

An Investigation of the Grafting of Acrylic Acid/Methyl Methacrylate Mixture onto Poly(ethylene terephthalate) Fibres

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ABSTRACT

The graft copolymerization of acrylic acid/methyl methacrylate (AA-MMA) onto poly(ethylene terephthalate) fibres has been studied using benzoyl peroxide (Bz_2O_2) as an initiator. The use of MMA as a comonomer increased the amount of AA introduced to the PET fibre up to 60% while the grafting of AA onto fibres alone gave low graft yields. This synergistic effect was found to be at its highest when an AA-MMA mixture having 30% AA (wt.) was used. The grafting increased the diameter and moisture regain of the fibres. The results of dyeability with the disperse dye suggested the diffusion into the fibre structure was moderately difficult when the graft yield reached 15-16%. The decomposition temperature values obtained from thermogravimetric analysis (TGA) showed that the thermal stability of poly(ethylene terephthalate) fibres decreased as a result of grafting.

Key Words:

copolymerization;
acrylic acid;
methyl methacrylate;
poly(ethylene terephthalate).

INTRODUCTION

Poly(ethylene terephthalate) (PET) fibres have poor chemical activity due to their high crystalline structure and lack of reactive functional groups. Graft copolymerization is one of the effective methods for improving undesirable properties

such as low moisture regain, difficulty in dyeing, and poor antistatic properties due to its high crystallinity, hydrophobicity, or for furnishing PET with new properties. It is generally thought that as a result of grafting. The essential fibre properties of

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the PET backbone are not affected but that the fibres acquire new properties, which depend upon the monomer and or monomers, grafted. Vinyl monomers such as acrylic acid [1-3] methacrylic acid [4] and acrylamide [5] can be grafted onto PET fibres by chemical [1,3,4,5] or radiation [2] initiation. Radiation grafting is easy to control, however, it gives a low radical yield and there is a problem of degradation of PET. Chemical methods are more advantageous as regards degradation of the main polymer. The grafting of monomer mixture onto PET fibres generally results in a synergistic effect. The monomer that cannot be grafted onto PET fibres alone at higher graft yields can be introduced into the PET structure to a significant extent using a comonomer [6-8].

This paper reports the grafting of acrylic acid/methyl methacrylate (AA-MMA) mixture onto PET fibres by the use of benzoyl peroxide (Bz_2O_2).

EXPERIMENTAL

Material

The MMA and AA used in this work were supplied by BDH Co. of England. PET Fibres (stretch ratio 2, 30 filaments, 110 dTex) were obtained from SASA Co., and Bz_2O_2 was obtained from Merck Chemical Co., Darmstadt, Germany. Sodium hydroxide, calcium chloride and the solvents (methanol, chloroform, acetone and benzene) were all of analytical grade and also supplied by Merck Chemical Co..

Approach

The experiments were carried out using multifilament PET fibres (30 filaments). The samples were prepared as small hank ($03 \pm 0.1g$) soxhlet-extracted for 6 h with acetone, and dried at ambient temperature.

Benzoyl peroxide (Bz_2O_2) was recrystallized twice from the methanol-chloroform mixture and dried in vacuum. Acrylic acid (AA) was vacuum-distilled over a column filled with copper wires at $30^\circ C$. Methyl-methacrylate (MMA) was washed three times with 5% NaOH, dried over $CaCl_2$, and finally distilled in vacuum at $46^\circ C$. AA and MMA, freshly distilled throughout the study, were kept in the dark.

The effects of various experimental conditions such as initiator and monomer concentrations, temperature,

and monomer mixture ratio were investigated.

A PET fibre sample was placed in a 100 mL 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 distilled water and then the mixture was immediately placed into a water bath at the polymerization temperature. After the desired polymerization time, the fibre sample was taken out of the tube and washed with water and soxhlet extracted with benzene for 8 h. Finally, the sample was dried until it maintained a constant weight [3,9,10].

Percent graft yield was calculated from the increase in the weight of the original

PET after grafting:

$$\text{graft yield (\%)} = \left[\frac{(w_2 - w_1)}{w_1} \right] \times 100 \quad (1)$$

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

To determine the moisture regain of the fibres, the fibres with various percents of graft production were placed in sulphuric acid of 65% with density of 1.275 g/mL for 24 h. Then the fibres dried in $100^\circ C$, and finally they were placed in vacuum desiccator and over P_2O_5 one hour and weighted. Then the percent of moisture regain was calculated by the following equation :

$$\text{Moisture regain (\%)} = \left[\frac{(M_n - M_0)}{M_0} \right] \times 100 \quad (2)$$

Here M_0 stands for the weight of dry fibres and \bar{M}_n for the weight of fibres in wet environment.

