Graft Copolymerization of Acrylamide on Swollen poly (Ethylene Terephthalate) Fibers Using Cerium Ammonium Nitrate Initiator

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GRAFT COPOLYMERIZATION OF ACRYLAMIDE ON SWOLLEN POLY(ETHYLENE TEREPHTHALATE) FIBERS USING CERIUM AMMONIUM NITRATE INITIATOR

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ABSTRACT

In this study the graft copolymerization of acrylamide (AAm) on swollen poly(ethylene terephthalate) (PET) fibers using cerium ammonium nitrate (CeAN) initiator was investigated. Five organic solvents, dimethylsulfoxide (DMSO), morpholine, acetic acid (HAc), *n*-butanol, and 1,2-dichloroethane (DCE), were used as swelling agents. DMSO was found to be the most suitable swelling agent. Solvent diffusion into the fibers was observed to increase with treatment time and temperature. The optimum graft yield was obtained when fibers were grafted after having been swollen in DMSO for a period of 1 hour at 140°C. Variation of graft yield with polymerization time and temperature, and monomer, initiator, and acid concentrations were investigated. Graft yields were observed to increase initially with polymerization time, then to level

off, and were found to increase up to a certain monomer and Ce^{4+} concentration, then to decrease slightly. The effect of grafting on such fiber properties as diameter, viscosity, and moisture gain were also investigated.

INTRODUCTION

Poly(ethylene terephthalate) (PET) is one of the most important synthetic fibers used in the textile industry. It possesses desirable fiber properties such as strength, high crisp, resistance to stretch, shrinkage, and abrasion. However, PET fibers suffer from the drawback of poor antistatic, soil release characteristics, difficult dyeability, and low moisture content because they are highly crystalline, markedly hydrophobic, and do not contain chemically reactive groups. Attempts have been made to eliminate these handicaps by chemical modification of PET fibers through grafting with vinyl monomers.

Vinyl graft polymerization onto PET fibers can be achieved either by radiation [1–8] or by chemical means [8–40, 46, 47]. PET macroradicals capable of initiating grafting can be created by subjecting the PET fibers to γ-rays from Co-60 or to high-energy electrons from accelerators. Grafting can be accomplished using either simultaneous or postirradiation techniques. Although grafting by radiation is easy to control, it causes low radical yield and degradation of the main polymer (above doses over 5 μrad) [1, 2].

Similarly, PET macroradicals can be formed under the influence of initiators. The PET can be oxidized to hydroperoxides [9, 10] at several points along the chain in a random manner. It is then allowed to decompose into active radicals in the presence of monomer either by heat or by a redox system.

There are many studies on grafting of vinyl monomers onto PET fibers in the literature. Grafting of styrene [11–15], acrylic acid, methacrylic acid [7, 16–19], vinyl acetate [5], acrylonitrile [7], or methyl methacrylate [5, 20–23] onto PET fibers has been reported. Studies concerning grafting of acrylamide are limited and generally patented [24–27], and these studies were carried out using either the radiation technique or with benzoyl peroxide (Bz_2O_2) as the initiator.

Tetravalent cerium (Ce^{4+}), a versatile oxidizing agent capable of reacting with almost all types of functional groups, has been extensively used for polymerization of vinyl monomers [23, 28–31]. On account of the high grafting efficiency compared to other known redox systems, this system has gained considerable importance in grafting vinyl monomers onto cotton, cellulose [32–34], wool [35, 36], silk [37], and nylon-6 [38–40]. In the present contribution we have aimed to study graft copolymerization of acrylamide (AAm) onto PET fibers using the Ce^{4+} initiator.

A factor that affects the grafting reaction is the pretreatment of the fiber or film before the reaction is started. These pretreatments have primarily involved swelling solvents.

