

Benzoyl-Peroxide-Initiated Graft Copolymerization of Poly(ethylene Terephthalate) Fibers with Acrylamide

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Synopsis

In this study the grafting of acrylamide onto poly(ethylene terephthalate) fibers with the help of benzoyl peroxide and the effects of the temperature and the concentrations of initiator and monomer were investigated. Some of the experiments were repeated several times in order to check the reproducibility. The optimum temperature for grafting was found to be 75°C. The graft yield was observed to increase with the monomer concentrations examined. The graft yield increased up to the benzoyl peroxide concentration approximately 0.05 g/50 mL, and then passed a plateau, before showing a decrease. The fiber diameter, intrinsic viscosity, and the moisture regain increased while the fiber density decreased with the graft yield.

INTRODUCTION

Poly(ethylene terephthalate) (PET) fiber is one of the most important synthetic fibers used in textile industry today. It possesses desirable fiber properties such as strength, high crisp, resistance to stretch, shrinkage, and abrasion, as well as undesirable features such as low moisture regain, difficulty of dyeing, etc., due to its crystalline structure, hydrophobic character, and lack of chemically reactive groups.

One of the most common methods used for the improvement of these undesirable features is grafting of vinyl monomers onto PET fibers. By this way, the PET fibers acquires some of the desired properties depending upon the monomer (or monomers) used for grafting. Vinyl monomers can be grafted onto PET fibers by using radiation or chemical methods. Although grafting by radiation is easy to control, it causes low radical yield and degradation of the main polymer (above doses over 5 Mrad).^{1,2} The nature of the grafted fibers are the same in the grafting of acrylic acid onto PET fibers in both radiation and chemical methods.³

There are many studies on the grafting of vinyl monomers onto PET fibers in the literature. For example, the grafting of styrene,^{1,4-6} acrylic acid and methacrylic acid,^{3,7,8} vinyl acetate,⁹ acrylonitrile,³ and bromostyrene¹⁰ onto PET fibers has been reported.

The studies concerning the grafting of acrylamide are generally patented.¹¹⁻¹⁶ For this reason, detailed information about the features of grafted fibers and conditions of grafting reaction are not clear. The aim of this study is to investigate the grafting of acrylamide onto PET fibers using benzoyl peroxide as an initiator.

EXPERIMENTAL

Materials

PET fibers (multifilament, 99 denier) were obtained from SASA Co. (Adana, Turkey). The fiber samples were washed with luke-warm water, Soxhlet-extracted for 6 h with acetone and dried at ambient conditions. Benzoyl peroxide (Bz_2O_2) was twice precipitated from chloroform solution in methanol and dried in a vacuum desiccator for 2 days.¹⁷ Benzene was crystallized cooling in the refrigerator. The crystallized part was used to prepare the Bz_2O_2 solutions. Acrylamide, xylene, carbon tetrachloride, and *m*-cresol were chemically pure grade.

Polymerization Procedure

The graft polymerization reactions were carried out in a 100-mL polymerization tube. The PET fibers were placed in a 45 mL deionized water containing monomer. Five milliliters of benzoyl peroxide solution prepared in benzene in desired concentration were added. The mixture was then put in a water bath (Lauda D 40 S, W. Germany, $\pm 0.1^\circ\text{C}$) adjusted to the polymerization temperature. The fibers were taken from the polymerization tube after a specified polymerization period and subjected to a prewashing procedure before being washed in boiling water for 4 h. The washing water was changed at least four times. They were Soxhlet-extracted with water for 6 h in order to remove the homopolymer which may remain as a film upon the surface of the fibers and subject them to a further washing procedure. The times for the fibers having various grafting ratios to reach constant weight were determined by preexperiments. The washing times were evaluated according to the results obtained in these experiments. The fibers then dried and weighed. The graft yield (%) value was based on the weight.

Measurement of Density

The densities of the fiber samples were determined at 23°C using the density gradient tube prepared by carbon tetrachloride and xylene. The levels of the glass floats (made by Davenport Ltd., the density of which is known within 1/10,000) and the fiber samples were determined by the help of a cathetometer (within a sensitivity of ± 0.01 mm).

Measurement of Diameter

The diameters of the fiber samples were measured by a Vanox (Olympus) microscope at a magnification of $400\times$. The diameters were measured, using at least five samples.

