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GRAFT COPOLYMERIZATION OF 2-HYDROXY ETHYL METHACRYLATE ON DIMETHYL SULFOXIDE PRETREATED POLY(ETHYLENE TEREPHTHALATE) FILMS USING BENZOYL PEROXIDE

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ABSTRACT

In this study, 2-hydroxy ethyl methacrylate (HEMA) monomer was grafted onto poly(ethylene terephthalate) (PET) films using benzoylperoxide (BP) initiator. PET films were pretreated in dimethyl sulfoxide (DMSO) for 1 hour at 140°C before the polymerization process was carried out. The change of grafting yield with polymerization time, temperature, initiator, and monomer concentrations were investigated. The optimum polymerization temperature, time, initiator, and monomer concentrations were found to be 85°C, 4 hours, 0.5 M and 2.2×10^{-2} M, respectively. The effects of initiator and monomer diffusion times onto grafting were also investigated, and found to cause an increase in the grafting yield. Kinetic parameters and the activation energy for the grafting were calculated. Water absorption capacity and intrinsic viscosity of the grafted films were determined. Further, the grafted films were subjected to FTIR spectroscopy, scanning electron microscopy (SEM), and mechanical tests.

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Key Words: Graft copolymerization; Poly(ethylene terephthalate) film; 2-Hydroxy ethyl methacrylate polymerization; Swelling assisted polymerization

INTRODUCTION

Poly(ethylene terephthalate) (PET) is a versatile, widely used commercial product in industry as fiber, film, and plastic resin. However, it has drawbacks such as high hydrophobicity of the surface, which causes high static electrification, low wettability, and poor adhesion. The generation of electrostatic charges on polymers has been mostly a nuisance in many fields associated with polymer. It causes serious damage in semiconductor manufacture, sometimes to human life through fire or explosion. Wetting properties of the polymeric material is also important for the production of filtration and pervaporation membranes. Many efforts have been made to minimize these handicaps, mostly by rendering polymer surfaces hydrophilic or electroconductive. The methods employed for this purposes include surfactant mixing or grafting with hydrophilic monomers.

Numerous publications are available where various methods of initiating graft polymerization have been proposed and comprehensively studied.[1−18] Uyama and Ikada [1] UV irradiated PET film and fabrics with various hydrophilic monomers. Their electrostatic properties were studied by measuring the triboelectric charges generated during mechanical rubbing of the materials. Hsieh and Wu improved the wettability of PET films by grafting acrylic acid (AA) onto glow-discharged PET films.[2] In the study of Uchida and Ikada,[3] quarternary amines were introduced onto PET film surfaces by UV-induced graft copolymerization. Graft copolymerization of anionic and cationic monomers (2-acrylamido-2-methyl propane sulfonic acid, AA, N,N-dimethylamino propyl acrylamide, dimethylaminoethyl methacrylate) onto the surface of PET film with a UV irradiation method was achieved in another study of Uchida et al.[4]

A chemical initiation method was also used for grafting of vinyl monomers onto PET films and found best fitting for this purpose due to the low degradation of the base polymer. However, studies concerning the use of this method are very limited,[11−14,16] since the chemical nature of PET does not allow the formation of its macrochains with an appreciable quantity of radical that can initiate the grafting, and the high extent of crystallization and ordering of amorphous regions retard monomer and initiator diffusion.

To facilitate the incorporation of monomers into the host polymer, swelling agents can be used to open the physical structure of the host polymer.[10,12−14,16,17,19,20] In our previous study, the effect of organic solvents, namely pyridine, dichloroethane (DCE), DCE/H_2O (20/80 v/v) and DMSO were used as swelling agents in the graft copolymerization of acrylamide

(AAm) [11] and 4-vinyl pyridine (4-VP) [12] onto PET films and reported that pretreatment of the films in DMSO for 1 hour at 140°C is the best condition. In the present study, we have also treated PET films with DMSO at the same conditions before the graft copolymerization, for the enhancement of grafting procedure.

There are a small number of studies concerning the graft copolymerization of 2-hydroxyl ethyl methacrylate (HEMA), which was chosen as the monomer for grafting onto the PET in this study. Shukla et al. studied photoinduced graft copolymerization of HEMA onto cotton yarn [21] and cotton cellulose.[22] Graft copolymerization of HEMA onto plasma-treated fabrics of cotton, silk, and PET was investigated by Hirotsu and Asai [23] and polymerizability was compared to that obtained with Ce(IV) catalyst. Abdel-Bary et al. [24] performed graft polymerization of HEMA onto PET fibers using benzoylperoxide (BP) as initiator in water and water/organic solvent mixture as the reaction medium.

As a part of the studies carried out on the graft copolymerization of HEMA onto PET; in this study, a chemical process is employed in which HEMA is incorporated into the PET matrix with the aid of DMSO, as the swelling agent, and BP, as the radicalic initiator.

EXPERIMENTAL

Materials

PET films (Hoksp) of 50 μm thickness were used for grafting. HEMA (Merck) was purified by vacuum distillation at 0.5 mm Hg at 85°C. BP was recrystallized from methanol and dried in a vacuum oven for 2 days. All the other reagents were Merck products and used as supplied.

