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Graft Copolymerization of Methyl Methacrylate onto Poly(Ethylene Terephthalate) Fibers Using Benzoyl Peroxide

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GRAFT COPOLYMERIZATION OF METHYL METHACRYLATE ONTO POLY(ETHYLENE TEREPHTHALATE) FIBERS USING BENZOYL PEROXIDE

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Key Words: Graft copolymerization; Poly(ethylene terephthalate) fibers; Methyl methacrylate; Benzoyl peroxide

ABSTRACT

The graft copolymerization of methyl methacrylate onto poly(ethylene terephthalate) fibers has been studied using benzoyl peroxide as initiator. The grafting reactions were carried out within the 70 to 90°C temperature range, and the variations of graft yield with monomer and initiator concentrations were also investigated. The overall activation energy for grafting was calculated as 34.1 kcal/mol. The results of dyeability with the disperse dye suggested that diffusion into the fiber struc-

ture was moderately difficult when the graft yield reached 14–15%. The maximum graft yield was obtained at a benzoyl peroxide concentration of 4.00×10^{-3} M. The decomposition temperature values obtained from thermogravimetric analysis show that the thermal stability of poly(ethylene terephthalate) fibers decreased as a result of grafting. Further, such change in the properties of methyl methacrylate grafted fibers as density, diameter, and moisture regain were also determined.

INTRODUCTION

Poly(ethylene terephthalate) (PET) is an important polymer that finds widespread uses in commerce and industry in the form of fibers, films, and plastic resins. PET possesses such desirable fiber properties as high strength and resistance to shrinkage and abrasion as well as such undesirable features as low moisture regain, difficulty in dyeing, and poor antistatic properties due to its high crystallinity, hydrophobicity, and lack of chemically reactive groups.

Graft copolymerization is one of the effective methods for improving these undesirable properties or for furnishing PET with new properties. It is generally thought that as a result of grafting, the essential fiber properties of the PET backbone are not affected but that the fibers acquire new properties which depend upon the monomer and/or monomers grafted.

Vinyl monomers such as acrylic acid [1–5], methacrylic acid [6, 7], acrylamide [8, 9], and *n*-vinyl-2-pyrrolidone [3] can be grafted onto PET fibers by chemical [1–3, 6, 8, 9] or radiation [4, 5, 10] initiation. Radiation grafting is easy to control; however, it gives a low radical yield and there is a problem of degradation of PET (above 5 Mrad) [10, 11]. Chemical methods are more advantageous as regards degradation of the main polymer [12].

Methyl methacrylate, which was chosen as the monomer in this study, has also been used by various workers for grafting onto PET. Experimental results of the grafting of methyl methacrylate onto PET with the use of potassium permanganate-oxalic acid [13], pentavalent vanadium [14], and tetravalent cerium [15] have been given by Nayak and coworkers. There are also reports concerning initiated grafting with the potassium bromate-thiourea system [16], the acetyl acetonate complex of tetravalent vanadium [17], and radiation [18].

However, there are no detailed studies in the literature concerning radical methyl methacrylate grafting onto PET fibers in aqueous media using benzoyl peroxide. Investigation of the factors affecting grafting (such as temperature, solvents, monomer and initiator concentrations) to determine the optimal conditions for grafting is as important as the investigation of the properties of grafted PET fibers.

The present paper deals with the grafting of methyl methacrylate onto PET fibers initiated by radicals resulting from thermal decomposition of benzoyl peroxide. Also, changes observed in the properties of grafted PET, such as density, diameter, thermal stability, and moisture regain, are reported here.

EXPERIMENTAL

Materials

PET fibers (stretch ratio 2, 28 filament) supplied by SASA Co. (Adana), were used during all experiments. Fiber samples prepared as small hanks were Soxhlet-extracted with acetone for 6 hours and dried at ambient conditions.

Monomer methyl methacrylate (MMA) (BDH) was washed three times with 5% NaOH, dried over CaCl₂, and finally distilled in vacuum at 46°C. Initiator benzoyl peroxide (Bz₂O₂) (Merck) was recrystallized twice from a methanol–chloroform mixture and dried over P₂O₅ in a vacuum desiccator. Blue BR (I.C.I.) was used in dyeing experiments as a disperse dye.

All the other chemicals such as acetone, dimethylsulfoxide, dimethylformamide, pyridine, and alcohols, were chemically pure grade and used as supplied by their manufacturers.

