

## Kinetics of graft copolymerization of acrylamide and 2-hydroxyethylmethacrylate monomer mixture onto poly(ethylene terephthalate) fibers

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**Abstract**—Poly(ethylene terephthalate) (PET) fibers were grafted with acrylamide (AAM) and 2-hydroxyethylmethacrylate (HEMA) using benzoyl peroxide ( $Bz_2O_2$ ) as initiator in aqueous media. PET fibers were swelled in dichloroethane (DCE) for 2 h at 90 °C to promote the incorporation and the subsequent polymerization of AAM/HEMA onto PET fibers. Variations of graft yield with time, temperature, initiator concentration and monomer mixture ratio were investigated. The optimum initiator concentration was found to be 10 mmol/L. The maximum graft yield was obtained (prep.) 273%. The optimum temperature and polymerization time were found to be 85 °C and 120 min, respectively. The rate of grafting was found to be proportional of the 1.39 and 0.37 powers of AAM/HEMA and  $Bz_2O_2$  concentrations, respectively. The grafted PET fibers were characterized by FTIR spectroscopy and scanning electron microscopy (SEM). Further changes in properties of grafted PET fibers such as water absorption capacity and diameter were determined. The dyeability of the PET fibers increased with an increase in grafting with acidic and basic dyes.

**Key words:** Poly (Ethylene Terephthalate) Fibers, 2-Hydroxyethylmethacrylate, Acrylamide, Graft Copolymerization, Monomer Mixture

### INTRODUCTION

Polyester fiber is a manufactured fiber in which the fiber forming substance is any long chain synthetic polymer composed at least 85% by weight of an ester of a dihydric alcohol and terephthalic acid [1]. The most widely used polyester fiber is made from the linear polymer poly(ethylene terephthalate), and this polyester class is generally referred to simply as PET. PET fibers are one of the most important synthetic fibers used in the textile industry and have good resistance to weak mineral acids, even at boiling temperature, and to most strong acids at room temperature, oxidizing agents, sunlight and micro organisms. One of the distinguishing characteristics of PET is attributed to the benzene rings in the polymer chain. The aromatic character leads to chain stiffness, preventing the deformation of disordered regions, which results in weak van der Waals interaction forces between chains. Due to this, PET is difficult to crystallize.

PET fibers are hydrophobic and do not contain chemically reactive groups, showing resistance to moisture, dye anions or cations [2-4]. Certain desirable properties such as dyeability with basic, direct, and other classes of dyes, adsorption, water absorbency, and improvement in antistatic, mechanical and thermal properties can be imparted to PET fiber by grafting with different vinyl monomers.

Graft copolymerization of vinyl monomers from their binary mixtures is of special importance to obtain polymers having properties of both monomers in comparison to graft copolymers obtained by the grafting of individual monomers [5-7]. The grafting from binary mixture of monomers has the advantage of introducing grafted chains with tailor-made properties for specific applications. The mutual effect

of monomers in the reaction mixture controls the fraction of individual monomer in the grafted chains and overall yield of grafting. This synergistic effect of comonomer enhances the fraction of monomer in the graft yield. Hence, this technique of graft copolymerization provides an opportunity to prepare tailor-made grafted chains of desired properties by using suitable monomers [8-10]. There are a few studies on the grafting of multiple monomers onto PET fibers [10-13].

Among various kinds of vinyl monomer grafting agents, acrylamide (AAM) and 2-hydroxyethylmethacrylate (HEMA) are the most popular and useful monomers that improve the characteristics of PET fibers. AAM/HEMA monomer mixture grafted PET fibers could exhibit dye ability, adsorption, and water absorbency, mechanical and thermal properties suitable for textile use.

The graft copolymerization of AAM [14] and HEMA [15] individually onto PET fiber has been reported, but using a binary mixture of AAM and HEMA is not available in the literature. The present paper deals with a view of studying factors affecting the graft copolymerization of a binary mixture of AAM and HEMA onto PET fibers. The grafted fibers were characterized by Fourier transform infrared (FTIR), and scanning electron microscopy (SEM) techniques. Also, the properties of the fibers, such as the water absorption capacity, dyeability, and diameter were determined.

### EXPERIMENTAL

#### 1. Materials

The PET fibers (122 dTex, middle drawing) used in these experiments were provided by SASA Co. (Adana, Turkey). The fiber samples were Soxhlet-extracted for 6 h with acetone and dried in a vacuum oven at ambient temperature. AAM and HEMA were purified by vacuum distillation.  $Bz_2O_2$  was twice precipitated from chlo-

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reform in methanol and dried in a vacuum oven for 2 days. Other reagents were used as supplied. All reagents were Merck products.

## 2. Swelling Procedure

A temperature-controlled oil bath was used for heating. The fiber samples were dipped into DCE for 2 h at 90 °C. After treatment, solvent on the fibers was removed by blotting between a filter paper and put into the polymerization medium.

## 3. Polymerization Procedure

Polymerization was carried out in a thermostated 50 mL tubes under reflux. The mixture containing the PET fiber sample ( $0.3 \pm 0.01$  g), an appropriate amount of AAm/HEMA mixture and  $\text{Bz}_2\text{O}_2$  at required concentration in 2 mL acetone was made up to 20 mL with deionized water. The mixture was immediately placed into the water bath adjusted to the polymerization temperature. At the end of the predetermined polymerization time, the grafted fibers were taken out. Residual solvent, monomers, freed from the poly(AAm), poly(HEMA) and poly(AAm-HEMA) were removed by boiling water for 4 h and Soxhlet-extracting the PET fibers in methanol for 96 h. The grafted fibers were then vacuum-dried at 50 °C for 72 h and weighed. The graft yield (GY) was calculated from the weight increase in grafted fibers as follows:

$$\text{GY (\%)} = [(w_g - w_i)/w_i] \times 100 \quad (1)$$

Where  $w_i$  and  $w_g$  denote the weights of the original (ungrafted) and grafted PET fibers, respectively. The rate of grafting ( $R_g$ ) was calculated by using the formula as follows:

$$R_g = (w_g - w_i)/(t \times V) \quad (2)$$

where  $t$  is the polymerization time (s) and  $V$  is the volume (L) of the overall reaction medium.