Hsieh et al. [41] studied the effects of swelling solvents on the polymerization of acrylic acid onto PET film by glow discharge. Uchida et al. [42] performed graft copolymerization of AAm by UV irradiation. They pretreated the PET film with benzoyl alcohol for enhancement of graft copolymerization. Xue et al. [43] pretreated PET films with 1,1,2,2-tetrachloroethane prior to the graft polymerization

of methacrylic acid using H_2O_2 as initiator, and they reported that the amount of add-on is increased as the swelling level increases. In our previous studies we also examined the effect of various solvents [1,2-dichloroethane (DCE); DCE/H_2O (20/80); dimethylsulfoxide (DMSO)] as swelling agents in the graft copolymerization of AAm [44] and 4-vinyl pyridine [45] on PET films using Bz_2O_2 as the initiator.

In this study we used DMSO (δ: 12.0), morpholine (δ: 10.8), DCE (δ: 9.1), n-butanol (δ: 11.4), and acetic acid (HAc, δ: 10.1) whose solubility parameters (δ) are close to those of PET (δ: 9.5 and 12.0) as swelling agents to promote the diffusion and incorporation of monomer and the subsequent polymerization of AAm using Ce^{4+} as the initiator. We determined the enhancing effects of solvents, temperature, reaction time, and monomer and initiator concentrations. The effects of graft yield on viscosity, fiber diameter, and moisture regain properties were evaluated.

EXPERIMENTAL

Materials

PET fibers (126 denier, 28 filament) were kindly supplied by SASA Synthetic Fiber Co. (Adana, Turkey). The fiber samples were first Soxhlet extracted with acetone for 6 hours and then dried to constant weight at ambient temperature. AAm, CeAN, H_2SO_4, and other reagents were Merck products and used as supplied.

Swelling Procedure

DCE, morpholine, DMSO, n-butanol, and HAc were used as swelling agents. Soxhlet extracted and dried PET fibers (0.200 $\pm$ 0.001 g) were placed into 100 mL Pyrex tubes. A temperature-controlled oil bath was used for heating. Fibers were dipped into the selected organic solvent for 3 hours at predetermined temperatures (75-140°C). After treatment, any solvent on the fiber was removed by blotting between filter paper, and the percent increase in weight was determined.

Polymerization Procedure

Pretreated PET fibers were dipped into a 100-mL polymerization tube containing an aqueous solution of AAm at a known concentration, and the tube was placed in an oil bath adjusted to the polymerization temperature. The desired concentrations of CeAN and H_2SO_4 were added, and polymerization was carried under nitrogen atmosphere with continuous stirring. At the end of the predetermined polymerization time the fiber samples were taken from the mixture and roughly washed with hot distilled water. They were then subjected to Soxhlet extraction with water for 6 hours, vacuum dried, and weighed. The percent increase of the dry fiber weight was taken as the graft yield.

Determination of Intrinsic Viscosity

The intrinsic viscosities of ungrafted and grafted PET fibers were determined in m-cresol using an Ubbelohde capillary viscometer mounted in a water bath at 25 $\pm$ 0.1°C.

Measurement of Diameter

The diameters of the fiber samples were measured by a Kyowa Microlux-11 microscope at a magnification of ×400. The measurements were carried out using at least five samples taken from different regions of the grafted fiber.

Determination of Moisture Regain

The fiber samples were conditioned at 20 ± 0.1°C in a medium having a relative humidity of 65% in order to evaluate the moisture regain value. The moisture regain capacity of PET fibers was determined from the weight increase.

FT-IR Spectrum

The FT-IR spectra of AAm-grafted PET fibers were recorded using a Perkin-Elmer Model 1710 Spectrophotometer with a KBr disk.

RESULTS AND DISCUSSION

Swelling of PET Fibers

PET fibers were swollen in DMSO, morpholine, HAc, n-butanol, and DCE for 3 hours at temperatures ranging from 75 to 140°C. The results are tabulated in Table 1. It is clear that the amount of swelling is quite dependent on temperature; the higher the temperature, the greater is the percent swelling. DMSO was found to be the most effective solvent for enhancing graft polymerization of AAm among the solvents employed. The effect of swelling time on graft copolymerization is illustrated in Fig. 1. It is obvious that the effect of treatment time was not as large as that of temperature. Maximum swelling was reached after 1 hour at 140°C. Similar results were observed by Şanlı et al. [44] and Xue et al. [43] on PET films.

