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# Preparation of Poly(ethylene terephthalate)-g-Methacrylamide Copolymers Initiated by Azobisisobutyronitrile: Characterization and Investigation of Some Properties

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Poly(ethylene terephthalate)-g-methacrylamide (PET-g-MAAm) copolymer was prepared by graft copolymerization in organic solvent/water mixtures by using azobisisobutyronitrile (AIBN) as an initiator. The highest graft yield was obtained in 20/80 (v/v) acetonitrile/water mixture as 30.0%. The effect of polymerization parameters such as the ratio of solvent/water mixture, concentrations of initiator and monomer, temperature and time on the graft yield was studied. The moisture regain of the PET fiber increased with grafting from 0.42% to 3.01%. Thermogravimetric data showed that the thermal stability of PET fibers decreased with grafting and 85% of total weight of 29.7% grafted fiber was lost at 500°C. On the other hand, fiber density decreased with increasing graft yield. At SEM micrographs, the layers oriented in the direction of fiber length were observed on the surface of PET fiber as a result of grafting.

**Keywords:** graft copolymer; azobisisobutyronitrile; poly(ethylene terephthalate); methacrylamide

## 1 Introduction

PET fibers are the most commonly used in textile industry as fiber and fabrics. Although the mechanical strength and chemical resistance of PET fibers are good, the disadvantages such as high crystallinity, hydrophobicity, difficulty in dyeing, high flammability and weak antistatic properties restrict their usage areas (1–3). These undesirable properties of PET fibers can be improved by preparing their graft copolymers with monomer having suitable functional groups (4–6).

Graft copolymerization is an effective technique used for modifying the properties of synthetic (7) or natural fibers (8). Grafting can be achieved by radiation (9, 10) or chemical methods (11–13).

The chemical methods have some advantages such as high radical yield and no degradation of PET chain over radiation grafting. There are numerous studies on the grafting of various monomers such as acrylic acid (14), acrylonitrile (15) and acrylamide (16) onto natural and synthetic fibers by this method. The change of physical and chemical properties of the grafted fibers was also reported in the literature (14–16).

In this study, MAAm which has a hydrophilic character was selected as monomer and grafted onto PET fibers by using AIBN which is a radical initiator. The effect of graft copolymerization parameters on the graft yield was investigated and the changes in the properties of grafted fibers such as density, diameter, moisture regain and thermal stability were reported.

## 2 Experimental

### 2.1 Materials

PET fibers (30 filament, 110 dTex) were supplied by ADVANSA-SASA Co. (Adana, Turkey). The fiber samples prepared as small bundles were first washed with warm water and then acetone for 6 h and dried in vacuum at 50°C. AIBN (Merck, Germany) was recrystallized from methanol and dried in vacuum. Methacrylamide (MAAm) (Merck, Germany) was recrystallized from benzene/methanol mixture and dried in vacuum. Other chemicals were used without further purification.

### 2.2 The Preparation of PET-g-MAAm Copolymer

0.3 g of PET fiber was taken into a 100 ml round bottom polymerization tube and a organic solvent/water mixture at certain ratio, monomer and AIBN solution in acetone at

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suitable concentration were added into the tube, respectively. Then, the polymerization tube containing the mixture was placed into a water bath kept at a constant temperature.

After the grafting, the fibers taken from the tube were washed with boiling water which is a solvent for PMAAm by frequently changing the water for 8 h. The fibers were then dried in a vacuum oven at 50°C until they had a constant weight.

The percentage graft yield was determined gravimetrically by the use of grafted and original weights of the PET fibers as follows:

$$\text{The percentage graft yield (\%)} = \left( \frac{w - w_o}{w_o} \right) \times 100$$

where  $w_o$  is the original weight of PET fiber and  $w$  is the weight of grafted fiber after the polymerization process.

### 2.3 Characterization

FTIR spectra of samples prepared as KBr pellets were obtained by using a Mattson 1000 model FTIR spectrometer.

A LINSEIS L81 model thermal analyzer was used for thermal analyses. The thermograms were recorded at a temperature range between 25°C and 650°C under nitrogen atmosphere, with a heating rate of 10°C min<sup>-1</sup>.