Polymerization Procedure

PET films were cut to dimensions of about 100 × 30 mm and had a weight of approximately 0.12 g. Before the polymerization reaction was carried out, the films were preswelled in DMSO for 1 hour at 140°C in a temperature controlled oil bath.[11] After this treatment, excess DMSO on the film was removed by blotting between a filter paper. DMSO pretreated PET films of known mass were put into the polymerization tube containing 24 mL of aqueous solution of HEMA at a known concentration, and nitrogen gas was allowed to pass through the solution for 45 min. Then the polymerization tube was placed into a thermostatted water bath. After thermal equilibrium was established, the desired concentration of BP (dissolved in benzene) was added. Graft polymerization was allowed to proceed for a specified period of time under a nitrogen atmosphere. At the end of the predetermined polymerization time, films were removed from the polymerization medium and residual solvent, monomer, and homopoly(HEMA) were extracted with methanol for 6 hours. PET films were then vacuum dried at 50°C for 72 hours and brought to a constant weight. The graft yield (%) was calculated gravimetrically as follows:

$$\text{Graft Yield}(\%) = [(w_g - w_i)/w_i] \times 100 \tag{1}$$

where w_i and w_g denotes the weights of the ungrafted and grafted PET films, respectively.

The rate of grafting (R_g) was found by using the formula [13, 25]:

$$R_g = [(w_g - w_i) \times 1000]/[M_w \times t \times V] \tag{2}$$

where M_w is the molecular weight of monomer, t is polymerization time (s) and V is the total volume (mL) of the overall reaction medium.

Determination of Water Absorption Capacity

PET films were immersed in distilled water, thermostated at 20°C ± 0.1°C for 48 hours, then blotted between a filter paper and weighed. They were vacuum dried at 50°C for 96 hours and brought to a constant weight and weighed again. Water absorption capacity was determined from the weight increase.

Determination of Intrinsic Viscosity

Intrinsic viscosity measurements were made in a phenol/tetrachloroethane (TCE) (1:1, m/m) solvent system using a Ubbelohde capillary flow viscometer mounted in a water bath maintained at 25°C ± 0.1°C.

Infrared Spectroscopy

FTIR spectra of ungrafted and HEMA-grafted PET films were recorded using a Mattson Model 1000 FTIR spectrophotometer. Samples were analysed as films cast from a phenol/TCE (1:1) solvent system onto NaCl plates.

Scanning Electron Microscopy

Scanning electron microscopy studies of the ungrafted and grafted PET films were performed using a JEOL Model JEM-100 CX II microscope.

Samples were coated with gold by a Polaron SC 502 sputter coater for examination.

RESULTS AND DISCUSSION

Effect of Time and Temperature on Grafting

Change of grafting yield (%) with time and temperature is presented in Figs. 1 and 2. As it is reflected from Fig. 1, the grafting is characterized by an initial fast rate, followed by a slower one and then leveled off after 4 hours of polymerization time with a saturation grafting yield value of 34%. This may be attributed to the saturation of the active PET backbone by homopoly(HEMA) and increase in medium viscosity. Similar results were observed in the graft polymerization of AAm,[11] 4-VP,[12] n-vinyl pyrrolidone,[13] methacrylic acid,[16] and 2-methyl-5-vinyl pyridine [26] onto PET films.

The effect of temperature on graft copolymerization of HEMA onto PET films was studied within the temperature range of 60–90°C, keeping monomer concentration (0.5 M , initiator concentration (2.2×10^{-2} M) and polymerization time (4 hours) constant (Fig. 2). The data indicate that the grafting yield percentage increases as the temperature increases from 60°C to

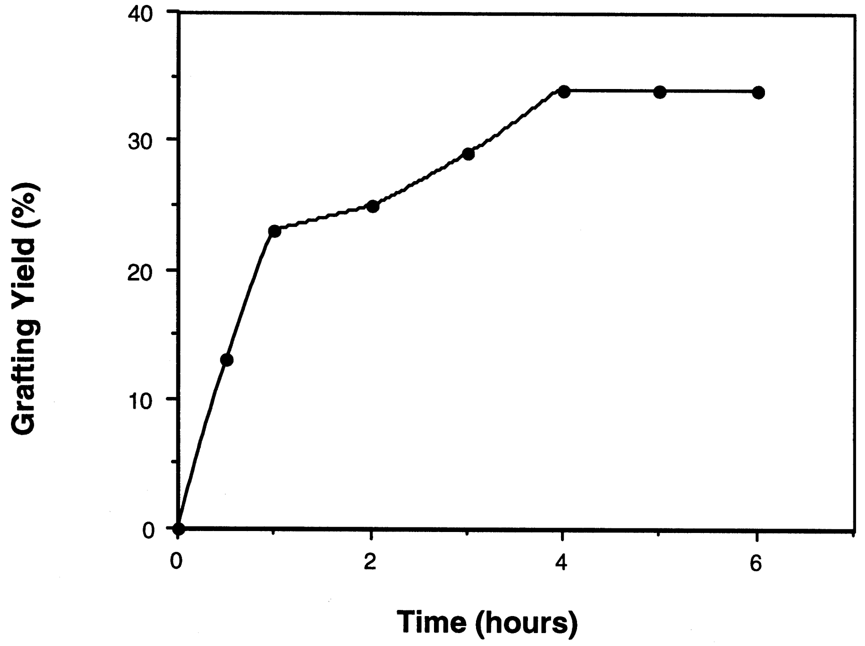

Figure 1. Variation of grafting yield with polymerization time. [HEMA] = 0.5 M, [BP] = 2.2×10^{-2} M, T = 85°C.

