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GRAFTING OF POLYESTER FIBERS

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ABSTRACT

Polyester monofilaments were grafted with methacrylic acid monomer in order to improve the water absorption and dye uptake characteristics. Kinetic parameters like percent grafting and grafting efficiency were measured as a function of concentration of monomer, initiator concentration, time of reaction, and temperature. The results show that the rate of grafting is proportional to the 0.167 power of the monomer concentration and the 0.545 power of the initiator concentration. The activation energy for grafting, calculated from an Arrhenius plot, was found to be 11.12 kcal·mol^{-1}. Water absorption and dye uptake were tremendously improved by grafting.

INTRODUCTION

Poly(ethylene terephthalate) (PET) fibers are highly crystalline, markedly hydrophobic, and do not contain chemically reactive groups. Grafting of hydrophilic monomers onto polyester fibers improves their dye uptake, water absorption, antistatic properties, and adhesion.

In general, there are serious difficulties in grafting monomers onto PET fibers. The chemical nature of PET does not allow formation on its macrochains of an appreciable quantity of radicals that can initiate grafting. Its high degree of crystallization and the order of its amorphous regions retard monomer diffusion.

In a heterogeneous polymer-monomer reaction system, diffusion controls chain growth and chain termination in the internal structure of the polymer. One way to facilitate diffusion is to open up the physical structure of the polymer by swelling in order to allow the monomer to enter in larger quantities.

There are many studies on the grafting of vinyl and other monomers onto PET fibers and films in the literature. The grafting of styrene [1–4], bromostyrene [5], acrylic and methacrylic acid [6–13], acrylamide [14, 15], vinyl acetate [16], acrylonitrile [10, 17], and methyl methacrylate [18, 19] onto PET fibers and films has been reported.

The grafting of methacrylic acid (MAA) onto PET fibers is presented in this study. The effect of such variables as monomer concentration, initiator concentration, backbone concentration, temperature of the reaction, and time of polymerization on the kinetic parameters of grafting are evaluated. The improvement in moisture absorption and the dyeability of the grafted fibers are also studied in detail. The thermal stability of PET fibers grafted with MAA is also studied.

EXPERIMENTAL

Materials

Poly(ethylene terephthalate) fibers from Swiss polyester Grilene fibers (type F-3) were used for grafting. Methacrylic acid was vacuum distilled. The polyester was first swollen at 90–95°C for 2–3 hours in a solvent/nonsolvent system consisting of 1,2-dichloroethane/water (20/80 v/v). Dichloroethane was completely removed from the fiber by treatment with boiling water. The swollen fibers were used for grafting [17].

Grafting Procedure

Swollen polyester fibers (1 g) were added to a solution containing a known weight of benzoyl peroxide in 10 mL benzene diluted with 80–90 mL water and with 50% MAA monomer in a three-necked round-bottomed flask fitted with a condenser and a nitrogen inlet. The round-bottomed flask was kept in an ultrasonic bath which was held at constant temperature. The contents of the flask were stirred at 15 minute intervals using an ultrasonicator. The reactions were performed as a function of monomer concentration, temperature, backbone concentration, initiator concentration, and time of reaction. After the stipulated period of time, the reaction was quenched by placing the reaction vessel in ice-cold water. The homopolymer present in the grafting reaction mixture was removed with boiling water. After extraction, the grafted fibers were filtered and dried in vacuum. The amount of graft added onto the fiber was determined gravimetrically. The percent grafting was calculated by using the formula

$$\text{percent grafting} = \frac{W_2 - W_1}{W_1} \times 100$$

where W_2 = weight of graft
W_1 = weight of backbone

The rate of grafting was found by using the formula

$$\text{rate of grafting } (R_g) = \frac{\text{weight of graft} \times 1000}{\text{molecular weight of monomer} \times \text{time in seconds} \times \text{volume of reaction}}$$

Determination of Moisture Regain

The fiber samples, dried over P_2O_5, were conditioned in a desiccator at 65% r.h. for 24 hours. The moisture regain values were determined from the dried and conditioned fiber weights.