Surface morphologies of the fiber samples were examined by using a JEOL-JSM 5600 model SEM.

The diameters of fiber samples were measured by using a Olympus BX51 model optical microscope and the average of measurements taken from five different regions of each sample was given as the result.

Density measurements were carried out by using a density column explained previously (17).

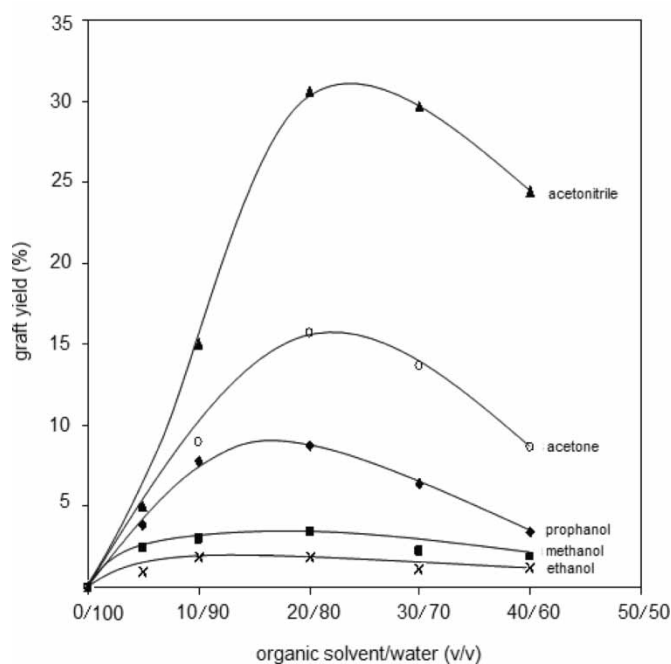
To determine the moisture regain properties of the fibers, they were kept in a chamber at a relative humidity of 65% and 20°C for 24 h. The moisture regain value was calculated from the differences in the weight of dry and conditioned fibers. This procedure was repeated three times for each sample.

## 3 Results and Discussion

### 3.1 Effects of Polymerization Medium on the Graft Yield

The type and amount of solvent used in the grafting of vinyl monomers onto PET fibers affect the graft yield (4, 17). For this reason, grafting was carried out in the presence of organic solvents such as methanol, ethanol, propanol, acetone and acetonitrile, in the beginning of the study. The graft yields obtained with various solvents and different ratios of organic solvent/water (v/v) mixtures are shown in Figure 1.

The graft yield increased up to the organic solvent/water (v/v) ratio of 20/80 for all the selected organic solvents and a decrease in the graft yield was observed for the



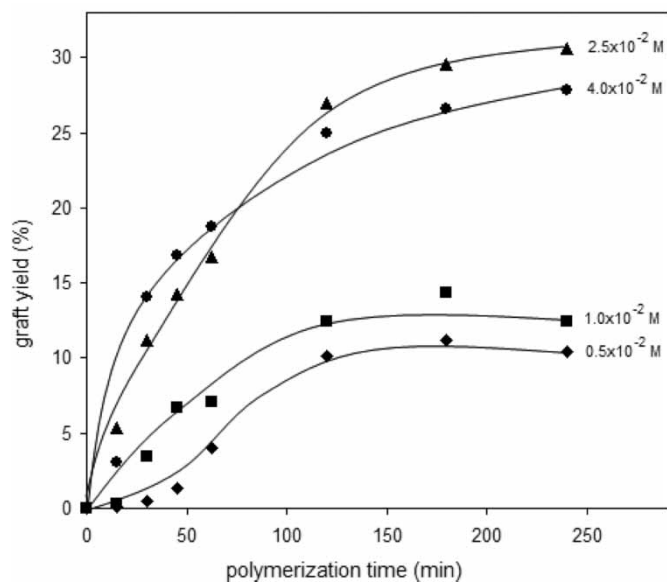
**Fig. 1.** Variation of graft yields with type of organic solvent and organic solvent/water ratio: (▲), acetonitrile; (○), acetone; (◆), propanol; (■), methanol; (x), ethanol, ([AIBN],  $2.5 \times 10^{-2}$  mol L<sup>-1</sup>; temperature, 85°C; time, 2 h; [MAAm], 0.75 mol L<sup>-1</sup>).

higher solvent amounts. Furthermore, the highest graft yield was obtained for acetonitrile. For this reason, further experiments were carried out with an acetonitrile/water ratio of 20/80 (v/v).