The fibre diameter was measured by electronic microscope at a magnification of 1000x from at least five different regions of each sample.

Dyeability of fibres was investigated by the use of dispersion dye including a pyridine structure (Figure 1).

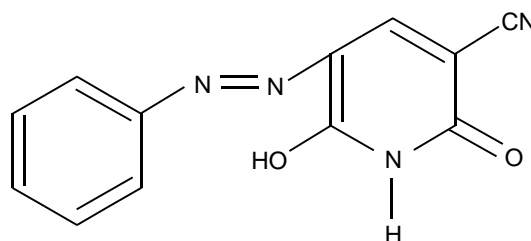


Figure 1. The dye molecular structure.

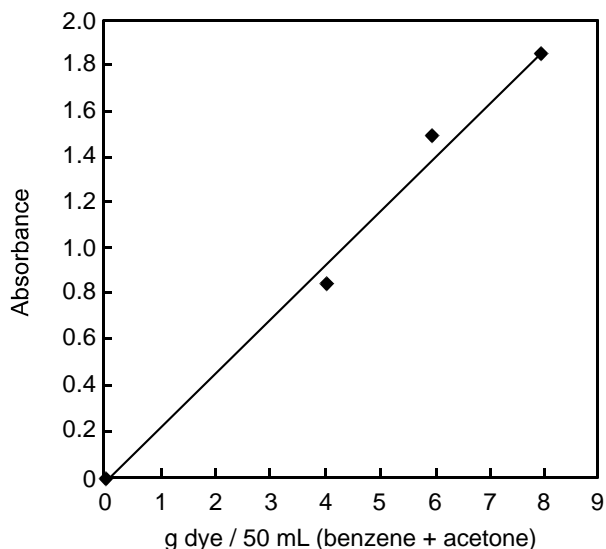


Figure 2. Calibration curve for disperse dye.

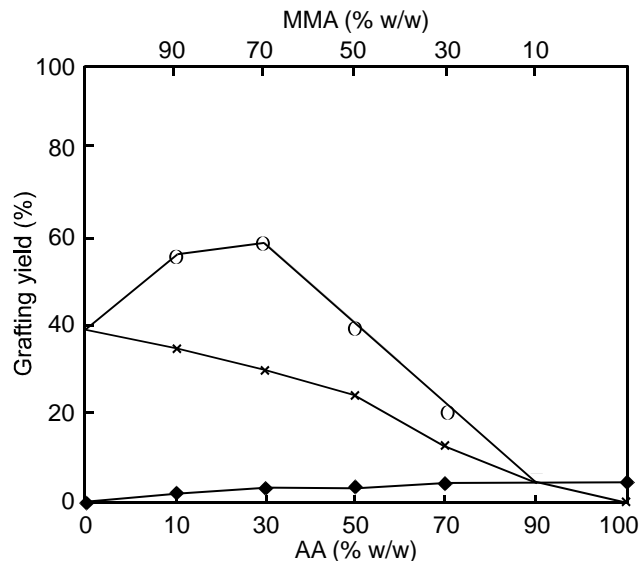
To do this, 8×10^{-4} g of dye was dissolved in 50 mL of a mixture of acetone and benzene (65% vol. acetone), and a calibration curve for concentration of dye was drawn by the use of UV-visible spectrometer in λ_{\max} (413 nm) (Figure 2). The amount of 0.1 g of fibres with various percents of graft products was placed in laboratory tubes, and then 8×10^{-4} g of dye, 3×10^{-4} g of biphenyl as a carrier and 50 mL of distilled water were added to the tubes. The tubes were placed in a water bath in 85°C for 1 h. After that the fibres were washed with 50 mL of solvent and the dye was extracted. Finally the amount of dye was measured by UV-visible spectrometer in λ_{\max} .

Apparatus

The samples were characterized by thermogravimetric analysis (TGA) (Linseis L81) in He atmosphere at the flow rate of 200 mL/min., between 25°C and 800°C and were uniformly heated at a $10^\circ\text{C}/\text{min.}$ heating rate, by Fourier Transformation Infrared (FTIR) (Perkin-Elmer model 1710 spectrophotometer), and the fibre diameters were measured with a Kyowa Microlux-11 microscope at a magnification of 1000x.