Dyeing Test

Two disperse dyes, Naviline brown 3 and Foron red S-FL, were made into a 2% solution in a methylene chloride:ethylene glycol solvent mixture (1:3). Fibers were immersed in the dye solution for 15 minutes, then washed with methylene chloride and ethylene glycol in order to remove excess dye adhering to the fiber. The fibers were dried thoroughly. The color was visually compared with that of control fibers in order to qualitatively grade the dye uptake for fibers with different percent grafting values.

Thermal Studies

The ungrafted and grafted fibers were subjected to thermogravimetric analysis using the Mettler TA 3000 system containing a TGA module. The analysis was carried out in a nitrogen atmosphere with a bubble rate of 200 mL/min using a program heating rate of 10°C/min.

RESULTS AND DISCUSSION

The kinetics of grafting of graft copolymer has been extensively studied in recent years. However, the study of the kinetics of grafted copolymers in the heterogeneous condition is of recent origin. The grafting yield and the extent of grafting depend upon a large number of variables. Therefore, the effect of variables on percent grafting was investigated. During this study, one of the variables was varied and the other parameters were kept constant.

Variation of Monomer Concentration

The effect of MAA concentration on percent grafting and rate of grafting is presented in Fig. 1. The results show that the percent grafting and rate of grafting decrease with a steep negative slope when the monomer concentration is increased.

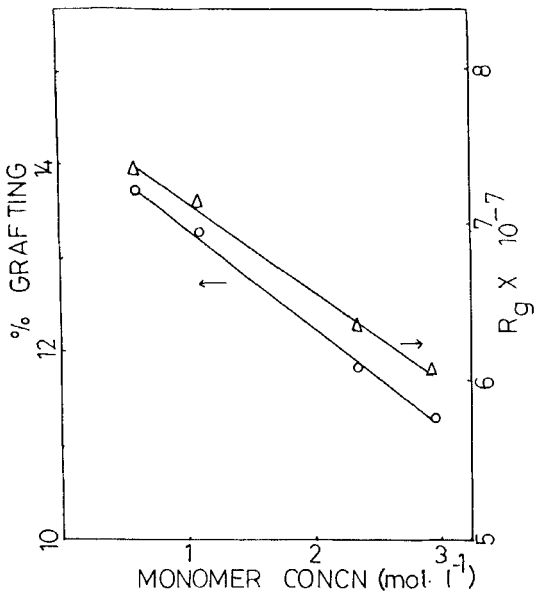

FIG. 1. Effect of monomer concentration on percent grafting and rate of grafting.

This may possibly be due to high homopolymer formation in the reaction. This increases the viscosity of the reaction medium, which retards monomer diffusion in the fiber. The rate of monomer diffusion is progressively affected by deposition on the fiber surface. Therefore, a decrease in percent grafting is observed at a higher monomer concentration.

Variation of Initiator Concentration

The effect of benzoyl peroxide concentration on percent grafting and rate of grafting is shown in Fig. 2. Percent grafting and rate of grafting increase with initiator concentration. An increase in benzoyl peroxide concentration increases the free radical formation, which in turn increases the number of reaction sites in the backbone. As a result, percent grafting increases with an increase in initiator concentration. The enhancement of grafting with increasing benzoyl peroxide concentration [15] is due to the primary free radical species (C_6H_5COO) and/or the secondary free radical species (C_6H_5) formed by the dissociation of benzoyl peroxide in the polymerization system, which participate essentially in the initiation of grafting.

