

Grafting of Acrylamide–Methacrylic Acid Mixture onto Poly(ethylene terephthalate) Fibers by Azobisisobutyronitrile

MELTEM ÇELİK and MEHMET SAÇAK*

Department of Chemistry, Faculty of Science, Ankara University, 06100 Tandoğan, Ankara, Turkey

SYNOPSIS

The chemical grafting of acrylamide–methacrylic acid (AAM–MAA) mixture onto poly(ethylene terephthalate) (PET) fibers using azobisisobutyronitrile as a chemical initiator was investigated. The use of MAA as a comonomer increased the amount of AAM introduced to the PET fiber up to 33.0%, while the grafting of AAM onto fibers alone gave low graft yields. This synergistic effect was found to be at its highest when an AAM–MAA mixture having 30 wt % AAM was used. The grafting increased dyeability with both acidic and basic dyes, and increased diameter and decreased the density of the fibers. The thermogravimetric analysis results revealed that the decomposition temperature of the fibers decreased with grafting. The electron micrographs showed that grafting changed the surface morphology of the fiber and a shell-like heterogeneous structure occurred at the surface at high graft yields. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Poly(ethylene terephthalate) (PET) fibers have poor chemical activity due to their high crystalline structure and lack of reactive functional groups. That is why PET fibers are modified by various methods, one of which is graft copolymerization. Vinyl monomers such as acrylamide (AAM),^{1,2} acrylic acid,^{3,4} and *N*-vinyl-2-pyrrolidone⁵ were grafted onto PET fibers by this method. Because the property acquired by the fiber is dependent upon the monomer used in grafting, monomers containing appropriate functional groups are generally chosen. The grafting of suitable vinyl monomers onto PET fibers was reported to improve their moisture regain,^{1–5} antistatic properties,⁶ nonflammability,⁷ and dyeability with acidic and basic dyes.^{6,8,9}

The grafting of monomer mixture onto PET fibers was also reported by various workers.^{9–13} Here the study purpose was to give the desired properties of these monomers, having different functional groups, simultaneously to the PET fibers. It is also

important to understand the basics of graft copolymerization reaction when a monomer mixture is used.

The grafting of monomer mixture onto PET fibers generally results in a synergistic effect. The monomer that cannot be grafted onto PET fibers alone at higher graft yields can be introduced into the PET structure to a significant extent using a comonomer.^{9–11,14} In monomer mixture grafting, one of the monomers may have a negative synergistic effect; however, the positive synergistic effect of the other generally overcomes this and the overall effect becomes positive.^{11,14} These synergistic effects are not selective to the grafting method and are observed in both chemical and radiation initiated grafting studies.¹⁰

This article reports the grafting of acrylamide–methacrylic acid (AAM–MAA) mixture onto PET fibers by the help of azobisisobutyronitrile (AIBN). The effects of various experimental conditions such as initiator and monomer concentrations, temperature, and monomer mixture ratio were also investigated. The grafted fibers were characterized by scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and infrared (IR) spectroscopy. The changes of dyeability, density, and diameters of grafted fibers were also investigated.

* To whom correspondence should be addressed.

EXPERIMENTAL

Materials

The experiments were carried out using multifilament PET fibers (30 filaments, 110 dTex) obtained from SASA Co. (Adana). The samples in small bundles (0.15 ± 0.01 g) were Soxhlet extracted with acetone for 8 h and dried at 50°C.

MAA (Merck) was saturated with NaCl, kept overnight, dried over CaCl₂, and vacuum distilled at 40°C using a copper wire filled column. Other monomer AAM (BDH) was recrystallized from acetone. AIBN (BDH) was recrystallized from methanol twice and dried in a vacuum desiccator over P₂O₅.

The acidic and basic dyes were chrome yellow FR (Kentaş Co.) and methylene blue (Merck), respectively. Other chemicals such as dimethylformamide and pyridine were chemically pure grade and used without further purification.

Graft Copolymerization

Fiber samples were placed into a 50-mL polymerization tube containing suitable amounts of AAM, MAA, or their mixture. Then, initiator dissolved in 1 mL toluene at suitable concentration was added to it and the mixture was brought up to 20 mL with deionized water and placed into a water bath (Lauda D 40 S, Germany), the temperature of which can be adjusted within $\pm 1^\circ\text{C}$. The fiber samples taken from the polymerization mixture after grafting were subjected to the following washing procedures according to the monomer used.

In AAM grafting, the fiber samples were washed with boiling water and then Soxhlet extracted with water for 8 h.

In MAA grafting, the fiber samples were washed with water (by frequently changing the water) for 24 h and then Soxhlet extracted with methanol for 8 h.

