Graft Copolymerization of an Itaconic Acid/Acrylamide Monomer Mixture onto Poly(ethylene terephthalate) Fibers with Benzoyl Peroxide

R. Coşkun,[1] M. Saçak,[2] M. Karakışla[2]

[1]*Chemistry Department, Yozgat Faculty of Science and Literature, Erciyes University, Yozgat, Turkey*
[2]*Chemistry Department, Faculty of Sciences, Ankara University, 06100 Ankara, Turkey*

ABSTRACT: A mixture of acrylamide (AAm) and itaconic acid (IA) was grafted onto poly(ethylene terephthalate) (PET) fibers with benzoyl peroxide in aqueous media. The effects of polymerization conditions such as the temperature, polymerization time, initiator concentration, and monomer mixture ratio on grafting were investigated. The maximum graft yield was 76.1% with an AAm/IA mixture ratio of 90/10 (mol/mol). The graft yield was as low as 3% in the single grafting of IA, whereas the use of AAm as a comonomer increased the amount of IA that entered the fiber structure to 33.5%. An increase in the temperature from 65 to 85°C increased the grafting rate and saturation graft yield. However, an increase in the temperature above 85°C decreased the saturation graft yield. The graft yield increased up to an initiator concentration of $1.0 \times 10^{-2}\ M$ and decreased afterwards. The grafting rate was 0.65th- and 0.74th-order with respect to the initiator and AAm concentrations, respectively. The densities, diameters, and moisture-regain values of the AAm/IA-grafted PET fibers increased with the graft yield. Similarly, there was an increase in the dyeability of the AAm/IA-grafted fibers with acidic and basic dyes. The grafted fibers were characterized with Fourier transform infrared and thermogravimetric analysis, and their morphologies were examined with scanning electron microscopy. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 1795–1803, 2005

Key words: fibers; graft copolymers; kinetics (polym.); polyesters

INTRODUCTION

Poly(ethylene terephthalate) (PET) fibers are important synthetic fibers that are commercially produced today and have superior fiber-forming properties such as the easy packaging of polymer chains with orientation and resistance against microorganisms, erosion, stretching, and acidic media.[1–3] In addition to these properties, PET has some drawbacks, such as lower moisture regain, difficulty in dyeing, and weak antistatic behavior.

One of the ways employed to improve these inferior properties of PET fibers or give them new properties is graft copolymerization. Monomers such as acrylamide (AAm),[4,5] acrylic acid,[6,7] methyl methacrylate,[8,9] and N-vinyl-2-pyrrolidone[10] with suitable functional groups have been successfully grafted onto PET fibers. There are also numerous studies on the grafting of multiple monomers onto PET fibers.[11–14]

The use of multiple monomers in graft copolymerization generally results in a synergistic effect. A polymer, which cannot be satisfactorily grafted to PET fiber when used alone, may be inserted into its structure to a significant extent with the help of the synergistic effect of a comonomer. It was reported that the graft yield of AAm alone on PET fiber was significantly increased by the use of methacrylic acid as a comonomer.[15] Additively, the simultaneous grafting of monomers with different functional groups serves the purpose of furnishing the fiber with the desired properties.

In graft copolymerization, the factors affecting the graft yield are also important. This study concerns the grafting of an AAm/itaconic acid (IA) monomer mixture onto PET fibers by the use of benzoyl peroxide (Bz_2O_2) and the determination of the factors that affect the graft yield. The grafted fibers were characterized by Fourier transform infrared (FTIR), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM) techniques. Also, the properties of the fibers, such as the moisture regain, dyeability, density, and diameter, were determined.

EXPERIMENTAL

Materials

The PET fibers used in the experiments (30 filament and 110 dTex) were obtained from SASA Co. (Adana,
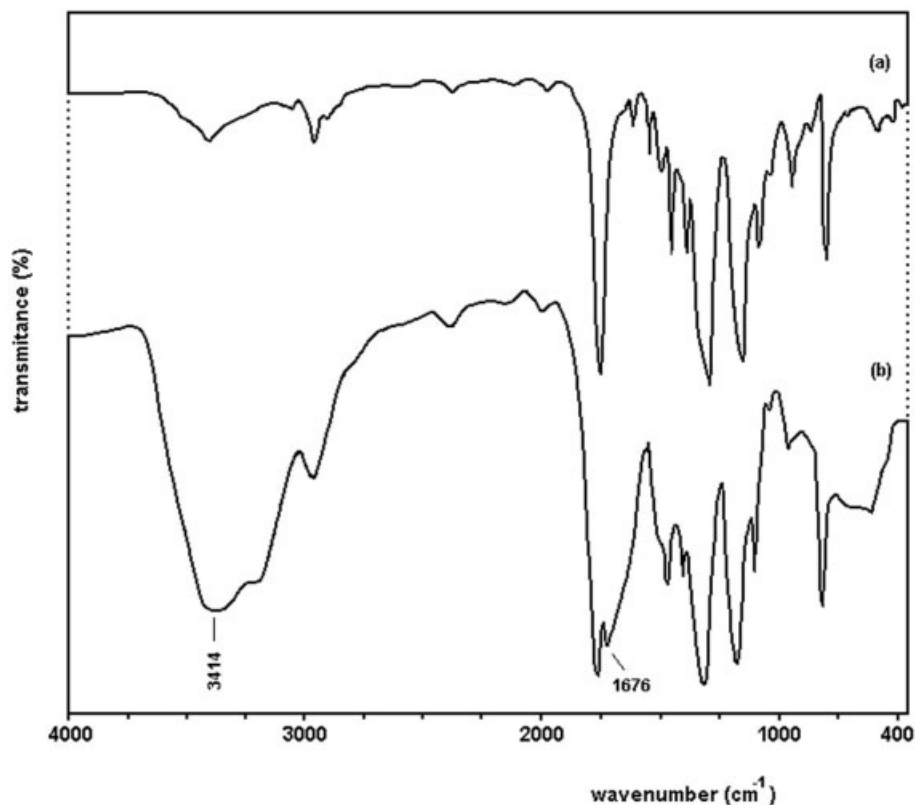

