

Ce(IV)-Initiated Graft Polymerization of Acrylic Acid onto Poly(ethylene terephthalate) Fiber

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ABSTRACT: Graft copolymerization of acrylic acid onto poly(ethylene terephthalate) (PET) fiber by a redox system using ceric (IV) initiator was studied with regard to various parameters of importance: acrylic acid concentration, ceric (IV) concentration, nitric acid concentration, reaction temperature, and reaction time. Based on the morphology of the PET fiber, it could be concluded that ceric (IV) in dilute nitric acid is a redox initiator for the surface graft copolymerization of the acrylic acid/PET system. The grafted PET fiber showed an increase in improved moisture regain to reach

900% at 39.5% graft yield. The dyeability with the basic dye and disperse dye significantly increased by 100 and 22%, respectively, as a result of the grafting onto PET fiber. Both tenacity and elongation gradually decreased by 51.2 and 28.9%, respectively, with increasing graft yield, which reduced the fiber service lifespan. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1952–1958, 2003

Key words: graft copolymers; PET fiber; ceric initiator; morphology; tensile properties

INTRODUCTION

There is a widespread use of fibers of synthetic origin in the textile industry today. Poly(ethylene terephthalate) (PET) fiber has a prominent place among these synthetic fibers because of its outstanding stability and excellent mechanical properties.¹ However, many superior properties of PET fiber and some of their features such as low moisture regain, difficulty of dyeing, and poor antistatic properties limit their fields of usage.²

In recent years, the scientific literature has revealed a growing interest in graft copolymerization on textiles as a method for modification of the properties of textile fabrics. Grafting is a well-established technique used to cause more or less extensive modification of properties and textile performance of PET fiber, as well as other synthetic and natural fibers. Although a lot of work has been done on graft copolymerization of vinyl monomers onto cellulosic and other textile fibers,^{3–7} much less has been reported on grafting of vinyl monomers onto PET fiber. Ceric salts in aqueous acidic solution are the well-known initiator of vinyl polymerization and graft copolymerization. In this

study, the effect of the changes of graft copolymerization conditions on the graft yield of acrylic acid onto PET fiber using ceric ammonium nitrate in nitric acid medium was examined. The changes in the physical properties of PET fiber grafted with acrylic acid such as moisture regain and dye uptake were also observed.

EXPERIMENTAL

Materials

The PET filament yarn (250 denier, 48 filaments) was provided by Oriental Fiber Co. (Nakornprathom, Thailand). The fiber sample was extracted with methanol to remove any material adhering to the surface by Soxhlet extraction at 338 K for 6 h. Acrylic acid (AA) was obtained from Siam Industry Co. (Thailand). The monomethyl ether hydroquinone (MEHQ) is frequently used as an inhibitor of AA. The inhibitor of AA monomer is particularly suitable for the manufacture of its polymer without pretreatment. Ceric (IV) ammonium nitrate (CAN), analytical grade, was obtained from Fluka (Buchs, Switzerland). Methanol, analytical grade, was obtained from Merck (Darmstadt, Germany). Nitric acid 70% (w/w), analytical grade, was obtained from Ajax (Australia). Methylene blue (basic dye), analytical grade, was obtained from Merck (Hohenbrunn, Germany). Hicron navy blue GRL-SF 200% (CI disperse blue 79) was obtained from Kangwal Polyester Co. (Petchaburi, Thailand).

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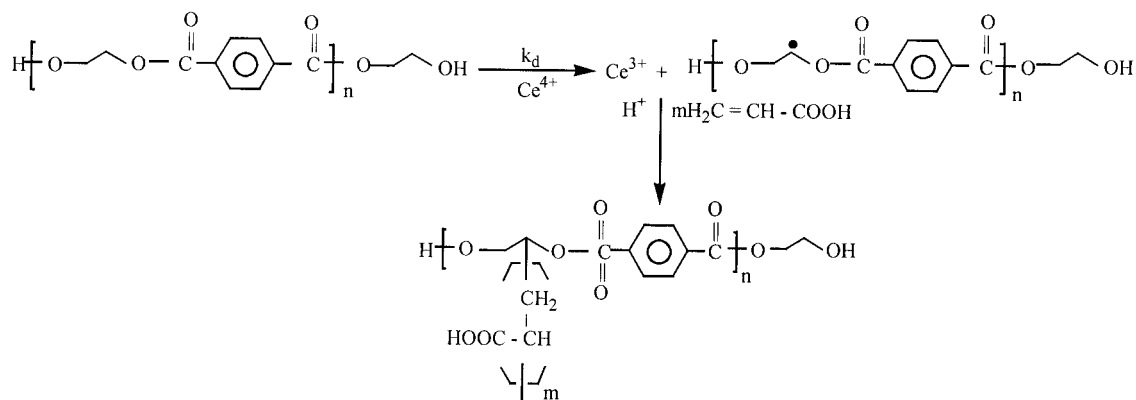


Figure 1 Schematic representation of the surface modification of PET fiber.