RESULTS AND DISCUSSION

Our results showed that if acrylic acid (AA) is used as a monomer, the maximum graft production is 5%, and



(◆)AA, (*) MMA, and (○) AA-MMA .

Figure 3. The grafting yields of AA, MMA, and AA-MMA. Mixture concentration of AA-MMA mixture is 0.1 mol/L, time, 2 h, temperature, 85°C , $[\text{Bz}_2\text{O}_2] = 4.0 \times 10^{-3}$ mol/L.

for methyl methacrylate (MMA) is 39% while the mixture of these two monomers in 70% of MMA by weight, has maximum yield (60%) (Figure 3). This is because the activity of MMA is higher than that of AA and the probability of grafting MMA monomer onto PET structure is higher than that of AA. Besides, the

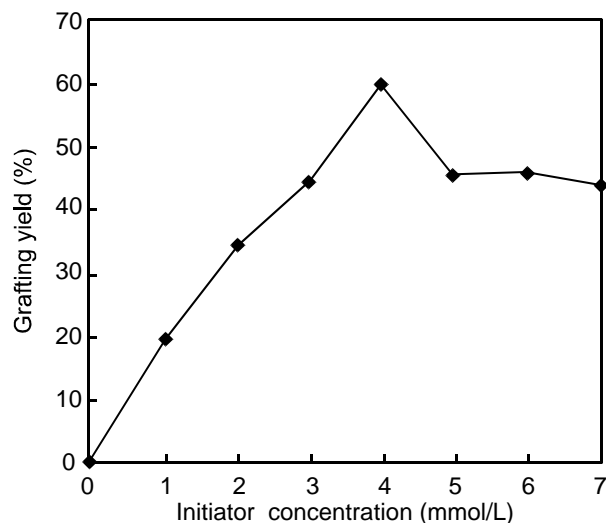


Figure 4. Effect of Bz_2O_2 concentration on the grafting yield. The concentration of 30% by weight AA containing AA-MMA: 0.1 mol/L, time: 2 h, and temperature: 85°C .

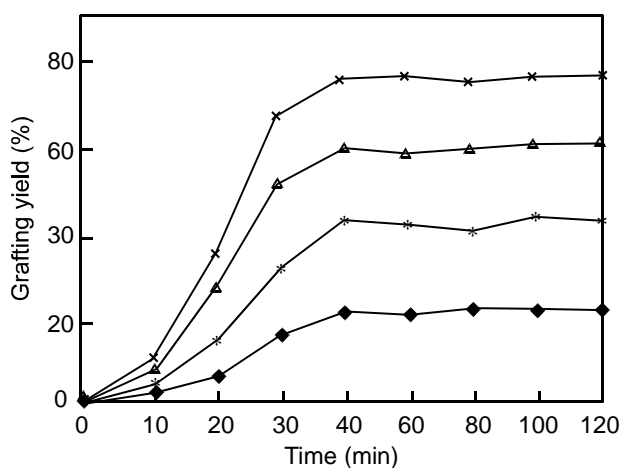
solvent of AA is water, and in aqueous environment, the quantity of AA homopolymer is greater than that of MMA generally speaking, the monomers with greater side chain have more activity.

By increasing the concentration of the initiator from 0.001M to 0.004M, and fixing the other variables such as temperature, time of reaction, concentration and percent of the mixture of monomers, grafting yield increased at first and then decreased (Figure 4). Since the number of radicals increased as a result of increasing the concentration of the initiator, the number of active sites in PET chain became greater, and the copolymerization and homopolymerization reactions increased as well. Also the extra increasing of Bz_2O_2 concentration causes the rate of terminal reactions to increase.

When the temperature was increased, the grafting yields and rates of reaction increased. In a temperature higher than glass transition temperature (T_g) ($70^\circ C$) of PET, the PET molecules went afar from each other and were inflated. So, the flexibility of the PET chain increased and made the grafting yield becoming greater. In addition, the diffusion to PET and the rate of dissociation of the initiator increased.