Graft Copolymerization

A PET fiber sample (0.30 ± 0.01 g) was placed in a 100-mL Pyrex polymerization tube containing the required concentrations of monomer and initiator in 5 mL acetone. The volume of the polymerization mixture was made up to 50 mL with deionized water and then the mixture was immediately placed into a water bath (Lauda D 40 S, Germany) at the polymerization temperature. The temperature was kept within ± 0.5°C, and the contents were stirred occasionally during graft copolymerization.

After the desired polymerization time, the fiber sample was taken out of the tube and washed with 50 mL acetone overnight at room temperature. It was then Soxhlet-extracted with benzene for 8 hours and with acetone for 6 hours to remove homopoly(MMA) from grafted PET fiber. Finally, the sample was dried until it maintained a constant weight.

Percent graft yield was calculated from the increase in the weight of the original PET after grafting:

$$\text{graft yield (\%)} = [(w_2 - w_1)/w_1] \times 100$$

where w_1 and w_2 denote the weights of the original and grafted PET, respectively.

Dyeing Procedure

The grafted and original fiber samples were dyed with Blue BR (I.C.I.) (0.80 g/L). The dyeing was carried out at 95°C for 1 hour using a material-to-liquor ratio of 0.6:100. The dye uptakes of the fiber samples were calculated from the amount of dye remaining in the dye bath by using a predetermined calibration curve. Solutions of Blue BR (disperse dye) were used in the concentration range 0.50×10^{-3} to 10.0×10^{-3} g dye/L to construct the calibration curve. The absorbances were taken at 622 nm with a Shimadzu 160 A Model UV spectrophotometer.

Measurement of Density and Diameter

The densities of the fiber samples were measured with a density gradient column prepared from carbon tetrachloride and xylene. Glass floats (made by Davenport Ltd.) whose densities are known at 23°C with an accuracy of 1/10,000 were used in the calibration of this column. The levels of the glass floats and the fiber samples in the column were determined using a cathetometer with ± 0.01 mm sensitivity.

The fiber diameters were measured with a Kyowa Microlux-11 microscope at a magnification of 1000 \times from at least five different regions of each sample.

Determination of Moisture Regain

Fiber samples dried over P₂O₅ were conditioned in a medium at 20°C with a relative humidity of 65% for 24 hours in order to evaluate the moisture regain value. This value was calculated from the differences in the weight of the conditioned fiber and the dry weight of the original fiber.

Thermogravimetric Analysis

Thermogravimetric analysis was performed with a Linseis L81 Model thermal analyzer in He atmosphere (flow rate 200 mL/min). The samples were uniformly heated at a 10°C/min heating rate, beginning from room temperature. Thermal analysis was carried out up to 450°C; higher temperatures had no bearing on morphological characteristics due to predominant degradation of PET.

RESULTS AND DISCUSSION

It is known that MMA has a tendency toward thermal polymerization [19]. We first examined whether there was any thermal grafting by using preexperiments. For this purpose the fiber sample was placed into a polymerization tube containing only water and monomer (no initiator) at 90°C (the highest temperature used in the study) and kept for 4 hours. Then the fiber sample was washed and weighed. No variation in sample weight was observed after several trials. This observation completely eliminated any questions about thermal grafting of MMA onto PET at our experimental conditions.

It was also observed that Soxhlet extraction of a sample with only either acetone or benzene was enough to remove homopoly(MMA) from the grafted fibers. For the complete removal of homopoly(MMA), however, both of these solvents were sequentially employed during our studies.

Effect of Temperature and Time

Figure 1 shows the effect of polymerization temperature and time on grafting. It is seen that increasing the polymerization temperature from 70 to 90°C causes a significant increase in the rate of grafting. Another observation is that no grafting occurs at 70°C even after 40 minutes (induction period). Raising the polymerization temperature to 75°C is accompanied by an improvement in grafting and a reduction

