.

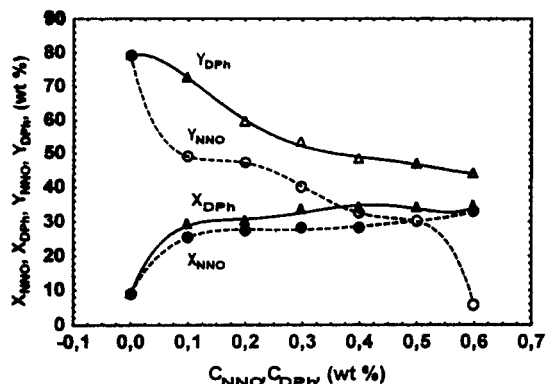


Figure 1 Dependence of degree of grafting of PAA on PP fibers (X_{NNO} , X_{DPH} curves) and homopolymer content (Y_{NNO} , Y_{DPH} curves) on C_{NNO} or C_{DPH} concentration (properly) in grafting solution. Grafting temperature (properly) 368 K; grafting time $\tau = 0.5$ h; concentration $C_{AA} = 7.5\%$ by wt.

The activated fibers were then treated with a grafting bath containing acrylic acid with a suitable concentration and additives to facilitate the grafting process such as diphenyl (DPH) and a dispersing agent (NNO), which also reduce the formation of homopolymer and so increase the degree of grafting.

Thus, the following were examined: the effects of quantities of the mentioned additives as well as the grafting temperature and time, and the concentration of acrylic acid on the degree of grafting poly(acrylic acid) (PAA) on PP fibers [X % by wt], and on the quantity of homopolymer being formed in the grafting bath [Y % by wt]. The results obtained are shown in Figures 1–4.

From the data illustrated in the mentioned figures it follows that when the additives (DPH and NNO) are absent in the grafting bath, already in the initial stage of the process, a considerable quantity of homopolymer is formed, which brings about an increase in the grafting bath viscosity and consequently a poor AA penetration into fibers. This results in a very low degree of grafting and a high quantity of PAA homopolymer formed almost of all the monomer used in the process. When DPH and NNO are added at the same time, the degree of PAA grafting (X) on PP fibers increases, while the quantity of homopolymer (Y) is considerably reduced during the grafting process. The best results are obtained when 0.4% by wt of DPH and NNO each is added to the grafting bath.

Then, the grafting temperature and time were examined. In the first series of experiments the

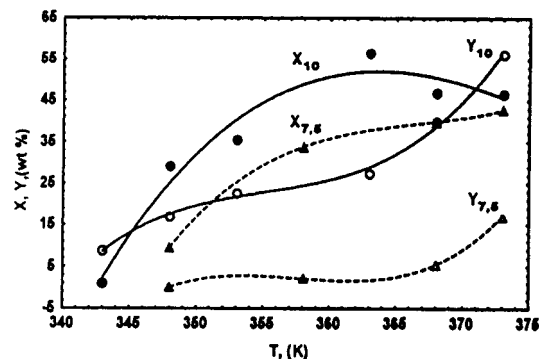


Figure 2 Dependence of degree of grafting of PAA on PP fibers (X) ($X_{7.5}$, $C_{AA} = 7.5\%$; X_{10} , $C_{AA} = 10\%$, curves) and homopolymer content (Y) ($Y_{7.5}$, Y_{10} curves) on grafting temperature (T). $\tau = 0.5$ h; $C_{AA} = 7.5\%$ by wt (curves $X_{7.5}$ and $Y_{7.5}$) and $C_{AA} = 10\%$ by wt (curves X_{10} and Y_{10}) with NNO (0.4%) and DPh (0.4%) in grafting solution.

grafting time was constant, 0.5 h, while the grafting temperature was changed from 343 to 373 K. The grafting process was carried out with a AA concentration of 10% by wt. Figure 2 shows the degree of PAA grafting on PP fibers and the total quantity of homopolymer formed during the process under the specified conditions. It has been found that a high degree of grafting and a negligible amount of homopolymer can be obtained with the used AA concentration at about 7.5% by wt, and temperature preferably within the range 343–363 K.