Determination of Moisture Regain

The fiber samples were conditioned at 20°C in a medium having a relative humidity of 65% in order to evaluate the moisture regain value. This value was calculated from the increase in the weight of the conditioned fiber and the dry weight of the original fiber.

Determination of Intrinsic Viscosity

The intrinsic viscosity values of the pure PET and grafted PET were determined in *m*-cresol at 25°C. Those determinations were carried out by using an Ubbelohde viscosimeter having a solvent flow time 149.6 s.

FTIR Spectrum

The FTIR spectrum was recorded by using a Perkin-Elmer Model 1710 spectrophotometer with a KBr disc.

RESULTS AND DISCUSSIONS

In this study the effect of temperature upon the graft yield was investigated keeping the other variables constant. Some of the experiments were repeated several times in order to examine the reproducibility of the results. The experimental results are shown in Table I. Figure 1 was obtained by taking the average values of data presented in Table I.

As seen in Table I, the reproducibility of the experiments is poor. This poor experimental reproducibility was also observed by the other workers in grafting styrene and ethyl acrylate onto wool¹⁸ and styrene onto nylon.¹⁹ This could have been caused by the entrapment of homopolymer within the fibers, in spite of the long extraction times used. In the grafting onto fibers, the homopolymer occluded in the grafted product is generally removed by the extraction with a selective solvent. Water is a good solvent for removing the occluded polyacrylamide from the grafted fibers without needing a second solvent.^{4,20,21} The increase in the weight of the original fiber samples is due to inclusion of the polyacrylamide within the PET fibers even after several

TABLE I
Effect of Polymerization Temperature and Time upon Graft Yield^a

Time (h)	Graft yield (%)			
	70°C	75°C	85°C	92°C
1/4		2.1	6.4	9.1
		3.0	3.7	
1/2		8.3	11.2	18.8
		5.3	7.6	16.3
				16.9
1	1.4	17.4	24.8	19.1
		19.9	18.8	
		15.6		
2	6.8	35.8	26.1	23.2
		3.8	31.7	18.2
		38.9		22.9
3	7.7	42.8	30.1	23.8
		40.6	25.4	19.1
			29.4	
4	15.0	40.2	31.3	18.9
		11.6	26.3	21.5
			38.3	

^a[Acrylamide] = 2 g/50 mL; [Bz₂O₂] 0.0484 g/50 mL.

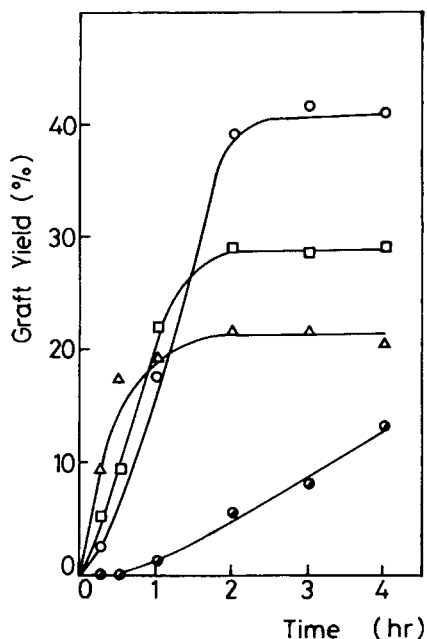


Fig. 1. Variation of graft yield with polymerization temperature: [acrylamide] = 2 g/50 mL; [Bz₂O₂] = 0.0484 g/50 mL; (●) 70°C; (○) 75°C; (□) 85°C; (△) 92°C.

extractions with water (Table I). Whether this substantial increase in the weight of the fibers is due to polyacrylamide chains chemically bonded to PET fibers or *in situ* polymerization is not clear. However, the mechanism of this polymerization reaction is believed to be a grafting reaction.

It can also be observed in Figure 1 that the saturation grafting value was reached at 75, 85, and 92°C. At 70°C there was an induction period of 30 min. The highest graft yield was obtained at 75°C around 40%. The increase of temperature was observed to increase the rate of grafting, but decrease the saturation grafting. In conclusion, the optimum temperature for grafting acrylamide onto PET fibers was found to be 75°C.