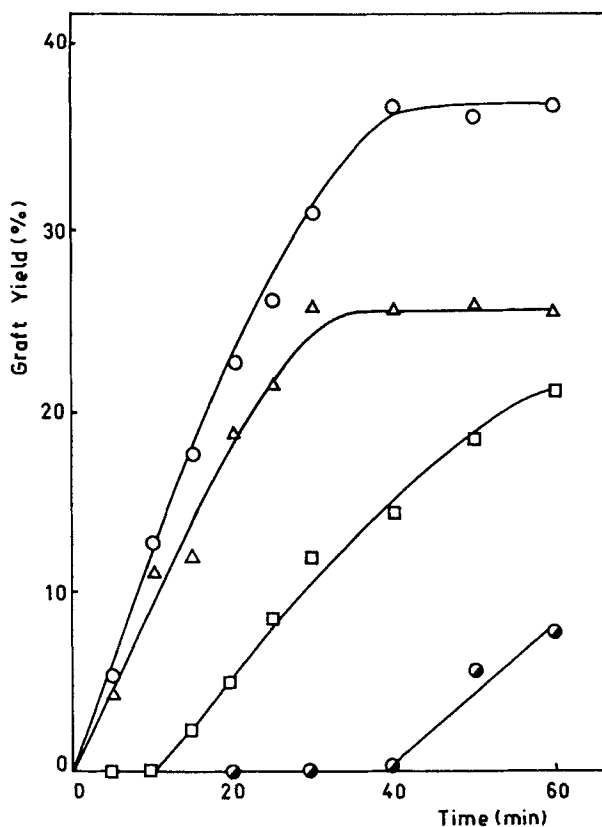


FIG. 1. Effect of polymerization temperature on graft yield: $[MMA] = 0.120$ M, $[Bz_2O_2] = 4.00 \times 10^{-3}$ M, (●) 70°C, (□) 75°C, (△) 80°C, (○) 90°C.

of the induction period. The latter amounts to only 10 minutes. Carrying out the polymerization at 80 and 90°C causes further enhancement in grafting, and no induction period was noticed.

It is clear that an increase in the polymerization temperature influences the rates of the initiation and propagation reactions. It also eases diffusion into the fiber structure and facilitates the swellability of PET fibers. These last effects are especially predominant at and above the glass transition temperature of PET (80°C). Since the polymer chains become more mobile at the glass transition temperature, the reactivity of PET will increase at this temperature and above, thereby giving rise to a higher graft yield [20].

On the other hand, the grafting reaction initially proceeds at a fast rate at 80 and 90°C, then decreases with time to a slower rate and at last levels off (saturation graft yield) (Fig. 1). The saturation graft yield of 25.7% at 80°C increases to 36.2% at 90°C.

By raising the temperature, monomer consumption will increase, depending on the rise in the rate of initiation and propagation. That is why the saturation graft yield at 80 and 90°C could be observed as a decrease in monomer concentration.

TABLE 1. The Values of the Initial Rates of Grafting (R_g) at Various Temperatures^a

Temperature, °C	$R_g \times 10^5$, mol/L·s	$1/T \times 10^3$, 1/°C	Log $R_g + 5$
75	2.945	2.874	0.4690
80	8.680	2.833	0.9385
85	10.618	2.793	1.0260
90	13.718	2.755	1.1373

^a[MMA] = 0.120 M; [Bz₂O₂] = 4.00 × 10⁻³ M.

The initial rates of grafting (R_g) calculated for the experimental temperatures are given in Table 1. The slope of log R_g vs $1/T$ graph shows that the overall activation energy for grafting is 34.1 kcal/mol in the 75 to 90°C range (Fig. 2).

Effect of Monomer Concentration

PET fibers were grafted using a Bz₂O₂ concentration of 4.0 × 10⁻³ M at 80°C for four different MMA concentrations. The experimental results are presented in

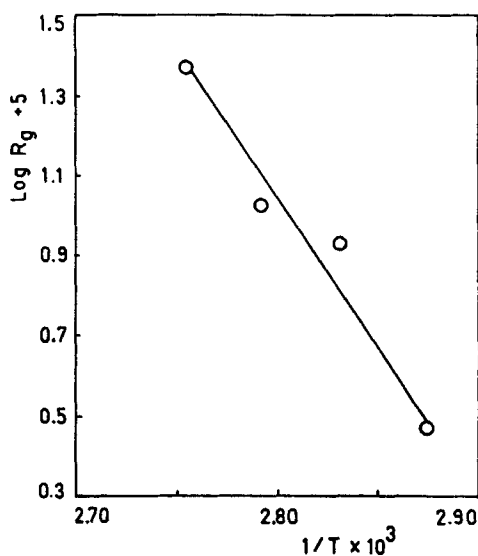


FIG. 2. Arrhenius plot of $1/T$ vs log R_g for grafting MMA onto PET fibers using Bz₂O₂.

