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GRAFTING OF METHACRYLIC ACID ONTO POLY(ETHYLENE TEREPHTHALATE) FIBERS USING AZOBISISOBUTYRONITRILE

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Key Words: Graft copolymerization; Poly(ethylene terephthalate) fibers; Methacrylic acid; Azobisisobutyronitrile

ABSTRACT

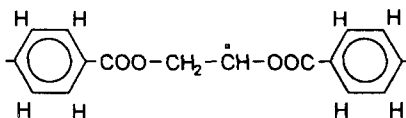
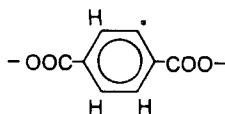
Poly(ethylene terephthalate) fibers were grafted with methacrylic acid using azobisisobutyronitrile. The graft yield was observed to increase between 60 and 90°C and reached 32% at 90°C. An increase in monomer concentration increased the graft yield. The optimum concentration for initiator was found to be 3.0×10^{-3} mol/L. Grafting decreased the density and increased the diameter of the fiber. Moisture regain and dyeabilities of the fibers with basic dyes increased due to —COOH groups introduced into the fiber structure through grafting. However, grafting resulted in a decrease in the decomposition temperatures of fibers. Micrographs revealed that the homogeneous appearance of the fiber surface changed with an increasing degree of grafting, and the surface took on a shell-like appearance at high graft yields.

INTRODUCTION

Graft copolymerization is a method to modify natural and synthetic polymers under selectively controlled conditions [1-4].

There are many reports upon chemical [5-9] and radiation [10, 11] initiated grafting studies for the modification of poly(ethylene terephthalate) (PET) fibers. The high crystallinity, highly oriented structure, lack of chemically active groups, and high glass transition temperature of PET fibers result in undesirable properties such as low moisture regain, accumulation of static charge, and high resistance to dyeing. Grafting aims to improve these adverse features.

The radiation method is quite simple. However, the application of high doses may result in PET degradation [12] and low radical yield [13]. ESR studies showed that the irradiation of PET with γ -rays gave the following radicals [14]:



These radicals, which act as grafting sites, can be chemically created by the use of such radical initiators as hydrogen peroxide [8], azobisisobutyronitrile (AIBN) [16], and benzoyl peroxide [5, 9, 15] at suitable conditions.

A number of studies concerning the grafting of vinyl monomers upon PET fibers using AIBN is quite limited, and the grafting of methyl methacrylate onto PET fibers using this initiator was recently reported by us [16].

This paper deals with the grafting of MAA onto PET fibers using AIBN initiator. It reports the moisture regain, dyeability, and density of grafted PET fibers as well as the effects of such factors as temperature and monomer and initiator concentrations on grafting. The grafted fibers were characterized by using thermogravimetric analysis, infrared spectroscopy, and scanning electron microscopy.

EXPERIMENTAL

Materials

The PET fiber (30 filament, 110 dTex) used in the experiments was obtained from SASA Co. (Adana) and Soxhlet-extracted with acetone for 6 hours before being used.

Methacrylic acid (MAA) (Merck) was treated with NaCl, dried over CaCl_2 and distilled in vacuum at 40°C . AIBN (BDH) was recrystallized twice from methanol and kept in vacuum desiccator over P_2O_5 . Methylene blue (Merck) was used without further purification.

Graft Copolymerization Procedure

The graft copolymerization procedure was detailed previously [6]. Fiber samples and monomer dissolved in 19 mL water at a suitable concentration were put in a 50-mL Pyrex polymerization tube placed in a water bath (Lauda D 40 S). One milliliter of toluene containing a suitable concentration of initiator was added to this mixture after it had reached the polymerization temperature. The time at which the initiator was first added was accepted as the starting point of copolymerization. The sample taken at the end of graft copolymerization was washed with water at room temperature for 24 hours since the solubility of polyMAA is quite high at low temperatures [22]. The sample was then Soxhlet-extracted for 8 hours with acetone, dried, and weighed. The percentage graft yield was calculated as follows:

$$\text{graft yield, \%} = \frac{(\text{original fiber weight}) - (\text{grafted fiber weight})}{(\text{original fiber weight})} \times 100$$

Dyeing

Ungrafted and grafted PET fibers with various amounts of MAA were dyed with methylene blue at 85°C for 2 hours. The dye concentration and the fiber/liquor ratio were 2 g/L and 1/100, respectively. The dyed samples were washed with water, and the dye was extracted from the fibers with dimethylformamide at 70°C.