## 4. Determination of the Amount of AAm in the Fibers Grafted with the AAm/HEMA Monomer Mixture

The amount of AAm inserted into the structure of fibers grafted with the AAm/HEMA mixture was determined via nitrogen analysis with LECO CHNS 932 element analyzer as follows:

$$\% \text{AAm content} = \frac{\% \text{N} \times M_{\text{AAm}}}{14} \quad (3)$$

where  $M_{\text{AAm}}$  is the molecular mass of AAm. The amount of HEMA was determined by the subtraction of the amount of AAm from the total graft.

## 5. Dyeing of the Fibers

Ungrafted and grafted fibers with various AAm/HEMA ratios were dyed with 50 ppm methylene blue solution at 85 °C for 2 h. The same procedure was repeated with congo red. The amount of dye was determined spectrophotometrically at 665 nm for methylene blue and at 497 nm for congo red by the use of calibration curves. The measurements were taken with an Ultrospec 2000 spectrophotometer.

## 6. Determination of Water Absorption Capacity

AAm/HEMA grafted PET fibers were immersed in distilled water at 20 °C for 48 h, blotted between a filter paper, and weighed. They were then vacuum dried at 50 °C for 72 h and weighed again. Water absorption capacity was determined from the weight gain of the fibers.

## 7. Measurement of the Fiber Diameter

The diameter of the grafted fibers was measured with a JOEL

Model JSM 5600 ( $\times 2,000$ ) microscope. The measurements were made in three different regions on each sample, and the average diameters were computed.

## 8. FTIR Spectrum

Fourier transform infrared (FTIR) spectra of AAm/HEMA grafted PET fibers were recorded using a Mattson model 1000 FTIR spectrophotometer with KBr discs.

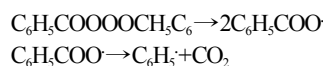
## 9. Scanning Electron Microscopy

SEM studies of the original and AAm/HEMA grafted PET fibers, coated with gold, were performed using a JOEL Model JSM 5600 microscope.

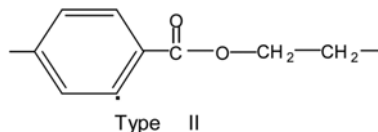
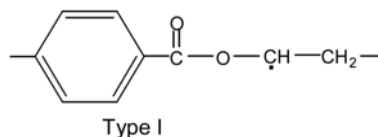
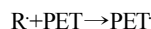
# RESULTS AND DISCUSSION

The electron spin resonance (ESR) carried out on PET revealed that two types of radicals were formed there. Their structures are given below (Type I, II) [16,17]. These radicals' sites can be created either by the direct interaction of the initiator with the fiber or by the transfer reactions between the active homopoly (AAm), or homopoly (HEMA) or copoly (AAm/HEMA) chains and PET fiber. Type II PET radicals are known to be predominant [18]. Graft copolymerization was carried out on these active radicals of PET fibers to add AAm, HEMA and AAm/HEMA mixed comonomers.

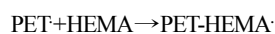
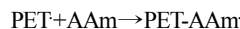
Chemical grafting involves the formation of active centers upon the PET backbone. Once these centers are formed, polymer chains start to grow on them, resulting in branches.  $(\text{C}_6\text{H}_5\text{CO})_2\text{O}_2$  undergoes thermal dissociation as:



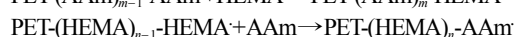
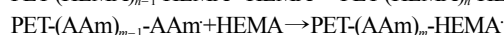
The  $\text{C}_6\text{H}_5\text{COO}\cdot$  and  $\text{C}_6\text{H}_5\cdot$  radicals formed in the polymerization medium may initiate the production of PET radicals:



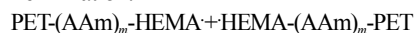
Also, the  $\text{C}_6\text{H}_5\text{COO}\cdot$  and  $\text{C}_6\text{H}_5\cdot$  and PET radicals may initiate the polymerization of AAm and HEMA:

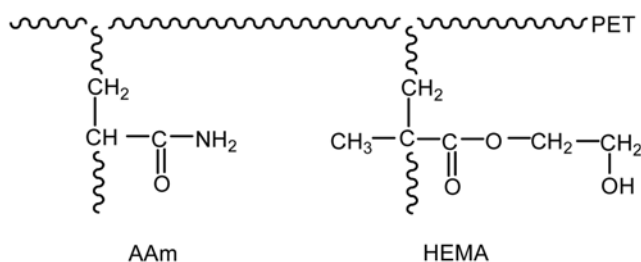


Propagation:

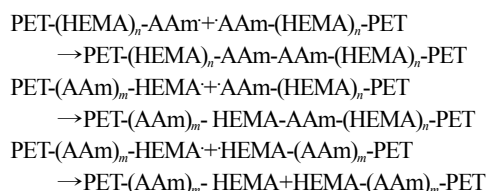


Termination:





**Scheme 1. AAm/HEMA grafted PET fibers.**

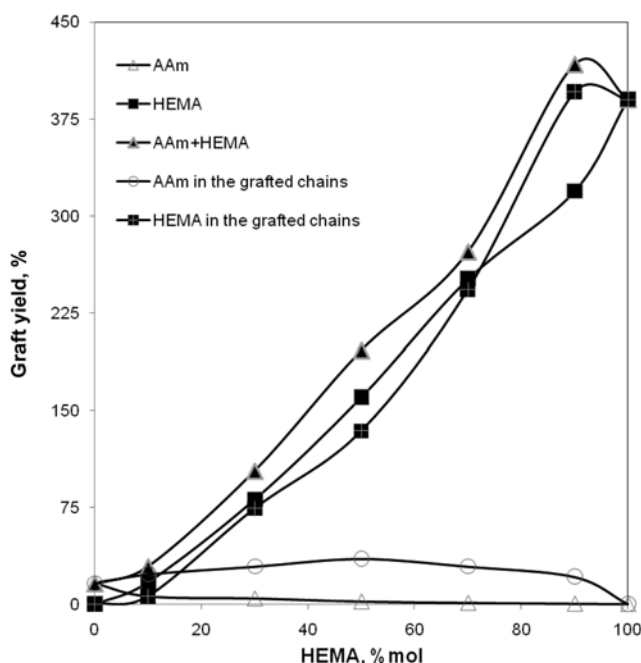


Where  $m$  and  $n$  are the values of the average sequence lengths of AAm and HEMA blocks in the grafted copolymer chains [9].

AAm/HEMA grafted PET fiber may be illustrated as in Scheme 1.

### 1. Effect of the Monomer Mixture Ratios on the Graft Yield

To investigate the effect of monomer mixture ratios on the grafting, the graft copolymerization was carried out at different mole ratios of AAm/HEMA comonomers by using  $\text{Bz}_2\text{O}_2$ . The AAm/HEMA mixture concentration was kept constant at 0.6 M. The maximum monomer concentration employed in single monomer grafting was also 0.6 M. As shown in Fig. 1 for grafting with AAm alone, the graft yield increased with the AAm concentration and reached 16% at 0.6 M. Similarly, the graft yield increased with increasing HEMA concentration in the grafting of HEMA alone, the maximum graft yield observed was 390%. The use of AAm and HEMA monomers together in grafting caused an increase in the graft yield.



**Fig. 1. Variation of graft yield with molar percentage ratio: [AAm/HEMA]=0.6 M;  $[\text{Bz}_2\text{O}_2]=8.0 \times 10^{-3}$  M;  $T=85^\circ\text{C}$ ;  $t=3$  h.**

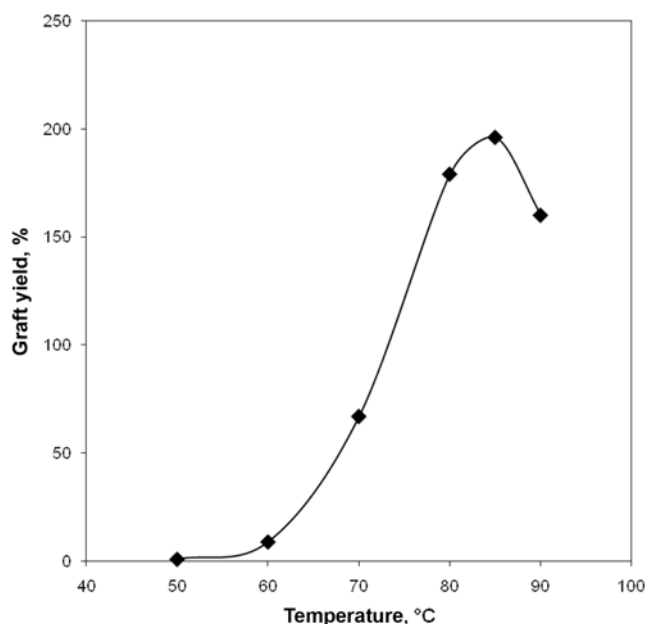
The graft yield was highly dependent on the monomer ratio, and the maximum graft yield (417%) was reached at an AAm/HEMA ratio of 10/90. Similar results were also observed in the grafting of PET fibers with itaconic acid/acrylamide [10], acrylamide/methacrylic acid [12] and itaconic acid/metacrylamide [11] monomer mixtures.

The polymer chains were grafted onto PET fibers. The side chains contained structural units coming from both AAm and HEMA. Graft copolymerization of vinyl monomers from their binary mixtures is of special importance to obtain polymers having properties of both monomers in comparison to graft copolymers obtained by the grafting of individual monomers. The graft yield of AAm on the side chains was determined by nitrogen analysis with an element analyzer. The amount of HEMA was then computed by the subtraction of the amount of AAm from the total amount grafted. Fig. 1 shows the percentages of graft yields of AAm and HEMA in the grafted chains. The graft yield of AAm increased to 35% when it was used with 0.3 M AAm.

The graft yield copolymerization of AAm in the presence of HEMA has shown a substantial increase in the graft yield in comparison to the graft yield found with individual monomers. The HEMA has shown a synergistic effect on AAm, hence affinity of AAm for grafting onto PET fibers has increased. The polymer chains grafted onto PET fibers from the mixture of AAm and HEMA were copolymeric in nature, which indicated that there was strong interaction between AAm and HEMA monomers responsible to prevent grafting of an individual monomer onto PET fibers.

### 2. Effect of Temperature

The graft polymerization of AAm/HEMA (50/50 mole) mixture onto PET fibers was studied at different temperatures ranging from 50 to  $90^\circ\text{C}$  (Fig. 2). It is clear that the graft yield increases with increasing the temperature from  $50^\circ\text{C}$  to  $85^\circ\text{C}$ ; further increase in the temperature decreases the graft yield. The PET regions are



**Fig. 2. Variation of graft yield with polymerization temperature: [AAm/HEMA]=0.6 M (50/50 mol);  $[\text{Bz}_2\text{O}_2]=8.0 \times 10^{-3}$  M;  $t=3$  h.**

more mobile, particularly at temperatures above the glass transition temperature (80 °C). Thus maximum graft yield is obtained in the region. The enhancement in grafting upon raising the polymerization temperature could be ascribed to higher rate of  $Bz_2O_2$  decomposition, and possible reaction between the growing homopolymers and copolymers chains radical with PET. It also increases the swellability of PET fiber and facilitates the diffusion of monomers into PET matrix, thus resulting in increased rates of grafting. The molecular weights of the grafted chains showed a continuous decreasing trend on increasing the temperature. Thus, lowering of grafting by raising the temperature above 85 °C could be due to the favoured chains termination reactions and increase in the formation of homopolymers and copolymers, as reflected from the grafting efficiency curve in Fig. 2. Similar results were obtained in the  $Bz_2O_2$  initiated graft polymerization of itaconic/metacrylamide mixture on PET fibers [11].