In monomer mixture grafting, the fiber samples were washed with water (by frequently changing the water) for 24 h and Soxhlet extracted with methanol and acetone for 8 and 4 h, respectively.

The fiber samples subjected to the above-mentioned washing procedures were weighed after being dried in vacuum until they reached a constant weight at 50°C; and the percentage graft yield was gravimetrically determined using the original and grafted fiber weights.

Determination of AAM Content

The AAM content in AAM-MAA grafted fibers was determined by nitrogen analysis using Kjeldahl's method. The MAA content was found by subtracting this value from the total graft yield.

Dyeing

The AAM-MAA grafted and ungrafted PET fibers were dyed with methylene blue (0.4 g/L) by taking a fiber/liquor ratio of 1/100 at 95°C for 2 h. The fiber samples taken from the dyeing bath were washed with water and the dye was extracted from the fiber by dimethylformamide at 70°C.

The dyeing process with acidic dye chrome yellow FR (1.5 g/L) was carried out for 2 h by keeping the fiber/liquor ratio at 1/100 at 95°C. The dyed fiber sample was washed with water and the dye was extracted from the fiber by 25% aqueous pyridine solution.

The optical density measurements were carried out using Shimadzu 160 A spectrophotometer at 644.5 nm for methylene blue and 404.5 nm for chrome yellow FR. The dye uptake values of the samples were calculated with the help of calibration curves previously constructed for each type of dye and weight of the fiber samples.

IR Spectra and SEM

The FTIR spectra of ungrafted and AAM-MAA grafted fiber samples were taken using a Matson 1000 FTIR spectrophotometer by pelleting with KBr. The SEM micrographs were taken with JEOL-JEM-100 CX II microscope.

TGA

The TGA were carried out in a He atmosphere with a flow rate of 200 mL/min between 25° and 650°C using a LINSEIS L81 thermal analyzer. The samples were heated at a rate of 10°C/min.

Measurement of Density and Diameter

The densities of fiber samples were determined using a density column (details were given elsewhere¹⁵). The diameters of the fiber samples were determined using a Nikon type 104 optical microscope at a magnification of $\times 600$. The diameters were measured from at least five different regions for each sample.

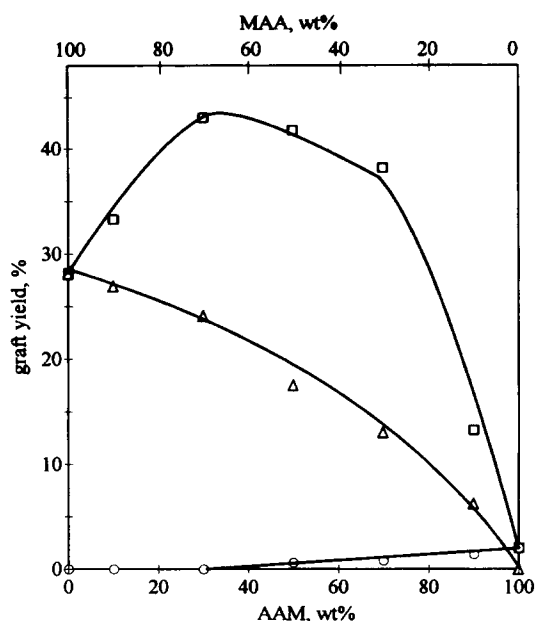


Figure 1 Graft yields of (○) AAM, (△) MAA, and (□) AAM-MAA mixture. Concentration of AAM-MAA mixture, 0.50 g/20 mL; time, 2 h; temperature, 85°C; [AIBN], 2.0×10^{-3} mol/L.

RESULTS AND DISCUSSION

Figure 1 shows the experimental results of grafting PET fibers with AAM, MAA, or their mixture using AIBN initiator. The weight ratio of the mixture was varied by keeping the total concentration of the monomer mixture at 0.50 g/20 mL. The concentrations of monomer in single monomer grafting were chosen as that in the monomer mixture.

As seen from Figure 1, in single MAA grafting the graft yield increases with MAA concentration and reaches 28.1% at a monomer concentration of 0.50 g/20 mL. On the other hand, the maximum graft yield in a single AAM grafting remains as low as 2.0%, even after a graft copolymerization time of 4 h. The increase of AAM concentration from 0.05 g/20 mL to 0.50 g/20 mL did not effect the graft yield to a significant extent.

The use of AAM and MAA monomer together in grafting caused a significant increase in graft yield. Graft yield was highly dependent on the monomer ratio and the maximum graft yield (43.0%) was obtained in a mixture containing 30 wt % AAM. The graft yield decreased when the weight percentage of AAM was chosen below 30 wt %, keeping the total monomer concentration constant at 0.50 g/20 mL. Similarly the increase of AAM concentration above 30 wt % gradually decreased the graft yield and a sharp decrease was observed in graft yield at an AAM ratio of 70 wt %.

