Grafting of Ethyl Acrylate onto Monofilament Polyester Fibers Using Benzoyl Peroxide

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Received 15 December 1997; accepted 26 March 1998

ABSTRACT: Ethyl acrylate was grafted onto monofilament poly(ethylene terephthalate) fibers using benzoyl peroxide as a chemical initiator. Breaking tenacity and densities of grafted fibers decreased while breaking elongation increased with the graft yield. Scanning electron micrographs showed that the fiber geometry and its diameter were not affected by grafting. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1701–1705, 1998

Key words: monofilament polyester fibers; grafting; ethyl acrylate; benzoyl peroxide

INTRODUCTION

The modification of natural and synthetic polymers by graft copolymerization has been very attractive in recent years.[1–4] One polymer under investigation for this method of modification is poly(ethylene terephthalate) (PET), especially in fiber form. Various vinyl monomers can be grafted onto PET fibers by chemical[5–11] or radiation[11–14] methods. PET fibers are difficult to dye, have low moisture regain, and have poor antistatic properties due to their lack of chemically active groups and their highly crystalline structures. These inferior properties were reported to be improved to some extent depending on the monomer grafted.[6,8,10–12]

The grafting of monomers onto PET fibers also affects their mechanical properties, such as breaking tenacity and breaking elongation. There are reports concerning the mechanical properties of PET fibers grafted with *N*-vinyl-2-pyrrolidinone,[12] vinyl acetate,[13] acrylic acid,[11] and acrylonitrile.[15]

This study reports the results of grafting ethyl acrylate onto monofilament PET fibers. The effects of ethyl acrylate grafting onto PET fibers, their breaking tenacity, breaking elongation, and densities were also investigated.

EXPERIMENTAL

Materials

Monofilament PET fibers (0.4 mm in diameter with a molecular weight of 26,000) were obtained from KORDSA Co. (İzmit, Turkey), cut in 3-cm-long pieces, and Soxhlet-extracted with acetone for 8 h before grafting. Ethyl acrylate (BDH, UK) was treated with 5% NaOH before being washed with water. It was then kept over Na_2SO_4 overnight and vacuum-distilled at 40°C. Benzoyl peroxide (Merck, Germany) was crystallized twice from a methanol–chloroform mixture. Dimethyl sulfoxide (DMSO; Merck, Germany) was used as supplied.

Graft Copolymerization

Monofilament PET fibers (0.20 ± 0.01 g), subjected to a prior swelling process in DMSO at 120°C for 30 min, were then transferred into the

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Contract grant sponsor: Ankara University Research Fund.

polymerization tube containing initiator and monomer at suitable concentrations, and filled to 20 mL with toluene. The mixture was bubbled with nitrogen for 20 min before being transferred into a water bath (D 40 S; Lauda, Berlin, Germany), the temperature of which can be adjusted within ±0.1°C. The system was bubbled with nitrogen throughout grafting.

The samples taken from the mixture after a predetermined copolymerization time were Soxhlet-extracted, first with acetone for 6 h then with ethanol for 8 h. The fiber samples thus freed from homopoly(ethyl acrylate) were dried under vacuum at 50°C and brought to constant weight. The percentage graft yield was calculated from the original and grafted fiber weights.

Breaking Tenacity, Breaking Elongation, and Density

The breaking tenacity and breaking elongation were measured using an Instron tensile tester at 65% relative humidity at 25°C. The jaw gap was 20 cm and the extension rate was kept constant at 10 cm/min.

The fiber densities were determined using a carbon tetrachloride–xylene density column, the details of which are outlined elsewhere.[7]

Scanning Electron Microscopy

Micrographs were taken with a JEOL model JEM-100 CX II scanning electron microscope.

RESULTS AND DISCUSSION

The swelling of the PET fibers used in grafting is an important criterion and facilitates the easy diffusion of reactants into the fiber matrix. Swelling of PET fibers can be carried out by two different procedures. The first is to add the swelling agent directly to the polymerization medium and carry out the grafting in the presence of swelling agents. In this case fiber structure is maintained swollen during the graft copolymerization. It has been reported that the swelling agents which were directly added to the polymerization medium may affect the grafting process positively or negatively.[13,16]

The second method is to use a swelling agent as a pretreatment prior to incorporation of the monomer and polymer. The use of fibers subjected to the preswelling process with dimethylformamide, DMSO, or chlorined hydrocarbons was reported to promote the grafting.[8,11,12,15] The use of swelling agents in grafting studies carried out on monofilament fibers is of great importance in obtaining the necessary structural flexibility for diffusion because their surface area is quite small compared with small-diameter multifilament fibers.

Table I Relation Between Graft Yield and Swelling Time in DMSO

Time (min)	Graft Yield[a] (%)
Unswollen fiber	0.7
5	1.2
10	3.4
15	6.5
20	8.8
30	8.4
40	8.6

Swelling temperature: 120°C.
[a] Ethyl acrylate, 4.61 mol/L; benzoyl peroxide, 1.50×10^{-3} mol/L; time, 4 h; temperature, 80°C.