Figure 1 FTIR spectra of (a) ungrafted and (b) 65.0% AAm/IA mixture grafted PET fibers.

Turkey). They were cut in bundles of certain weights, Soxhlet-extracted with acetone for 6 h, and dried at 50°C.

IA (Merck, Germany) and AAm (BDH, England) were used after recrystallization. Bz_2O_2 (Merck) was recrystallized twice from a methanol and chloroform mixture and dried in a vacuum desiccator. The basic and acidic dyes employed were methylene blue (Merck) and Scarlet Red B (Bayer, Germany), respectively.

Graft copolymerization

Fiber samples (0.300 ± 0.001 g) were placed in a 50-mL polymerization tube, and an appropriate amount of IA, AAm, or their mixture was added to it. Then, Bz_2O_2, dissolved in 2 mL of acetone, was added to the tube. The mixture was made up to 20 mL with deionized water and placed in a water bath at the polymerization temperature (kept within ±1°C). The fiber samples taken at the end of polymerization were freed from the homopolymer or homopolymers through washing with boiling water for 4 h (the washing water was changed four times) and Soxhlet-extracted for 6 h. The washed fibers were dried at 50°C *in vacuo*. The graft yield (G%) was calculated by the use of the weights of the original and grafted fibers with the following formula:

$$G\% = \frac{W_g - W_o}{W_o} \times 100$$

where W_g is the dry weight of the grafted fiber (g) and W_o is the dry weight of the original fiber (g).

The rate of grafting (R_g) was calculated as follows:

$$R_g = \frac{W_g - W_o}{Vt}$$

where V is the volume of the solution (L) and t is the grafting time (s).

Determination of the amount of AAm in the fibers grafted with the AAm/IA monomer mixture
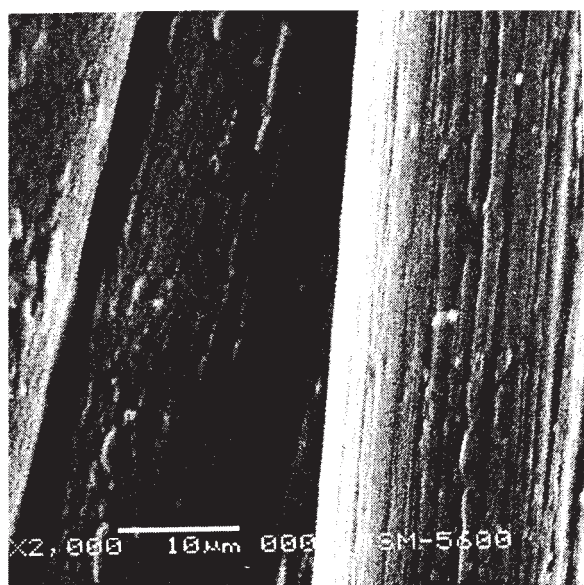
The amount of AAm inserted into the structure of fibers grafted with the AAm/IA mixture was determined via nitrogen analysis with the Kjeldahl method as follows:

$$\% \text{ AAm content} = \frac{(\text{Nitrogen}\%) \times M_{\text{AAm}}}{14}$$

where M_{AAm} is the molecular mass of AAm
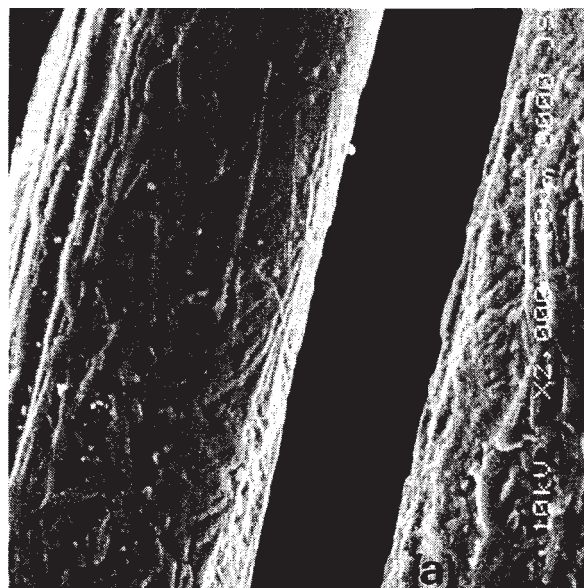
(a)