Graft copolymerization

The graft copolymerization reaction was carried out in a 100-cm³ three-neck round-bottom flask. A PET sample weighing 1.0 g was impregnated with 15 cm³ AA for about 20 min, and 8 cm³ nitric acid (50% w/w) was then added. After adding nitric acid for 20 min, 2 cm³ CAN solution was added into the reaction mixture and the time was noted. The grafting reaction was carried out in a nitrogen atmosphere under heating within the temperature range of 323 ± 1 K for 1 h. Then, the reaction was stopped by quenching the vessel with ice water. After the reaction, the homopolymer of AA was removed from the graft copolymer by methanol in a Soxhlet extractor at 338 K for 48 h. Poly(acrylic acid) (PAA) was precipitated by methanol. The graft yield was calculated as follows:

$$\text{Graft yield (\%)} = \frac{(\text{Weight of grafted fiber} - \text{weight of fiber})}{\text{Weight of fiber}} \times 100 \quad (1)$$

Characterization

Fiber/graft morphology

The surfaces of 40% graft yield of the AA-grafted-PET fiber and the ungrafted PET fiber were coated with a thin layer of gold to provide electric conductivity. A scanning microscope (JSM-5800LV, JEOL, Peabody, MA) was used for surface morphology characterization at 15 keV acceleration voltage. The micrographs were taken at different angles of view with different magnifications.

Tensile properties

The denier of samples was tested on a Lenzing Vibroskop 400 (Lenzing Co., Ltd., Austria) at a tension weight of 300 mg with a fiber length of 24 mm. Te-

nacity, elongation, and load of samples were tested on a Lenzing Vibrodyn 400 at the testing speed of 100 mm min⁻¹ using a gauge length of 10 mm.

Moisture regain

The moisture regain of the samples was determined by exposing the fibers (1.0 g) to 65% relative humidity at 293 K in a humidity-temperature chamber for 5 days. The samples were weighed in the conditioned state, then dried at 383 K for 12 h in an oven and weighed again. Each sample was repeated for three replications.

Dyeability

The samples were dyed with 0.2 g L⁻¹ methylene blue (100 cm³), allowed to stand for 2 h at 373 K, and with 0.2 g L⁻¹ Hicron Navy Blue GRL-SF 200% (100 cm³) for 2 h at 403 K by Phisit dyeing apparatus (Bangkok, Thailand). The material/liquor ratio was 0.2/100. The dye remaining on the sample was washed with distilled water. The washing solution was mixed with the dye left in the pot. This solution was measured for the methylene blue absorbance at 663 nm wavelength and the Hicron navy blue GRL-SF 200% absorbance at 545 nm wavelength versus distilled water as a blank on Unicam 5625 UV/Vis spectrometer (Unikam, UK). The concentrations of the methylene blue and Hicron navy blue GRL-SF 200% undyed were determined from the calibration curve and the concentration of the dye on the fiber was calculated.

RESULT AND DISCUSSION

The grafting of AA onto PET fiber was conducted to develop the material properties that accommodated a high-density surface of carboxyl groups. The overall process involved the treatment of PET fiber with AA in acidic medium of CAN. This led to the formation of graft copolymer and homopolymer. A schematic dia-

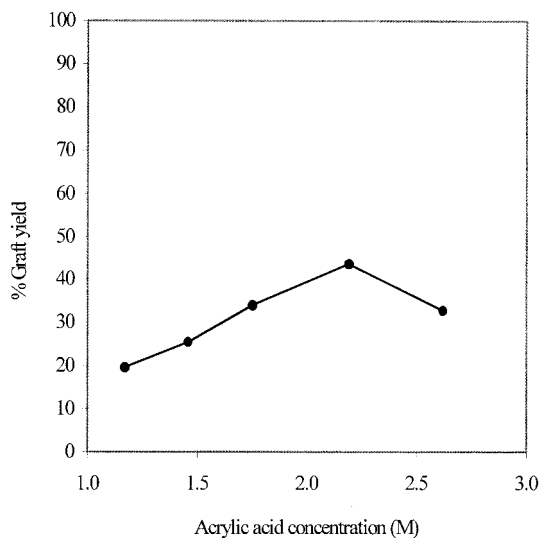


Figure 2 Effect of acrylic acid concentration on graft yield.

gram for the modification of PET backbone is depicted in Figure 1.