We used PET fibers preswollen with DMSO at 120°C for 30 min in grafting. It was found that a 20-min swelling period was enough for effective grafting. As seen in Table I, prolonged swelling times did not change grafting to a significant extent.

Figure 1 shows the relation between the graft yield and monomer concentration. The increase in monomer concentration increases the graft yield. However, the graft yield does not change significantly after a monomer concentration of 4.61 mol/L.

The increase in monomer concentration increases the number of monomer molecules diffused into the fiber matrix. This facilitates the chance for PET macroradicals and active grafted side chains to find monomer molecules. The observation that high monomer concentrations do not increase graft yield further can be attributed to monomer adsorption onto PET fibers and/or the deposition of homopoly(ethyl acrylate) onto the fiber surface.

Figure 2 shows the relation between temperature and graft yield. The graft yield was examined between 65 and 90°C, and we observed that the optimum temperature for grafting was around 80°C.

The increase in temperature facilitates the diffusion of monomer into fiber; increases the rate of initiation, transfer, and propagation reactions;

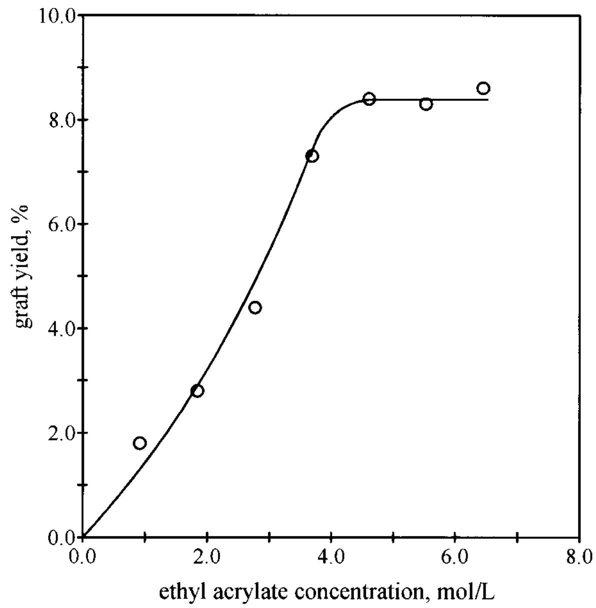

Figure 1 Variation of graft yield with ethyl acrylate concentration. Benzoyl peroxide, 1.50×10^{-3} mol/L; time, 4 h; temperature, 80°C.

and increases the rate of dissociation of the initiator. All these factors promote the grafting. The grafting is particularly effective around the glass transition temperature because PET macromolecules are promoted to radical reactions.[17]

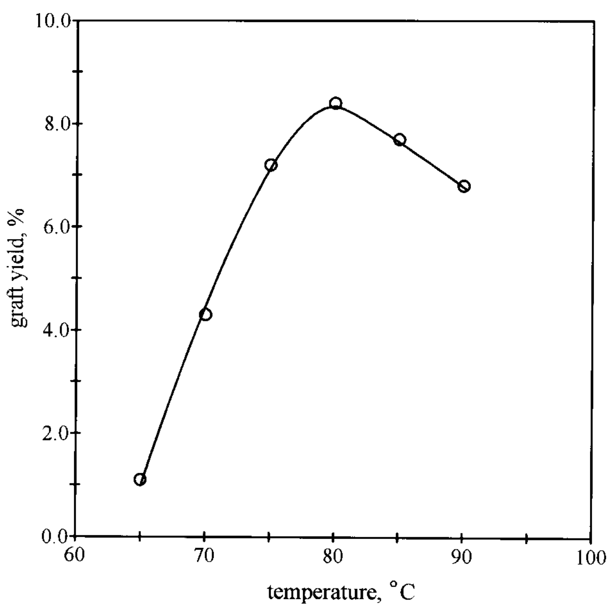

Figure 2 Variation of graft yield with temperature. Ethyl acrylate, 4.61 mol/L; benzoyl peroxide, 1.50 $\times 10^{-3}$ mol/L; time, 4 h.

Table II Effect of Ethyl Acrylate Grafting on Breaking Tenacity and Breaking Elongation of PET Fiber

Graft Yield (%)	Breaking Tenacity (cN/tex)	Breaking Elongation (%)
0.0	51.2	15.1
1.6	50.3	15.6
2.7	49.4	16.1
3.6	47.7	16.9
4.5	45.9	18.3
6.1	40.6	19.3
7.4	38.0	20.0
7.9	33.6	20.3
8.6	30.0	21.1

The further rise in temperature, however, increases the rate of termination reactions and causes the graft yield to decrease.[10,11,15,17]

Table II shows the effect of ethyl acrylate grafting on the breaking tenacity and the breaking elongation values of PET fibers. At 8.6% grafting, the breaking tenacity of PET fibers drops from 51.2 cN/tex to 30.0 cN/tex.

