

4-Vinylpyridine and 2-hydroxyethylmethacrylate monomer mixture graft copolymerization onto poly(ethylene terephthalate) fibers using benzoyl peroxide

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Summary

Poly(ethylene terephthalate) (PET) fibers were grafted with 4-vinyl pyridine (4-VP) 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 4-VP/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 8×10^{-3} mol/L. The maximum graft yield was obtained 280%. The optimum temperature and polymerization time was found to be 85°C and 100 min. respectively. The rate of grafting was found to be proportional of the 1.5 and 0.3 powers of 4-VP/HEMA and Bz_2O_2 concentrations, respectively. The grafted PET fibers were characterized by thermo gravimetric analysis and scanning electron microscopy (SEM). Further changes in properties of grafted PET fibers such as water absorption capacity, intrinsic viscosity and diameter were determined. The dye ability of the PET fibers increased with an increase in grafting with diazo and basic dyes.

Introduction

PET fiber is a aromatic polyester the PET chain is nominally linear which is widely used in packaging, fiber, and engineering applications. This polymer may be synthesized by a variety of means, including the reaction of ethylene glycol with dimethyl terephthalate. 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. However the interactive forces create inflexible tight packing among macromolecules, well developed crystallinity and do not contain chemically reactive groups, showing resistance to moisture, dye anions or cations [1-3]. Certain desirable properties such as dye ability with basic, direct, and other classes of dyes, 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 [4-9]. 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 [10-15].

The graft copolymerization of 4-VP [16] and HEMA [17] individually onto PET fiber has been reported, but using a binary mixture of 4-VP 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 4-VP and HEMA on to PET fibers. The grafted fibers were characterized by Fourier transform infrared (FTIR), differential scanning calorimetry (DSC), and scanning electron microscopy (SEM) techniques. Also, the properties of the fibers, such as the water absorption capacity, dyeability, viscosity, and diameter, were determined.

Experimental

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. 4-VP and HEMA was purified by vacuum distillation. Bz_2O_2 was twice precipitated from chloroform in methanol and dried in a vacuum oven for 2 days. Other reagents were used as supplied. Sudan IV reagent was Aldrich product. All reagents were Merck products.

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.

Polymerization procedure

Polymerization was carried out in a thermostated 50 mL tubes under reflux. The mixture containing the PET fiber sample ($0.3 \pm 0.01g$), appropriate amount of 4-VP/HEMA mixture and Bz_2O_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(4-VP), poly(HEMA) and poly(4-VP-HEMA) were removed by 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:

$$G Y (\%) = [(w_g - w_i) / w_i] \times 100 \quad (1)$$

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.

Determination of the amount of 4-VP in the fibers grafted with the 4-VP/HEMA monomer mixture

The amount of 4-VP inserted into the structure of fibers grafted with the 4-VP/HEMA mixture was determined via nitrogen analysis with LECO CHNS 932 element analyzer as follows:

$$\%4\text{-VP content} = \frac{(\text{Nitrogen}\%) \times M_{4\text{-VP}}}{14} \quad (3)$$

where $M_{4\text{-VP}}$ is the molecular mass of 4-VP. The amount of HEMA was determined by the subtraction of the amount of 4-VP from the total graft.

Dyeing of the fibers

Ungrafted and grafted fibers with various 4-VP/HEMA ratios were dyed with 25 ppm methylene blue solution at 85°C for 2 h. The same procedure was repeated with sudan IV. The amount of dye was determined spectrophotometrically at 665 nm for methylene blue and at 515 nm for sudan IV by the use of calibration curves. The measurements were taken with an Ultrospec 2000 spectrophotometer.

Determination of intrinsic viscosity

Intrinsic viscosity measurements were carried out for 4-VP/HEMA grafted PET fibers in *m*-cresol, using an Ubbelohde capillary flow viscometer mounted in a water bath maintained at 35.0 ± 0.1°C.

Determination of water absorption capacity

4-VP/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.

Measurement of the fiber diameter

The diameter of the grafted fibers was measured with a JEOL Model JSM 5600 (x1500) microscope. The measurements were made in three different regions on each sample, and the average diameters were computed.