Contribution of Monomers in Grafted Chains

In Table I the graft yields of single AAM and MAA grafting data were added to each other and compared with those when the monomers were grafted together taking the same corresponding concentrations. It is obvious that the graft yields obtained with the monomer mixture are much higher than the single monomers grafting combined. This is the case for all the AAM-MAA mixtures investigated.

As seen from Table I the single graft yields of AAM and MAA with concentration of 0.25 g/20 mL

Table I Graft Yield of Single Monomer Grafting and Contribution of Monomers in AAM-MAA Mixture Grafted PET Fibers

Initial Weight Ratio of AAM and MAA Used ^a		Graft Yield of Monomers (%)			Contribution of Monomers in Grafted Chains (%)		
AAM	MAA	Single AAM	Single MAA	Total	AAM ^b	MAA ^c	Total
0.0 (0.00)	100 (0.50)	0.0	28.1	28.1	0.0	28.1	28.1
10 (0.05)	90 (0.45)	0.0	26.9	26.9	21.3	12.1	33.3
30 (0.15)	70 (0.35)	0.0	24.1	24.1	27.6	15.4	43.0
50 (0.25)	50 (0.25)	0.6	17.5	18.1	29.8	12.0	41.8
70 (0.35)	30 (0.15)	0.8	13.0	13.8	33.0	5.2	38.2
90 (0.45)	10 (0.05)	1.4	6.2	7.6	12.5	0.7	13.2
100 (0.50)	00 (0.00)	2.0	0.0	2.0	2.0	0.0	2.0

^a Values in parentheses show the monomer concentration in g/20 mL.

^b Estimated by Kjeldahl's method.

^c Calculated by subtracting AAM graft yield from total graft yield.

onto PET fibers are 0.6 and 17.5%, respectively. When these graft yields are added the total graft yield is 18.1%. However the graft yield was found to be 41.8% when the mixture having the same monomer concentrations was used. These results clearly indicate the positive synergistic effect of the use of AAM-MAA onto the graft yield.

In fibers grafted with various AAM-MAA mixtures, the AAM content of the side chains was determined by nitrogen analysis and the MAA content was calculated by subtracting this value from the gravimetrically determined total graft yield. The graft yields thus calculated are also tabulated in Table I.

These results clearly displayed that while AAM alone cannot be grafted onto PET fibers using AIBN to a significant extent, it can be inserted into PET fibers with the use of MAA comonomer. For instance, there was no grafting with AAM alone at a concentration of 0.15 g/20 mL onto PET fibers. However, when 0.35 g/20 mL MAA is added to AAM at the same concentration, the share of AAM in the total graft yield rises to 27.6%.

There is a definite positive synergistic effect for the case of AAM and it is valid for all AAM-MAA ratios. The highest synergistic effect was observed at an AAM concentration of 70 wt %.

However, there is a negative synergistic effect for the case of MAA, and its graft yield is lower in the use of the mixture than alone. The single monomer grafting of 0.35 g/20 mL MAA onto PET fibers gives a graft yield of 24.1%. The addition of 0.15 g/20 mL AAM (which corresponds to 30 wt % AAM) decreases its share to 15.4% in total grafting.

These two opposing synergisms are the determining factors in the total effect and are positive. The positive effect for AAM dominates the negative effect for MAA and the total graft yield increases.

Effect of Initiator and Monomer Concentrations on Grafting

Figure 2 shows the effect of AIBN concentration on the grafting of monomer mixture. The graft yield rapidly increases up to 2.0×10^{-3} mol/L AIBN concentration and gradually decreases above this value. This dependence of graft yield upon the initiator concentration is a typical behavior, and is frequently observed in free radical grafting of various monomers onto PET fibers.^{2,6,15}

The increase in AIBN concentration increases the radical concentration in the medium that cleaves a hydrogen from the PET main chain and creates

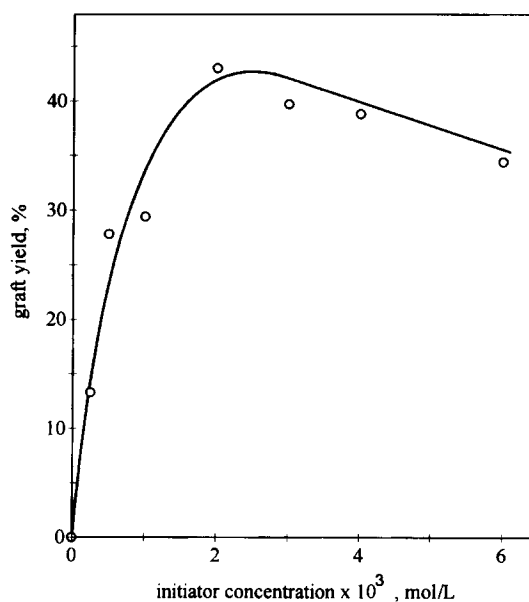


Figure 2 Effect of AIBN concentration on the grafting. Concentration of 30 wt % AAM containing AAM-MAA mixture, 0.50 g/20 mL; time, 2 h; temperature, 85°C.