Effect of Polymerization Time and Temperature on Grafting

The effect of polymerization time and temperature upon the graft yield is presented in Fig. 2. Obviously the extent of polymerization increases as the reaction temperature increases from 70 to 90°C. An induction period of 2 hours was ob-

TABLE 1.   Effect of Temperature on Swelling (t = 3 hours)

Temperature, °C	Swelling, %				
	DMSO	Morpholine	HAc	n-Butanol	1,2-Dichloroethane
75	25.09	25.95	21.35	15.00	13.93
80	30.32	21.81	11.55	13.85	16.33
90	45.31	36.03	27.27	27.74	—
100	53.25	42.07	30.01	32.11	—
140	78.80	—	—	—	—
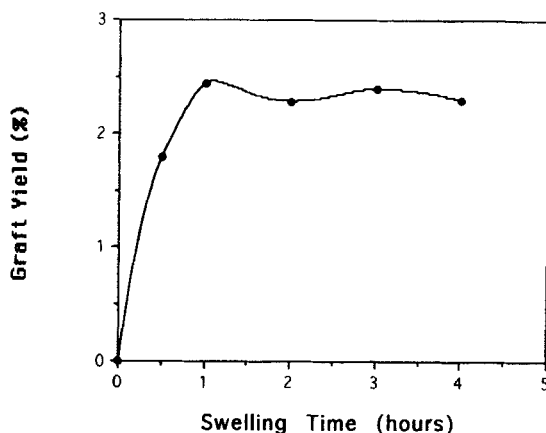
FIG. 1. Change of graft yield with swelling time. $T_{swelling}$ = 140°C, $T_{grafting}$ = 70°C, $t_{grafting}$ = 3 hours, $[Ce^{4+}]$ = 2 × 10^{-2} M, $[AAm]$ = 0.5 M, $[H^+]$ = 0.1 M.

served at 90°C and became longer with decreasing temperature. The enhancement in polymer add-on by raising the polymerization temperature could be attributed to the favorable effect of temperature on 1) enhancement of the swellability of the fiber, 2) increase in the mobility of monomer and initiator, 3) higher rate of diffusion of monomer and initiator from the solution phase to the fiber phase, and 4) higher rate of initiation and propagation on the graft. Besides the above parameters, PET attains its glass transition temperature (T_g) at 80–85°C. Since the PET segments become more mobile at T_g, the reactivity of PET is expected to increase at this temperature and above, thereby giving rise to higher polymer add-on.

Slowing down the polymer add-on during later stages of the reaction (after 6 hours) could be associated with the diffusion barrier caused by the formation of homopoly(acrylamide), the depletion in monomer and initiator concentration, as
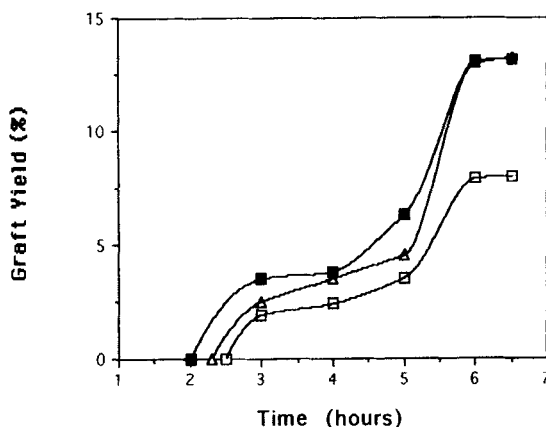