FTIR spectrum

Fourier transform infrared (FTIR) spectra of 4-VP/HEMA grafted PET fibers were recorded using a Mattson model 1000 FTIR spectrophotometer with KBr discs.

Differential scanning calorimetry

Thermal analyses were performed with Perkin Elmer Sapphire Differential Scanning Calorimeter (DSC). Sample weights ranged from 3.0 to 9.0 mg. The samples were heated from 30°C to 300°C at a heating rate of 10°C/min. The intercept points of slopes were taken as glass transition temperatures (T_g).

Scanning electron microscopy

SEM studies of the original and 4-(VP)/HEMA grafted PET fibers, coated with gold, and were performed using a JEOL Model JSM 5600 microscope.

Result and discussion

Effect of the monomer mixture ratios on the graft yield

Figure 1 shows the graft yields obtained by the grafting of PET fibers with 4-VP, HEMA, their mixtures, and their components of graft yield with Bz_2O_2 . The 4-VP/HEMA mixture concentration was kept constant at 0.5 M. The maximum monomer concentration employed in single monomer grafting was also 0.5 M. As shown in Figure 1 for grafting with 4-VP alone, the graft yield increased with the 4-VP concentration and reached 82% at 0.5 M. Similarly, the graft yield increased with increasing HEMA concentration in the grafting of HEMA alone, the maximum graft yield observed 210%. The use of 4-VP and HEMA monomers together in grafting caused a significant increase in the graft yield. The graft yield was highly dependent on the monomer ratio, and the maximum graft yield (318%) was reached at a 4-VP/HEMA ratio of 10/90. Similar results were also observed in the grafting of PET fibers with itaconic acid/acrylamide [12], acrylamide/methacrylic acid [20] and acrylic acid/ styrene [21] monomer mixtures.

The polymer chains grafted onto PET fibers. The side chains contained structural units coming from both 4-VP 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 4-VP on the side chains was determined by nitrogen analysis with element analyzer. The amount of HEMA was then computed by the subtraction of the amount of 4-VP from the total amount grafted. Figure 1 shown percentages graft yields of 4-VP and HEMA in the grafted chains. The graft yield of 4-VP increased to 151% when it was used with 0.45 M 4-VP. Similarly The graft yield of HEMA increased to 291% when it was used with 0.45 M HEMA.

The graft yield copolymerization of 4-VP 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 4-VP, hence affinity of 4-VP for grafting onto PET fibers has increased. The polymer chains grafted onto PET fibers from the mixture of 4-VP and HEMA were copolymeric in nature which has indicated that there was strong interaction between 4-VP and HEMA monomers responsible to prevent grafting of an individual monomer onto PET fibers. The high efficiency of grafting of comonomers onto PET fibers has also been attributed to initiator, which were exclusively involved in the formation of radicals at

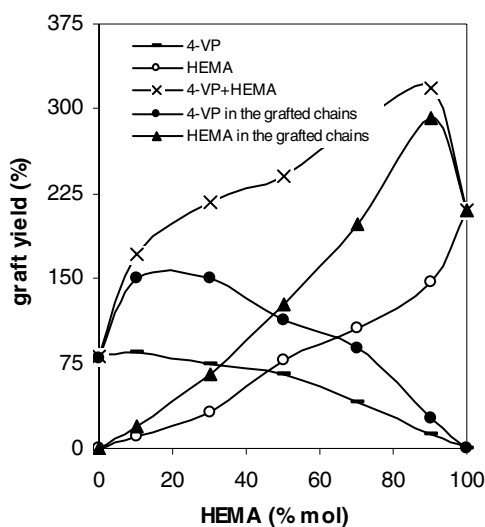


Figure 1. Variation of graft yield with molar percentage ratio: [4-VP/HEMA] = 0.5 M; [Bz₂O₂] = 8.0 × 10⁻³ M; T = 75°C; t = 2 h.