active sites on the PET macromolecules. In addition the increase in initiator concentration increases the number of active homopolyAAM, homopolyMAA, and poly(AAM-co-MAA) chains in the medium. These active polymeric chains cause the formation of a higher number of active sites by chain transfer reactions with main PET chains.

However, the increase of AIBN concentration above a certain value (2.0×10^{-3} mol/L and above) makes the radical concentration excessive in the medium causing the rate of termination reactions to increase and graft yield to decrease.

The effect of monomer concentration upon the graft yield was investigated using an AIBN concentration of 2.0×10^{-3} mol/L and 30 wt % AAM containing mixture. The results are plotted in Figure 3.

The results show that the increase in monomer concentration causes an increase in the saturation graft yield and grafting rate. The time to reach the saturation graft yield was around 40–50 min for every monomer concentration investigated and no induction period was observed.

The increase in monomer concentration increases the number of monomer units diffused into the PET matrix and the outer solution. This increases the chance of active sites on the PET fibers to add AAM and MAA molecules and increase the graft yield. The saturation graft yield is around 5.5% when total monomer concentration of 0.05 g/20 mL was used.

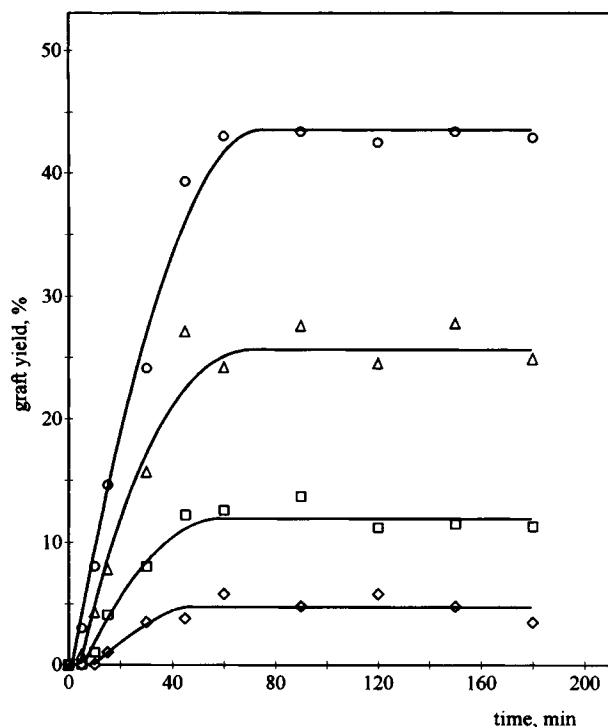


Figure 3 Effect of monomer mixture concentration on the grafting. (○) 0.50 g/20 mL; (△) 0.30 g/20 mL; (□) 0.10 g/20 mL; (◇) 0.05 g/20 mL. Concentration of AAM in AAM-MAA mixture, 30 wt %; [AIBN], 2.0×10^{-3} mol/L; time, 2 h; temperature, 85°C.

This value goes up to 43% when the total monomer concentration is increased to 0.50 g/20 mL.

Effect of Temperature and Time on Grafting

Figure 4 shows the effect of polymerization temperature upon grafting of the AAM-MAA mixture onto PET fibers between 65° and 90°C. The temperature increased the saturation graft yield and the grafting rate provided that all other variables were kept constant. At 65°C there was no grafting for 60 mins at 80°C an induction period of 5 min was observed.

The increase in temperature increases: the dissociation rate of AIBN; initiation, propagation, and termination rates; monomer mobility; and the diffusion of monomer into the fiber. All the factors, except the increase in the rate of termination reaction, increase the graft yield. Our results indicate that between 65° and 90°C the graft yield promoting effects are operative.

Another consequence of the temperature rise, especially above the glass transition temperature (80°C), is increasing in the swellability and mobility

of PET fibers. This increases the ability of PET macromolecules to give radicalic reactions.¹⁶ Indeed when one examines Figure 3 one can see that the saturation graft yield increases from 28% at 80°C to 65% at 90°C. Similarly the rate of grafting 5.5%/30 min at 75°C rapidly increases to 9.2%/30 min at 80°C and 53.1%/30 min at 90°C.