In the next series, the grafting temperature was constant (363 K), and the grafting time was

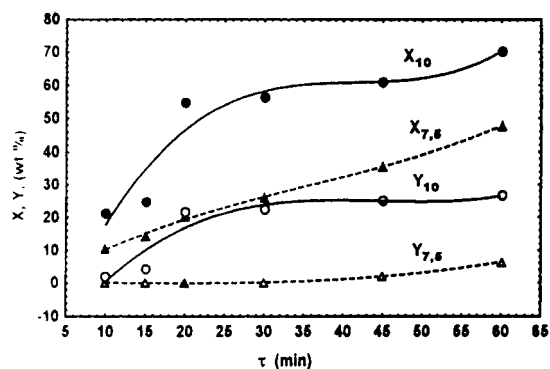


Figure 3 Dependence of degree of grafting of PAA on PP fibers ($X_{7.5}$, X_{10} curves) and homopolymer content ($Y_{7.5}$, Y_{10} curves) on time of grafting (τ). $T = 363$ K; $C_{AA} = 7.5\%$, and $C_{AA} = 10\%$, DPh and NNO—0.4% by wt each.

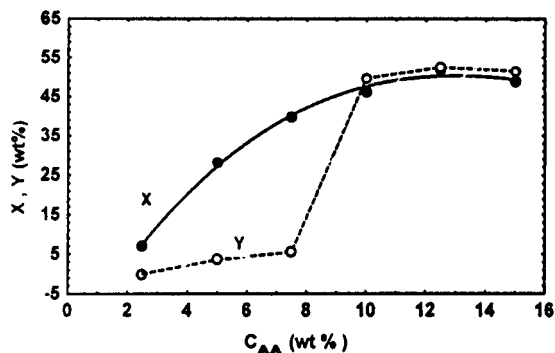


Figure 4 Dependence of degree on PP fibers (X curve) and homopolymer content (Y curve) on concentrating AA (C_{AA}) in grafting solution. $T = 368$ K; $\tau = 0.5$ h, DPH and NNO—0.4% each.

changed from 10 to 60 min, using AA concentrations of 7.5% and 10% by wt. The results of this series are illustrated in Figure 3. Although high degree of grafting can be obtained with a 10% (by wt) AA concentration, the concentration of 7.5% by wt provides the minimum quantity of homopolymer.

Figure 4 shows the results obtained with constant grafting temperature and time and variable AA concentration. It can be seen that the use of AA concentration above 7.5% by wt in the grafting bath is not effective due to the formation of higher quantities of homopolymer than those in the case of lower concentration of acrylic acid.

Moisture Absorption and Swelling of the Grafted PP Fibers

The incorporation of a different polymer as a side chain to the main chain of the polymer under

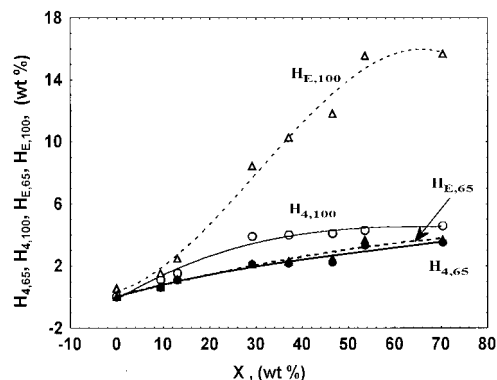


Figure 5 Dependence of absorption moisture (H) on degree of grafting PAA on PP fibers according PN-71-P-04635 (4 and 48 h in a deccicator, 65% RH and 100% RH). $H_{4,65}$ —absorption of moisture after 4 h, 65% RH in deccicator; $H_{4,100}$ —absorption of moisture after 4 h, 100% RH in deccicator; $H_{E,65}$ —absorption in equilibrium (48 h), 65% RH in deccicator; $H_{E,100}$ —absorption in equilibrium (48 h), 100% RH in deccicator.

modification can change its mechanical as well as physical and chemical properties. Thus, it was of interest to check the behavior of the grafted PP fibers in terms of their moisture absorption and swelling. The results obtained are shown in Table I and illustrated by Figures 5 and 6.