### 3. Effect of Polymerization Time

The effect of polymerization times on grafting yield was investigated by changing the polymerization time (from 15 to 150 min), keeping the monomer and initiator concentration and temperature constant. As it is reflected from Fig. 3, graft yield progressively increases with the increase in polymerization time up to 120 min, then levels off reaching a 196% saturation grafting value. The increasing trend in graft yield on increasing the polymerization time was due to the formation of new chains and the increase in size of growing chains onto the PET fibers. Levels off reaching may be attributed to the formation of a diffusion barrier, an increase in the medium viscosity due to the homopolymers, copolymers formed in the polymerization medium. Similar results were observed in the graft copolymerization of AAm [14], 4-vinyl pyridine [19] on PET fibers.

### 4. Effect of Initiator Concentration

Fig. 4 shows the effect of  $Bz_2O_2$  concentration on the rate of grafting as the  $Bz_2O_2$  concentration increased. The graft yield increases significantly by increasing the  $Bz_2O_2$  concentration up to  $10.0 \times 10^{-3}$  M,

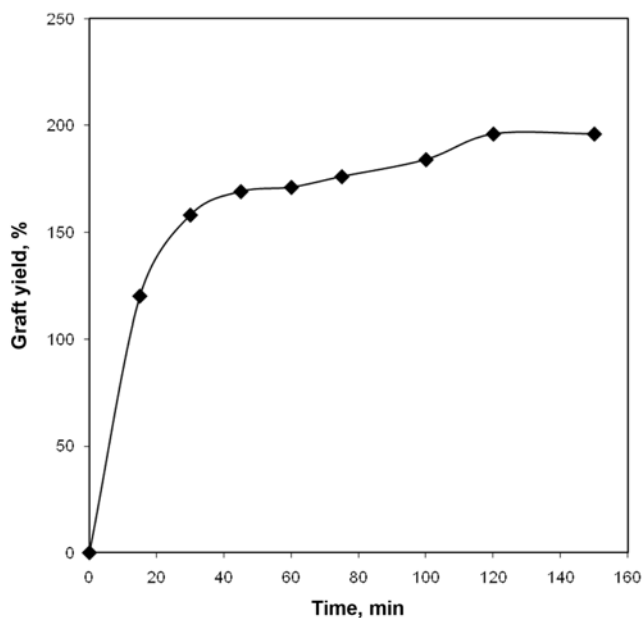


Fig. 3. Variation of graft yield with polymerization time: [AAm/HEMA]=0.6 M (50/50 mol) [ $Bz_2O_2$ ]= $8.0 \times 10^{-3}$  M; T=85 °C.

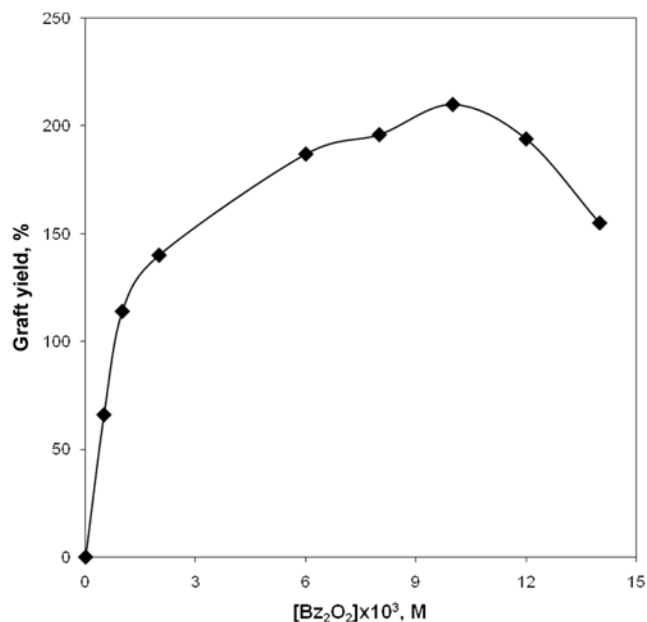


Fig. 4. Effect of initiator concentration on graft yield: [AAm/HEMA]=0.6 M (50/50 mol); T=85 °C; t=2 h.

and then falls down upon further increase in initiator concentration. This is a typical behavior reported in many other studies [10].