Fig. 3 which shows that both the rate of grafting and saturation graft yield increase as the concentration of MMA increases. For instance, the saturation graft yield of 2.2% at 0.019 M MMA increases to 25.9% at 0.120 M MMA. Also, the grafting reaction proceeds without any induction period at 0.120 M MMA. The reverse is the case at other MMA concentrations, where induction periods of varying extents are observed.

A rise in the concentration of MMA will increase the available MMA molecules diffusing into the PET fiber structure. Hence, the chance for the PET macroradicals and growing grafted side chains to react with monomer molecules will increase, which will result in an increase of saturation graft yield. Leveling off of grafting at all MMA concentrations could be associated with depletion in MMA concentration as well as with reduction in active sites on the PET backbone as polymerization proceeds.

Effect of Initiator Concentration

The effect of Bz_2O_2 concentration on grafting is shown in Fig. 4. Bz_2O_2 at different concentrations (0.25×10^{-3} to 8.00×10^{-3} M) was added to the polymerization system, and the reaction was allowed to proceed at $80^\circ C$ for 1 hour. It is

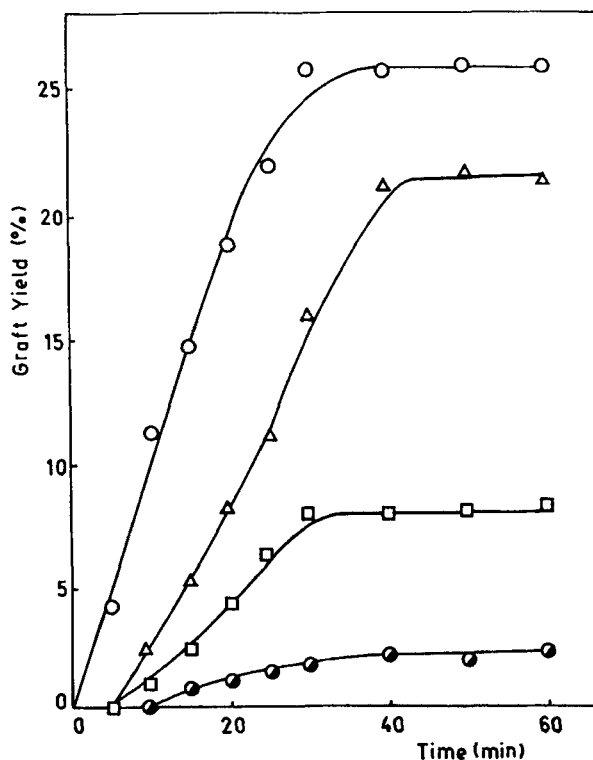


FIG. 3. Variation of graft yield with the monomer concentration: $[Bz_2O_2] = 4.00 \times 10^{-3}$ M; temperature, $80^\circ C$; [MMA]: (●) 0.019 M, (□) 0.039 M, (△) 0.078 M, (○) 0.120 M.

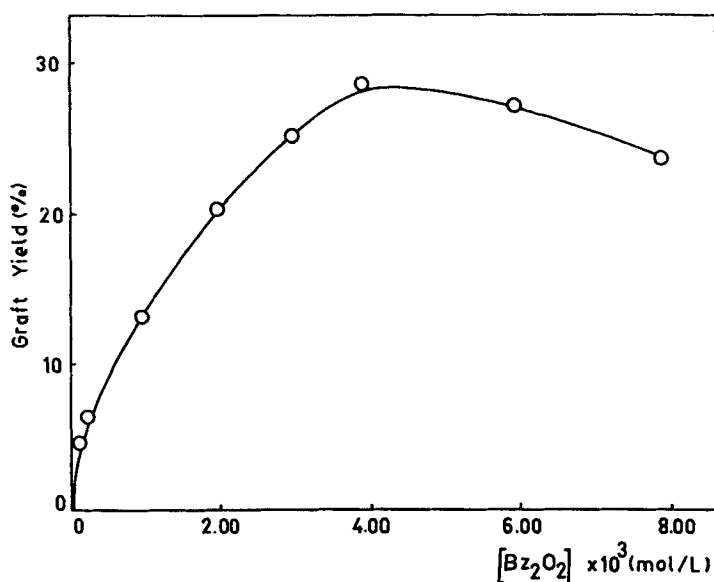


FIG. 4. Variation of graft yield with the initiator concentration: [MMA] = 0.120 M; temperature, 80°C; time, 1 hour.

seen that increasing the Bz₂O₂ concentration up to approximately 4.00×10^{-3} M is accompanied by substantial increase in the graft yield. The graft yield value passes through a maximum (28.3%) at this concentration, and slightly decreases at higher initiator concentrations. A similar trend has been reported for grafting acrylic acid [2] and acrylamide [8] onto PET fibers.