The yield of PAA-grafted-PET was considerably influenced by the functions of monomer, initiator, acid concentration, and reaction conditions. The influences of these parameters on the graft yield are discussed below.

Effect of monomer concentration

The effect of monomer concentration on the graft yield is shown in Figure 2. It is seen that the graft yield increases steadily with the increasing AA concentration from 1.17 to 2.19M, and then decreases with further increases in AA monomer concentration. More AA molecules diffuse into the PET fiber and the excess amount resides in the outer solution. This increases chances for the PET macroradicals and growing grafted side chains of AA to encounter more monomer units to add and increase the graft yield. However, the decreasing trend of the graft yield was also found when further increases in the concentration of AA had been added. The greater the monomer concentration in the aqueous phase, the greater the amount of homopolymer attributed to the competition between the homopolymerization and graft copolymerization, where the former prevails over the latter at higher AA concentration and at the expense of the latter.⁶ The PAA homopolymer accumulated increases the medium viscosity, which inhibits the AA diffusion to the active site on the macroradicals, thus leading to the decrease in graft yield.

Effect of initiator concentration

The results obtained by changing the initiator concentration for the graft copolymerization are presented in

Figure 3. It is observed that increasing Ce^{4+} concentration from 0.49 to $1.82 \times 10^{-3} M$, the graft yield increases, and thereafter the graft yield decreases considerably. The variation of Ce^{4+} produces a vast change in the number of free radicals generated.⁸ The higher ceric ion concentration increases the degree of decomposition of the complex of Ce^{4+} . These primary free radicals abstract hydrogen radicals from the active centers on PET and produce PET macroradicals, which lead to the formation of graft copolymer and thus increase the graft yield. However, a further increase in initiator concentration ($>1.82 \times 10^{-3} M$) causes the following outcomes^{9,10}: (1) for the abundant free radicals in the aqueous phase, AA homopolymer could be particularly formed in the solution, which might terminate the growing chains; (2) free radicals formed on the main chain of PET could be oxidized, and thus terminate the reactive sites; (3) the graft copolymerization and homopolymerization of AA compete with each other in the system, depending on the direct attack of free radicals to either the PET or to the monomer. The net result is that a higher concentration of initiator results in the production of more free radicals in the acid medium, thereby reducing the graft yield resulting from excessive Ce^{4+} concentration taking part in the termination of growing graft chains. At high ceric ion concentration, the propagating radical with the hydroxyl end group loses a hydrogen radical to form a polymer molecule with an olefinic end group. This end group can possibly graft further with acrylic acid to give some short grafts at the polymer chain end, as shown in Figure 4.

As mentioned above, homopolymer formation takes place simultaneously with graft copolymerization at the expense of the graft reaction. To attain a good

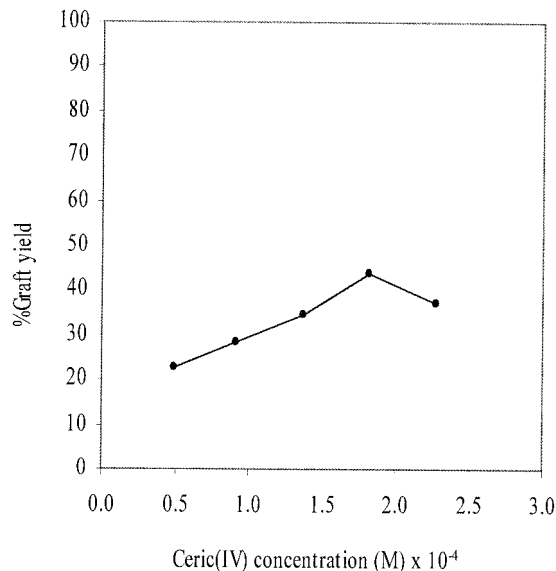


Figure 3 Effect of ceric initiator concentration on graft yield.