The interpretation of the solvent effect on the graft yield is quite complicated. For example, solvent molecules can participate in the reactions such as initiation, chain transfer or termination which occurred during polymerization. Furthermore, since the solubility of homoPMAAm formed in the graft copolymerization medium would decrease with the increasing amount of organic solvent, homoPMAAm could cover the surface of the fiber as a layer. As a result, the diffusion of monomer, initiator and other reactives into the fiber is restricted and a decrease in the graft yield could be observed.

### 3.2 Effect of AIBN Concentration on the Graft Yield

The effect of AIBN concentration on the graft yield was studied in the concentration range of  $0.5 \times 10^{-2}$  –  $4.0 \times 10^{-2}$  mol L<sup>-1</sup> AIBN (Figure 2). The graft yield increased up to the initiator concentration of  $2.5 \times 10^{-2}$  mol L<sup>-1</sup> and the highest graft yield which is 29.7% was reached at this concentration. A slight decrease in the graft yield was observed at AIBN concentrations higher than this value. The increase in the AIBN concentration increases the number of radicalic types, such as homopolymeric and copolymeric active chains. Thus, the termination reactions accelerate and the graft yield decreases (18).

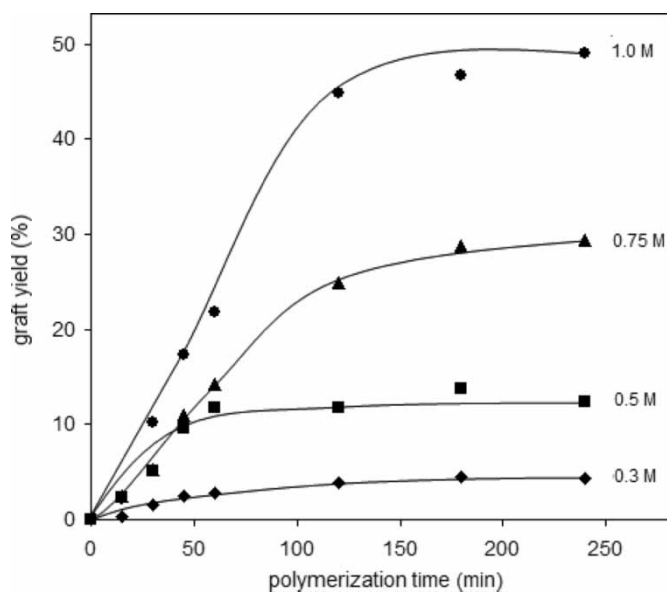


**Fig. 2.** Variation of graft yields with AIBN concentration ( $\text{mol L}^{-1}$ ): ( $\blacklozenge$ ),  $0.5 \times 10^{-2}$ ; ( $\blacksquare$ ),  $1.0 \times 10^{-2}$ ; ( $\blacktriangle$ ),  $2.5 \times 10^{-2}$ ; ( $\bullet$ ),  $4.0 \times 10^{-2}$  ( $[\text{MAAm}]$ ,  $0.75 \text{ mol L}^{-1}$ , temperature,  $85^\circ\text{C}$ ).

### 3.3 Effect of MAAM Concentration on the Graft Yield

Figure 3 shows the change in the graft yield with the MAAM concentration. As seen from the figure, the graft yields of 4.4% at the lowest MAAM concentration of  $0.3 \text{ mol L}^{-1}$  and 49.0% at the highest MAAM concentration of  $1.0 \text{ mol L}^{-1}$  were reached after 2 h.