(b)

Figure 2 SEM micrographs of AAm/IA mixture grafted PET fibers at a magnification of 2000×. The graft yields were (a) 10.0 and (b) 27.8%.

The amount of IA was determined by the subtraction of the amount of AAm from the total graft.

Measurement of the fiber density and diameters

The density of the fibers was determined by the use of a density column prepared with xylene and carbon tetrachloride, as described previously.[16] The diameters of the grafted fibers were measured with an Olympus BX51 optical microscope. The measurements were made in five different regions on each sample, and the average diameters were computed.

Dyeing of the fibers

Ungrafted and grafted fibers with various AAm/IA ratios were dyed with 0.75 g/L methylene blue solution at 85°C for 2 h. The fiber samples taken from the dyeing bath were thoroughly washed with hot water, and the dye absorbed by the fibers was extracted with dimethylformamide at 80°C. The same procedure was repeated with acidic dye at a dye concentration of 1.5 g/L (Scarlet Red B). In the case of acidic dyeing, the dye was extracted with a 25% pyridine solution at 90°C from the fiber. The amount of extracted dye was determined spectrophotometrically at 680 nm for methylene blue and at 532 nm for Scarlet Red B by the use of calibration curves. The measurements were taken with a Shimadzu 160 A spectrophotometer (Japan).

Determination of the moisture-regain values of the fibers

The fiber samples were kept in a chamber with a relative moisture of 65% at 20°C for 24 h. The samples were then removed from the medium, weighed, dried at 50°C *in vacuo*, kept in a desiccator containing P_2O_5 for 2 h, and weighed again. The conditioning chamber with a relative moisture of 65% was prepared with sulfuric acid (density = 1.275 g/cm^3).

SEM

The SEM micrographs of the fibers were taken with a JEOL JSM-5600 scanning electron microscope (Japan) after their surfaces were covered with gold.

TGA

The thermal analysis of the fiber samples was carried out with a Linseis L81 thermal analyzer between 25 and 700°C under a helium atmosphere at a flow rate of 200 mL/min. The samples were heated at a rate of 10°C/min.

FTIR spectroscopy

The FTIR spectra of the fiber samples were recorded with a Mattson 1000 FTIR spectrophotometer (UK) after being pelletized with KBr.

RESULTS AND DISCUSSION

FTIR spectra

The spectra of ungrafted and 65% AAm/IA-grafted PET fibers are given in Figure 1. A comparison of these
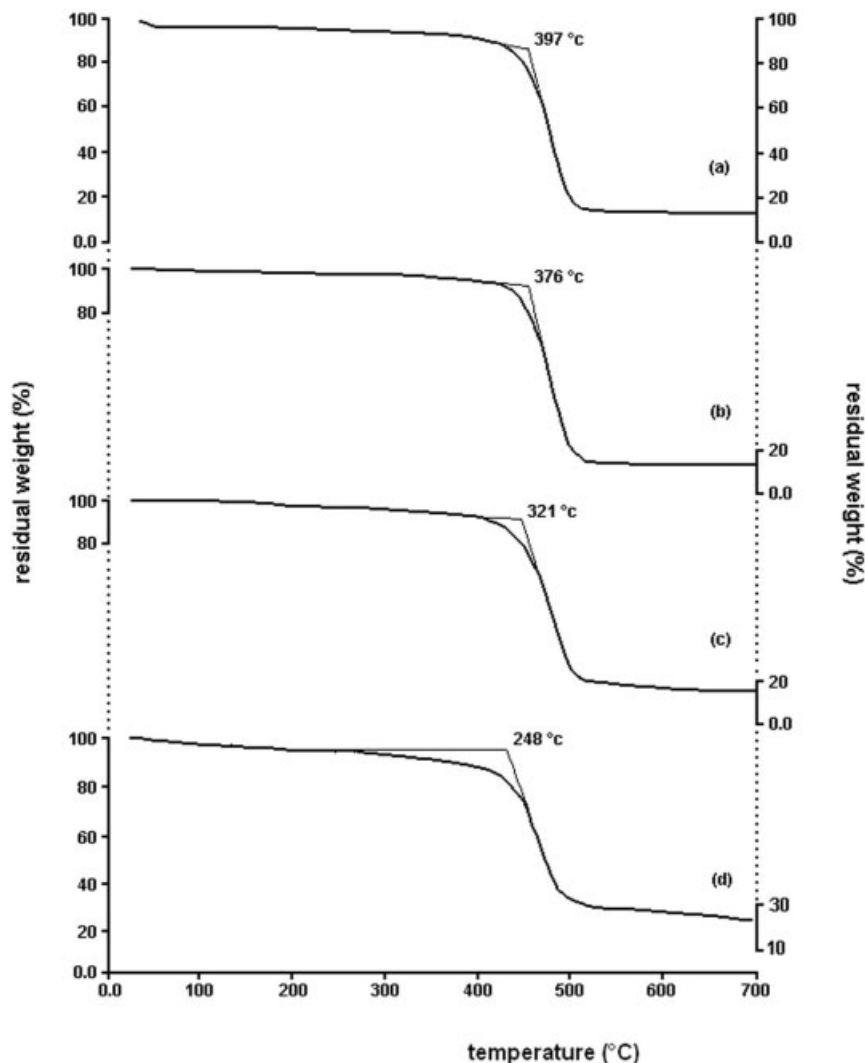
Figure 3 Thermograms of PET fibers grafted with various AAm/IA mixtures. The graft yields were (a) 0.0, (b) 4, (c) 11.3, and (d) 28.3%.