From these data it follows that the moisture absorption and swelling in water of the grafted PP fibers increase with the degree of grafting, thus depending on the amount of incorporated carboxyl groups, being also dependent on the exposure time and the relative humidity value during testing.

The values of moisture content of the modified PP fibers at specified RH values and their swell-

Table I Swelling in Water and Moisture Sorption for PP Fibers Grafted with PAA at an Equilibrium State at 65 and 100% Relative Humidity

No.	Hygroscopicity, in % by wt				Swelling of Fibers wt %
	After 4 h		After 48 h		
	65%	100%	65%	100%	
PP-untreated	0.0364	0.0366	0.0368	0.0549	0.8330
PP-PKA(9.43)	0.6145	1.1124	0.6381	1.5858	4.9634
(13.11)	1.0911	1.5245	1.1415	2.5013	8.4606
(29.15)	2.1094	3.8892	2.1249	8.4377	15.6065
(37.08)	2.1671	3.9870	2.2885	10.2813	19.1157
(46.57)	2.2156	4.0753	2.4769	11.7998	23.6370
(53.56)	3.3163	4.2897	3.6642	15.5496	31.2808
(70.34)	3.4964	4.5924	3.6934	15.6927	36.0913

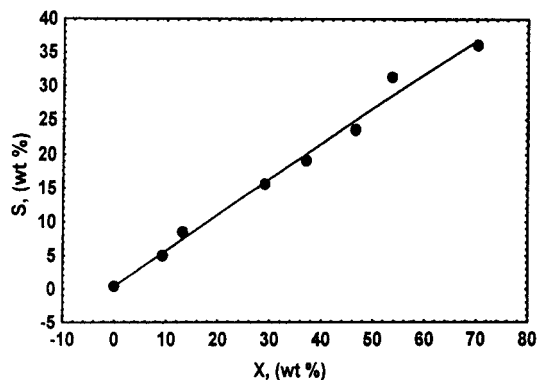


Figure 6 Dependence of swelling (S) in water of grafting PP fibers on degree of grafting PAA (X).

ing can be given in the form of the following equations:

$$H_{4,65} = 0.079 + 0.07 \cdot X - 0.00031 \cdot X^2 \quad (2)$$

$$H_{4,100} = -0.066 + 0.155 \cdot X - 0.001 \cdot X^2 \quad (3)$$

$$H_{E,65} = 0.048 + 0.077 \cdot X - 0.00034 \cdot X^2 \quad (4)$$

$$H_{E,100} = -0.73 + 0.351 \cdot X - 0.002 \cdot X^2 \quad (5)$$

$$S = 0.593 + 0.52 \cdot X \quad (6)$$

where $H_{4,65}$ and $H_{4,100}$ means the moisture content of the modified PP fibers at 65% and 100% RH, respectively, after swelling for 4 h at the given RH, % by wt; $H_{E,65}$, $H_{E,100}$ are the moisture content at equilibrium at 65% and 100% RH, respectively, % by wt; S is the swelling of the modified PP fibers, % by wt; and X is the degree of grafting, % by wt.

It is important that knowing the above functions and the value of degree of grafting (X), one can calculate the values of moisture absorption or swelling for specified conditions.

CONCLUSION

1. An effective method for grafting poly(acrylic acid) on polypropylene fibers has been developed.
2. The effects of additives facilitating the grafting process (diphenyl and NNO dis-

persing agent) and the reaction parameters such as grafting temperature and time and acrylic acid concentration on the degree PAA grafting and the quantity of homopolymer formed during the process were examined and the found relationships were describe with mathematical equations.

3. The lowest quantity of homopolymer formed during poly(acrylic acid) grafting was found when the process was carried out for 45 min, using acrylic acid with a concentration not exceeding 7.5% by wt at 363–368 K.
4. The effect of grafting degree on the moisture absorption and swelling of the grafted polypropylene fibers was examined, and the findings were described by means of mathematical equations.

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