The dye uptake values of the fibers were determined by using a preconstructed calibration curve and the original weight of the fiber. The optical density measurements were carried out by using a Shimadzu 160 A Model spectrophotometer at 644.5 nm.

Characterization of the Grafted Fibers

The infrared spectra of the fiber samples were taken with a Matson 100 Model FT-IR using KBr pellets. The micrographs of the fibers were obtained by using a JEOL-JEM 100 CX II Model scanning electron microscope (SEM) after being covered with gold.

Thermogravimetric analyses were performed by the use of a Linseis L 81 Model thermal analyzer. The samples were heated up to 550°C starting from the room temperature at a heating rate of 10°C/min in a 200 mL/min He atmosphere.

The density measurements were made by using a density gradient column prepared from carbon tetrachloride and xylene. The details were previously outlined [16].

The fiber diameters were determined under a Nikon Type 104 Model optical microscope. The measurements were made at five different regions for each sample.

The samples were conditioned at 20°C in a medium having 65% moisture for 24 hours for the moisture regain measurements. The moisture regain value was calculated from the difference between the weights of the conditioned and unconditioned samples.

RESULTS AND DISCUSSION

The homopolymer of the monomer used for grafting also forms in the polymerization medium. The general procedure to remove the homopolymer from the grafted fiber is by extraction of the fiber with a suitable solvent.

Although highly time- and solvent-consuming, this method is preferable to others since it does not damage the fiber. The grafted fiber samples are then dried and weighed. The increase in the weight of the sample is taken as a measure of grafting, and the graft yield is calculated based upon this increase.

Supporting evidence for the grafting is also obtained from infrared [3, 4, 6, 17], NMR [17], and thermogravimetric analysis [18, 19] studies. Figure 1 shows the FT-IR spectra of 37.5% MAA grafted and ungrafted PET fibers. The grafted fiber gives a broad band located between 3000 and 3500 cm^{-1} , originating from the hydroxyl groups of MAA. The infrared spectrum is obviously not sufficient to show the binding sites where polyMAA side chains are attached to the PET backbone. However, there is no current technique capable of showing the availability of these binding points. The change in many properties of the fiber, such as moisture regain, density, dyeability with the grafting, and the permanent increase in the weight of the fiber even after prolonged extraction periods to remove the homopolymer, are a few conclusive indications that grafting was actually taking place.

Effect of Time and Temperature on Grafting

Figure 2 shows the change of graft yield with temperature and time. An increase of temperature from 60 to 90°C has an increasing effect upon the grafting rate and graft yield. No grafting was observed at temperatures below 60°C, even after a period of 120 minutes, due to the low rate of initiator dissociation and the difficulty of diffusion of the monomer into the PET backbone. The grafting remained at a very low level of 3.3% at 60°C after 120 minutes. There is also an induction period of 60 minutes at this temperature. The graft yield increased up to 6.2% at 65°C, and the induction period at this temperature was observed to be 10 minutes. The graft yield steadily increased and there was no induction period observed at the other temperatures employed.

An increase in temperature increases the decomposition rate of AIBN and therefore the radical concentration. PET macromolecules become much more susceptible to radical reactions above the glass transition temperature ($\sim 80^\circ\text{C}$) [20]. The graft yield and grafting rate increased up to 32.1% and 27.9%/20 minutes, respectively, with temperature due to the combined action of these two effects at 90°C. This kind of effect of temperature and time upon the graft yield was also observed in the grafting of methyl methacrylate [7, 16] and acrylic acid [6, 15] upon PET fibers.

The fact that graft yield remains constant after a certain period at high temperatures (i.e., saturation graft yield) can be attributed to the depletion in monomer concentration in the polymerization medium. The monomer molecules are consumed by both the grafting and homopolymerization reactions. An increase in temperature will increase the rate of both these reactions.