FIG. 2. Variation of graft yield with polymerization time and temperature. $[Ce^{4+}]$ = 2 × 10^{-2} M, $[AAm]$ = 0.5 M, $[H^+]$ = 0.1 M, T = 70°C (□), 80°C (△), 90°C (■).
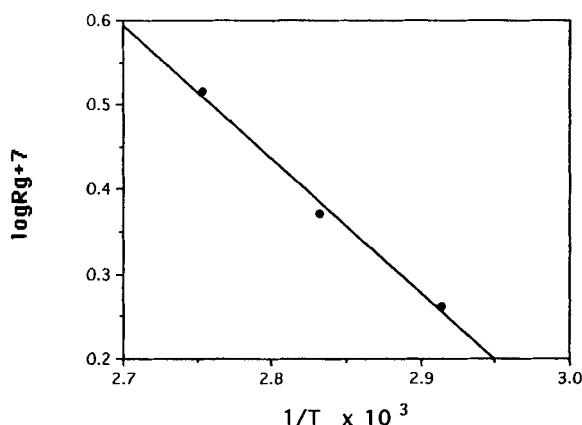
FIG. 3.   Variation of the rate of polymerization with temperature.

well as the decrease of the number of available active sites on the PET backbone and the fast rate of termination. Similar results were reported for glycidyl methacrylate [46], AAm [24, 44], methyl methacrylate [18], and methylvinyl pyridine [8] graft polymerization on PET fibers. From the Arrhenious plot of log R_g vs $1/T$ (Fig. 3), the overall activation energy was computed to be 7.25 kcal/mol·K.

Effect of Monomer and Initiator Concentrations

The effect of the variation of monomer concentration on the graft yield was evaluated by changing the concentration of AAm in the 0.1–1.0 M range and keeping the concentrations of all other reagents constant (Fig. 4). It is clear that the polymer add-on is directly related to the AAm concentration up to 0.5 M. As the monomer concentration increases above this value, there is a substantial reduction
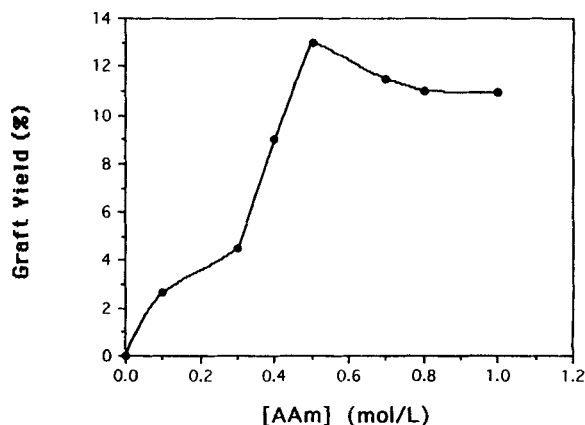
FIG. 4.   Effect of monomer concentration on graft yield. $[Ce^{4+}] = 2 \times 10^{-2}$ M, $[H^+] = 0.1$ M, $T = 80°C$, $t = 6$ hours.

in polymer add-on. That is, 0.5 M is the optimal concentration for achieving maximum polymer add-on.

The decrease in graft yield at higher AAm concentrations could be attributed to the probable adsorption of monomer on PET fibers which impedes diffusion of the initiator inside the fibers and thereby lowers the polymer add-on. Homopolymerization prevails over polymerization with PET fibers at higher AAm concentrations, whereupon the graft yield decreases.

Figure 5 represents the effect of different concentrations of Ce^{4+} on the graft yield. From this figure it is evident that graft yield rapidly increases up to an initiator concentration of 2.0×10^{-2} M, and slightly decreases at higher concentrations.

Since the oxidation potential of ceric ion is very high and polyester fibers have no pendant groups which can be easily oxidized, it is probable that the free radicals on the fiber are created as a result of interaction of the metal ion with the fiber matrix according to the following reaction:

$$PET + Ce^{4+} \rightarrow PET\cdot + Ce^{3+} + H^+$$

Pradhan et al. [23] suggested a reaction mechanism for the graft copolymerization of methyl methacrylate on PET fibers using Ce^{4+} as initiator. They reported that there was a progressive enhancement of the graft yield with increasing Ce^{4+} concentration. This mechanism was supported by our work up to 2.0×10^{-2} M $[Ce^{4+}]$. However, a further increase of the initiator concentration probably caused the termination reactions to dominate and the graft yield to decrease. This typical behavior was observed in many other studies [9, 18, 44, 45].