Effect of Temperature

The percent grafting and the rate of grafting increase with an increase of temperature up to an optimum temperature and then slowly decrease (Fig. 3). The data indicate that the grafting yield increases with temperature up to 70°C; a further increase in temperature decreases the percent grafting. Similar results were obtained for polyester fibers grafted with acrylic acid, acrylonitrile, vinyl acetate, acrylamide,

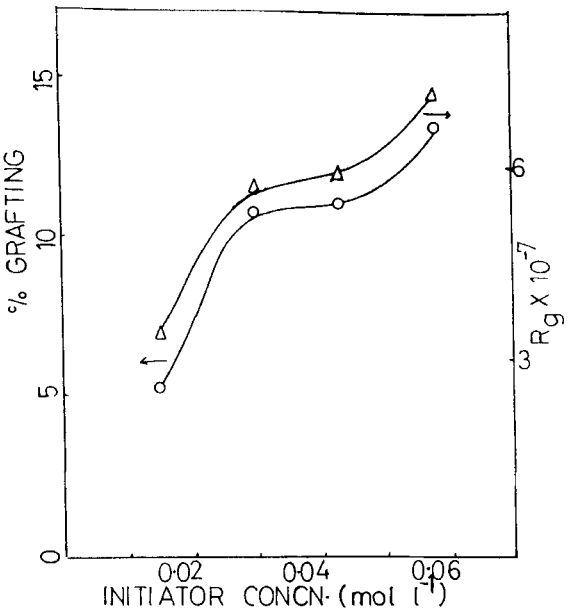

FIG. 2. Effect of initiator concentration on percent grafting and rate of grafting.

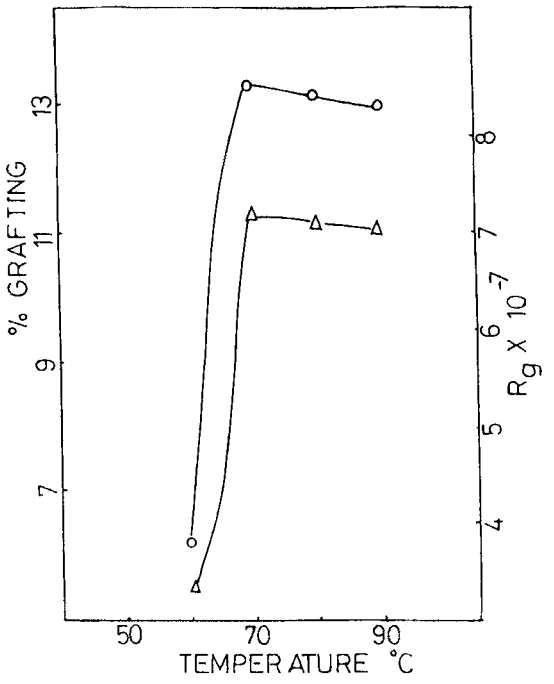

FIG. 3. Effect of variation of reaction temperature on percent grafting and rate of grafting.

etc. by other workers [6, 14, 15, 17]. In the chemical method of grafting using benzoyl peroxide initiator, there may possibly be two competitive processes taking place: homopolymerization and graft copolymerization. Although the initial rate of grafting increases with temperature, saturation grafting decreases [17]. This may be due to the decrease in monomer concentration in the swollen state because the rate of monomer consumption due to homopolymerization is higher at higher temperatures. The polymer swells in its own monomer, and hence the monomer available for grafting decreases as the temperature increases and consequently the rate of grafting decreases. The maximum grafting yield was obtained at 70°C, which is near the glass transition temperature of poly(ethylene terephthalate) (T_g = 65°C). The polymer chains whose activities are increased around the glass transition temperature tend to give radical reactions much more easily [2]. The increase in temperature increases the initiation and propagation rates of graft copolymerization along with the decomposition rate of the initiator. The increase in temperature also increases the mobility of the monomer molecules. The increase in temperature increases the swellability of the PET fibers and the mobility of the reactive species. Since more and more radicals combine as the temperature is increased, they cannot take part in the initiation of graft copolymerization. Moreover, with an increase of temperature, randomness increases with the predominance of chain termination. All these effects result in increases of the grafting rate and grafting yield with an increase in temperature. Similar results are reported in the literature [2, 19, 20].