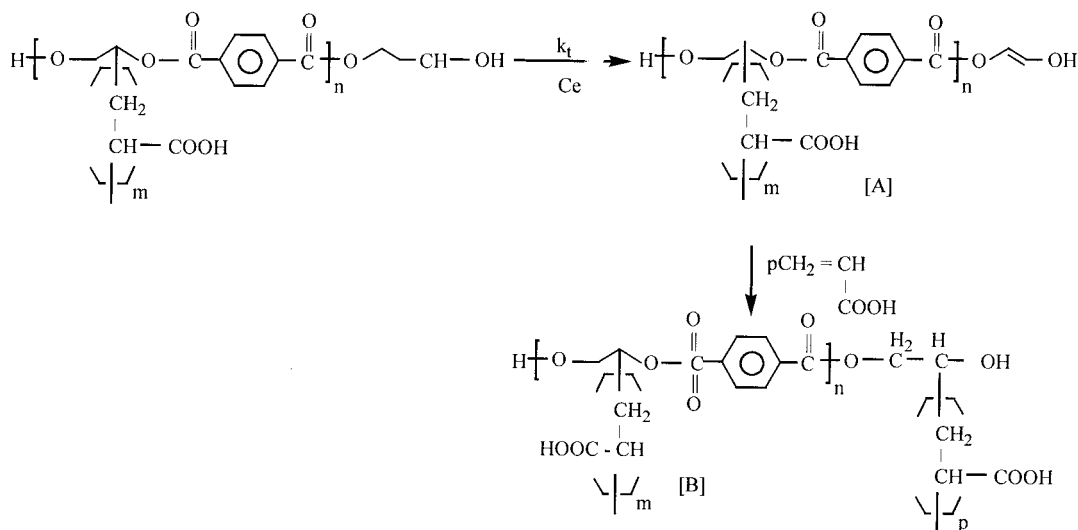


Figure 4 Role of high ceric (IV) concentration on propagating grafted chains: [A] termination of chain end; [B] reinitiating for further grafting.

property of graft copolymer, the homopolymer should be removed. The most commonly employed method for the removal of this homopolymer from the grafted fiber is extraction in a good solvent for the homopolymer, whereas the graft copolymer remains unaffected. In this research, methanol was employed for the extraction of homopolymer by the Soxhlet extraction method. The extraction time was determined based on the extraction time at which the fiber weight remained unchanged.

The homopolymer content and the graft yield were determined at four levels of graft yield, from 22.6 to 41.6%. The relation between the homopolymer content and the grafting yield of acrylic acid onto PET fiber is shown in Figure 5. The graft yield decreases when the

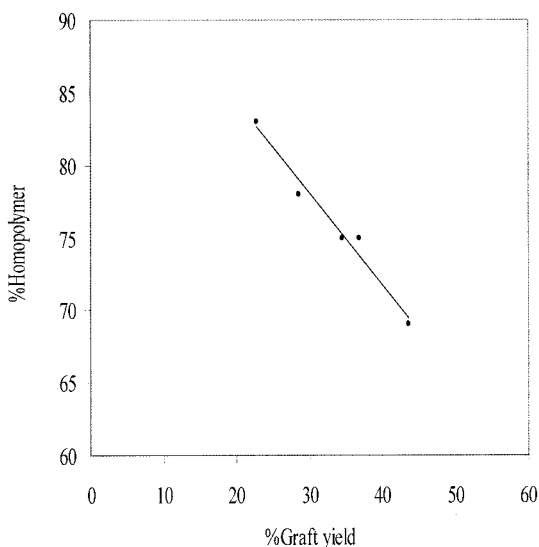


Figure 5 Relationship between homopolymer content and graft yield.

homopolymer content increases. The homopolymer content in the reaction bath brings about an increase in its viscosity because of the presence of macromolecules, which hinders the diffusion of free vinyl monomer onto the fiber and decreases the grafting degree on fiber.