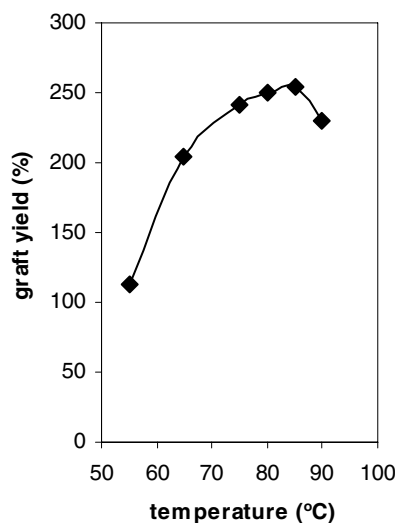


Figure 2. Variation of graft yield with polymerization time: [4-VP/HEMA] = 0.5 M (50/50 mol); [Bz₂O₂] = 8.0 × 10⁻³ M; t = 2 h.

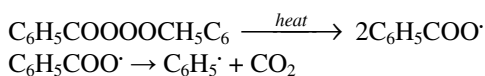
PET fibers backbone to facilitate grafting of a monomer rather than in the formation of radicals at monomers to produce ungrafted homopolymer and copolymer in the reaction mixture [11].

Effect of temperature

The effect of temperature on the graft polymerization of 4-VP/HEMA (50/50 mol) mixture onto PET fibers was studied by varying temperature between 55–90°C (Figure 2). It is clear that the graft yield increases with increasing the temperature from 55°C to 85°C; further increase in the temperature decreases the graft yield. The PET regions are 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 Bz₂O₂ decomposition, and possible reaction between the growing homopolymers and copolymers chains radical with PET. It also increases swell ability 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 Figure 2. Similar results were obtained in the Bz₂O₂ initiated graft polymerization of itaconic/acrylamide mixture on PET fibers [12].

The following mechanism was proposed [11]:

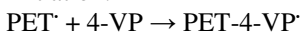
Radical formation:



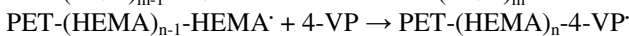
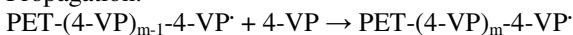
The $C_6H_5COO\cdot$ and $C_6H_5\cdot$ radicals formed in the polymerization medium may initiate the production of PET radicals:



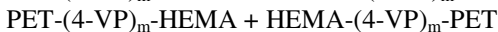
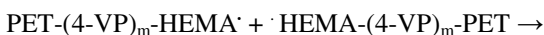
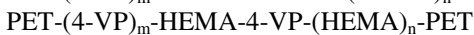
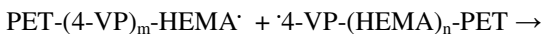
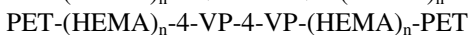
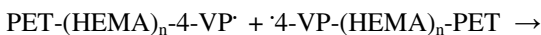
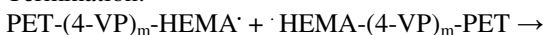
Initiation:



Propagation:



Termination:



Where m and n are the values of the average sequence lengths of 4-VP and HEMA blocks in the grafted copolymer chains.

Effect of polymerization time

Grafting of PET fibers was carried out at various polymerization times, keeping the monomer and initiator concentration and temperature constant. As it is reflected from Figure 3, graft yield progressively increases with the increase in polymerization time up to 100 min then levels off reaching a 255% 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 observed in the graft copolymerization of AAm [22, 23], n-vinyl-2-pyrrolidone [24], 4-VP [16], 2-Methyl-5-vinyl pyridine [25] on PET fibers.

Effect of initiator concentration

Figure 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 8.0×10^{-3} M, and then fall down upon further increase in initiator concentration. This is a typical behaviour reported in many other studies [16, 26].

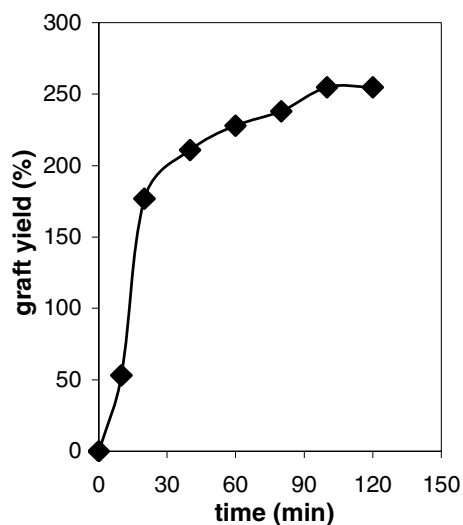


Figure 3. Variation of graft yield with polymerization time: [4-VP/HEMA]=0.5 M (50/50 mol); $[Bz_2O_2] = 8.0 \times 10^{-3}$ M; $T = 85^\circ C$.