Schamberg and Hoigne⁴ observed that the maximum graft yield was obtained near the glass-transition temperature in their grafting studies onto various polymers. The polymer chains whose activities are increased around the glass-transition temperature tend to give radical reactions much more easily. Since more and more radicals combine as the temperature is increased, they cannot take place in the initiation of graft polymerization. Furthermore, the chain termination begins to predominate due to the increase in temperature. Therefore, a lower graft yield is obtained.

Effect of Acrylamide Concentration

The variation of graft yield with the concentration of acrylamide was investigated by carrying out the polymerization at four different concentrations for 4 h (Fig. 2). The grafting reaction takes place rapidly at first, then slows down, and levels off. The rate of grafting leveled off after 120 min for all acrylamide concentrations except for 0.5 g/50 mL (at which an induction

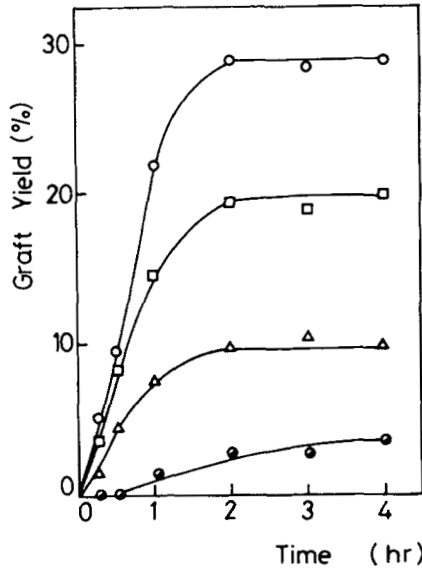


Fig. 2. Variation of graft yield with acrylamide concentration: $[Bz_2O_2] = 0.0484$ g/50 mL; temperature = $85^\circ C$; time = 2 h; [acrylamide] = g/50 mL; (○) 2; (□) 1.5; (△) 1; (●) 0.5.

period of 30 min was observed). The fact that grafting yield remains at a certain level can be explained by the significant reduction of the monomer concentration in the system (i.e., the acrylamide concentration diffused into the PET fibers and the external solution decreased).

Effect of Initiator Concentration

The effect of concentration of benzoyl peroxide upon the graft yield was shown in Figure 3. As seen in the figure, the graft yield increases up to the

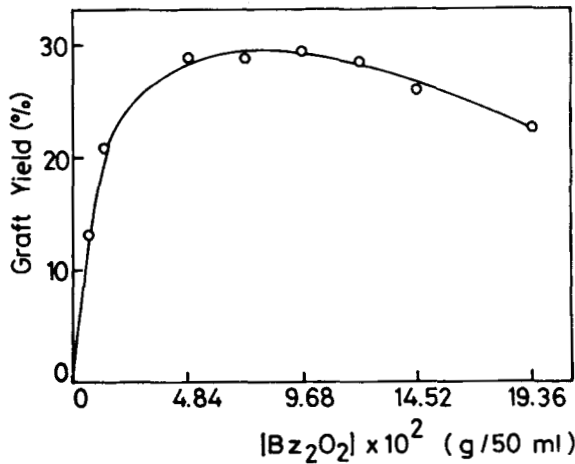


Fig. 3. Variation of graft yield with benzoyl peroxide concentration. [acrylamide] = 2 g/50 mL; temperature = $85^\circ C$; time = 2 h.

TABLE II
Moisture Regain and Intrinsic Viscosity Values of Grafted PET Fibers

Graft yield (%)	Moisture regain (%)	Intrinsic viscosity (dL/g)
Ungrafted	0.42	0.067
5.1	0.71	
9.1	0.95	0.148
19.1	1.89	
21.8	2.56	0.325
28.9	3.10	0.538
38.7	3.81	
41.7	3.90	

benzoyl peroxide concentration of 0.05 g/50 mL, then passes through a plateau, and decreases starting from the concentration of 0.0968 g/50 mL.

The primary free radical species ($C_6H_5COO\cdot$) and/or the secondary free radical species ($C_6H_5\dot{C}$) formed by the dissociation of benzoyl peroxide take place in various reactions in the medium of polymerization. These free radicals can form PET macroradicals by the hydrogen abstraction, take a role in the termination reactions (with the growing polymer chains or PET macroradicals), or combine with other free radical species. At low benzoyl peroxide concentrations the formation of PET macroradicals is favored, while at high initiator concentration other two reactions predominate decreasing the graft yield.