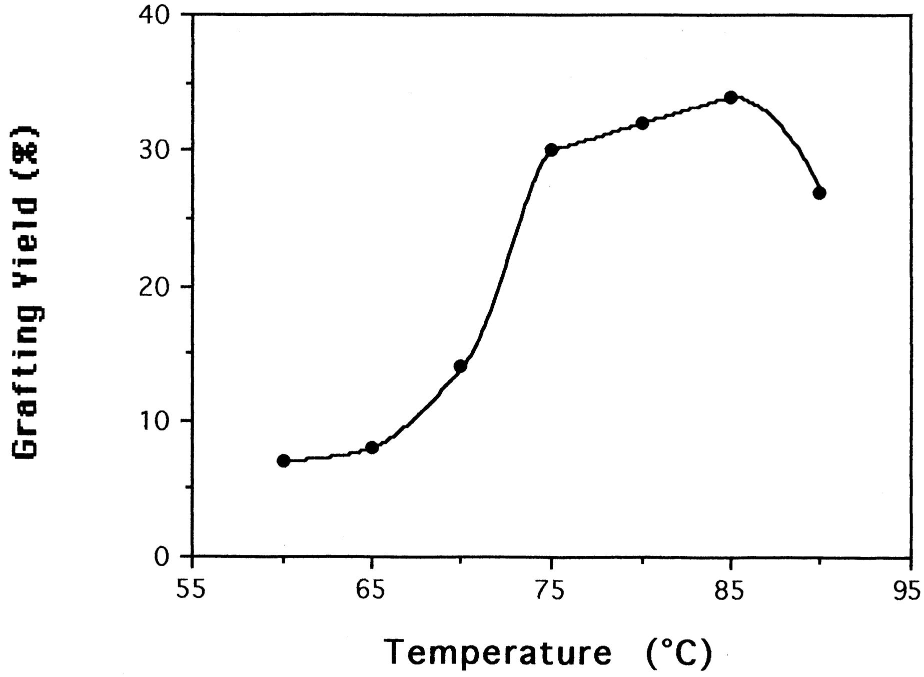

Figure 2. Change of grafting yield with polymerization temperature. [HEMA] = 0.5 M, [BP] = 2.2 × 10^{-2} M, t = 4 hours.

85°C and reaches to 34%; a further increase in temperature decreases the percent grafting. The enhancement in grafting upon rising the polymerization temperature could be ascribed to an increase in the decomposition rate of BP and therefore, increase in the radical concentration and a possible reaction between the growing homopolymer chain radical with PET. PET macromolecules also become much more susceptible to radical reactions above the glass transition temperature (~ 80°C).[27] Lowering of the grafting by raising the temperature above 85°C could be ascribed to a fast rate of termination. This kind of temperature effect upon the grafting yield was also observed in the literature.[11,12,14,20]

Variation of Initiator and Monomer Concentrations

The effect of initiator concentration was studied by changing the BP concentration from 0.5 × 10^{-2} M to 3.0 × 10^{-2} M. The results show that the grafting yield increases with increasing the BP concentration (Fig. 3) up to 2.0 × 10^{-2} M and then falls down upon further increase in BP. This is a typical behavior observed in many studies.[9–13,20,15,28–30] The enhancement in grafting yield by increasing BP concentration up to certain