Bz₂O₂ decomposes at a reasonable rate beginning from about 55–60°C to give a primary free radical species (C₆H₅COO[·]) and/or secondary free radical species (C₆H₅[·]). These free radicals can appear in various reactions in the polymerization medium. They can form PET macroradicals by hydrogen abstraction from the PET backbone, take a role in the termination reactions (with the growing polymer chains or PET macroradicals), or combine with other free radical species. PET macroradicals can also be formed by the transfer reactions of growing homopoly(MMA) chains with the PET backbone [the increase in the free radical concentration increases the number of active poly(MMA) chains]. The ultimate effects of all these reactions determine the magnitude of grafting.

Our experimental results suggest that when Bz₂O₂ concentration does not exceed 4.00×10^{-3} M, the formation of PET macroradicals by transfer reactions or direct hydrogen abstraction from the PET backbone will be favored. At a high initiator concentration, termination reactions will predominate and the graft yield will decrease.

Effect of Orientation

To examine the effect of orientation upon graft yield, PET fibers mechanically stretched at room temperature with a stretch ratio of 2 were used in the graft

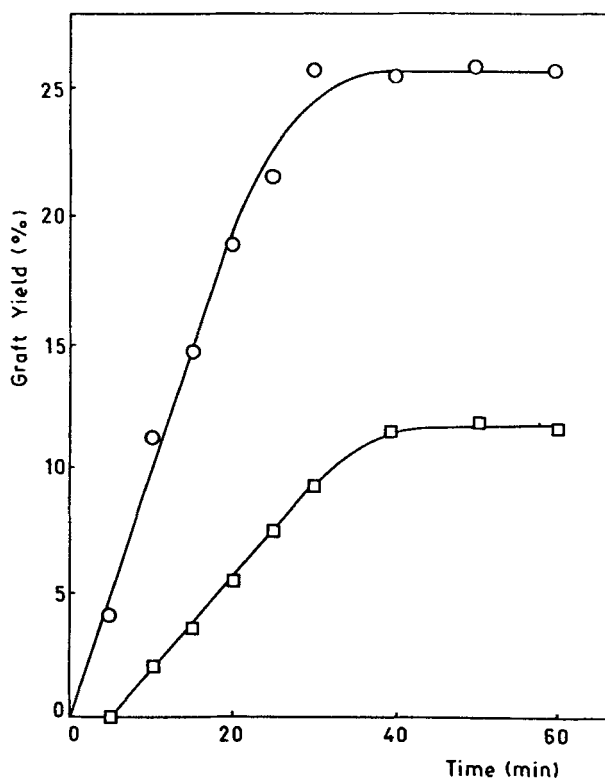


FIG. 5. Effect of orientation on graft yield: (○) unoriented PET; (□) oriented PET; temperature, 80°C; [MMA] = 0.120 M; [Bz₂O₂] = 4.00 × 10⁻³ M.

copolymerization. The results are given in Fig. 5 in which the oriented fiber samples were subjected to graft copolymerization at the same conditions employed with the unstretched PET fibers.

The molecular orientation of fibers is the alignment of long-chain molecules relative to the fiber axis. As the chains of the fiber pack closely together during orientation, it becomes increasingly difficult for other molecules to penetrate between them. As a result of orientation, the number of domains that can accept the grafted side poly(MMA) chains will decrease. Thus, the graft yield decreases due to the effect of these factors, as expected. From Fig. 5 it can be seen that both the saturation graft yield and the rate of grafting decrease with orientation. The graft yield of 26.0% that was obtained with unstretched fiber at 1 hour decreases to 12.1% with the stretched fiber. Also, an induction period of 5 minutes is observed in the oriented fiber.

Effect of Reaction Medium

Solvents added to the graft copolymerization medium have important effects upon graft yield [2, 6, 13-15]. In this part of study, the effect of solvents on the graft yield was investigated by adding various alcohols and some organic solvents to

the reaction medium. The grafting procedure was carried out at different water/solvent ratios (v/v) by keeping the total volume of the reaction system at 50 mL.