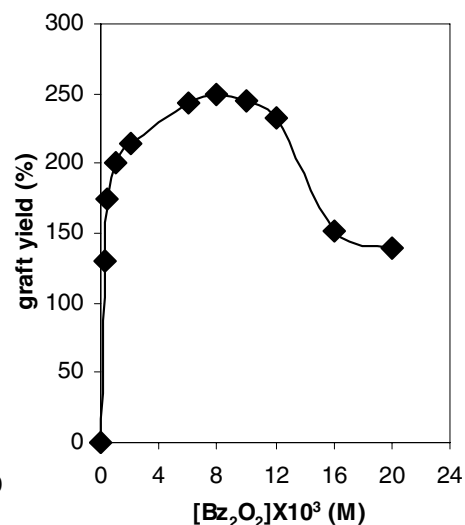


Figure 4. Effect of initiator concentration on graft yield : [4-VP/HEMA] = 0.5 M (50/50 mol); $T=85^\circ C$; $t=100$ min.

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 is chain transfer reaction between active homopolymers, copolymers chains and PET macromolecules. These chains-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 [16].

Effect of the monomer mixture concentration

Figure 5 show the change in the graft yield with change in the 4-VP/HEMA mixture concentration. The 4-VP/HEMA ratio kept constant at 50/50 mol. Variation of grafting yield with monomer mixture concentration was studied in the range of 0.1-0.6 M by keeping all the other conditions constant. The percentage of grafting was found to increase steadily with the monomer concentration up to 0.6 M then PET fibers was deformed. As the monomer mixture concentration increases, the diffusion of monomers molecules into the PET structure increases, leading to a higher grafting yield (280%). 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 and thereby enhancing grafting [17].

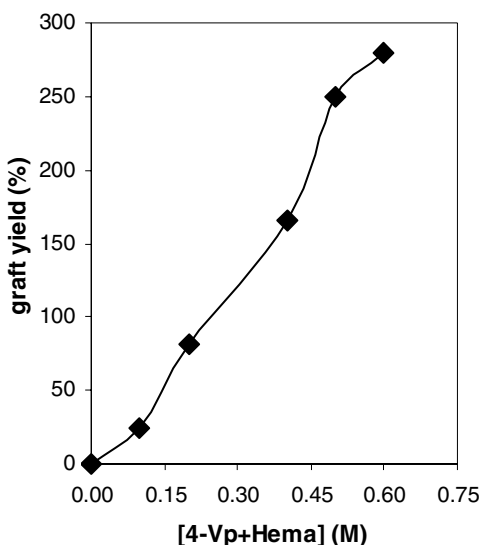


Figure 5. Effect of monomers mixture concentration on graft yield: 4-VP/HEMA= 50/50 mol; $[Bz_2O_2] = 8.0 \times 10^{-3}$ M; $T = 85^\circ C$; $t = 100$ min.

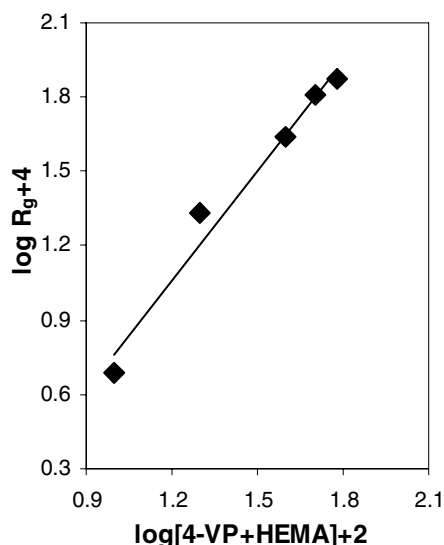


Figure 6. Rates of grafting (R_g) vs. [4-VP/HEMA]: $[Bz_2O_2] = 8.0 \times 10^{-3}$ M; $T = 85^\circ C$; $t = 100$ min.