The enhancement of grafting by increasing the  $Bz_2O_2$  concentration to a certain limit implies that primary free radical species ( $C_6H_5COO\cdot$ ) and/or secondary free radical species ( $C_6H_5\cdot$ ) may participate essentially in the direct abstraction of hydrogen atom from the PET backbone to yield a polyester macroradical capable of initiating the grafting. Another factor that creates suitable sites for grafting

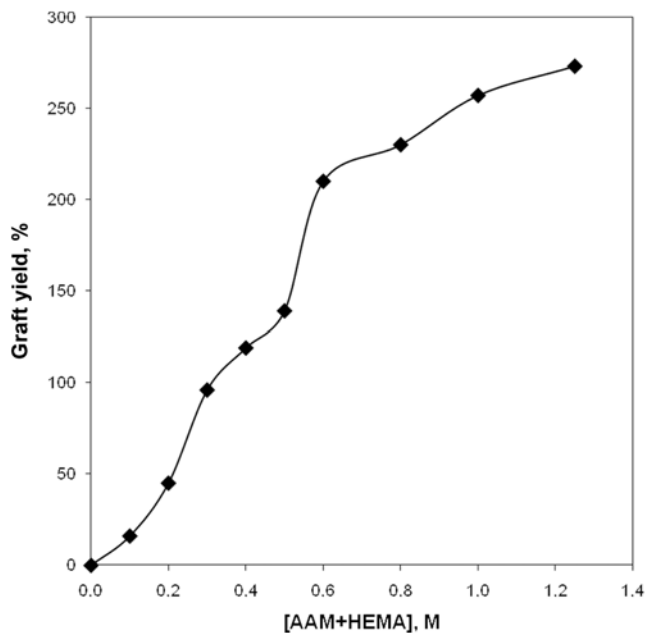


Fig. 5. Effect of monomers mixture concentration on graft yield: AAm/HEMA=50/50 mol; [ $Bz_2O_2$ ]= $10.0 \times 10^{-3}$  M; T=85 °C; t=2 h.

is chain transfer reaction between active homopolymers, copolymers chains and PET macromolecules. These chain-transfer and hydrogen abstraction reactions have an increasing effect upon the graft yield. Above this limit, the termination process with the growing homopolymers and copolymers chains, the combination of the free radical species and the termination process with the polyester macroradicals prevail over the initiation process [19].

### 5. Effect of the Monomer Mixture Concentration

Fig. 5 shows the change in the graft yield with change in the AAm/HEMA mixture concentration. The AAm/HEMA ratio remained constant at 50/50 mol. Variation of grafting yield with monomer mixture concentration was studied in the range of 0.1-1.25 M by keeping all the other conditions constant. The percentage of grafting was found to increase steadily with the monomer concentration up to 1.25 M, then PET fibers were deformed. As the monomer mixture concentration increases, the diffusion of monomer molecules into the PET structure increases, leading to a higher grafting yield (273%). In addition, the increase of graft yield could be also associated with the gel effect brought about by the solubility of polyHEMA in its own monomer. As a result, termination of the growing grafted chain radical by coupling may be hindered. Besides, the gel effect

perhaps causes swelling of PET fibers and facilitates diffusion of monomer to the growing grafted chains as well as formation of active sites on the PET backbone, thereby enhancing grafting [15].

### 6. Kinetics of Grafting

It is obvious that the mechanism of the graft copolymerization is quite complex due to the propagation, termination, homopolymerization and copolymerization reactions. However, kinetically, the rate of graft copolymerization ( $R_g$ ) with respect to monomer and initiator concentrations can be written as follows [13]:

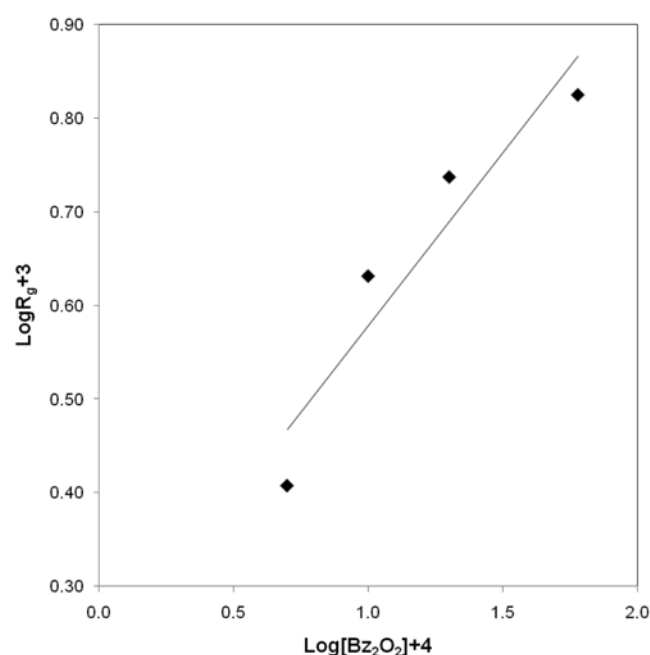
$$R_g = k [AAm/HEMA]^m [Bz_2O_2]^n \quad (4)$$

where  $m$ , and  $n$  can be experimentally determined. The experimental results showing the change of the initial rate of grafting with  $Bz_2O_2$  concentration (Table 1) in the range of  $0.5 \times 10^{-3}$  to  $6.0 \times 10^{-3}$  M (keeping the concentration of AAm/HEMA mixture constant, 0.6 M 50/50 mol) were related by plotting  $\text{Log}R_g$  vs.  $\text{Log}[Bz_2O_2]$ . Fig. 6 shows that the rate of grafting was proportional to 0.37 power of  $Bz_2O_2$  concentration. Similarly, at constant  $Bz_2O_2$  concentration the initial rates of grafting obtained at various AAm/HEMA concentrations (Table 2) were related by plotting  $\text{Log}R_g$  vs.  $\text{Log}[AAm+HEMA]$

**Table 1. Kinetic data showing the change of the initial rate of grafting with  $Bz_2O_2$  concentration**

$[Bz_2O_2] \times 10^3$ mol L <sup>-1</sup>	Grafting yield (%)	$\text{Log}[Bz_2O_2]+4$	$R_g \times 10^4$ g L <sup>-1</sup> s <sup>-1</sup>	$\text{Log}R_g+3$
0.5	66	0.7	25.59	0.41
1.0	114	1.0	42.81	0.63
2.0	140	1.3	54.61	0.74
6.0	187	1.8	64.83	0.83