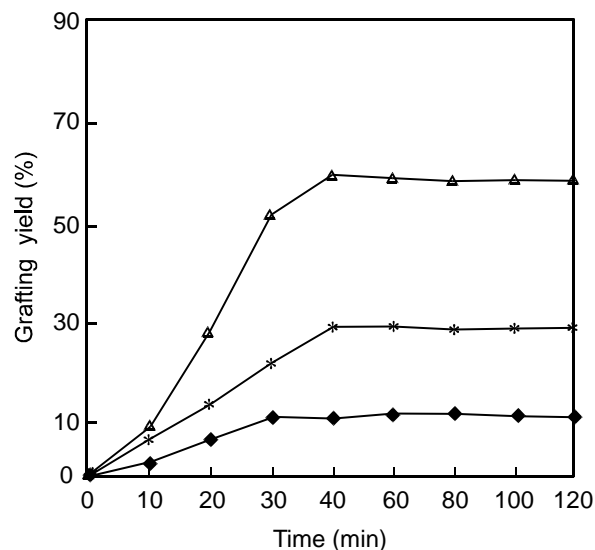
The most suitable time for copolymerization reaction was 40 min. After this time, the viscosity of environment increased because of homopolymerization reaction in system, and this made an inhibition of diffusion to PET chain (Figure 5).

The polymerization reaction was carried out by



$65^\circ C$ (\blacklozenge), $75^\circ C$ (*), $85^\circ C$ (\triangle), and $90^\circ C$ (x).

Figure 5. Effect of temperature and time on the grafting yield. Concentration of 30% AA containing AA-MMA mixture: 0.1 mol/L, $[Bz_2O_2]$: 4.0×10^{-3} mol/L.



0.05M (\blacklozenge), 0.075M (*), and 0.1 M (\triangle).

Figure 6. Effect of monomer mixture concentration on the grafting yield. Concentration of AA in AA-MMA mixture, 30%, $[Bz_2O_2]$: 4.0×10^{-3} mol/L, time: 2 h, and temperature: $85^\circ C$.

various concentrations of the monomer. Maximum yield of grafting was obtained at 0.1M of the monomer (Figure 6).

By increasing the yield of grafting, the fibres gained much more moisture, and in 58.9% of graft production, it reached 1.15%. This property of uncopolymerized PET fibres was about 0.4%. Because of the existence of the polar group of COOH in AA structure grafted to PET chain, the ability of absorption of water increased (Table 1).

When the yield of graft production was increased, the diameter of fibres changed from 2.56 (uncopolymerized fibres) to $3.096 \text{ mm} \times 10^{-2}$ (grafted production with 58.9%) (Table 2).

Table 1. The variation of moisture regain with grafting percent.

Grafting yield (%)	Moisture (%)
0.0	0.4
5.0	0.46
11.6	0.50
40.7	0.65
58.9	1.15
66.9	1.17
75.0	1.20

Table 2. The variation of diameter of PET fibres with grafting yield percent.