The segments in the amorphous regions of PET fibers may be disoriented as a result of grafting. The explored reaction parameters (i.e., time) and preswelling process might also have a role. The decrease in orientation, which is one of the most important fiber characteristics responsible for good mechanical behavior, decreases the fibers' breaking tenacity. The reorientation of these disoriented regions under the influence of stretching force increases the breaking elongation of the fiber, as seen in Table II. The breaking elongation value of ungrafted PET is 15.1%, which increases to about 21.1% at 8.6% grafting.

Table III shows the changes in fiber density with grafting. The graft yield was observed to

Table III Density Values of Ethyl Acrylate-Grafted PET Fibers

Graft Yield (%)	Density (g/cm^3)
Ungrafted	1.3775
2.8	1.3712
4.4	1.3675
7.3	1.3530
8.6	1.3519

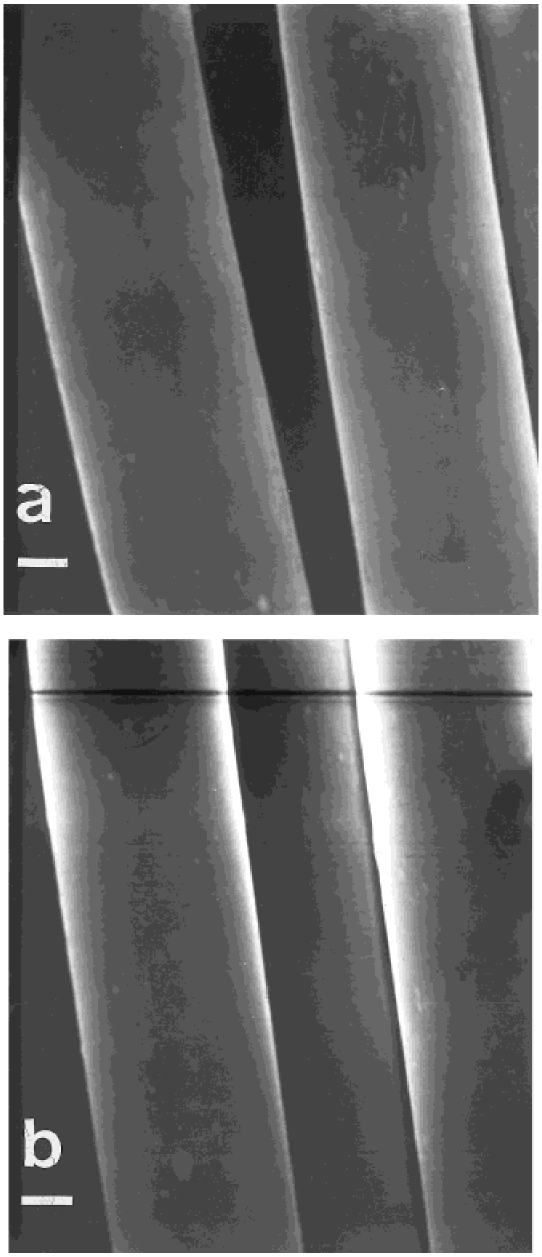

Figure 3 Micrographs of (a) ungrafted and (b) 8.6% ethyl acrylate–grafted PET fibers (bar = 0.1 mm).

decrease the fiber density. The fiber density decreased from its original value of 1.3775 to 1.3519 g/cm^3 at the highest graft yield, 8.6%.

The decrease in the fiber density with grafting reveals that the entrance of side poly(ethyl acrylate) chains separates the main PET chains and causes a certain expansion in volume of fiber.

Scanning electron microscope investigation of ungrafted and 8.6% ethyl acrylate–grafted PET fibers showed that grafting caused no deformation in fiber geometry whatsoever, as seen in Figure 3. Also, we observed no change in the fiber diameters measured from the micrographs.

CONCLUSIONS

This study showed that ethyl acrylate can be grafted onto monofilament PET fibers using benzoyl peroxide as a chemical initiator. From our experimental results, the following conclusions can also be drawn.

- The optimum temperature for grafting was 80°C. The graft yield decreases if the temperature goes above or below this value.
- The extent of grafting was found to be affected by monomer concentration. The graft yield does not change significantly after a monomer concentration of 4.61 mol/L.
- Swelling of monofilament PET fibers in DMSO before graft copolymerization is an important criterion. We found that a 20-min swelling period at 120°C was enough for effective grafting, and that prolonged swelling times did not change grafting to a significant extent.
- Scanning electron micrographs showed that the fiber geometry and its diameter were not affected by grafting.
- Finally, breaking tenacity and densities of grafted fibers decreased, while breaking elongation increased with the graft yield.

The authors thank Ankara University Research Fund for its financial support of this work.

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