spectra shows a broad peak at 3414 cm^{-1} coming from the merge of the —OH[17] group of IA and the —NH stretching peak[15] of AAm, which was not observed for the ungrafted fiber. There was also a carbamide peak at 1676 cm^{-1} coming from AAm. These results show that IA and AAm homopolymers were introduced into the fiber structure.

SEM results

The effect of the grafting on the PET surface was investigated with SEM micrographs. The SEM micrographs of the ungrafted PET fibers and PET fibers grafted with 10.0% and 27.8% AAm/IA mixtures are shown in Figure 2. The morphology of the uniform surface of the ungrafted PET fiber[15] was changed to a layered, shell-like structure with grafting [Fig. 2(a,b)].

TGA

Thermograms of ungrafted and AAm/IA-grafted PET fibers are presented in Figure 3. The thermograms indicate that the thermal decomposition temperatures of the fibers decreased after grafting. The thermal decomposition temperature of ungrafted PET fiber (397°C) decreased to 376, 321, and 248°C upon grafting with 4, 11.3, and 28.3% graft yields, respectively.

Effect of the monomer mixture ratios on the graft yield

Figure 4 shows the graft yields obtained by the grafting of PET fibers with IA, AAm, and their mixtures with Bz$_2$O$_2$. The AAm/IA mixture concentration was kept constant at 1.5 mol/L. The maximum monomer concentration employed in single monomer grafting was also 1.5 mol/L.
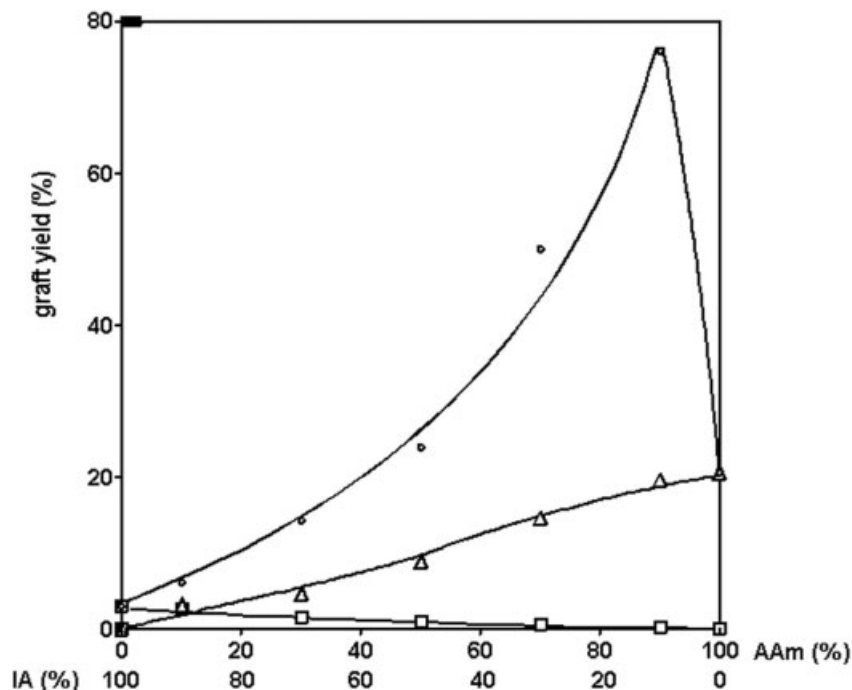
Figure 4 Variation of the grafting percentage with changes in the molar percentage ratio: ($\triangle$) AAm, ($\square$) IA, and ($\bigcirc$) AAm/IA (temperature = 85°C, time = 2 h, [Bz$_2$O$_2$] = 1.0 × 10^{-2} mol/L, AAm/IA = 50/50).