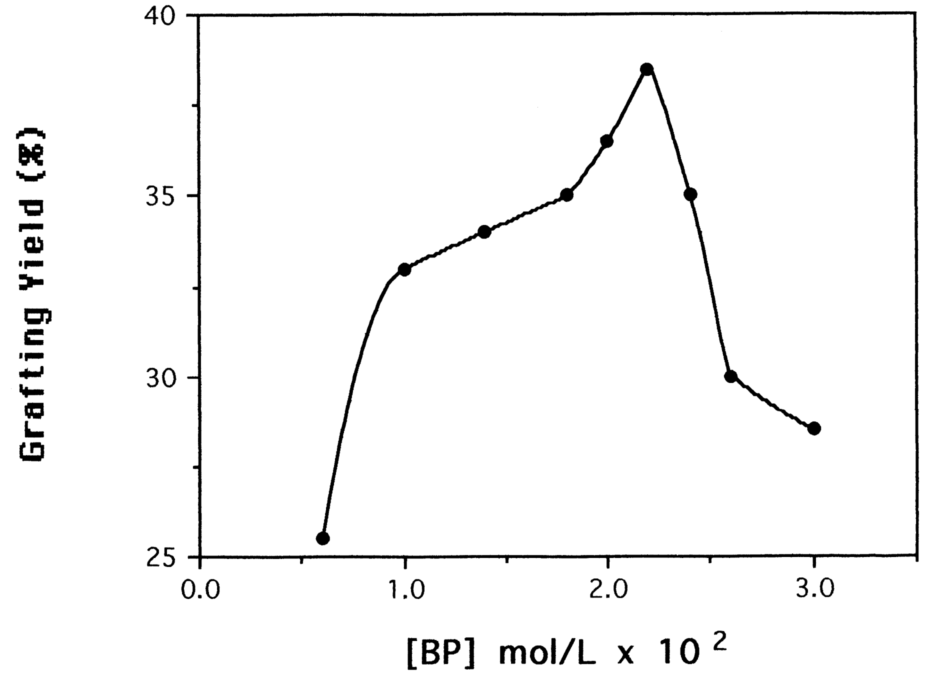

Figure 3. Effect of initiator concentration on grafting yield. [HEMA] = 0.5 M, T = 85°C, t = 4 hours.

limit suggests that BP decomposes to yield benzoyl radicals, which may create suitable active sites for grafting by abstracting hydrogen atoms from the PET backbone, which facilitate the addition of monomers. Another factor that creates suitable sites for grafting is chain transfer reactions between active homopoly(HEMA) chains and PET macromolecules. Both of these processes have a promoting effect on the grafting procedure, which is expected to increase with the increase in the BP concentration. However, a further increase in the initiator concentration (above 2.0×10^{-2} M) causes the termination reactions to dominate and decreases the grafting yield.

Figure 4 represents the effect of HEMA concentration on the grafting yield by varying the HEMA concentration from 0.1 M to 0.8 M at 85°C for a polymerization time of 4 hours. As seen from the figure, the grafting yield increased up to 0.5 M HEMA concentration and remained constant with a further increase in the monomer concentration. The fact that the grafting yield increases as the monomer concentration increases can be explained by the increase in the number of monomer molecules diffused into the PET structure, which lead to a higher grafting yield. The leveling off of the grafting after saturation yield (38.5%) could be associated with accumulation of the homopoly(HEMA) in the reaction medium, which

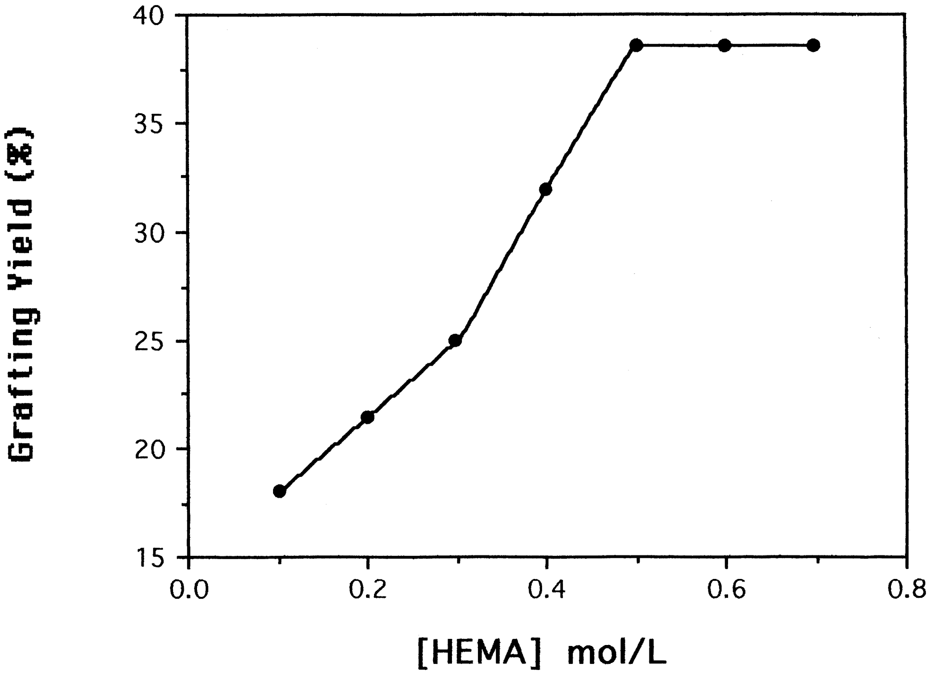

Figure 4. Effect of monomer concentration on grafting yield. [BP] = 2.2×10^{-2} M, T = 85°C, t = 4 hours.

increases the viscosity and retards the monomer diffusion into PET film.[11–13,28,30]

Effect of Initiator and Monomer Inclusions

In polymerizing a monomer in a polymer, the diffusion of the monomer and the initiator into the polymer backbone controls chain growth and chain termination in the internal matrix of the host polymer. To facilitate the incorporation of HEMA and BP into the PET matrix, besides swelling the PET films in DMSO to open up the physical structure, PET films were dipped into a 0.5 M HEMA and 2.2×10^{-2} M BP solution for 1 to 7 days at 20°C before the graft copolymerization was carried out (Figs. 5 and 6). As seen from Fig. 5, the grafting yield was increased with increasing initiator diffusion time up to 3 days, reaching to a grafting yield of 42%, then decreased. This may be attributed to the decrease in the efficiency of the initiator.[31]