Effect of Backbone Concentration

Figure 4 shows the effect of backbone concentration on percent grafting and rate of grafting. The grafting percentage decreases with an increase of backbone concentration. This may be due to the effects collectively produced by homopolymer formation and monomer concentration. In the case of the rate of grafting, the value decreases up to a concentration of 1.5 g and then the rate of polymerization slightly increases.

Variation of Reaction Time

The percent grafting increases with an increase of reaction time (Fig. 5). This trend is similar to that obtained for acrylonitrile and acrylic acid monomer grafted to polyester fibers [6, 17]. The graft copolymerization rate increases to a maximum value after 4 hours of reaction time and continuously decreases after that.

Kinetics of Grafting

The relationship between the rate of grafting (R_g) with the monomer and initiator concentrations in a grafting system [21] can be written as

$$R_g = k[\text{monomer}]^m[\text{initiator}]^n$$

where m and n can be experimentally determined. The experimental results showing the change of the rate of grafting with concentration of Bz_2O_2 (keeping the concentration of MAA constant) was related by plotting log R_g vs log[Bz_2O_2]. Figure

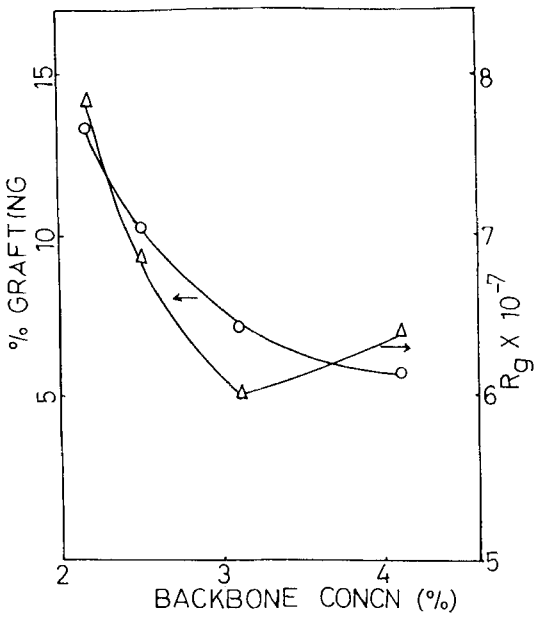

FIG. 4. Effect of backbone concentration on percent grafting and rate of grafting.

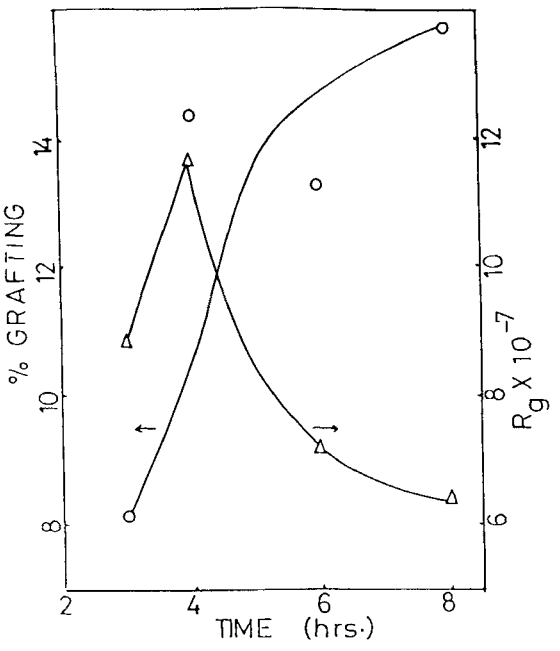

FIG. 5. Effect of reaction time on percent grafting and rate of grafting.