[AAm/HEMA]=0.6 mol L<sup>-1</sup> (50/50 mol); T=85 °C; t=2 h

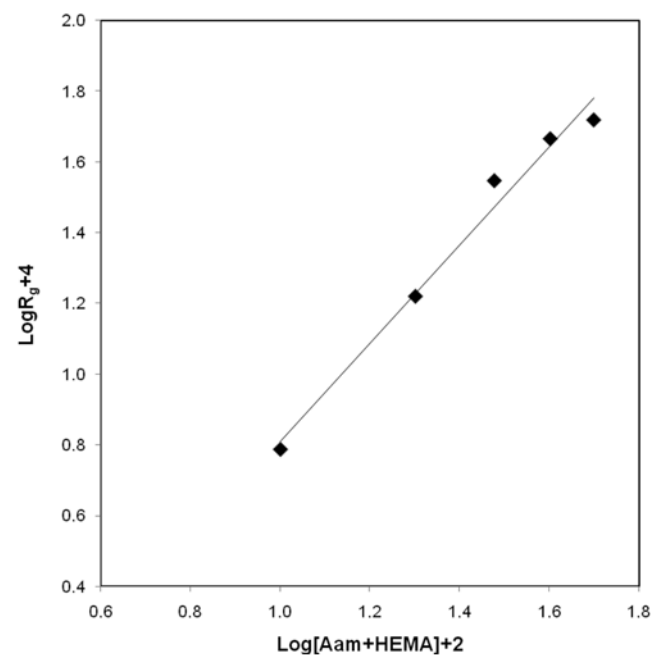


**Fig. 6. Rates of grafting ( $R_g$ ) vs.  $[Bz_2O_2]$ : [AAm/HEMA]=0.6 M (50/50 mol); T=85 °C; t=2 h.**

**Table 2. Kinetic data showing the change of the initial rate of grafting with AAm/HEMA (50/50 mol) concentration**

$[AAm/HEMA]$ mol L <sup>-1</sup>	Grafting yield (%)	$\text{Log}[AAm+HEMA]+2$	$R_g \times 10^4$ g L <sup>-1</sup> s <sup>-1</sup>	$\text{Log}R_g+4$
0.1	16	1.0	6.14	0.79
0.2	45	1.3	16.60	1.22
0.3	96	1.5	35.19	1.55
0.4	119	1.6	46.21	1.67
0.5	139	1.7	52.24	1.72

$[Bz_2O_2]=10.0 \times 10^{-3}$  mol L<sup>-1</sup>; T=85 °C; t=2 h



**Fig. 7. Rates of grafting ( $R_g$ ) vs. [AAm/HEMA]:  $[Bz_2O_2]=10.0 \times 10^{-3}$  M; T=85 °C; t=2 h.**

(Fig. 7), which shows that the rate of grafting was proportional to the 1.39 power of AAm/HEMA concentration in the range of 0.1–0.5 M AAm/HEMA concentration. Therefore, the grafting rate of AAm/HEMA and PET fibers using the  $Bz_2O_2$  initiator can be written as

$$R_g = k[A\text{Am}/\text{HEMA}]^{1.39} [Bz_2O_2]^{0.37} \quad (5)$$

There are no kinetic data concerned with the grafting of AAm/HEMA using  $Bz_2O_2$  in the literature. However, many researchers have investigated the kinetics of the grafting of various vinyl monomers onto PET fibers using different initiators. For instance, Coşkun et al. [13] reported that the grafting rate was proportional to the 0.89 and 0.47 powers of monomer and initiator concentrations, respectively, in the grafting of crotonic acid/metacrylamide onto PET fibers using a  $Bz_2O_2$  initiator. In our previous study [19], the orders with respect to monomer and initiator concentrations were determined as 1.5 and 1.0.

As seen from the given references above, the dependence of the rate of grafting on initiator and monomer concentrations varies with the types of initiator and monomer mixture grafted onto PET backbone.

### 7. Dyeability

PET fibers do not contain suitable functional groups that can interact with dye molecules. Only they can be dyed with disperse dyes. Thus dyeability of ungrafted PET fibers with acidic and basic dyes is negligible. Grafting PET fibers with AAm/HEMA monomer mixes its dyeability properties with both acidic and basic dyes because it inserts into the fibers structure of the functional groups of  $-NH_2$ - and  $CO-O-R-OH$  groups, which can interact with acidic and basic dyes. Dyeability of grafted PET fibers with acidic dye (congo red) and basic dye (methylene blue) is shown in Fig. 8. Fig. 8 shows that the grafted PET fibers with the acidic dye increased to 5.96 mg of dye/g of fiber after grafting with 103% AAm/HEMA (70/30

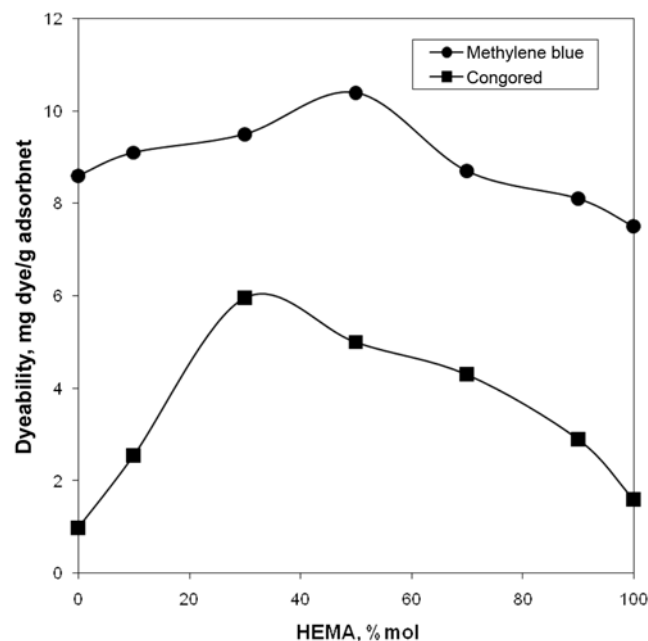


Fig. 8. Dyeability of fibers grafted with AAm/HEMA mixture at various ratios.

mol). The grafted PET fibers with the basic dye increased to 10.4 mg of dye/g of fiber after grafting with 196% AAm/HEMA (50/50 mol).