Effect of Monomer and Initiator Concentrations on Grafting

The effect of initiator concentration upon graft yield was investigated by increasing the AIBN concentration from 0.3×10^{-3} to 8.0×10^{-3} mol/L while keeping all other conditions constant. The results are shown in Figure 3. It is seen that the graft yield rapidly increases up to an AIBN concentration of 3.0×10^{-3}

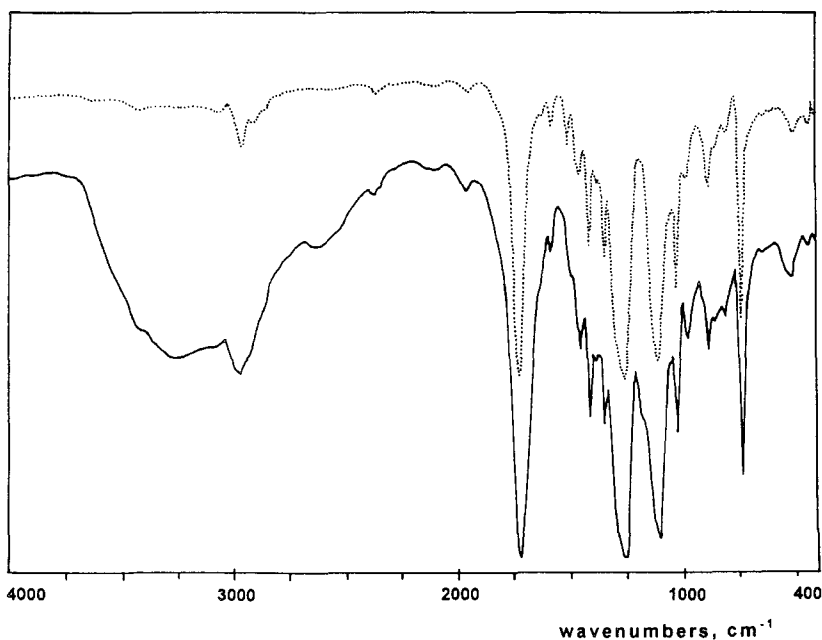


FIG. 1. FT-IR spectra of ungrafted (\cdots) and 37.5% (—) methacrylic acid grafted PET fibers.

mol/L and reaches a maximum graft yield value of 25.9%. A slow decrease in graft yield was observed at higher initiator concentrations.

An increase in AIBN concentration will obviously increase the number of isobutyronitrile radicals formed as a result of AIBN decomposition. These free radicals abstract hydrogen atoms from the PET backbone, creating active sites which facilitate the addition of monomers. These radicals also initiate MAA homopolymerization in the outer solution.

Another factor which creates suitable sites for grafting reactions to take place are the chain transfer reactions between the active MAA homopolymer chains and the PET macromolecules.

Both these processes have a promoting effect upon grafting. In our study the graft yield was found to increase up to an AIBN concentration of 3.0×10^{-3} mol/L due to the combined effect of these two factors. A further increase in AIBN concentration increases the radical species in the medium, which promotes the termination reactions. The gradual decrease in the graft yield at AIBN concentrations above 3.0×10^{-3} mol/L can be attributed to the increase in the rate of termination reactions.

Figure 4 shows that an increase in monomer concentration increases the graft yield. The saturation graft yield increases from 6.2% at a monomer concentration of 0.05 mol/L to 37.5% at a monomer concentration of 0.50 mol/L. An increase in the monomer concentration also increases the grafting rate. There was no induction period for any of the four MAA concentrations employed.