Effect of acid concentration

Figure 6 shows the effect of nitric acid concentration on grafting of AA onto PET fiber in the presence of Ce^{4+} initiator. It is observed that the increases of nitric acid concentration in the reaction mixture enhanced the percentage graft yield. A further increase of the nitric acid concentration led to the decrease of percentage grafting, which was attributed to the reduction of

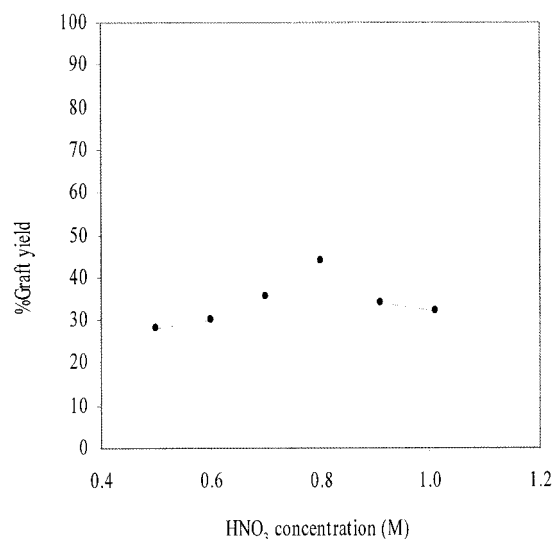


Figure 6 Effect of nitric acid concentration on graft yield.

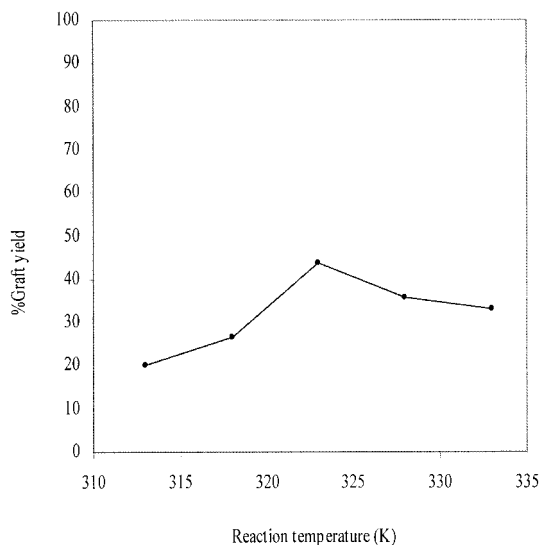


Figure 7 Effect of reaction temperature on graft yield.

the ceric–PET complex. For higher percentage grafting, the acid enhanced the oxidizing power of the initiator. The acid also acted as a catalyst in the hydrolysis of PET, leading to uncoiling of the chains and improvement of the monomer's accessibility onto its active sites.

Mechanistically, the acid enhancement effect in grafting, based on considerable work,^{11–16} was attributed to a partitioning phenomenon. In terms of this concept, increased partitioning of monomers occurs in the graft region of the backbone polymer when acid is dissolved in the bulk grafting solution, thus permitting higher concentrations of the monomer to be available for grafting at a particular site. The role of the acid partition in the grafting reaction initiated by ceric ions causes an increase in the grafting yield. Unfortunately, inclusion of acid also accelerates homopolymerization in the bulk solution and a reduction in grafts. Generally, the extent of this improved monomer partitioning depends on the polarity of monomer, the substrate, and the concentration of the nitric acid present. The positive effect of acid enhancement is that both a partitioning phenomenon and ceric ion initiation acted in concert to optimize the graft yield. At a higher concentration of acid, apart from increased homopolymerization, the effect of acid hydrolysis on the PET backbones as another possible cause for the lowering in graft yield could be observed.

Effect of reaction temperature

Graft copolymerization of AA onto PET fiber was investigated at five different temperatures (i.e., 313, 318, 323, 328, and 333 K), and the results are shown in Figure 7. It is proposed that in the early stages of the reaction, homopolymer formation was very limited

and the concentration of AA monomer around the growing chain was maintained. This causes a fast chain initiation and propagation, leading to a high graft yield.

A further increase in temperature decreased the graft yield. This indicated that at higher temperature, the collision between monomer free radicals also increased, wherein the homopolymer formation becomes predominant. The graft copolymerization occurs with poor selectivity and various hydrogen abstractions. At the higher temperature, it is certain that chain termination and chain-transfer reactions were accelerated, thereby decreasing the graft yield.