Table 2 shows the effect of various solvents on graft yield. All the solvents employed were found to have a negative effect on graft yield. Also, an increase in the amount of solvent in a water/solvent mixture further decreased the graft yield regardless of the type of solvent employed. The grafting was completely inhibited at a water/ethanol, water/butanol, and water/dimethylformamide ratio of 10/90 (v/v). Similarly, a 50%(v) or more addition of pyridine and dimethylsulfoxide into the polymerization medium completely inhibited the grafting reaction.

The variation of grafting upon changing the proportions of the solvent can be explained by the following factors: (a) miscibility of monomer, (b) capability of swelling of PET fiber, (c) formation of solvent radical and/or hydrogen and hydroxyl radicals from water under the influence of the primary radical species of the initiating system, and (d) termination of the grafted chain radicals and PET macroradicals via chain transfer. Since the first three of these factors have a positive effect on the diffusion of monomer to active sites upon the PET backbone, they facilitate grafting. However, the effect of factor (d) is to lower the rate of initiation of grafting, thereby leading to a decrease in grafting.

It is clearly seen that the effects of solvents added to the graft copolymerization medium are highly complicated and depend on many factors. For instance, in the grafting of glycidyl methacrylate onto PET fibers in 80% dimethylformamide (aq), it was reported that the use of Bz_2O_2 increased the graft yield [21], while a change of initiator (hydrogen peroxide instead of Bz_2O_2) in the same system had a decreasing effect [22]. Our results suggest that the aqueous media is favorable for the grafting of MMA onto PET fibers using Bz_2O_2 .

Some Properties of MMA-Grafted PET Fibers

Table 3 exhibits the variation of density and diameter of PET fibers with graft yield. According to this table, grafting increases the diameter but decreases the density of the fibers. A density of 1.3722 g/cm^3 and a diameter of $1.36 \times 10^{-2} \text{ mm}$

TABLE 2. Effects of Some Solvents on Graft Yield^a

Water/solvent ratio (v/v)	Graft yield, %				
	Ethanol	Butanol	DMF ^b	DMSO ^b	Pyridine
100/00	25.9	25.9	25.9	25.9	25.9
90/10	18.2	10.8	18.5	12.3	11.1
70/30	11.6	7.1	8.7	6.3	3.3
50/50	2.2	1.2	4.5	0.0	0.0
30/70	0.8	0.6	2.8	0.0	0.0
10/90	0.0	0.0	0.0	0.0	0.0

^a[MMA] = 0.120 M; [Bz_2O_2] = 4.00×10^{-3} M; time, 1 hour; temperature, 80°C.

^bDMF = dimethylformamide; DMSO = dimethylsulfoxide.

TABLE 3. Density and Diameter Values of MMA-Grafted PET Fibers

Graft yield, %	Density, g/cm ³	Diameter, mm × 10 ⁻²
0.0	1.3722	1.36
5.2	1.3663	1.45
10.0	1.3615	1.57
15.6	1.3574	1.61
20.6	1.3570	1.71
24.3	1.3521	1.83
32.3	1.3477	1.98
36.8	1.3345	2.03

of ungrafted PET fiber change to 1.3345 g/cm³ and 2.03 × 10⁻² mm for 36.8% (maximum graft yield obtained in this study) MMA-grafted PET fiber, respectively. This shows that the contribution of grafting upon fiber volume is higher than the fiber weight. Although poly(MMA) has a lower density than PET (1.1870 and 1.3722 g/cm³, respectively), one should also be aware of the contribution of the opening structure of the PET fiber due to grafting onto the decreasing density.

The moisture regain values of MMA-grafted PET fibers are shown in Fig. 6. The moisture regain value of ungrafted PET fiber is 0.42%. It increases to 0.56% at 14.8% graft yield and shows a decrease above this graft yield.