As shown in Figure 4 for grafting with AAm alone, the graft yield increased with the AAm concentration and reached 20.6% at 1.5 mol/L. Similarly, the graft yield increased with increasing IA concentration in the grafting of IA alone. However, the maximum graft yield remained as low as 3%. Similar results were observed in the grafting of IA upon polypropylene fibers.[18,19]

The use of AAm and IA monomers together in grafting caused a significant increase in the graft yield. The graft yield was highly dependent on the monomer ratio, and the maximum graft yield (76.1%) was reached at an AAm/IA ratio of 90/10. Similar results were also observed in the grafting of PET fibers with acrylic acid/styrene[11] and AAm/methacrylic acid[15] monomer mixtures.

This synergistic effect was observed in every mixture ratio. For instance, the graft yields obtained by the single grafting of the monomers at an AAm concentration of 1.35 mol/L and an IA concentration of 0.15 mol/L, corresponding to a 90/10 AAm/IA ratio, were 9.0% for AAm and 1.0% for IA. In other words, the total graft yield for the individual grafting of the monomers at these concentrations was 19.9%. On the other hand, the graft yield reached 76.1% with the use of the monomer mixture with a 90/10 AAm/IA ratio (Fig. 4).

Distribution of the monomers in the grafted chains

On the fibers grafted with the AAm/IA mixture, the side chains contained structural units coming from both AAm and IA. The number of AAm units on the side chains was determined by nitrogen analysis with the Kjeldahl method. The amount of IA was then computed by the subtraction of the amount of AAm from the total amount grafted. Table I gives the percentages of IA and AAm in the grafted chains and inserted into the structure of the PET fibers with the use of different monomer mixtures.

As shown in the table, although it was not possible to graft IA on PET fibers to a significant extent, the use of AAm as a comonomer had a synergistic effect on the grafting of IA onto PET fibers. The graft yield was as low as 1.6% when IA was grafted alone onto PET fibers; its concentration was 0.45 mol/L (corresponding to a 70/30 AAm/IA ratio; Fig. 4). The graft yield of IA increased to 33.5% when it was used with 1.05 mol/L AAm (Table I). The amount of IA inserted into the structure of the PET fibers was more than the amount of AAm. It has been reported that a growing radical of IA has a greater affinity toward its own monomer and that a growing comonomer radical of AAm prefers to combine with IA.[20,21]

Effect of the temperature and time on the graft yield

The effects of the polymerization temperature on the grafting of the AAm/IA mixture onto PET fibers are shown in Figure 5. Increasing the temperature from 65 to 85°C increased the saturation graft yield and rate of grafting. The highest graft yield, 29%, was obtained at 85°C, and it decreased to 23.3% at 95°C. An increase in

TABLE I
Distribution of AAm and IA in Poly(AAm/IA) Grafted to PET Fibers

AAm/IA	Distribution of monomers in PET fiber (%)			Distribution of monomers in grafted chains (%)	
	AAm[a]	IA[b]	Total graft yield	AAm	IA
0.0/100	—	3.0	3.0	—	100
10/90	1.0	5.1	6.1	16.4	83.6
30/70	3.0	11.3	14.3	20.9	79.1
50/50	5.3	18.6	23.9	22.2	77.8
70/30	23.4	33.5	56.9	41.3	58.7
90/10	58.1	18.0	76.1	76.1	23.9
100/0.0	20.6	—	20.6	100	—

[a] Estimated by Kjeldahl's method.
[b] Calculated by the subtraction of the AAm graft yield from the total graft yield.

the temperature increased the dissociation rate of Bz_2O_2, the mobility of the molecules, the swelling of the PET fibers, and the diffusion of monomer molecules into the PET structure.[22] A decrease in the graft yield at temperatures above 85°C may have been due to an increase in the rates of termination reactions.[11,23]

Effect of the initiator concentration on the graft yield

The effect of the Bz_2O_2 concentration on the grafting percentage of an AAm/IA (50/50) mixture to PET fibers is shown in Figure 6. The graft yield increased to

28.9% at a Bz_2O_2 concentration of 1.0×10^{-2} mol/L and decreased at initiator concentrations higher than this value. The increase in the Bz_2O_2 concentration increased the number of radical species, such as homopolymeric and copolymeric active chains. Thus, the rate of the termination reactions increased, and the graft yields decreased.[15,24]