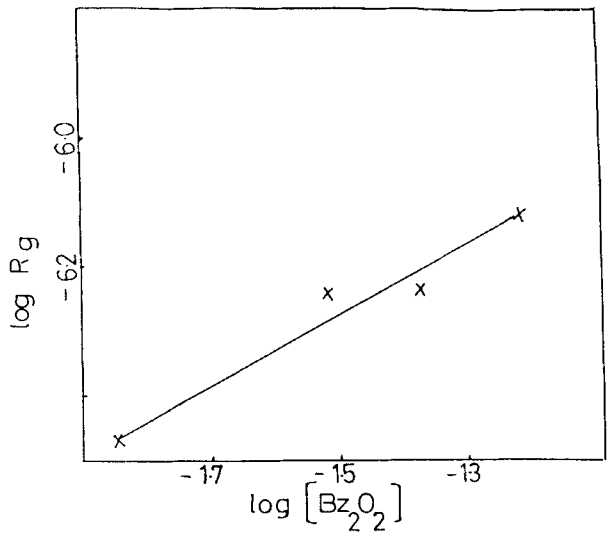

FIG. 6. The relation between rate of grafting and initiator concentration at constant monomer concentration.

6 shows that the rate of grafting was proportional to the 0.545 power of Bz_2O_2 concentration.

Similarly, at constant initiator concentration, the rate of grafting obtained at various MAA monomer concentrations was related (Fig. 7). Figure 7 shows that the rate of grafting was proportional to the 0.167 power of MAA concentration. Therefore, the grafting rate of MAA onto PET fibers using benzoyl peroxide can be written as

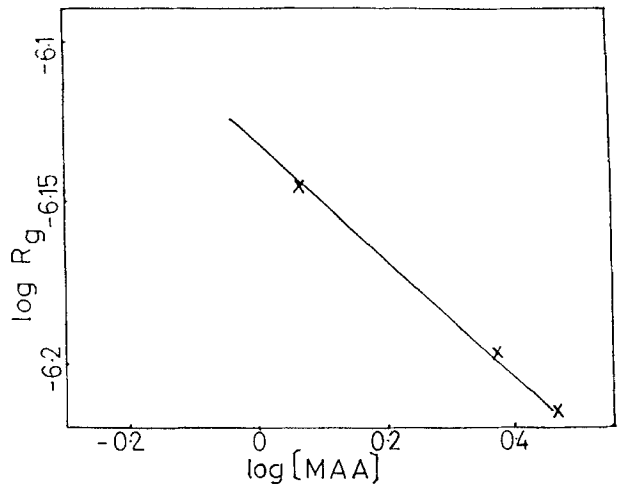

FIG. 7. The relation between rate of grafting and monomer concentration at constant initiator concentration.

$$R_g = k[\text{MAA}]^{0.167}[Bz_2O_2]^{0.545}$$

The k value obtained for the grafting reaction was 3.287×10^{-6}. The activation energy for grafting, calculated from an Arrhenius plot of log R_g vs $1/T$, was found to be 11.12 kcal/mol.

Moisture Sorption Studies

The percent moisture sorption of grafted fibers is shown in Table 1. The results show that there is a threefold increase in moisture uptake in the case of grafted fibers when compared with ungrafted PET fibers. The percent moisture absorbed increases with an increase of percent grafting up to a maximum value and then decreases. This may be due to blocking of the pores in the fibers after an optimum grafting by the graft molecules [6]. It was reported [21] that grafting starts from the fiber surface and proceeds toward the center. Because of this, the formation of a packed structure starts from the subsurface regions of fibers [22]. The increase in moisture sorption values was due to (—COOH) hydrophilic groups which enter the fiber structure as a result of MAA grafting. The initial rate of increase slows down at higher grafting values, possibly due to the barrier effect produced by the structure [21].