Effect of reaction time

Figure 8 shows the effect of reaction time on graft yield. It is observed that by increasing the reaction time from 30 to 60 min, the graft yield increases, and thereafter the graft yield decreases considerably. In the beginning, the rate of grafting increases and reaches a maximum when the reaction time is 60 min. This increase can be explained as follows¹⁷: (1) the higher contact time of monomer molecules with the PET macroradical sites; (2) an increase in the length of PAA grafted chain or the longer kinetic chain length; (3) an increase in the number of grafted chains. When the time of reaction proceeds beyond 60 min, the graft yield decreased gradually. Similar observations were also reported earlier.^{18,19} The reactive sites exposed to the AA were reduced as the result of the increase in viscosity of the solution. This situation induced diffusion difficulties for AA to react with the reactive sites. However, the monomer–PET copolymerization takes place during the first 60 min when the rate of grafting increases.

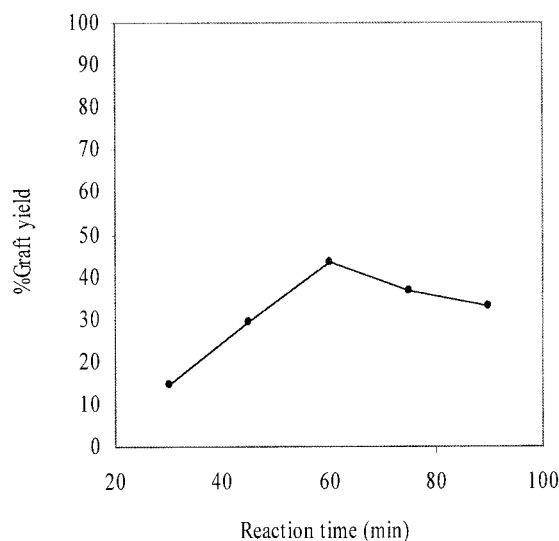


Figure 8 Effect of reaction time on graft yield.

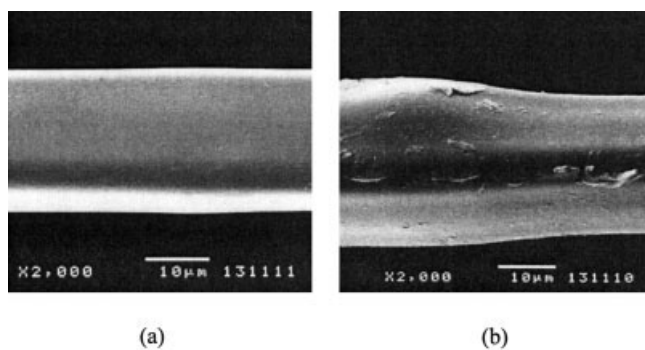


Figure 9 Scanning electron micrographs of AA-grafted-PET fiber. Graft yield: (a) 0%; (b) 43.6%.

Characterization

Fiber morphology

The morphological structure of PET-g-PAA fiber initiated by ceric (IV) was investigated by scanning electron microscopy. Figure 9(a) and (b) show the scanning electron micrographs of PET fiber and grafted fiber at $\times 2000$ magnification. Drastic dimension changes after AA grafting are observed.

The surface of the ungrafted PET [Fig. 9(a)] was smooth, showing the typical features of the control PET fiber. However, the electron photomicrograph illustrates a coating of the AA-grafted-PET fiber [Fig. 9(b)]. A thin and uneven layer of grafting film is deposited, indicating a predominantly surface grafting. As stated, the dimension of the treated fiber is changed, which becomes thicker and less shiny.

Tensile properties

The effects of acrylic acid grafting on the tenacity, the breaking elongation, and breaking load of PET fiber are tabulated in Table I.

Table I shows changes in tensile properties of fiber with grafting. Breaking tenacity, breaking load, and breaking elongation of PAA-grafted-PET fiber decreased with increasing graft yield. Grafting on the PET fiber resulted in a general loss of tensile performance of the PET fiber, in good agreement with previously reported results.²⁰ The segments in the crys-

TABLE II
Moisture Regain Values of AA-grafted-PET Fiber

Graft yield (%)	Moisture regain (%)
0.0	0.2
9.0	0.6
20.1	0.8
31.1	1.0
39.5	2.0

talline regions of PET fiber could be disoriented as a result of the grafting. The decrease in orientation, which is one of the most important fiber characteristics, is responsible for good mechanical behavior, a decrease in fiber strength, extensibility, and toughness.

Moisture regain

The moisture regain of the ungrafted and the grafted PET fiber was investigated and the results are shown in Table II.