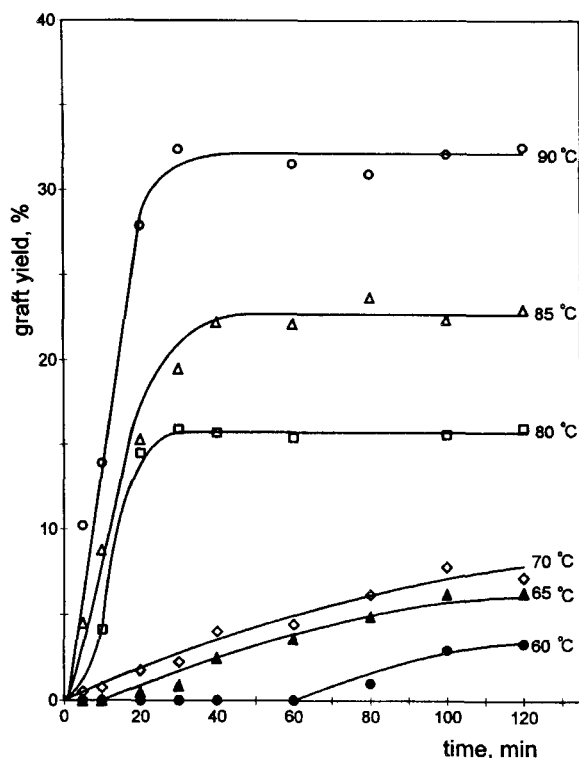


FIG. 2. Effect of temperature and time on grafting: [methacrylic acid], 0.35 M; [azobisisobutyronitrile], 3.0×10^{-3} M.

An increase in monomer concentration increases the number of MAA molecules diffused into PET macromolecules, which enables active PET macromolecules to easily find monomer units to add, and this promotes the grafting process.

Scanning Electron Microscopy

Figure 5 shows SEM micrographs of ungrafted and 37.5% MAA-grafted PET fibers at a magnification of 2000.

The homogeneous and smooth surface of ungrafted PET fiber (Fig. 5a) acquired a shell-like structure due to the deposition of grafted polymer at high grafting (Fig. 5b).

Figure 6 shows SEM micrographs of ungrafted and 37.5% MAA-grafted PET fibers at a magnification of 500. These micrographs are quite useful for evaluating the changes which may occur in fiber geometry as a result of grafting. An increase in fiber diameter is quite apparent as the graft yield increases. However, the increase in diameter causes no deformation in fiber shape.

The effect of MAA grafting upon PET diameter and density are tabulated in Table 1.

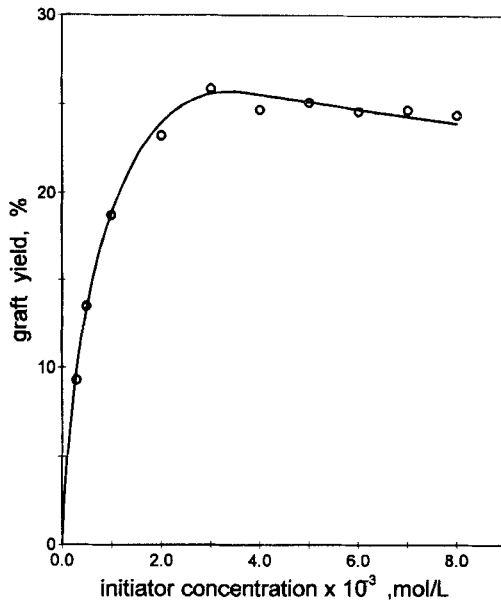


FIG. 3. Effect of azobisisobutyronitrile concentration on grafting: [methacrylic acid], 0.35 M; time, 2 hours; temperature, 85°C.

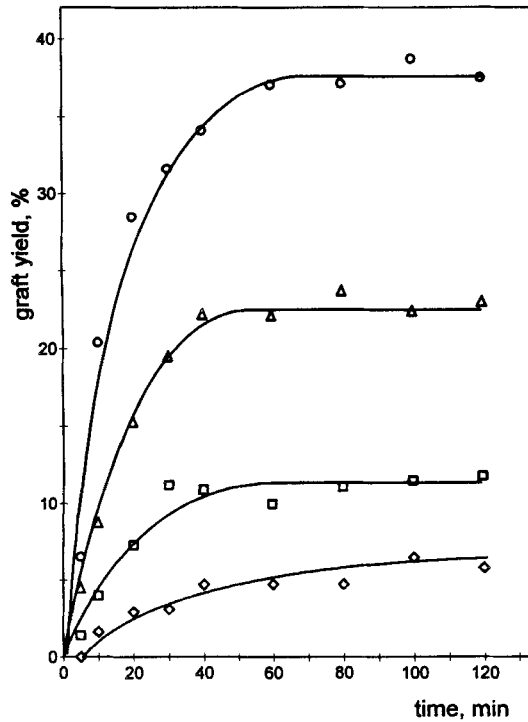


FIG. 4. Effect of methacrylic acid concentration on grafting: [azobisisobutyronitrile], 3.0×10^{-3} M; temperature, 85°C; (\diamond) 0.05 M; (\square) 0.10 M; (\triangle) 0.35 M; (\circ) 0.50 M.