Experimental results showing the effects of AAm and Ce^{4+} concentrations on the rate of grafting (R_g) are illustrated in Figs. 6 and 7. Kinetic investigation revealed that R_g was proportional to the 0.87 power of AAm and the 1.73 power of Ce^{4+} concentrations.
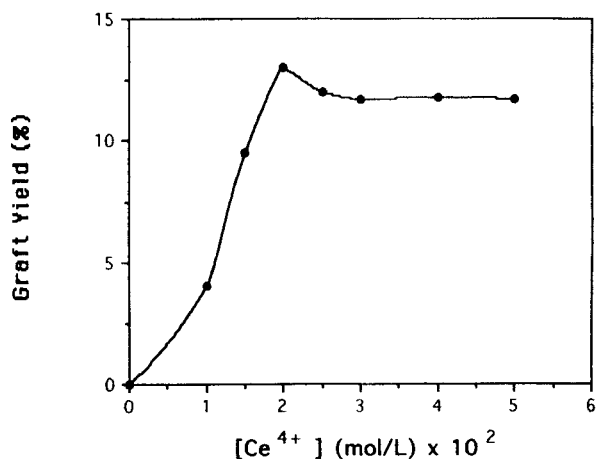

FIG. 5.   Effect of initiator concentration on graft yield. [AAm] = 0.5 M, $[H^+]$ = 0.1 M, $T = 80°C$, $t = 6$ hours.
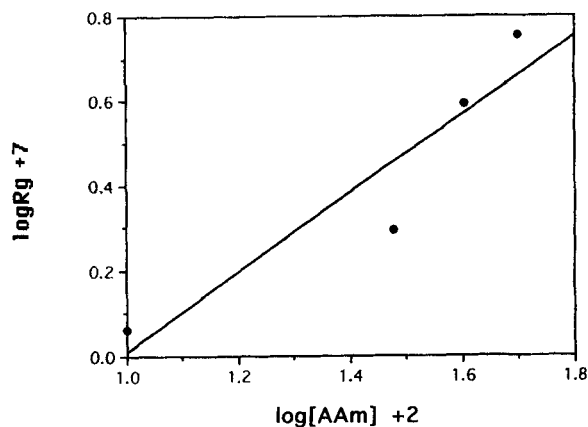
FIG. 6.   Change of rate of polymerization with monomer concentration.

Effect of Acid Concentration

The effect of acid concentration on the graft yield was studied by changing the sulfuric acid concentration from 0.05 to 0.3 M. The results obtained are presented in Table 2. They indicate that the graft yield increases with increasing acid concentration. The oxidizing ability of Ce^{4+} ion is known to increase with increasing acid concentration. At higher acid concentrations a large number of free radicals are produced, which increases the grafting yield. Similar results were obtained during graft copolymerization of methyl methacrylate onto PET fibers while using the same initiator [23].
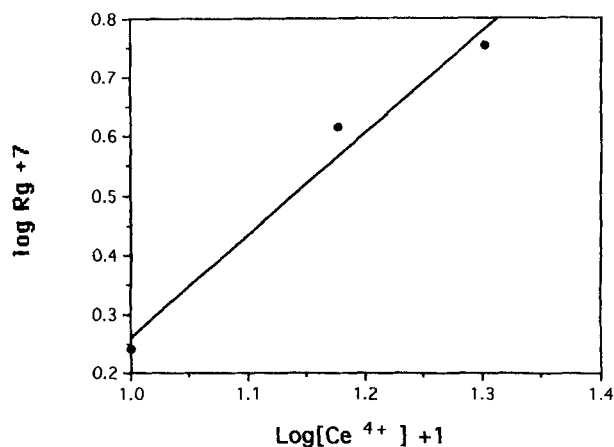
FIG. 7.   Change of the rate of polymerization with initiator concentration.

TABLE 2.   Effect of Acid
Concentration on Graft Yield[a]

H_2SO_4, mol/L	Graft yield, %
0.05	3.43
0.15	4.18
0.20	5.38
0.30	6.13

[a]$[Ce^{4+}] = 2.0 \times 10^{-2}$ M, [AAm] =
0.5 M, t = 6 hours, T = 80°C.