SOME PROPERTIES OF AAM-MAA MIXTURE GRAFTED PET FIBERS

Dyeability

PET fibers can only be dyed with disperse dyes because they do not contain functional groups that may interact with dye molecules. Grafting with AAM and MAA enables one to introduce $-\text{NH}_2$ and $-\text{COOH}$ groups that can interact with acidic and basic dyes, respectively. Therefore the grafting of these two monomers together improves the dyeability of the PET fiber with both acidic and basic dyes.

The acidic and basic dye uptake values of grafted fibers with 30 wt % AAM mixture at a fixed total

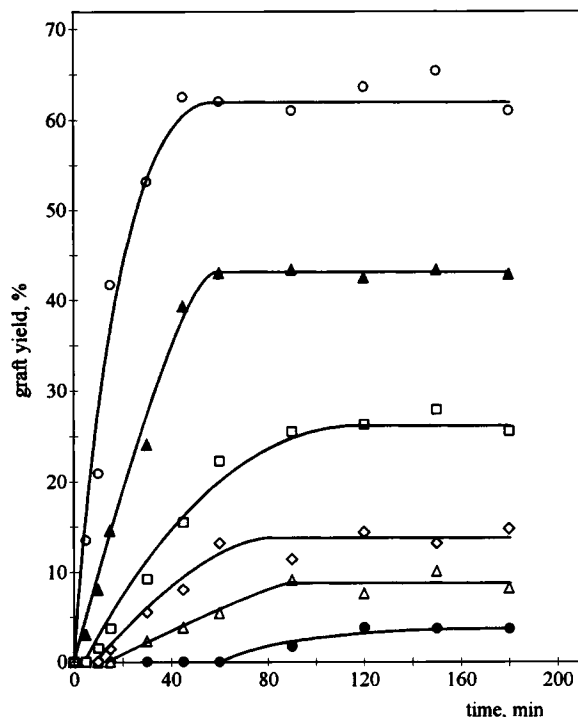


Figure 4 Effect of temperature and time on the grafting. (●) 65°C; (△) 70°C; (◇) 75°C; (□) 80°C; (▲) 85°C; (○) 90°C. Concentration of 30 wt % AAM containing AAM-MAA mixture, 0.50 g/20 mL; [AIBN], 2.0×10^{-3} mol/L.

Table II Dyeability of Fibers Grafted Using 30 wt % AAM Containing AAM-MAA Mixture

Graft Yield ^a (%)	Weight of AAM in Grafted Chains ^b (g)	Weight of MAA in Grafted Chains ^c (g)	Dye Uptake × 10 ³ (g Dye/g Fiber)	
			Basic Dye	Acidic Dye
0.0	—	—	0.05	0.01
11.4	0.0106	0.0059	0.17	0.48
22.3	0.0209	0.0117	0.55	1.04
29.4	0.0278	0.0155	0.96	1.51
43.0	0.0381	0.0212	2.65	4.78
53.1	0.0449	0.0251	3.52	8.20
63.6	0.0575	0.0321	5.33	9.89

^a Concentration of AAM-MAA mixture, 0.50 g/20 mL; time, 2 h; temperature, 85°C; [AIBN], 2.0×10^{-3} mol/L.

^b Estimated by Kjeldahl's method.

^c Calculated by subtracting AAM content from the weight differences between original and grafted fiber weights.

concentration of 0.50 g/20 mL monomer are tabulated in Table II. The same table also contains the AAM and MAA contents introduced into the fiber structure calculated with nitrogen analysis. The results indicate that the dyeability of PET fiber with both of these dyes increased with the increase in graft yield because it increases the number of necessary functional groups for dyeing in the fiber structure.

The dye uptake values of the fibers grafted with mixtures having different AAM-MAA ratios are listed in Table III. When the monomer mixture ratio is changed, the AAM and MAA contents introduced into the fiber structure become independent of the total graft yield. For instance the 43.0% grafted fiber with 30 wt % AAM containing AAM-MAA mixture has a chrome blue FR dye uptake value of 4.78×10^{-3}

g dye/g fiber. On the other hand the dye uptake value of the fiber grafted with 70 wt % AAM containing AAM-MAA mixture is much higher, 9.37×10^{-3} g dye/g fiber, due to a higher amount of AAM molecules introduced into the fiber structure. Similarly the dye uptake values of basic dyes are proportional to the MAA units introduced into the fiber structure as a result of grafting.

Grafting generally changes the supermolecular structure of the PET fibers that affects their properties such as moisture regain and dyeability. Some dye molecules can penetrate into the fiber due to its open structure and higher dyeability is obtained. However, it is obvious that the contribution of this effect into the total dye uptake will be quite small compared with that created by the functional groups as a result of grafting.