An induction period was not observed at four different monomer concentrations studied. From the initial slopes of the curves, the increase in monomer concentration increases



**Fig. 3.** Variation of the graft yields with MAAM concentration ( $\text{mol L}^{-1}$ ): ( $\bullet$ ), 1.00; ( $\blacktriangle$ ), 0.75; ( $\blacksquare$ ), 0.50; ( $\blacklozenge$ ), 0.30 ( $[\text{AIBN}]$ ,  $2.5 \times 10^{-2} \text{ mol L}^{-1}$ ; temperature,  $85^\circ\text{C}$ ).

both the rate of grafting and the saturation graft yield. At high MAAM concentration, the number of monomer units diffused into PET fibers increases. Thus, the possibility of monomer molecules finding of PET macroradicals and active PMAAM side chains also increases. As a consequence of this effect, the graft yield increases.

### 3.4 Effects of Temperature and Time upon the Graft Yield

The change in the graft yield with temperature and polymerization time was studied by keeping the MAAM and AIBN concentrations constant, and the results were shown in Figure 4. An induction period of 60 min and 15 min was observed at the lower temperatures used, namely  $65^\circ\text{C}$  and  $75^\circ\text{C}$ , respectively.

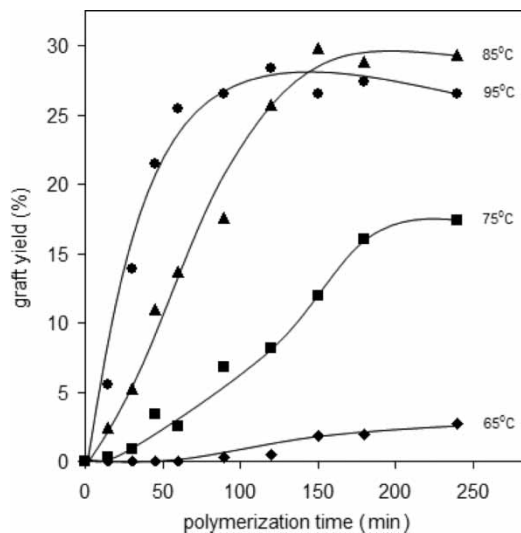
Increasing the temperature from  $65^\circ\text{C}$  to  $85^\circ\text{C}$  increased the graft yield from 1.9% to 29.7%, respectively. An increase in the temperature increases the decomposition rate of AIBN, the mobility of monomer molecules and PET ( $T_g = 80^\circ\text{C}$ ) chains, and the diffusion ability of reactants into the fiber structure. The graft yield increases depending on these effects.

The decrease in the graft yield observed at temperatures above  $85^\circ\text{C}$  (26.5% at  $95^\circ\text{C}$ ) is the result of acceleration of termination reactions (4, 19).

### 3.5 Density, Diameter and Moisture Regain

Table 1 shows the density, diameter and moisture regain values of ungrafted PET and PET-g-MAAM fiber.

The density of the PET fibers decreased after grafting. For example, the density of ungrafted PET fiber, which is  $1.3470 \text{ g cm}^{-3}$ , decreased down to  $1.3195 \text{ g cm}^{-3}$  after 29.7% grafting. The decrease observed in the density of



**Fig. 4.** Variation of the graft yields with polymerization temperature and time. ( $\blacklozenge$ ),  $65^\circ\text{C}$ ; ( $\blacksquare$ ),  $75^\circ\text{C}$ ; ( $\blacktriangle$ ),  $85^\circ\text{C}$ ; ( $\bullet$ ),  $95^\circ\text{C}$  ( $[\text{AIBN}]$ ,  $2.5 \times 10^{-2} \text{ mol L}^{-1}$ ;  $[\text{MAAm}]$ ,  $0.75 \text{ mol L}^{-1}$ ).