Evaluation of Some Properties of Grafted Fibers

Intrinsic Viscosity

The intrinsic viscosities of PET fibers were determined in *m*-cresol at 25°C. The results are tabulated in Table 3. The intrinsic viscosity was shown to increase with the graft yield, thus indicating evidence of grafting. A similar behavior was reported during the benzoyl-peroxide-initiated graft copolymerization of AAm monomer onto PET fibers [24] and radiation-initiated graft copolymerization onto nylon-6 [47].

Diameters of Grafted Fibers

The variation of the diameters of PET fibers with the graft yield is shown in Table 4. The data indicate that the fiber diameter increases as the graft yield increases. This may be attributed to the possible accumulation of grafted chains in between the polymer chains [24].

Moisture Regain

The percentage of moisture regain was found to increase with the percentage of grafting attained (Table 5). Grafting with AAm not only brings about an opening of the structure but it also increases the hydrophilicity of the fiber as a result of the introduction of polar groups (i.e., amide groups into the fiber matrix).

TABLE 3.   Intrinsic Viscosity Data for
Grafted PET Fibers

Graft yield, %	Intrinsic viscosity, dL/g
0.0	0.055
3.51	0.124
4.40	0.200
6.30	0.359
13.11	Not dissolved in *m*-cresol

TABLE 4. Variation of Fiber Diameters with Graft Yield

Graft yield, %	Diameter μm
0.00	15.79
2.65	21.05
4.54	23.68
6.30	27.63
10.17	34.21

TABLE 5. Moisture Regain Values of Grafted PET Fibers

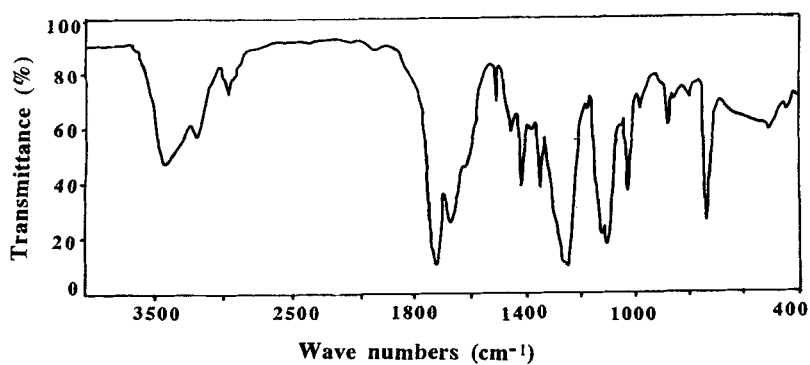| Graft yield, %	Moisture regain, %
0.00	0.50
2.29	0.69
4.40	0.97
6.30	1.10
13.50	1.92

FIG. 8.   FT-IR spectrum of AAm-grafted PET fiber.

FT-IR Spectrum

The FT-IR spectrum of AAm-grafted PET fiber is presented in Fig. 8. The absorptions at 3200–3330, 1625, and 1660–1670 cm^{-1} are typical of $-N-H$ stretchings, $-C=O$ (amide), and $-C=N-$ resonance peaks due to amide groups, respectively.

CONCLUSIONS

We have shown that acrylamide can be grafted onto PET fibers using cerium ammonium nitrate as the initiator. From our experimental results, the following conclusions can also be drawn.

1. DMSO was found to be the most suitable swelling agent, and pretreatment of the fibers for a period of 1 hour at 140°C was observed to be the best condition for the swelling procedure.
2. Grafting became much more effective at temperatures around and above the glass transition temperature of PET.
3. An acrylamide concentration of 0.5 M was found to be the optimal monomer concentration for achieving maximum polymer add-on.
4. To obtain high graft yield, the optimum initiator concentration was found to be 2.0×10^{-2} M.
5. Finally, intrinsic viscosity, diameter, and moisture regain values of the fibers increase with increasing graft yield.

ACKNOWLEDGMENT

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