The experimental data obtained at the 20th minute of polymerization, related to the change in the graft yield with the initiator concentration, are tabulated in Table II, and these data were used to plot log R_g + 4 against log $[Bz_2O_2]$ + 3 (Fig. 7). The slope of the graph showed that the rate of grafting was 0.65th-order with respect to the Bz_2O_2 concentration.
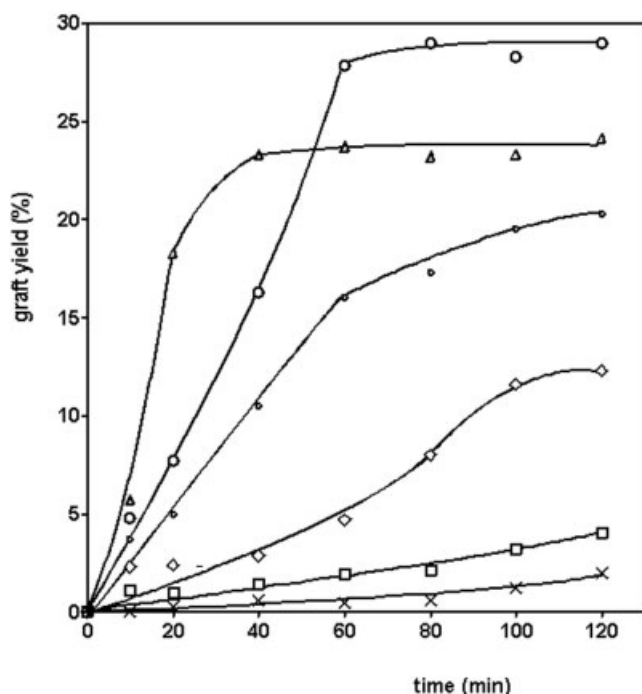

Figure 5 Effects of temperature and time on grafting: (×) 65, (□) 70, (◇) 75, (°) 80, (△) 85, and (○) 95°C ([AAm/IA] = 1.5 mol/L, $[Bz_2O_2]$ = 1.0×10^{-2} M).
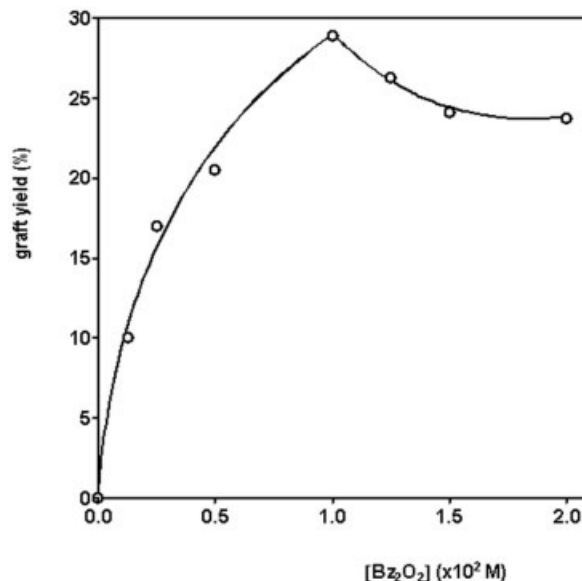
Figure 6 Effect of the Bz_2O_2 concentration on the grafting percentage ([AAm/IA] = 1.5 mol/L, temperature = 85°C, time = 2 h).

TABLE II
Dependence of R_g on the Bz_2O_2 Concentration

Graft yield (%)[a]	log [Bz_2O_2] + 3	$R_g \times 10^4$ (g of monomer $L^{-1}s^{-1}$)	log R_g + 4
1.3	0.49	1.67	0.22
2.3	0.78	2.92	0.47
3.7	1.08	4.58	0.66
4.0	1.26	5.25	0.72

[a] Values obtained at 20 min; AAm/IA = 50/50 (mol/mol).

Effect of the monomer mixture concentration on the graft yield

Figure 8 shows the change in the graft yield with changes in the AAm/IA mixture concentration. The AAm/IA ratio was kept constant at 50/50. Increasing the monomer mixture concentration from 0.5 to 2.5 mol/L increased the graft yield and rate of grafting. The saturation graft yield was reached in 60–80 min with every monomer concentration employed, and no induction period was observed.

The data obtained at the 20th minute of polymerization, which show the change in the rate of grafting with the concentration of AAm/IA, are tabulated in Table III. With the data tabulated in Table III, log R_g + 4 was plotted against log [AAm/IA] (Fig. 9). The slope of the graph showed that the graft yield was 0.74th-order with respect to the AAm concentration.

Therefore, the rate-of-grafting equation of the AAm/IA mixture onto PET fibers can be written as follows:

$$R_g = k[\text{AAm}]^{0.74}[\text{Bz}_2\text{O}_2]^{0.65}$$

where, k is the rate constant of graft copolymerization.
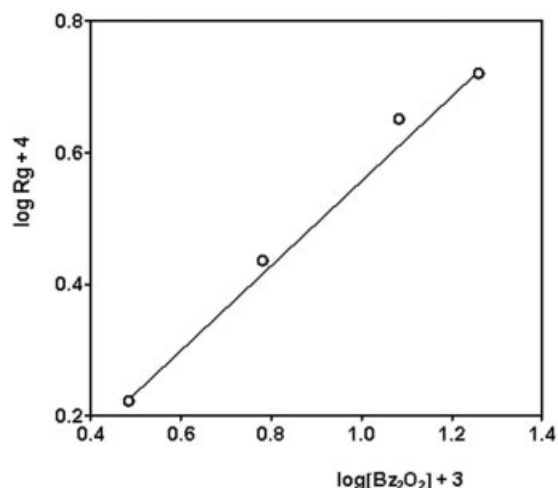