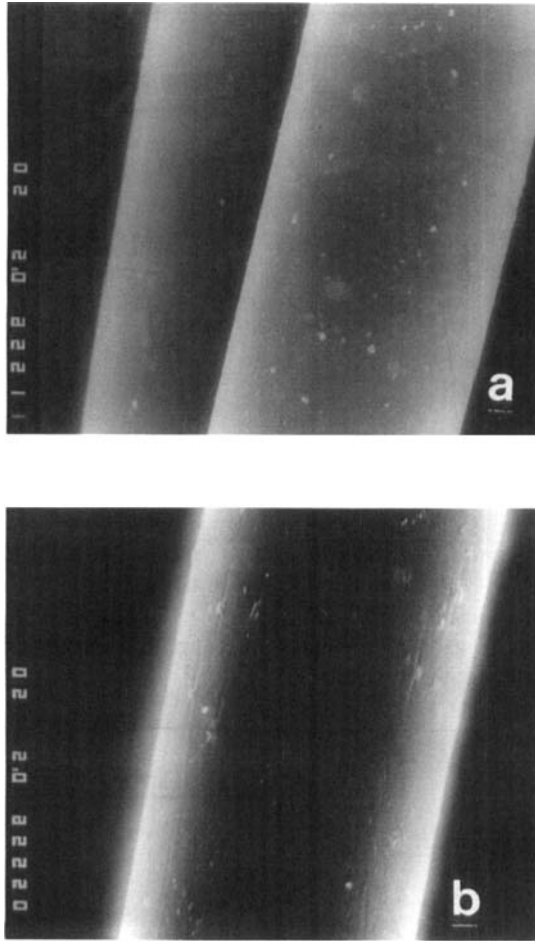


FIG. 5. SEM micrographs of (a) ungrafted and (b) 37.5% methacrylic acid grafted PET fibers at a magnification of 5000.

As mentioned above, grafting causes an increase in fiber diameter and a decrease in fiber density. This shows that the contribution of *grafting upon fiber volume* is much higher than its contribution to fiber weight. It is probable that polyMAA side chains separate the PET backbone chains from each other and cause a much higher increase in its volume than in its weight.

Moisture Regain and Dyeability

PET fibers have low moisture regain (0.42%) due to their hydrophobic character. They cannot be dyed with basic dyes due to their lack of suitable functional groups which may interact with dye molecules. The introduction of hydrophilic $-\text{COOH}$ groups as a result of MAA grafting improves both the moisture regain and dyeability with basic dyes, as seen in Table 2. The dye uptake value of $0.15 \times$

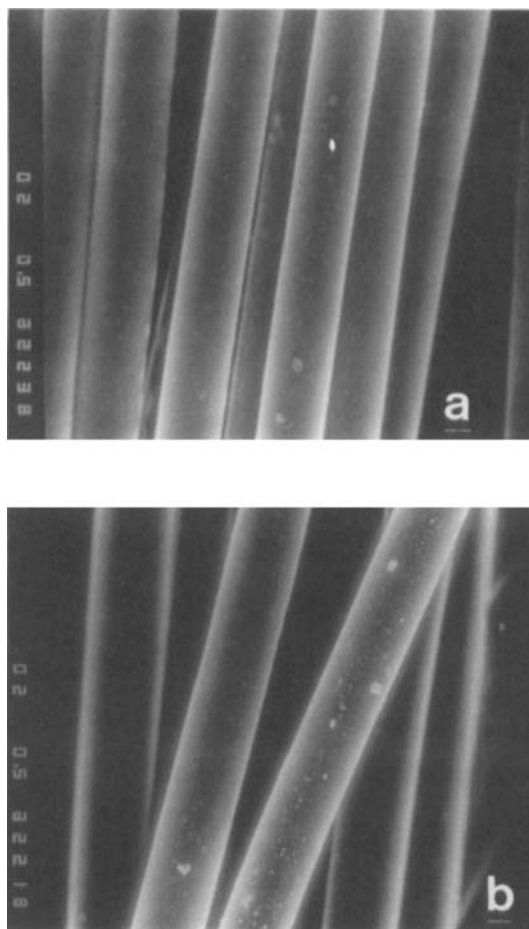


FIG. 6. SEM micrographs of (a) ungrafted and (b) 37.5% methacrylic acid grafted PET fibers at a magnification of 500.