Table III Dyeability of Fibers Grafted with Varying Compositions of AAM-MAA Mixture

Initial Weight Ratio of AAM and MAA Used ^a		Graft Yield (%)	Weight of AAM in Grafted Chains ^b (g)	Weight of MAA in Grafted Chains ^c (g)	Dye Uptake × 10 ³ (g Dye/g Fiber)	
AAM	MAA				Basic Dye	Acidic Dye
00	100	28.1	—	0.0422	7.03	0.08
10	90	33.3	0.0275	0.0156	1.01	1.48
30	70	43.0	0.0381	0.0212	2.65	4.78
50	50	41.8	0.0554	0.0223	3.05	9.52
70	30	38.2	0.0527	0.0083	0.38	9.37
90	10	13.2	0.0205	0.0012	0.07	1.12
100	00	2.0	0.0030	—	0.05	0.07

^a Concentration of AAM-MAA mixture, 0.50 g/20 mL; time, 2 h; temperature, 85°C; [AIBN], 2.0×10^{-3} mol/L.

^b Estimated by Kjeldahl's method.

^c Calculated by subtracting AAM content from the weight differences between original and grafted fiber weights.

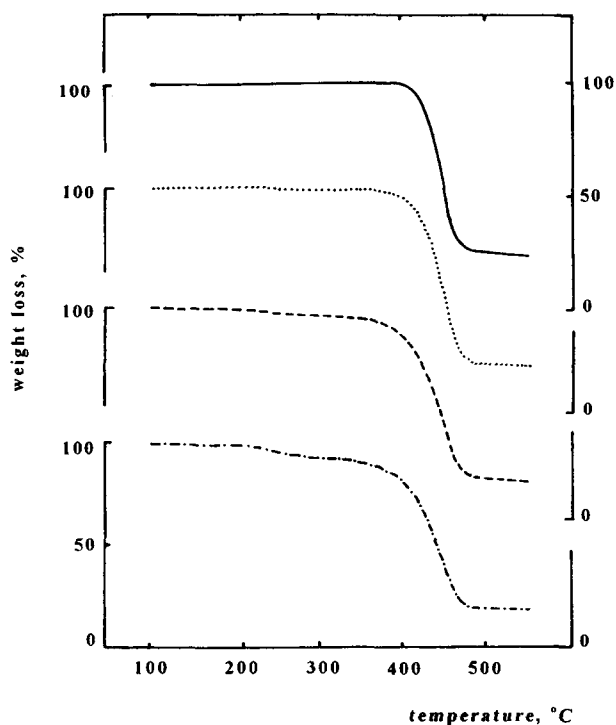


Figure 5 Thermograms of AAM-MAA mixture grafted PET fibers. (—) ungrafted; (· · ·) 11.4%; (---) 43.0%; (- · - ·) 63.6%.

TGA

The thermal behavior of PET fibers grafted with 30 wt % AAM containing AAM-MAA mixtures was investigated by comparing their primary thermo-

grams (Fig. 5). When the primary thermograms for the 100°–550°C temperature range are examined the grafting effect of the decomposition temperature of the PET fiber can be seen. The decomposition temperature of 383°C for the ungrafted PET fiber decreases to 368°C for 11.4% grafting and 333°C for 63.6% grafting. The decreases in weight observed around 200°C in the thermograms of grafted fibers is typical for poly(MAA), and is due to unzipping of polymer chains.¹⁷

IR Spectra

Figure 6 gives the FTIR spectra of ungrafted and grafted fibers with 43.0% AAM-MAA mixture. The N—H stretching band between 3200 and 3300 cm^{-1} observed in the case of single AAM grafting² and the OH stretching band at 3440 cm^{-1} in the case of single MAA grafting⁸ overlaps and forms a broad band between 3000 and 3500 cm^{-1} .

Also the ester carbonyl peak at 1680 cm^{-1} observed in the ungrafted fiber has a shoulder due to the effect of amide and acid carbonyl groups in the grafted fibers.

SEM

The effect of AAM-MAA mixture grafting upon the surface morphology of PET fibers was investigated by SEM. Figure 7(a) gives the surface micrographs of ungrafted PET fibers and the PET fibers grafted with 63.6% AAM-MAA mixture at a magnification