### 8. Water Absorption Capacity

It is known that PET fibers are hydrophobic and have very low chemical reactivity and water adsorption properties due to chemical structure and high crystallinity. In this study, the rise of water absorption capacity is attempted by graft polymerizing AAm/HEMA mixture onto PET fibers. The percent water absorption of AAm/HEMA grafted PET fibers was determined from the weight increase, and results obtained are shown in Fig. 9. As seen from the graph,

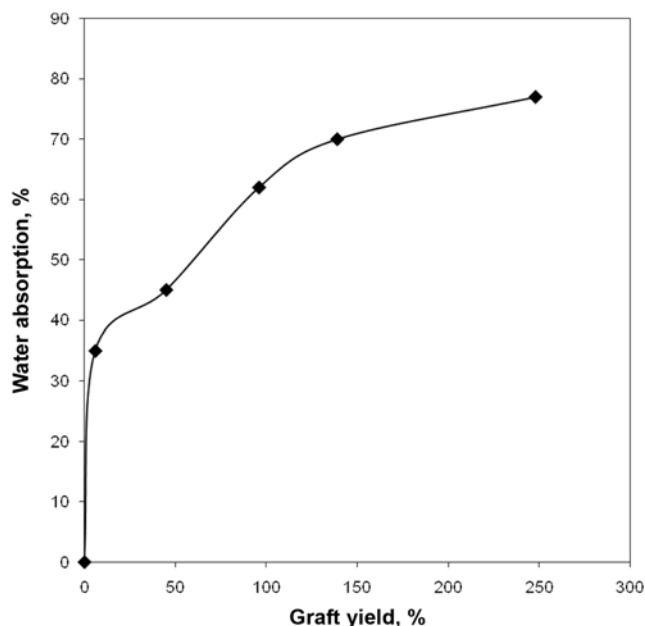


Fig. 9. Change of water absorption capacity with graft yield.

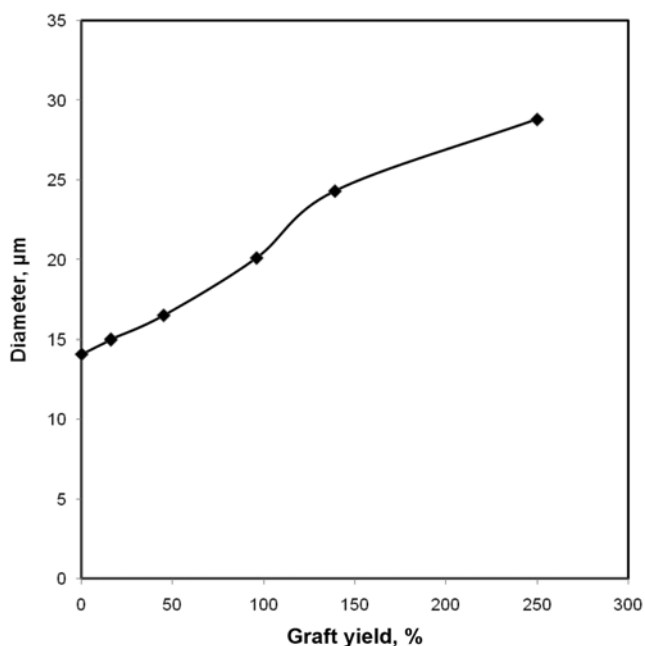


Fig. 10. Change with the graft yield of diameter of the AAm/HEMA mixture grafted PET fibers.

the percent water adsorption of AAm/HEMA grafted PET fibers is increased with increasing grafting yield and reached to a maximum value of 77% at the percent water adsorption at 250% grafting yield. The increase in the percent water absorption values was due to hydrophilic groups ( $\text{-NH}_2$  and  $\text{-OH}$ ) which enter the fibers structure as a result of AAm/HEMA grafting. The initial rate of increase slows at higher grafting values, possibly due to the dense hydrogen bonds that may form in the PET structure as a result of grafting with the AAm/HEMA monomer mixture.

### 9. Diameter

The diameter values of PET fibers grafted with different amounts of AAm/HEMA are given in Fig. 10. According to this table, grafting increases the diameter of the fibers. For instance, the diameter of  $14.1\text{ }\mu\text{m}$  of ungrafted PET fibers changes to  $28.8\text{ }\mu\text{m}$  of 250% AAm/HEMA grafted fiber. This shows that the contribution of grafting upon fiber volume is higher than upon fiber weight. Similar results were observed during the grafting of methyl methacrylate onto PET fibers [20].

### 10. FTIR Spectrum

The FTIR spectra of ungrafted and AAm/HEMA grafted PET fibers are given in Fig. 11. It is seen that the peaks of the ungrafted PET (Fig. 11(a)) can be assigned as follows:  $3429\text{ cm}^{-1}$  (OH),  $2963\text{ cm}^{-1}$  and  $2906\text{ cm}^{-1}$  (C-H asymmetric and symmetric in C-H,  $\text{CH}_2$  groups),  $1711\text{ cm}^{-1}$  (C=O),  $1410\text{ cm}^{-1}$  ( $\text{CH}_2$ ). After the grafting with AAm/HEMA, the spectrum of the AAm/HEMA grafted PET fibers (Fig. 11(b)) changed. A comparison of these spectrum shows a broad peak at  $3430\text{ cm}^{-1}$  coming from the merge of the  $\text{-OH}$  groups of HEMA. The new peak at  $1664\text{ cm}^{-1}$  wavenumber indicates the existence of carbamide ( $\text{O}=\text{C-NH}$ ) conjugated sequences in the grafted fibers [11], which was not observed in the ungrafted PET fibers, hence providing strong proof for the grafting of both monomers onto PET fibers.