The effect of inclusion of HEMA on the grafting yield is shown in Fig. 6. As reflected from the graph, grafting yield was increased with increasing monomer inclusion up to 5 days, reached to a maximum of 45%, then leveled off. These results are consistent with the previous studies on the graft

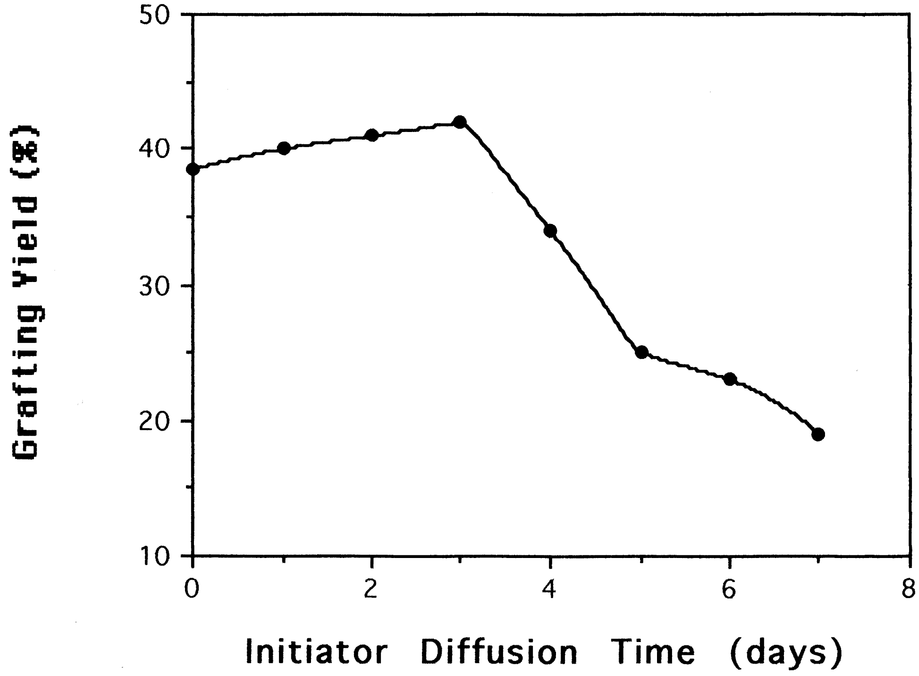

Figure 5. The change of grafting yield with initiator diffusion. [HEMA] = 0.5 M, [BP] = 2.2 × 10^{-2} M, T = 85°C, t = 4 hours.

copolymerization of AAm [12,14] and n-vinyl-2-pyrrolidone [13] grafting onto PET films.

Kinetics of Grafting

The relation of the rate of grafting (R_g) with the monomer and initiator concentrations can be written as [13,14]:

$$R_g = k[\text{HEMA}]^m[\text{BP}]^n \qquad (3)$$

where m and n can be experimentally determined.

The results for dependence of initial rate of grafting upon the [HEMA] in the range of 0.1 M to 0.4 M, keeping the other variables constant, are given in the form of log–log plot in Fig. 7. The order of grafting with respect to HEMA, determined from the slope of the plot in Fig. 7, is 0.4.

Likewise, Fig. 8 shows kinetic investigation of the effect of [BP] on the initial rate of grafting by changing the [BP] from 6.0 × 10^{-3} M to 2.2 × 10^{-2} M. As is evident, R_g is proportional to the 0.4 power of [BP]. Therefore, the grafting rate equation can be written as:

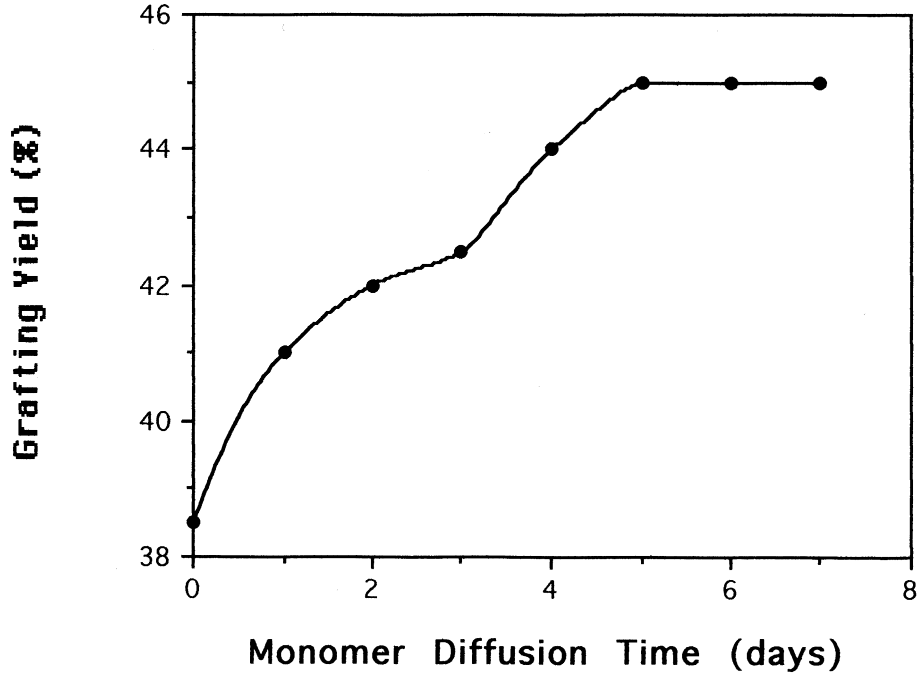

Figure 6. The change of grafting yield with monomer diffusion. [HEMA] = 0.5 M, [BP] = 2.2×10^{-2} M, T = 85°C, t = 4 hours.

$$R_g = k[\text{HEMA}]^{0.4}[\text{BP}]^{0.4} \tag{4}$$

The overall activation energy for grafting of HEMA onto PET film using the BP initiator was found to be 20 kcal/mol from the Arrhenius plot of log R_g vs 1/T (Fig. 9).

In the literature, there are no kinetic data concerning the grafting of HEMA onto PET film using BP as a radicalic initiator. However, many researchers have investigated the kinetics of the grafting of various vinyl monomers onto PET films and fibers using different initiators.[13,14,20,25,32–34] It has been understood from the literature studies that, the dependence of the rate of grafting on monomer and initiator concentrations varies with the types of initiator and monomers grafted onto the PET backbone.

Determination of Some Properties of HEMA-Grafted PET Films

Water Absorption Capacity

PET has a very low chemical reactivity and water absorption properties due to its chemical structure and high crystalinity. In this study, improvement

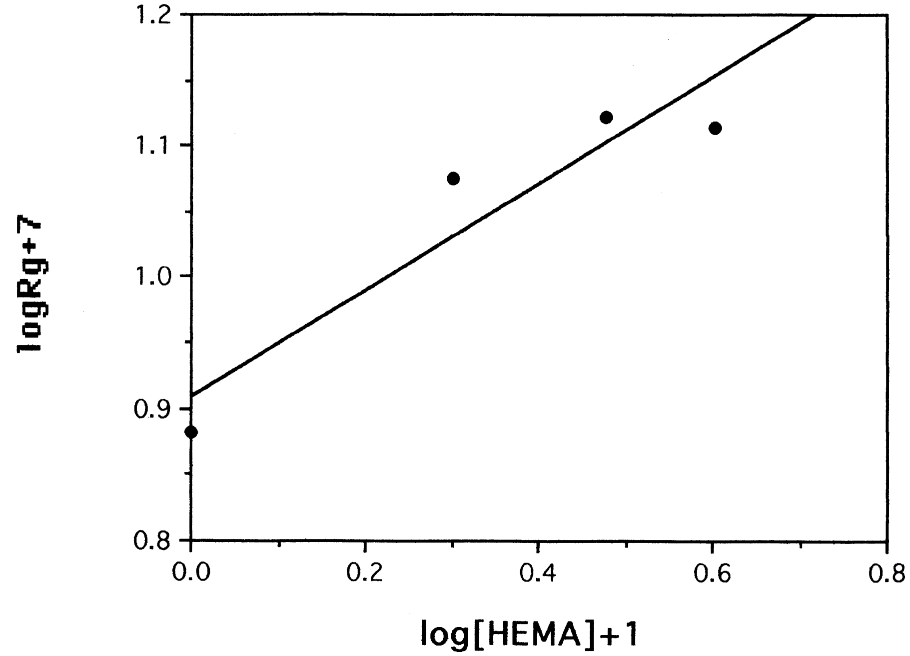

Figure 7. The change of rate of grafting with monomer concentration. [BP] = 2.2 × 10^{-2} M, T = 85°C, t = 4 hours.