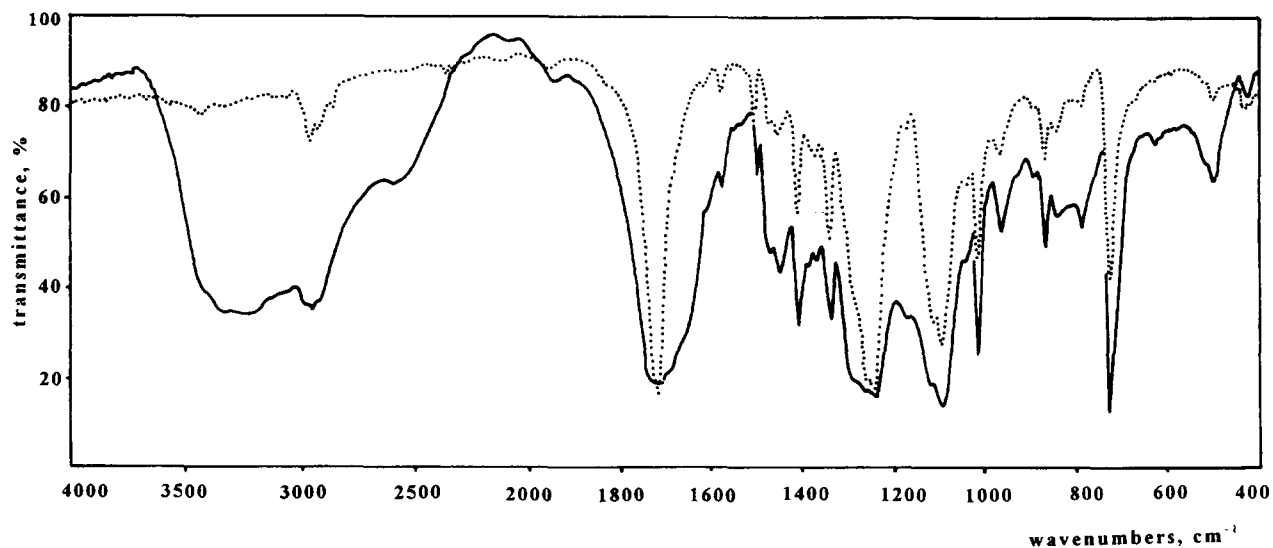


Figure 6 FTIR spectra of (· · ·) ungrafted and (—) 43.0% AAM-MAA mixture grafted PET fibers.

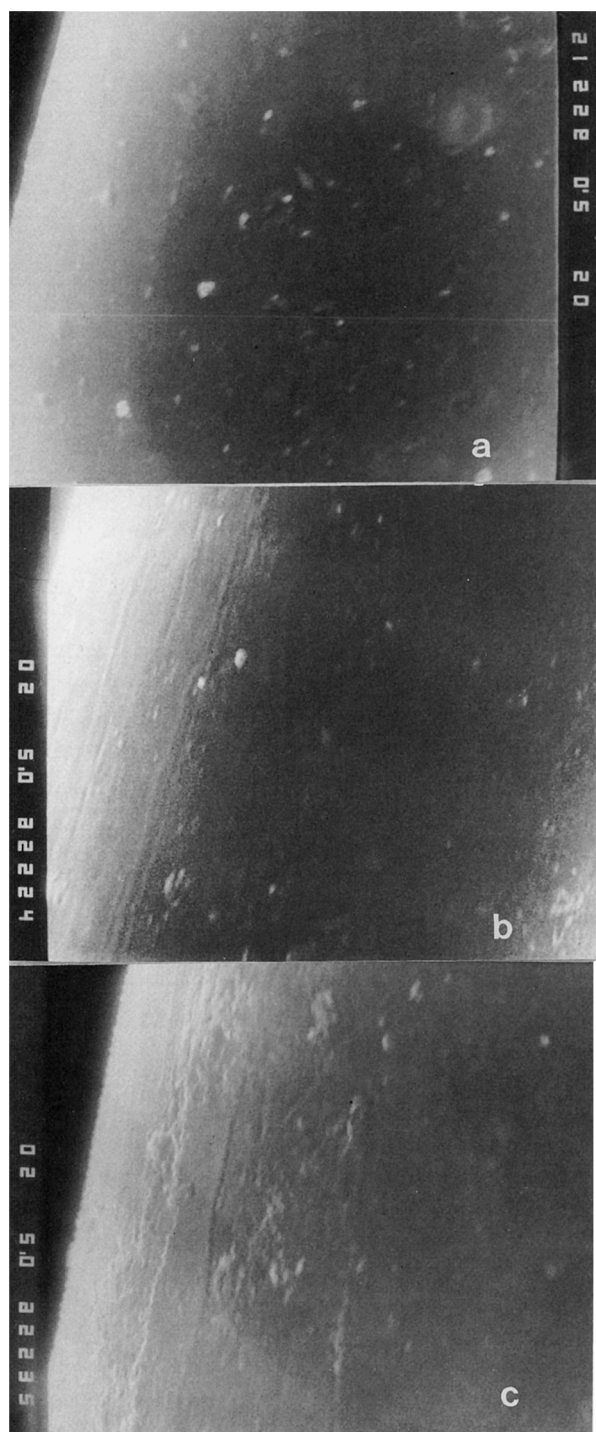


Figure 7 SEM micrographs of AAM-MAA mixture grafted PET fibers at a magnification of $\times 5000$: (a) ungrafted; (b) 22.3%; (c) 63.6%.

of $\times 5000$. The surface of ungrafted PET fiber is highly homogeneous and uniform except for some impurities. On the other hand a change in surface

morphology for 22.3% grafting was observed. Although the surface maintains its smooth and homogeneous structure, there is a tendency to form layers parallel to the fiber length.