**Table 1.** The change of the density, diameter and moisture regain values of PET fiber with the graft yield

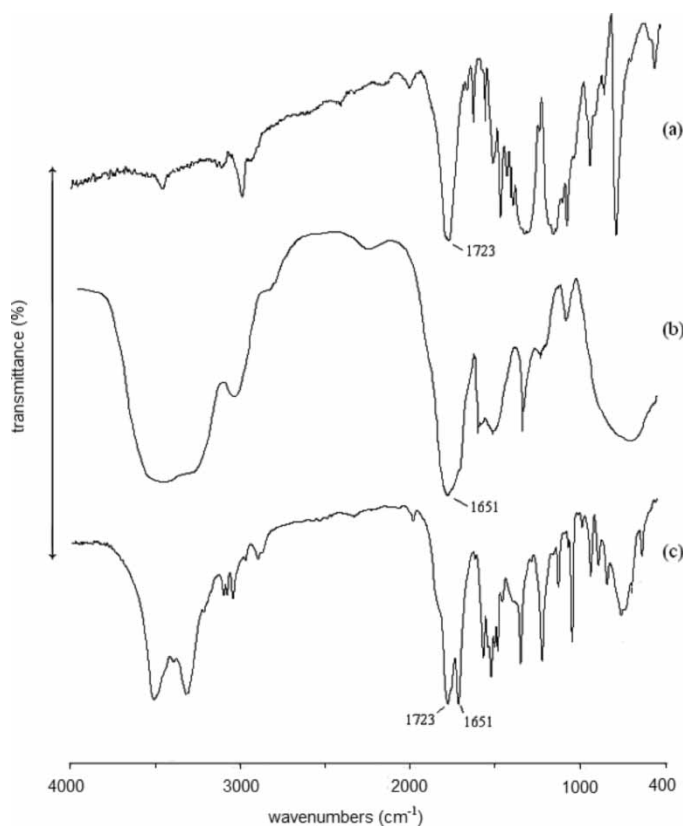
Graft yield (%)	Density (g cm <sup>-3</sup> )	Moisture regain (%)	Diameter × 10 <sup>3</sup> (cm)
0.0	1.3470	0.42	2.69
5.2	1.3440	0.58	2.76
11.0	1.3398	1.66	3.88
22.0	1.3220	1.79	4.26
29.7	1.3195	3.01	4.38

PET fiber with the increase in diameter, in spite of the increase of its weight, can be explained by that the contribution of grafted chain to fiber volume is higher than its contribution to the weight of fiber.

The hydrophilic character of MAAM due to the amide group in its structure contributed to the improvement of moisture regain property of the PET fibers. The moisture regain value of ungrafted PET fiber which is 0.42% increased up to 3.01% at 29.7% grafting (Table 1).

### 3.6 FTIR Spectra

Figure 5 shows the FTIR spectra of ungrafted PET fiber, poly(MAAM) homopolymer and PET-g-MAAM copolymer fiber containing 29.7% MAAM. The peak observed at

**Fig. 5.** FTIR spectra of (a) ungrafted PET fiber, (b) poly(MAAM) and (c) 29.7% MAAM-grafted PET fiber.

1723 cm<sup>-1</sup> for grafted PET fiber (Figure 5c) is ester carbonyl (C=O) peak which was also observed in the spectrum of ungrafted PET fiber (Figure 5a). The peak at 1651 cm<sup>-1</sup> in the spectrum of grafted PET fiber is due to the amide carbonyl group of MAAM (Figure 5b). The N-H stretching band observed between 3200 cm<sup>-1</sup> and 3500 cm<sup>-1</sup> in the spectrum of poly(MAAM) (Figure 5b) was also observed in the spectrum of grafted PET fiber (Figure 5c).

### 3.7 Thermograms

Thermograms of ungrafted and 29.7% MAAM-grafted PET fibers are shown in Figure 6. The weight loss for the grafted PET fiber was observed at two phases at the temperatures of 290°C and 330°C. The weight loss at 290°C is due to poly(MAAM), because its chains degrade between 170°C and 300°C (20). The second weight loss at 330°C can be attributed to the degradation of PET chains.

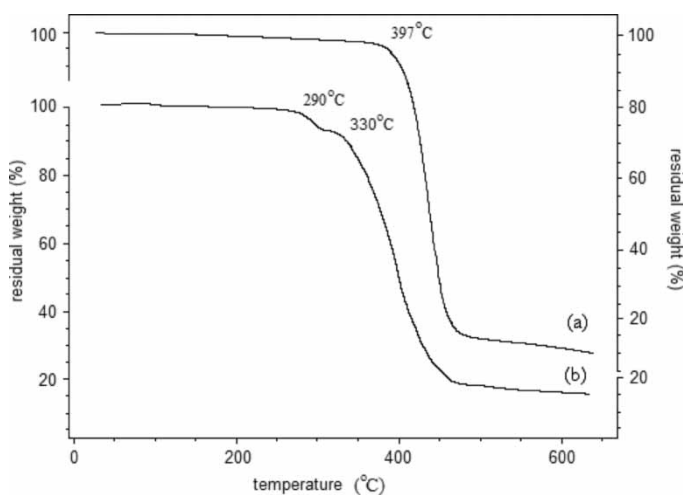
The weight loss of ungrafted PET fiber starting at 397°C reached up to the level of 89% at 500°C. The weight loss of PET-g-MAAM copolymer at 500°C is 85%.