Dyeing Test

Fibers with different percent graft levels and ungrafted samples were stained using two disperse dyes, Naviline brown and Foron red, and the stained samples were visually evaluated. The results are presented in Table 2. It is evident from Table 2 that as percent grafting increases, the intensity (dye uptake) also increases.

Thermal Stability

The TGA curves obtained for ungrafted and fibers grafted with 5.75 and 15.75% MAA grafts are presented in Fig. 8 as Curves a, b, and c, respectively. For ungrafted fibers, decay started at 220°C, the peak temperature was 438°C, and the end temperature was 479°C. During this decay process, 84% of the material was degraded. For fibers grafted with 5.75% graft, decay started at 205°C. The peak and end temperatures were 433 and 477°C, respectively. The weight loss was

TABLE 1. Absorbed Moisture Levels of PET Fibers

Percent grafting	Moisture, %
0	0.40
5.75	1.00
9.60	1.28
13.30	1.78
15.75	1.72

TABLE 2. Qualitative Results Obtained from Dyeing Tests[a]

Percent grafting	Naviline brown	Foron red
0	Very light	Very light
5.75	Light	Light
9.60	Medium	Intermediate
13.30	Intermediate	Intermediate
15.75	Dark	Dark

[a]Sequence of evaluations: very light, light, intermediate, medium, dark, very dark.

85.75%. This suggests that due to grafting, thermal stability of PET fibers was slightly reduced.

Fibers grafted with 15.75% MAA showed interesting results. Unlike the other two samples, decomposition took place in stages (peak temperatures of 220, 224, 350, 407, and 432°C), and weight losses at these temperatures were 8, 7.9, 5.3, 35.47, and 47%, respectively. The thermogram shows there may be the association/formation of a new compound during the decay process, i.e., the deformed products

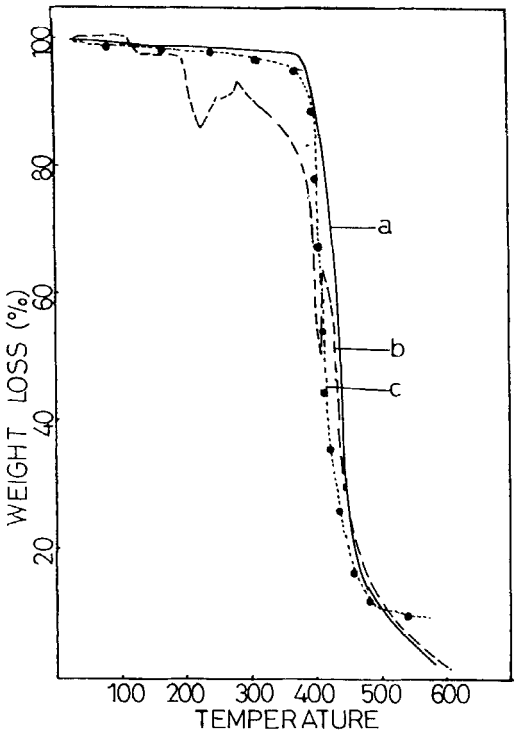

FIG. 8. Thermograms of PET fibers: (a) untreated, (b) 5.75% grafted, (c) 15.75% grafted.

combine to form into new compounds, which is why the thermogram shows a weight increase. This effect was seen in two temperature ranges. The starting, peak, and end temperatures for the first association mechanism were at 235, 239, and 292°C, respectively. During this reaction process, an 11.9% weight increase was observed. The starting, peak, and end temperatures for the second association process were 411, 413, and 416°C, respectively. Here, an 8.8% weight increase was observed. These studies suggest that although stability is lowered at low MAA content, it is increased at higher MAA content due to the rearrangement that takes place in the polyester graft system.

CONCLUSIONS

PET fibers were grafted with MAA after swelling the fibers with 1,2-dichloroethane/water. As a result of grafting, water absorption and dye uptake were increased to a greater extent. At higher percent grafting levels, some rearrangement/association takes place in the fiber.

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