The moisture regain value of the hydrophobically ungrafted PET fiber is 0.2%, which increases to 2.0% at 39.5% graft yield. It was thus increased by 900% moisture regain. The AA used as the grafting monomer increases the hydrophilic characteristics of the fiber by the inclusion of some polar carboxylic groups ($-\text{COOH}$) into PET fiber, which increase the moisture regain character of the fiber. It can also be claimed that the AA-grafted-PET fiber structure has a strong influence in the increase in the moisture regain value of the fiber.

Dyeability

The dyeability of the ungrafted and the acrylic acid-grafted-PET fiber with various graft levels is presented in Table III. The dye uptake of methylene blue was increased by 100% dyeability of PET fiber grafted with 43.5% acrylic acid, whereas the dye uptake of disperse dye for PET fiber grafted with 43.2% acrylic acid was increased by only 22% dyeability.

In the dyeing of PET-g-PAA fiber, the methylene blue (basic dye) reacted with the carboxylic groups

TABLE I
Effect of Acrylic Acid Grafting on Tensile Properties of PET Fibers^a

Graft yield (%)	Denier	Breaking load (g force)	Decrease in breaking load (%)	Breaking tenacity (g/den)	Decrease in breaking tenacity (%)	Breaking elongation (%)	Decrease in breaking elongation (%)
0.0	5.03 \pm 0.21	13.17 \pm 0.65	0.00	2.62 \pm 0.11	0.00	164.9 \pm 10.6	0.0
9.7	5.62 \pm 0.22	11.04 \pm 0.58	16.17 \pm 5.21	1.97 \pm 0.11	24.81 \pm 5.45	150.2 \pm 18.7	8.9 \pm 12.4
19.3	6.15 \pm 0.19	11.17 \pm 0.47	15.19 \pm 4.16	1.82 \pm 0.08	30.53 \pm 4.14	145.5 \pm 8.2	11.8 \pm 5.61
29.4	6.58 \pm 0.24	10.94 \pm 0.44	16.93 \pm 3.98	1.66 \pm 0.08	36.64 \pm 4.49	133.3 \pm 12.5	19.2 \pm 9.39
40.0	6.73 \pm 0.28	8.62 \pm 0.32	34.55 \pm 3.75	1.28 \pm 0.04	51.15 \pm 2.42	117.3 \pm 5.6	28.9 \pm 5.0

^a Number of repeats is 20.

TABLE III
Dyeability of the AA-grafted-PET Fiber with Methylene Blue and Disperse Dye

Dyeability with methylene blue		Dyeability with disperse dye	
Graft yield (%)	Dye uptake $\times 10^{-3}$ (g dye/g fiber)	Graft yield (%)	Dye uptake $\times 10^{-3}$ (g dye/g fiber)
0.0	1	0.0	77
16.3	315	16.9	87
22.0	446	19.2	88
31.7	529	30.4	93
43.5	724	43.2	94

present in the grafted chains and chain ends of the polymer. The interaction force such as dipole-dipole can be considered to contribute to the dye-fiber adsorption.²¹ This could be the increase in the number of -COOH groups, which provides the higher dyeability.

The grafting changed in voids and structural appearance of the fiber. These changes had their own contributions to increasing the dyeability of the disperse dye. The nature of the interaction between the disperse dye and PET-g-PAA fiber is that, in contrast to that of methylene blue (basic dye) and the fiber, the disperse dye is essentially nonionic, and thus there is not any ion-ion interaction between the dye and the treated fiber. The disperse dye can directly take either a colloidal portion or an adsorption at mechanistic sites on the polymer segments, which are in the mobile phase because of the thermal motion. Thus, the dye molecules penetrated through the disoriented (amorphous parts) regions of the fiber. The graft copolymerization of acrylic acid proceeds with the incorporation of amorphous poly(acrylic acid) chains in the noncrystalline regions of the fiber. With the increase in amorphous domain attributed to the grafting, the disperse dye molecules can easily approach the reactive sites in the disordered regions.

CONCLUSIONS

AA can be easily graft-copolymerized onto PET fiber using a ceric (IV) initiator in dilute nitric acid. The reaction variables, such as concentrations of monomer, initiator, and nitric acid, and polymerization temperature and time, significantly affect the graft yield. It could be concluded that ceric (IV) in dilute nitric acid

is a redox initiator for the surface graft copolymerization of the acrylic acid/PET system. The grafted PET fiber showed an increase in improved moisture regain and the dyeability with the basic dye and disperse dye. The tensile properties gradually decreased with increasing graft yield.

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