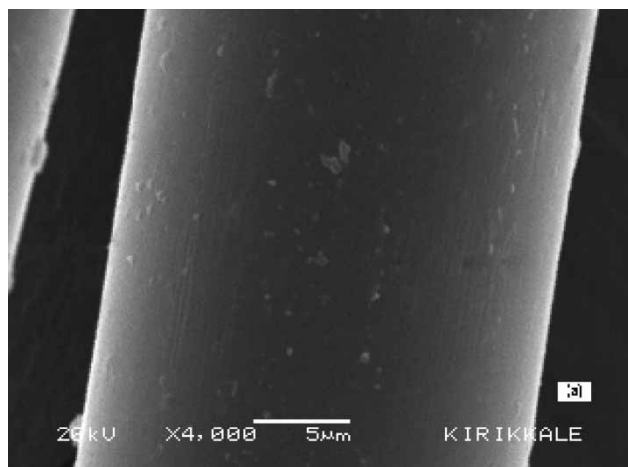
While the residue of grafted fiber at 500°C increases, decomposition temperature of PET fiber decreases from 397°C to 330°C with grafting. Therefore, it can be said that the grafting has an adverse effect on the thermal stability of PET fibers.

### 3.8 SEM Study

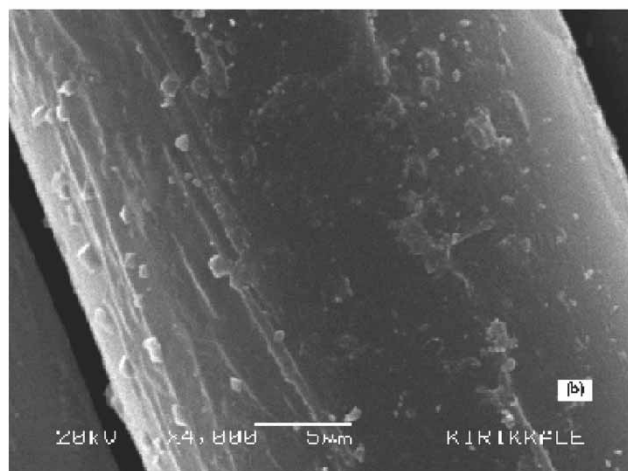
The micrographs of the ungrafted and 29.7% MAAM grafted PET fibers are given in Figure 7. As is seen from the micrographs, grafting of MAAM onto PET fiber affected the surface morphology of fiber.

The surface of ungrafted PET fiber is smooth (Figure 7a). However, the surface of PET fiber was coated with the

**Fig. 6.** Thermograms of (a) ungrafted and (b) 29.7% MAAM-grafted PET fiber.



(a)



(b)

**Fig. 7.** SEM micrographs of a) ungrafted and b) 29.7% MAAM-grafted PET fiber ( $\times 4000$  magnification).

layers arranged parallel to the length of fiber after grafting (Figure 7b).

As a result of grafting, the increase in the fiber diameter (Table 1) can be clearly seen from SEM micrographs of ungrafted and grafted fibers (Figure 7). In addition, the fiber geometry has not changed and no deformation occurred by grafting.

#### 4 Conclusions

Grafting of MAAM onto PET fiber was achieved by a chemical method using an AIBN initiator. It was observed

that the type of solvent affected the graft yield, and acetonitrile/water mixture at the ratio of 20/80 (v/v) was found to be the most suitable grafting medium. Similarly, the graft yield was also affected with the parameters such as temperature, initiator and monomer concentrations. The grafting increased moisture regain and diameters, and decreased the density of fibers. In addition, the thermal stability of the PET fibers was decreased by grafting.

#### 5 Acknowledgments

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