Figure 7 Plot of log R_g + 4 versus log [Bz_2O_2] + 3 ([AAm/IA] = 1.5 mol/L, temperature = 85°C, time = 20 min).
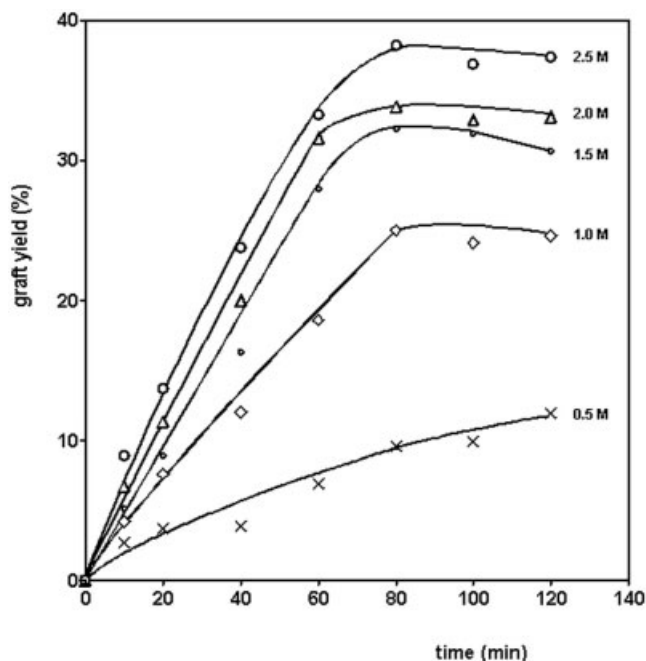

Figure 8 Effect of the concentration of the AAm/IA mixture on the grafting percentage: (×) 0.5, (◇) 1.0, (•) 1.5, (△) 2.0, and (○) 2.5 mol/L (AAm/IA = 50/50, [Bz_2O_2] = 1.0 × 10^{-2} mol/L, temperature = 85°C).

Investigation of some properties of the grafted fibers

Diameter and density

The changes in the diameter and density values of the AAm/IA grated PET fibers are given in Table IV. The density and diameter of the PET fibers increased with increasing graft yield and reached 1.3915 g/cm³ and 2750 × 10^{-3} cm, respectively, at a graft yield of 19.6%. The simultaneous increases of the fiber density and diameter can be explained by the contribution of the grafted side chains to the mass of the fiber being more than their contribution to its volume.[7]

Changes in the moisture regain

Figure 10 depicts the changes in the moisture regain of AAm/IA-grafted fibers with the graft yield. The mois-

TABLE III
Dependence of R_g on the AAm/IA Mixture Concentration

Graft yield (%)[a]	log [AAm/IA]	$R_g \times 10^4$ (g of monomer $L^{-1} s^{-1}$)	log R_g + 4
3.7	0.70	4.58	0.66
7.6	1.00	9.58	0.98
8.9	1.18	11.25	1.05
10.3	1.30	12.96	1.11

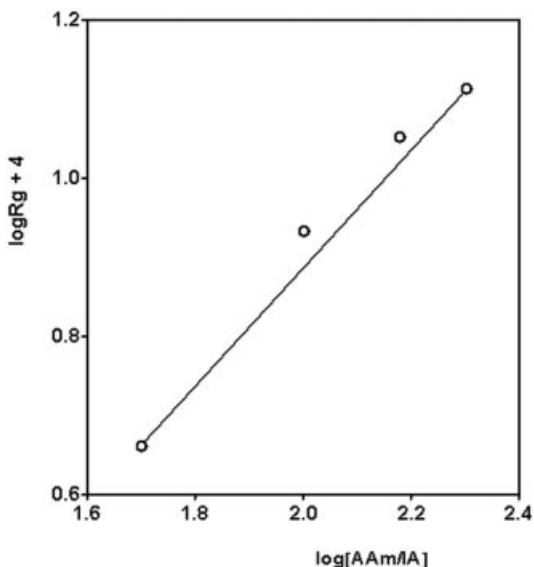[a] Values obtained at 20 min; AAm/IA = 50/50 (mol/mol).

Figure 9 Plot of $\log R_g + 4$ versus $\log$ [AAm/IA] (AAm/IA = 50/50, $[Bz_2O_2] = 1.0 \times 10^{-2}$ mol/L, temperature = 85°C, time = 20 min).