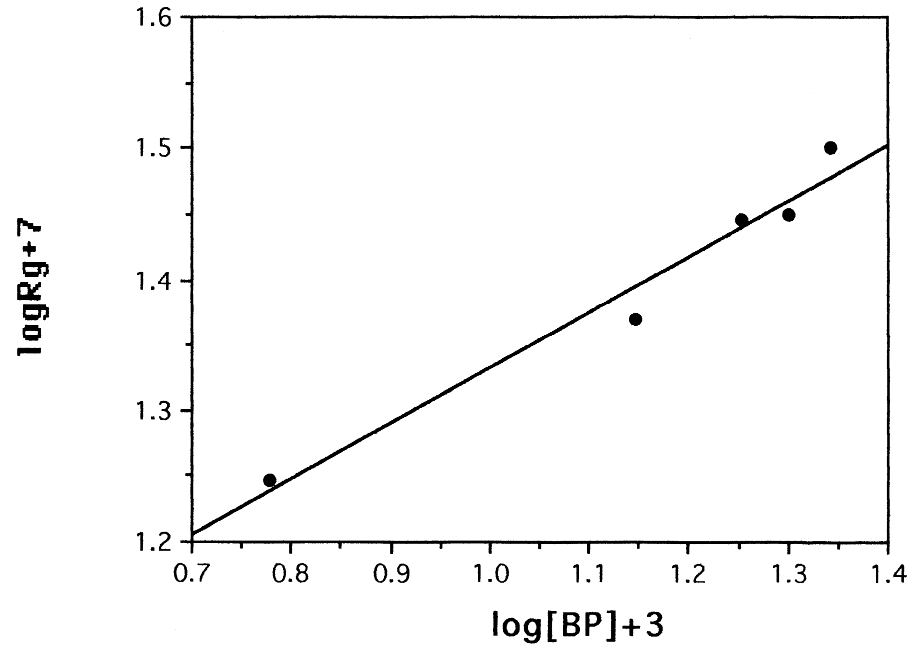

Figure 8. The change of rate of grafting with initiator concentration. [HEMA] = 0.5 M, T = 85°C, t = 4 hours.

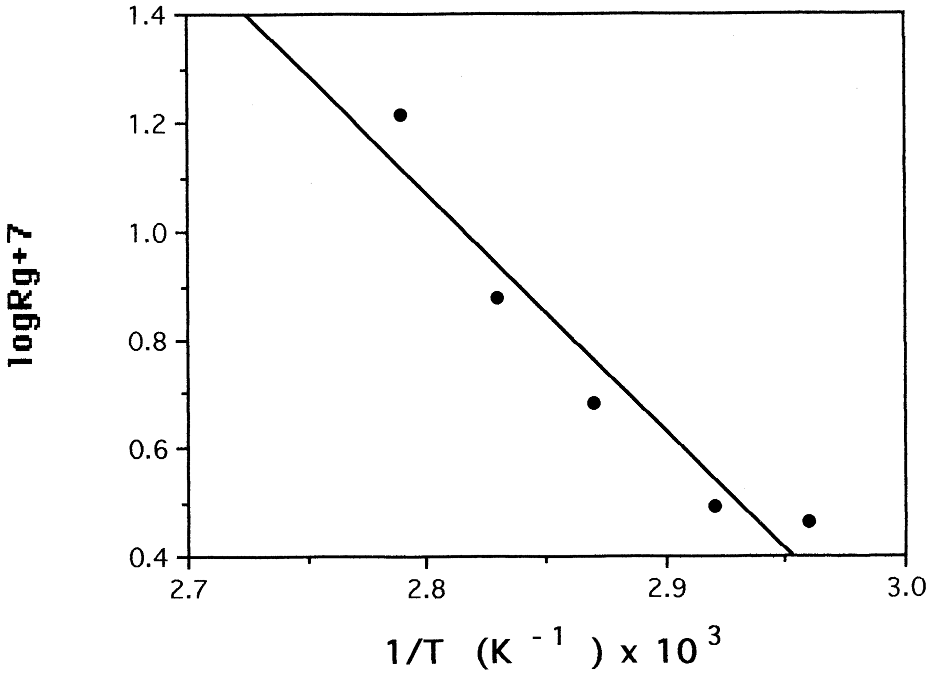

Figure 9. The change of rate of grafting with temperature. [HEMA] = 0.5 M, [BP] = 2.2 × 10^{-2} M, T = 85°C, t = 4 hours.

of water absorption capacity is attempted by copolymerizing a vinyl monomer, HEMA, onto PET film. Water absorption capacity of HEMA-grafted PET films was determined from the weight increase, and results obtained are shown in Fig. 10. As seen from the graph, water absorption capacity of HEMA-grafted PET films is increased with increasing grafting yield and reached to a saturation value of 35% water absorption capacity at 30% grafting yield.

Grafting with HEMA not only brings about an opening of the structure but also increases the hydrophilicity of the film due to the introduction of polar groups. Similar results were observed in the graft copolymerization of HEMA onto PET fibers and fabric.[35]

Intrinsic Viscosity

Intrinsic viscosity [η] data obtained from HEMA-grafted PET films are given in Table 1. As seen from the table, limit viscosity number was increased with increasing grafting yield, showing evidence of grafting. Similar results were obtained during the graft copolymerization of vinyl monomers onto PET films and fibers.[11–14,20]