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 [16].

$$R_g = k [4\text{-VP/HEMA}]^m [Bz_2O_2]^n \quad (4)$$

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 0.0 to 2.0×10^{-3} M (keeping the concentration of 4-VP/HEMA mixture constant, 0.5 M 50/50 mol) were related by plotting $\text{Log}R_g$ vs. $\text{Log}[Bz_2O_2]$. Figure 7 shows that the rate of grafting was proportional to 0.3 power of Bz_2O_2 concentration. Similarly, at constant Bz_2O_2 concentration the initial rates of grafting obtained at various 4-VP/HEMA concentrations (Table 2) were related by plotting $\text{Log}R_g$ vs. $\text{Log}[4\text{-VP+HEMA}]$ (Figure 6), which shows that the rate of grafting was proportional to the 1.5 power of 4-VP/HEMA concentration in the range of 0.1–0.6 M 4-VP/HEMA concentration. Therefore, the grafting rate of 4-VP/HEMA and PET fibers using the Bz_2O_2 initiator can be written as

$$R_g = k [4\text{-VP/HEMA}]^{1.5} [Bz_2O_2]^{0.3} \quad (5)$$

There are no kinetic data concerned with the grafting of 4-VP/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, Çoşkun et al. [12] reported that the grafting rate was proportional to the 0.74 and 0.65 powers of monomer and initiator concentrations, respectively, in the grafting of itaconic acid/acrylamide onto PET fibers using a Bz_2O_2 initiator. In our previous study [16], in the graft copolymerization of 4-VP onto PET fibers using Bz_2O_2

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

$[Bz_2O_2] \times 10^3$ $mol L^{-1}$	Grafting Yield (%)	$\text{Log}[Bz_2O_2]+4$	$R_g \times 10^3$ $g L^{-1} s^{-1}$	$\text{Log}R_g+3$
0.25	130	0.40	3.24	0.51
0.50	175	0.70	4.31	0.64
1.00	200	1.00	4.86	0.69
2.00	215	1.30	5.97	0.78

$[4\text{-VP/HEMA}] = 0.5 \text{ mol L}^{-1}$ (50/50 mol); $T = 85^\circ\text{C}$; $t = 100 \text{ min}$.

Table 2. Kinetic data showing the change of the initial rate of grafting with 4-VP/HEMA (50/50 mol) concentration

$[4\text{-VP/HEMA}]$ $mol L^{-1}$	Grafting Yield (%)	$\text{Log}[4\text{-VP+HEMA}]+2$	$R_g \times 10^4$ $g L^{-1} s^{-1}$	$\text{Log}R_g+4$
0.1	24	1.00	4.94	0.69
0.2	81	1.30	21.59	1.33
0.4	165	1.60	43.31	1.64
0.5	250	1.70	64.79	1.81
0.6	280	1.78	73.33	1.87

$[Bz_2O_2] = 8.0 \times 10^{-3} \text{ mol L}^{-1}$; $T = 85^\circ\text{C}$; $t = 100 \text{ min}$.

initiator, 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.

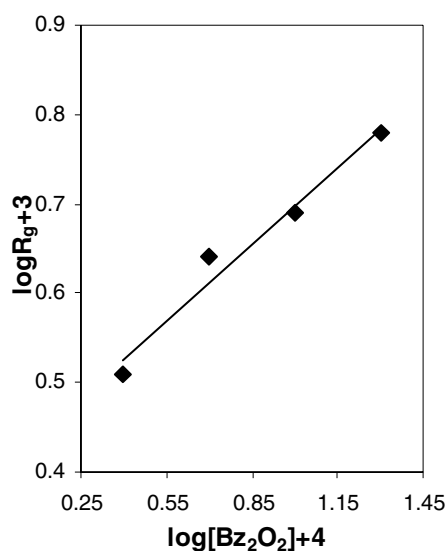


Figure 7. Rates of grafting (R_g) vs. $[Bz_2O_2]$: $[4\text{-VP/HEMA}] = 0.5 \text{ M}$ (50/50 mol); $T = 85^\circ\text{C}$; $t = 100 \text{ min}$.