EVALUATION OF SOME PROPERTIES OF GRAFTED FIBERS

Moisture Regain and Intrinsic Viscosity

In Table II the moisture regain is seen to increase with the graft yield. The moisture regain of PET fibers is relatively low. The moisture regain value of the ungrafted PET fiber was found to be 0.42% (at 20°C at 65% relative humidity). The values of moisture regain increased to 3.90% at 41.7% graft yield. This can be attributed to the hydrophilic nature of the grafted monomer and the structural changes due to grafting.

The intrinsic viscosity measurements were carried out in *m*-cresol at 25°C. The intrinsic viscosity was seen to increase depending upon the graft yield (Table II).

TABLE III
Density and Diameter Values of Grafted PET Fibers

Graft yield (%)	Diameter (cm $\times 10^{-3}$)	Density (g/cc)
Ungrafted	2.6851	1.3745
19.8	2.9292	1.3726
28.9	3.0268	1.3671
41.7	3.1733	1.3607

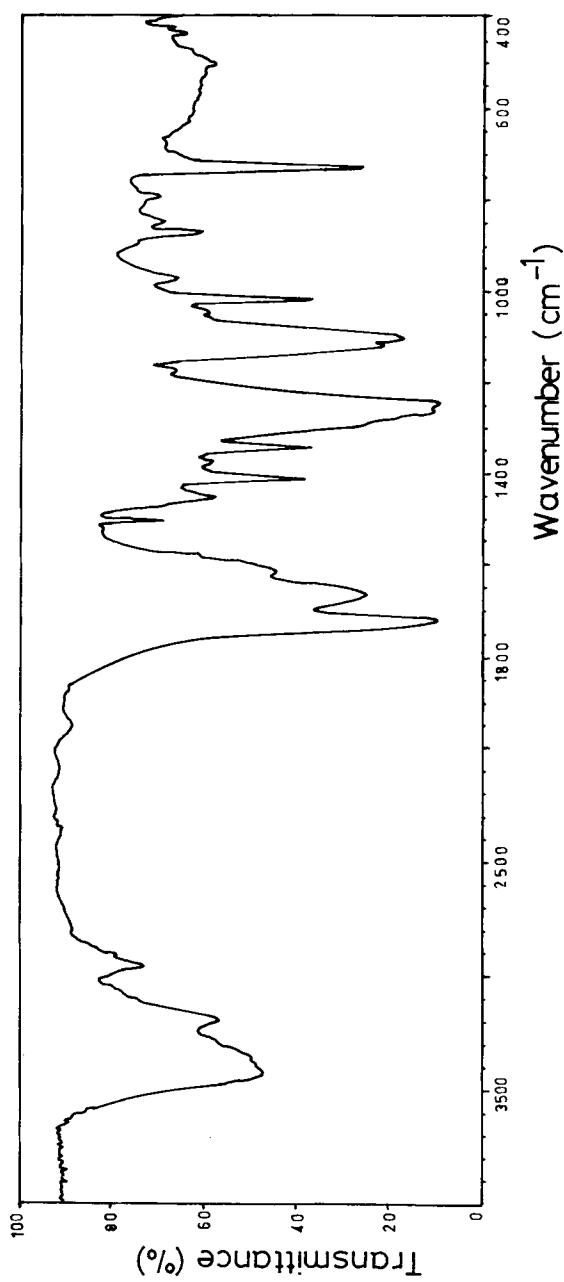


Fig. 4. FTIR spectrum of PET fiber grafted with 19.1% acrylamide.

Diameter and Density

Table III shows the variation of the densities and diameters of the PET fibers grafted with varying amounts of acrylamide. As is clearly seen, the fiber diameters increased and the fiber densities decreased with the increasing graft yield. A possible explanation is that the grafted polymer chains are accommodated in between the completely linear main polymer chains, which results in an increase in diameter. Their contribution to the weight is much less than their contribution to the volume. These polymer chains are most likely located on the regions close to the surface of the PET fibres.

FTIR Spectrum

Figure 4 shows the FTIR spectrum of the sample grafted with 19.1% acrylamide. The absorptions at 3200–3330, 1660–1670, and 1625 cm^{-1} are typical of those —N—H stretching, —C=O (amide), and —C=N— resonance peaks coming from the amide group, respectively.

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