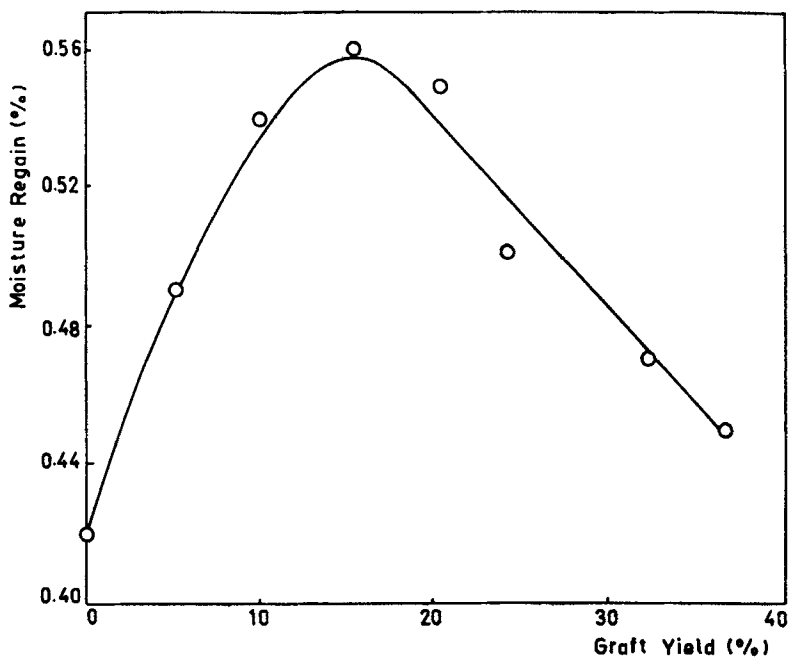


FIG. 6. Moisture regain values of MMA-grafted PET fibers.

The moisture regain of a textile fiber can be increased by introducing suitable hydrophilic groups to the fiber structure. Nevertheless, there is no difference in the hydrophilicity of MMA compared to PET. If the moisture regain value depends upon the number of MMA units inserted into the fiber structure with grafting, this value must also continuously increase above the graft yield of 14.8%. Thus, at this point another factor must be considered as affecting the moisture regain of MMA-grafted PET.

Moisture regain can also be enhanced by opening up the fiber structure as a result of grafting, thus offering additional accessibility for water molecules [13, 14]. On the contrary, there are also some reports that the fiber structure might be tighter when the graft yield reaches a certain grafting level. For example, Uchida et al. [23] reported that the structure became much more densely packed at the subsurface regions by grafting of PET films with acrylamide. They have given a model figure showing the physical structure of the surface region of grafted PET film.

It was also reported that the structural properties of PET fibers were changed due to grafting of acrylic acid, especially at the subsurface regions [2]. The grafting predominated at the subsurface regions acts as a barrier over 8–10% graft yield that impedes diffusion into the fiber structure. Similar behavior has been observed in the grafting of acrylic acid onto PET films [3]. It was pointed out that the difficulty of diffusion into films had resulted from both the tightness of the surface structure and partial crosslinking at the subsurface regions.

Since disperse dye molecules are physically inserted in the fiber structure, the level of dyeability of a fiber with disperse dye is the result of the tightness of the fiber structure. Thus, by dyeing MMA-grafted PET fibers with Blue BR (disperse

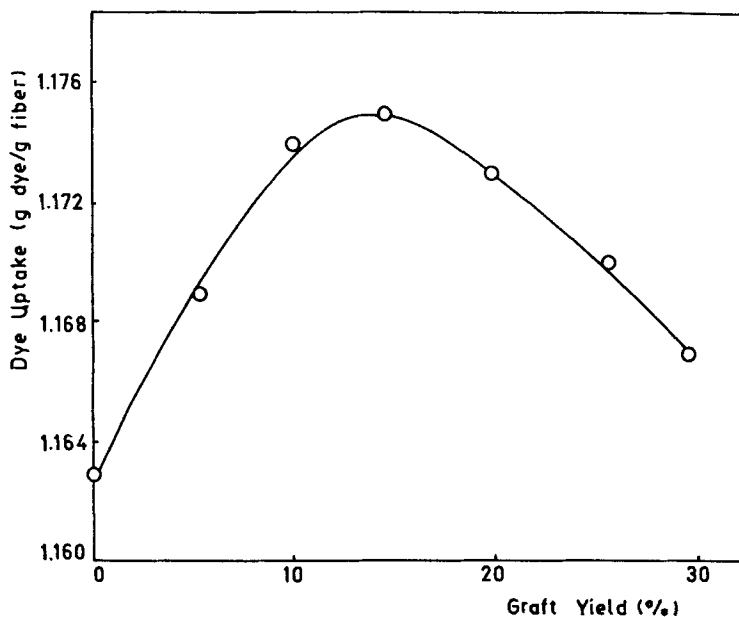


FIG. 7. Dye uptake values of MMA-grafted PET fibers. Disperse dye, Blue BR.