At 63.6% grafting the surface apparently changes, the smooth and uniform structure is destroyed, and the surface acquires a layered shell-like structure [Fig. 7(c)]. This observation indicates that at higher grafting there may be chemical and/or physical adhesion on the fiber surface.

Figure 8 gives the SEM micrographs of ungrafted and 63.6% AAM-MAA grafted fibers at a magnification of $\times 500$. This magnification gives an idea about the fiber geometry. As seen from the Figure 8(a,b), the high level grafting does not affect the fiber geometry, only increasing its diameter.

The diameter and density values of AAM-MAA mixture grafted PET fibers are tabulated in Table IV. The fiber densities decreased with the increasing graft yield. A possible explanation is that the side chains are accommodated between the main PET

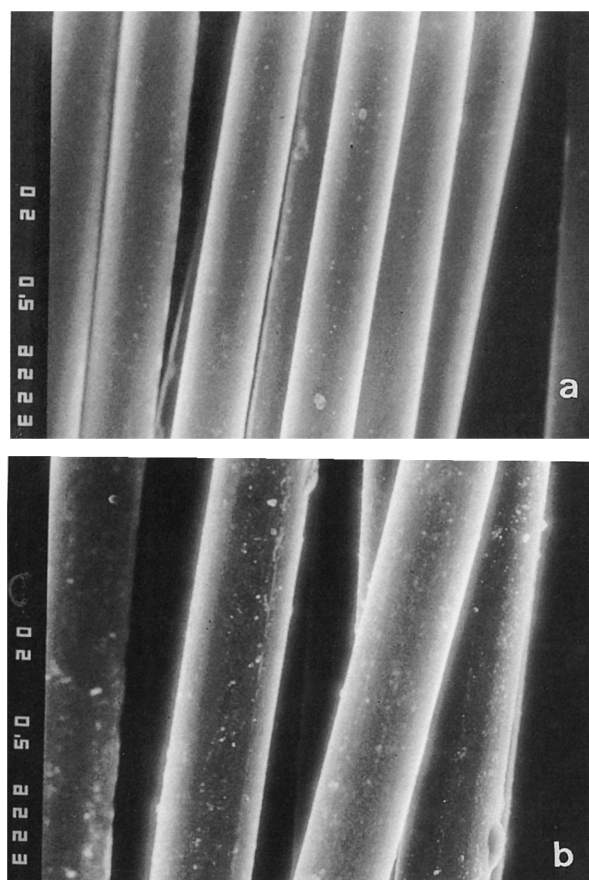


Figure 8 SEM micrographs of AAM-MAA mixture grafted PET fibers at a magnification of $\times 500$: (a) ungrafted; (b) 63.6%.

Table IV Density and Diameter of AAM-MAA Grafted PET Fibers

Graft Yield (%)	Density (g/cm ³)	Diameter (cm × 10 ⁻³)
Ungrafted	1.3748	2.587
4.8	1.3740	2.714
11.4	1.3720	—
29.4	1.3686	2.990
43.0	1.3636	3.098
53.1	1.3600	—
63.6	1.3587	3.649

chains, which results in an increase in diameter. The decrease observed in density with the increase in diameter was most probably due to the contribution of grafted chain to the weight of fiber being less than their contribution to the volume.

CONCLUSION

Our experimental results showed that single AAM grafting with AIBN remained at a very low level of 2.0%. However, the addition of MAA as comonomer was observed to have a synergistic effect on the introduction of AAM monomers into the PET fibers. The use of MAA as a comonomer is an alternative way of inserting AAM into the fiber structure.

The grafting of PET fibers with these two monomers improves the dyeability of the PET fibers with both acidic and basic dyes. The dye uptake values of grafted fibers are closely dependent upon the number of AAM and MAA units introduced into the fiber structure.

The ratio of AAM-MAA in the monomer mixture is an important factor in graft yield. The optimum AIBN concentration was found to be 2.0×10^{-3} mol/L using the optimum mixture ratio at 85°C. It was also observed that to obtain high graft yields one had to use higher temperatures. However, the increase in the graft yield decreases its decomposition temperature.

We are grateful to Ankara University Research Fund for their financial support of this work (Project Number 93-25-00-34).

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Received April 5, 1995

Accepted June 25, 1995