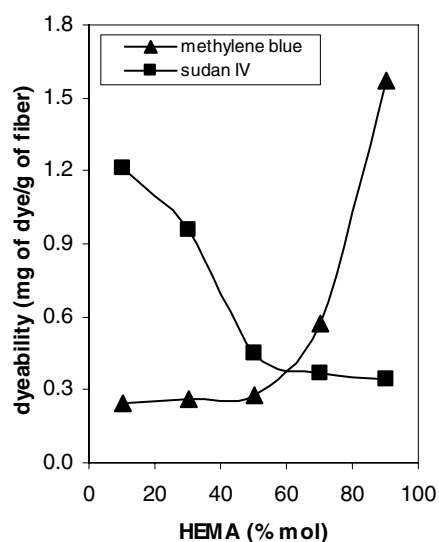


Figure 8. Dye ability of fibers grafted with 4-VP/HEMA mixture at various ratios: $[4\text{-VP/HEMA}] = 0.5 \text{ M}$; $[Bz_2O_2] = 8.0 \times 10^{-3} \text{ M}$; $T = 85^\circ\text{C}$; $t = 100 \text{ min}$.

Dyeability

PET fibers do not contain suitable functional groups that can interact with dye molecules. Only they can be dyed with disperse dyes. Thus dye ability of ungrafted PET fibers with diazo basic dyes is negligible. Grafting PET fibers with 4-VP/HEMA monomer mixtures its dye ability properties with both diazo and basic dyes because it inserts into the fibers structure of the functional groups of $-\text{CN}-$, $-\text{CO}-\text{O}-\text{R}-\text{OH}$ groups, which can interact with diazo and basic dyes, respectively. Dye ability of grafted PET fibers with diazo dye (sudan IV) and basic dye (methylene blue) is shown at Figure 8. The Figure 8 shows that the grafted PET fibers with the diazo dye increased to 1.21 mg of dye/g of fiber after grafting with 171% 4-VP/HEMA (90/10 mol). At higher graft yield, the dye ability with diazo dyes showed a decrease as a result of the decrease in the 4-VP content of the grafted fibers. The dye ability of the PET fibers grafted with the 4-VP/HEMA monomer mixture with basic dyes, however, increased with increasing HEMA content on the graft chains. The dye ability reached 1.57 mg of dye /g of fibers at a graft yield of 318% 4-VP/HEMA (10/90 mol).

Water absorption capacity

It is known that PET fibers are hydrophobic in nature and has very low chemical reactivity and water adsorption properties due to its chemical structure and high crystallinity. In this study, rise of water absorption capacity is attempted by graft polymerizing 4-VP/HEMA mixture onto PET fibers. The percent water absorption of 4-VP/HEMA grafted PET fibers was determined from the weight increase, and results obtained are shown in Figure 9. As seen from the graph, the percent water adsorption of 4-VP/HEMA grafted PET fibers is increased with increasing grafting yield and reached to a maximum value of 46% the percent water adsorption at 280% grafting yield. The increase in the percent water absorption values was due to hydrophilic

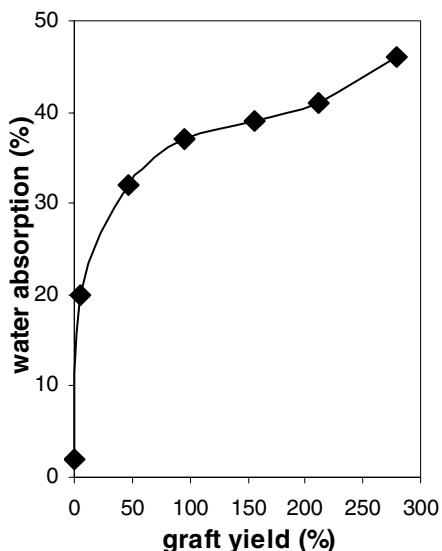


Figure 9. Change of water absorption capacity with graft yield.