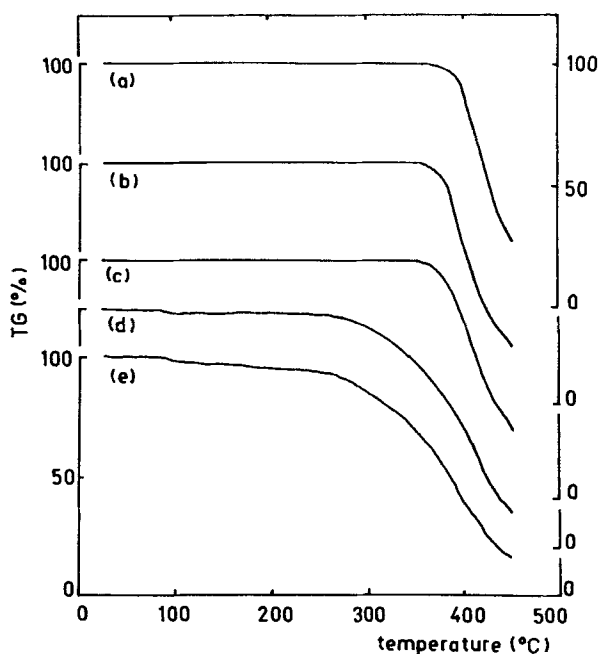


FIG. 8. Thermograms of MMA-grafted PET fibers. Graft yield: (a) 0%, (b) 5.2%, (c) 15.2%, (d) 24.3%, (e) 36.8%. Rate of heating, 10°C/min; atmosphere, 200 mL/min of He.

dye), we tried to clarify whether a diffusion barrier occurred at a graft yield higher than 14–15%. The results from dyeing experiments are shown in Fig. 7 where it is seen that the dye uptake value of MMA-grafted fibers increased up to 14–15% graft yield and then decreased at higher graft yields. This finding suggests that the diffusibility of dye molecules into the fiber structure moderately decreases above a graft yield of 14–15%, similar to moisture regain values (Figs. 6 and 7).

Thermogravimetric curves of ungrafted and various degrees of MMA-grafted PET fibers are shown in Fig. 8. As mentioned in the Experimental Section, thermograms were recorded only up to 450°C because experimentation had no bearing on morphological characteristics due to the predominant degradation of PET. Thus we aimed only to determine the decomposition temperature of the samples. It is clearly seen that the decomposition temperature is influenced by grafting. The decomposition temperature of ungrafted PET fibers is 365°C whereas it was 359, 353, 271, and 267°C in the case of MMA-grafted PET with 5.2, 15.2, 24.3, and 36.8% graft yields respectively. These series of data show that MMA-grafted PET fibers began to decompose earlier than the ungrafted PET fibers. At high graft yield, it is observed that the decomposition temperature of MMA-grafted PET sharply decreases. The decrease in thermal stability up to 450°C in MMA-grafted PET fibers may be due to the early decomposition of poly(MMA), thus decreasing the overall thermal stability of the grafted samples.

CONCLUSIONS

We have shown that MMA can be grafted onto PET fibers using Bz_2O_2 as the initiator. From our experimental results, the following conclusions can also be drawn.

1. Temperature and monomer concentrations affect graft yield values. It is necessary to increase them to obtain high graft yields. Grafting becomes much more effective at temperatures around and above the glass transition temperature of PET.
2. To obtain high graft yield, the optimum initiator concentration is 4.00×10^{-3} M.
3. Aqueous media is favorable for the grafting of MMA onto PET fibers compared to the solvents used in this study. Since the effect of solvents on graft yield is highly complicated and dependent upon many factors, it is very difficult to rule out the effect of solvents.
4. A graft yield above 14–15% acts as a barrier that impedes diffusion into the fiber structure. Thus moisture regain and dyeability with disperse dyes of MMA-grafted PET decrease at a graft yield higher than 14–15%.
5. The rate of grafting and saturation graft yield decrease due to orientation. The percent decrement of saturation graft yield is approximately 50% in oriented fibers when compared to unoriented fibers.
6. Finally, the thermal stability of PET fibers decreases when MMA is grafted onto them.

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