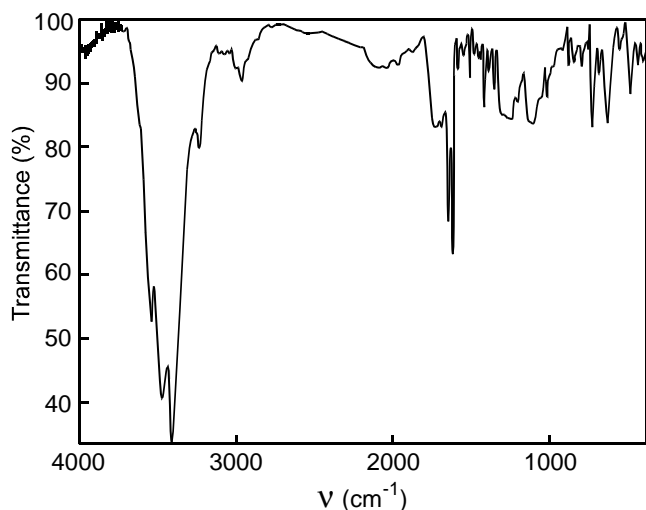
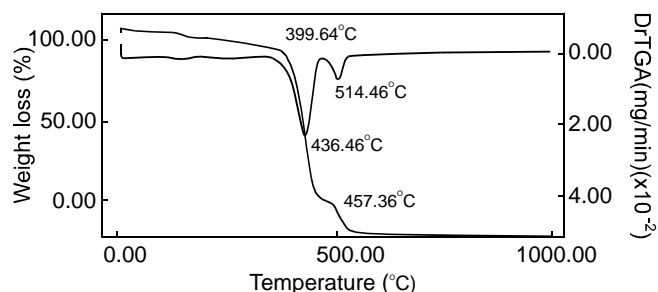
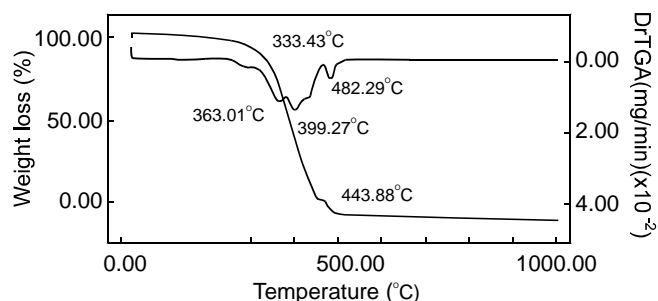
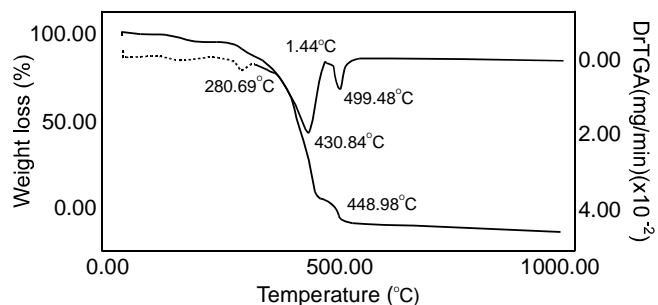
Grafting yield (%)	Diameter of fibre (mm × 10 ⁻²)
0.0	2.560
5.0	2.672
21.2	2.772
40.7	2.776
58.9	3.096
75.0	3.187

Table 3. The variation of disperse dye with percent of grafting yield.

Grafting yield (%)	Fibres/dye (g/g)
0.0	0.52
5.0	1.04
21.2	0.72
40.7	0.38
58.9	0.4

The results obtained from FTIR spectrum of PET showed a peak at 3300-3450 cm⁻¹ region related to OH group, and a peak about 1770 cm⁻¹ related to C=O and RCOO groups. These peaks showed that the AA and MMA molecules have been grafted to PET fibres.

The results obtained from DTA method of thermal stability of fibres showed that the thermal decomposition temperature for AA grafted to PET was 333.43°C.

**Figure 7.** FTIR Spectrum of AA-MMA mixture (30% AA, 70% MMA) grafted to PET fibre.**Figure 8.** Thermograms of AA grafted to PET fibres (3.7%).**Figure 9.** Thermograms of MMA grafted to PET fibers (30%).**Figure 10.** Thermograms of AA-MMA mixture (30% AA- 70% MMA) grafted to PET fibres (58.9%).

By increasing the degree of copolymerization, the flexibility of the fibres increased and thermal stability decreased. The AA molecules can form hydrogen bonding, so the thermal stability of AA is more than that of MMA. Thermal decomposition temperature of 58.9% of the mixture of monomers grafted to PET decreased to 280.69°C. So, by comparing the thermograms shown in Figures 8-10 with each other, we can conclude that by increasing the percentage of the grafted copolymerization, the thermal stability decreases. In addition, the monomers that can form hydrogen bonding produce homopolymers that can be easily dissolved in water. These monomers form fewer side bonds with PET fibres. The produced copolymers have higher ther-

mal stability. These copolymers are significant in industry.

PET Fibres do not contain chemically reactive groups. Hence, this material cannot combine with the dye cations and anions. So, the dyeability of PET fibres was investigated by the use of a disperse dye. The results showed that by increasing the percentage of grafted products, their dyeability increases to 5%-grafted product and then it decreases. So the amount of dye diffusing to PET fibres, does not react with these fibres. When the percentage of grafted products increase, the number of free sites through which the dye diffuses to the fibres decreases. So, only the physical dyeability is possible in these copolymerization products (Table 3).

CONCLUSION

- Our experimental results showed that single AA grafting with (Bz₂O₂) remained at a very low level of 5%. However, the addition of MMA as comonomer was observed to have a synergistic effect on the introduction of AA monomers into the PET fibres. The use of MMA as a comonomer is an alternative way of insertion AA into the fibre structure.
- Optimum grafting conditions were obtained by taking the initiator concentration as 4.0×10^{-3} M, monomer concentration as (AA 30% + MMA 70%) at 90°C for 40 min.

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