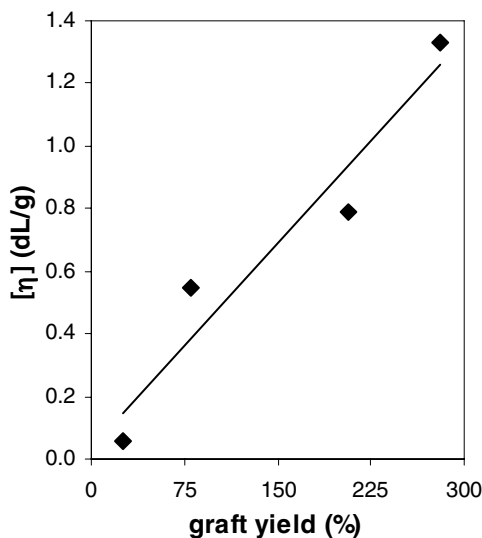


Figure 10. Variation of intrinsic viscosity with graft yield.

groups which enter the fibers structure as a result of 4-VP/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 4-VP/HEMA monomer mixture [12].

Intrinsic viscosity measurements

Intrinsic viscosity $[\eta]$, data obtained from 4-VP/HEMA grafted PET fibers are plotted in Figure 10. As reflected from the graph, intrinsic viscosity was increased with the increasing graft yields, showing an evidence of grafting. Similar results were observed during the grafting of 4-vinylpyridine onto PET fibers [16].

Diameter

The diameter values of PET fibers grafted with different amounts of 4-VP/HEMA are given in Table 3. According to this table, grafting increases the diameter of the fibers. For instance, the diameter of 12.3 μm of ungrafted PET fibers change to 35.7 μm of 280% 4-VP/HEMA grafted fiber. This shown 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 [27].

Table 3. Change with the graft yield of diameter and T_g of the 4-VP/HEMA mixture grafted PET fibers

Grafting Yield (%)	Diameter (μm)	T_g ($^{\circ}\text{C}$)
Ungrafted	12.3	82.30
25	14.3	84.52
81	20.1	124.82
165	25.1	129.57
250	31.9	147.97
280	35.7	186.55

Differential scanning calorimetry

Thermal analysis results of original and grafted PET fibers are given in Table 3. As seen from the table, as the amount of grafted 4-VP/HEMA (280%) increase, T_g of the grafted PET fibers also increase. The results of the DSC analysis show that 4-VP/HEMA grafted PET fibers thermal stability are better than that of PET fibers, because of a crosslinked network structure in grafted PET fibers.

FTIR spectrum

The FTIR spectrum of ungrafted and 4-VP/HEMA grafted PET fiber is shown in Fig. 11. FTIR spectrum of ungrafted PET fibers (Fig 11a) shown absorptions at 1711 cm^{-1} , 1410-1577 cm^{-1} and 2963 cm^{-1} , which are typical to those of C=O, C=C, aliphatic C-H, and aromatic C-H stretching, respectively [28]. A comparison of these spectrum shown a broad peak at 3292 cm^{-1} coming from the merge of the -OH groups of HEMA. 1600 cm^{-1} in the spectrum is due to the resonance peak of the 4-VP groups. Hence provided strong proof for the grafting of both monomers onto PET fibers.

Micrographs of grafted PET fiber

The scanning electron micrographs of ungrafted and 4-VP/HEMA grafted (280%) PET fibers are shown in Figure 12. The ungrafted PET fiber surface (Fig. 12a) exhibited a smooth and relatively homogeneous surface. At 280% graft yield, The grafted side chain seems to cover of the PET fibers (Fig. 12b), and showing another proof of grafting.

Conclusions

Maximum percent grafting (280%, 4-VP/HEMA 50/50 mol) was obtained when the polymerization was carried at the following conditions: $[Bz_2O_2] = 8.0 \times 10^{-3}$ M; $[4-VP/HEMA] = 0.6$ M (50/50 mol); $t = 100$ min and $T = 85^\circ C$. The presence of HEMA monomer in the reaction mixture has increased the extent of graft polymerization of the 4-VP onto PET fibers due to its synergistic. The rate of grafting was found to be proportional of the 1.5 and 0.3 powers of 4-VP/HEMA and Bz_2O_2 concentrations, respectively. It was recognized that, diameter, water absorption capacity, intrinsic viscosity and glass transition temperature increased with the increasing graft yield. The dye ability of the 4-VP/HEMA grafted PET fibers increased with an increase in grafting with diazo and basic dyes. The dye adsorption of the grafted fibers was very depended on the number of 4-VP and HEMA groups inserted into the PET fibers structure.