Figure 10 Moisture-regain values of AAm/IA-grafted PET fibers.

ture regain of ungrafted PET fiber was very low (0.42%) because of its hydrophobic character. As shown in Figure 10, the moisture regain of PET fibers grafted with the AAm/IA mixture increased with the graft yield. This was due to the insertion of carboxyl and amide groups into the fiber structure. The enlargement of the fiber structure due to the grafting process also had an effect on the increase in the moisture regain. However, this increase in the moisture regain of the AAm/IA-grafted PET fibers was not very much in comparison with similar studies in the literature.[5,7,11] This low value can be attributed to the dense hydrogen bonds that may form in the PET structure as a result of grafting with the AAm/IA monomer mixture.

Dyeability

PET fibers can only be dyed with disperse dyes because they do not contain suitable functional groups that can interact with dye molecules. Grafting PET
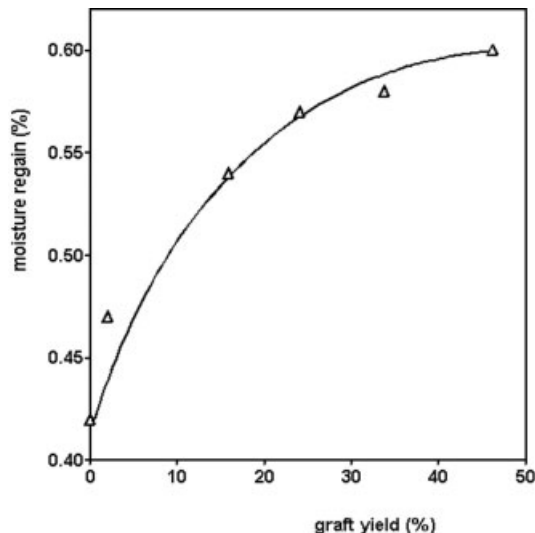
fiber with AAm/IA monomer mixtures increases its dyeability properties with both acidic and basic dyes because it inserts into the fiber structure of the functional groups of —COOH and —NH$_2$ groups, which can interact with basic and acidic dyes, respectively. The data related to the dyeing experiments are listed in Table V.

The table indicates that the dyeability of ungrafted PET fibers with acidic and basic dyes is negligible. The dyeability value of 0.27 mg of dye/g of fiber of ungrafted PET fiber with the basic dye increased to 2.30 mg of dye/g of fiber after grafting with 56.9% AAm/IA (0.1014 g of IA). At higher graft values, the dyeability with basic dyes showed a decrease as a result of the decrease in the IA content of the grafted fibers (Table I) and became 0.64 mg of dye/g of fiber at a grafting value of 76.1% AAm/IA.

The dyeability of the PET fibers grafted with the AAm/IA monomer mixture with acidic dyes, on the other hand, increased with increasing AAm content on the grafted chains. The dyeability reached 1.55 mg of dye/g of fiber at a grafting value of 76.1% AAm/IA (0.1755 g of AAm; Table V).

CONCLUSIONS

The factors affecting the grafting and some properties of AAm/IA-grafted PET fibers were investigated in detail. As shown by the experimental results, the single grafting of IA with Bz$_2$O$_2$ remained at a very low level of 1.6%. However, the addition of AAm as a comonomer had a synergistic effect on the introduction of IA monomers into the PET fibers. The optimum Bz$_2$O$_2$ concentration was 1.0×10^{-2} mol/L with a 50/50 AAm/IA ratio at the optimum temperature (85°C).

TABLE IV
Change with the Graft Yield of the Density and Diameter of the AAm/IA Mixture Grafted PET Fibers

Graft yield (%)	Density (g/cm^3)	Diameter $\times 10^3$ (cm)
0.0	1.3470	2.585
10.0	1.3821	2.687
19.6	1.3915	2.750
25.0	1.3958	2.800
27.8	1.3980	2.844
38.7	1.4006	2.878

TABLE V
Dyeability of Fibers Grafted with the AAm/IA Mixture at Various Ratios

AAm/IA (mol/mol)	Graft yield (%)	Weight of AAm in grafted chains (g)	Weight of IA in grafted chains (g)	Dye uptake (mg of dye/g of fiber)	
				Acidic dye	Basic dye
—	0.0			0.01	0.27
10/90	6.1	0.0047	0.0132	0.14	1.42
30/70	14.3	0.0090	0.0339	0.61	1.92
50/50	23.9	0.0160	0.0562	1.02	2.09
70/30	56.9	0.0707	0.1014	1.24	2.30
90/10	76.1	0.1755	0.0544	1.55	0.64

The grafting of PET fibers with these two monomers affected some properties. The dyeability of the PET fibers increased with an increase in grafting with both acidic and basic dyes. The dye-uptake values of the grafted fibers were very dependent on the number of IA and AAm units inserted into the fiber structure. However, the moisture regain showed very little increase with grafting. The thermal stability of the PET fibers decreased when the AAm/IA mixture was grafted onto them.

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