TABLE 1. Density and Diameter Values of MAA-Grafted PET Fibers

Graft yield, %	Density, g/cm ³	Diameter, cm × 10 ⁻³
Ungrafted	1.3748	2.587
6.2	1.3738	—
11.3	1.3711	2.721
18.7	1.3669	2.932
30.9	1.3618	3.120
37.5	1.3571	3.303

TABLE 2. Moisture Regain and Dye Uptake Values of MAA-Grafted PET Fibers

Graft yield, %	Moisture regain, %	Dye uptake $\times 10^3$, g dye/g fiber
Ungrafted	0.42	0.15
6.2	1.18	1.81
11.2	1.93	2.26
18.7	1.91	3.33
30.9	3.30	4.53
37.5	4.33	5.98

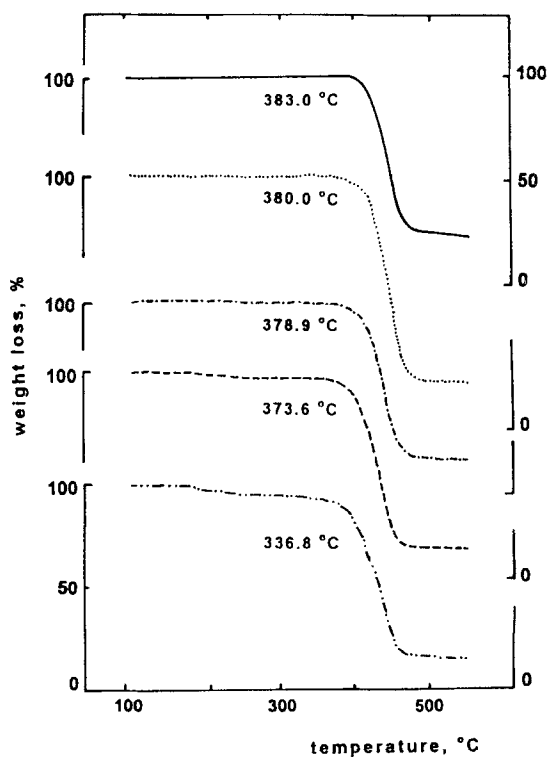


FIG. 7. Thermograms of methacrylic acid grafted PET fibers. Graft yield: (—) 0.0%; (···) 11.3%; (-·-·) 18.5%; (---) 30.9%; (- - - -) 37.5%. The decomposition temperatures are indicated within the figure.

10^{-3} g dye/g fiber for the ungrafted fiber increases up to 5.98×10^{-3} g dye/g fiber for 37.5% MAA-grafted fiber.

Thermogravimetric Analysis

Figure 7 shows thermograms of MAA-grafted PET fibers. An initial weight loss is observed in thermograms of grafted fibers around 200°C, which is due to polyMAA chain unzipping; it decomposes around 350°C [21].

The decomposition temperature of PET decreases from 383.0 to 336.8°C at 37.5% grafting. This indicates that grafting decreases the thermal stability of PET fibers, which may be due to the early decomposition of polyMAA compared to PET.

CONCLUSION

Our results show that MAA can be grafted upon PET fibers using AIBN initiator. Higher graft yields require higher temperature and monomer concentration. On the other hand, there is an optimum initiator concentration value (3.0×10^{-3} mol/L) for maximum graft yield.

Grafting improved the moisture regain and dyeability of the fiber with basic dyes. However, it decreased their decomposition temperature. Grafting also affected the fiber density and diameter. The chemical and/or physical deposition of polyMAA at high graft yield modified the fiber surface but did not cause any deformation in fiber geometry.

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