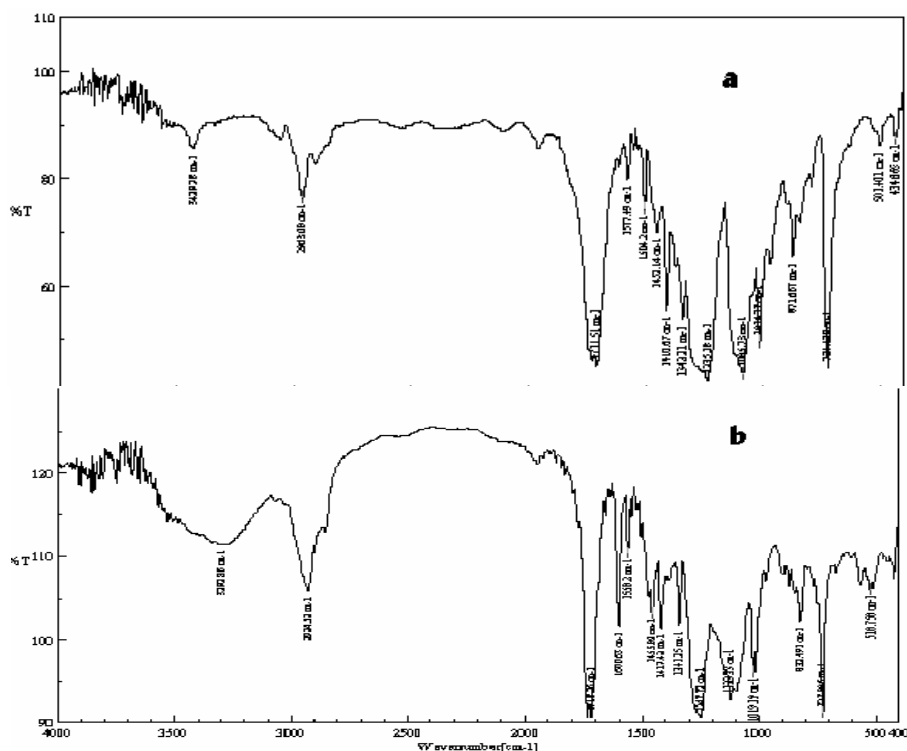


Figure 11. FTIR spectrum of a) ungrafted b) 280% 4-VP/HEMA mixture grafted PET fiber.

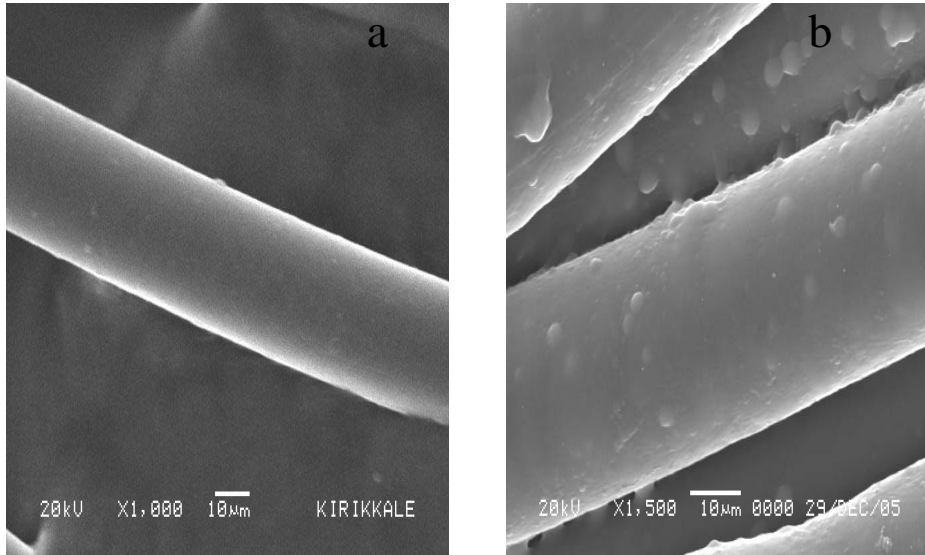


Figure 12. SEM micrographs of (a) ungrafted and (b) 4-VP/HEMA (280%, 50/50 mol) grafted PET fibers.

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