### 11. Micrographs of Grafted PET Fiber

The scanning electron micrographs of ungrafted and AAm/HEMA

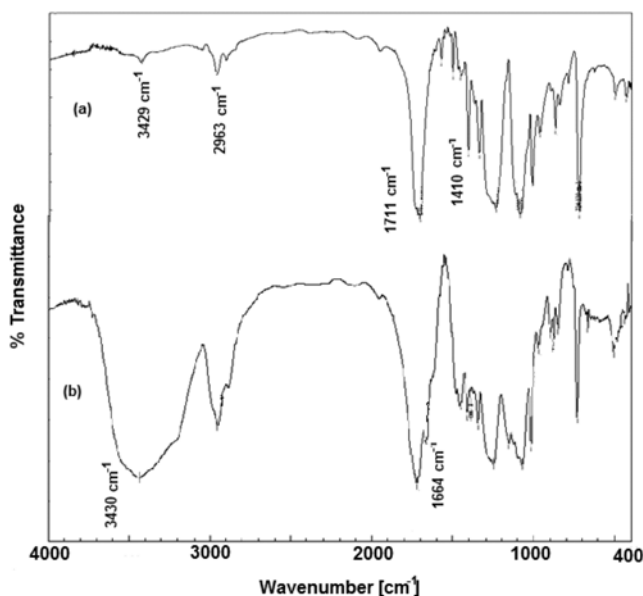
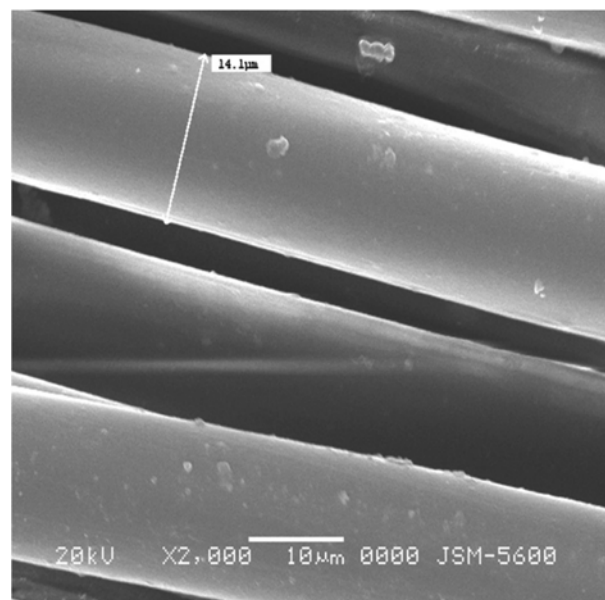
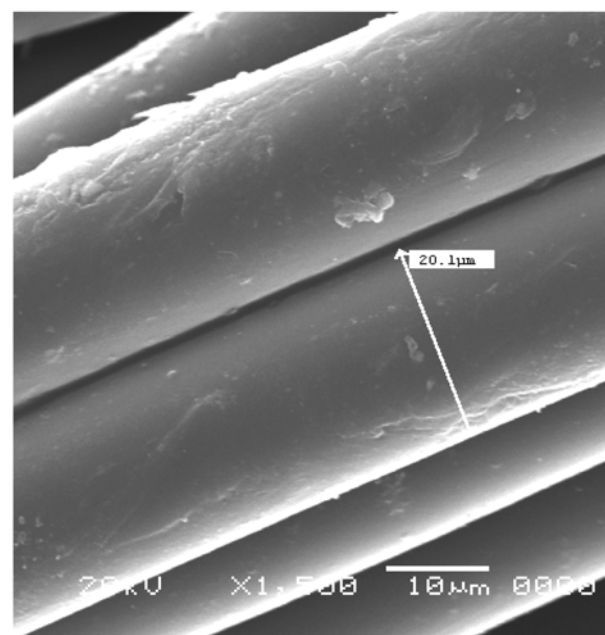


Fig. 11. FTIR spectra of: (a) ungrafted, (b) (96%) AAm/HEMA grafted PET fibers.



(a)



(b)

Fig. 12. (a) SEM micrograph of ungrafted PET fibers. (b) SEM micrograph of (96%) AAm/HEMA grafted PET fibers.

grafted (96%) PET fibers are shown in Fig. 12. The ungrafted PET fiber surface (Fig. 12(a)) exhibited a smooth and relatively homogeneous surface. At 280% graft yield, the grafted side chain seems to cover the PET fibers (Fig. 12(b)), showing another proof of grafting.

### CONCLUSIONS

Maximum percent grafting (273%, AAm/HEMA 50/50 mol) was obtained when the polymerization was carried at the following conditions:  $[\text{Bz}_2\text{O}_2]=10.0\times 10^{-3}\text{ M}$ ;  $[\text{AAm/HEMA}]=1.25\text{ M}$  (50/50 mol);  $t=120\text{ min}$  and  $T=85^\circ\text{C}$ . The presence of HEMA monomer in the reaction mixture increased the extent of graft polymerization of the

AAM onto PET fibers due to its synergistic effect. The rate of grafting was found to be proportional of the 1.38 and 0.37 powers of AAm/HEMA and Bz<sub>2</sub>O<sub>2</sub> concentrations, respectively. It was recognized that diameter and water absorption capacity increased with the increasing graft yield. The dyeability of the AAm/HEMA grafted PET fibers increased with an increase in grafting with acidic and basic dyes. The dye adsorption of the grafted fibers was very dependent on the number of AAm and HEMA groups inserted into the PET fibers' structure.

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