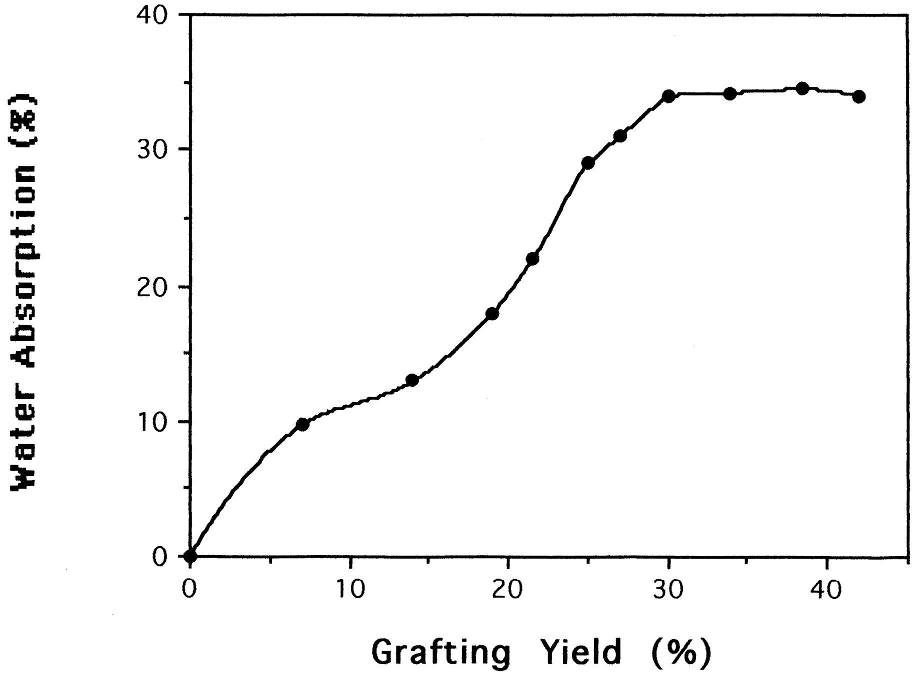

Figure 10. Effect of grafting yield percentage on water absorption capacity. T = 20°C, t = 48 hours.

FTIR Spectrum

The FTIR spectra of ungrafted and HEMA-grafted PET films are presented in Fig. 11. FTIR spectrum of ungrafted PET (Fig. 11a) shows absorptions at 1724 cm^{-1}, 1400–1600 cm^{-1}, 2967–2909 cm^{-1} and 3060 cm^{-1}, which are typical to those of C=O, C=C, aliphatic C-H, and

Table 1. Intrinsic Viscosity Data of HEMA Grafted PET Films

Graft Yield (%)	[η] (dL/g)
0	0.05
8	0.16
27	0.42
31	0.77
35	0.83
38	1.02
42	1.46

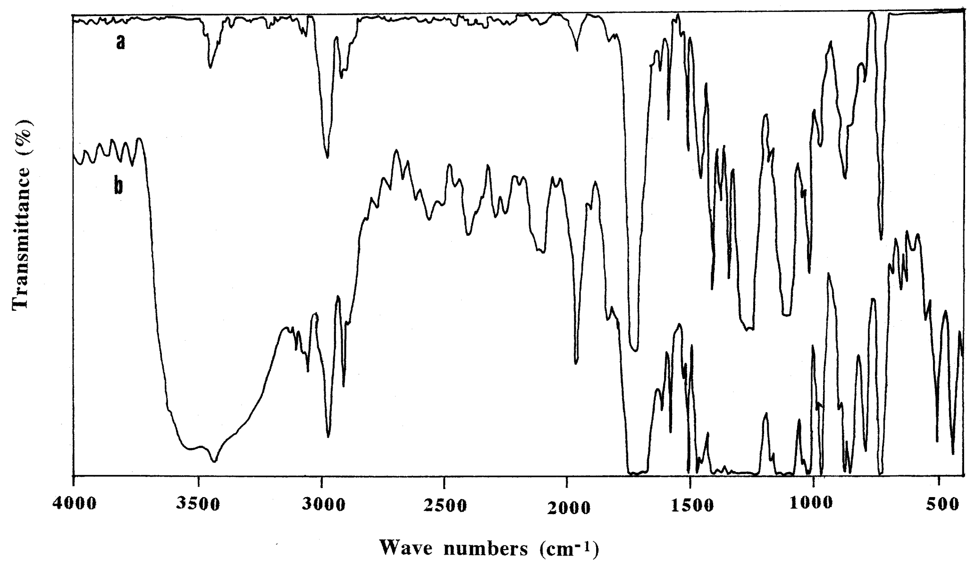

Figure 11. FTIR spectra of PET films. (a) Ungrafted, and (b) HEMA grafted.

aromatic C-H stretchings, respectively. However, in the FTIR spectrum of HEMA-grafted PET film (Fig. 11b), in addition to the above absorptions, the broad resonance peak observed at 3400–3560 cm^{-1} is due to -OH groups of poly(HEMA) chains. This also provides proof of grafting.

Microstructure of Grafted Copolymers

Scanning electron micrographs of ungrafted and HEMA-grafted PET films are presented in Fig. 12. It was seen from the SEM results that, although ungrafted PET film surface has a smooth and relatively homogeneous appearance, after HEMA grafting onto the amorphous regions of PET film surface as side chains (Fig. 12b), film surface has gained a heterogeneous appearance, which shows another proof of grafting.

Tensile Properties

Studies emphasizing improvement of the mechanical properties of PET are limited.[36–38] Table 2 lists the tensile properties of the HEMA-grafted PET films. HEMA-grafted PET films showed an increase in the percentage elongation and stress at break with increasing grafting to 34%. DMSO is a strong reactive solvent for PET, which may induce irreversible modification of the polymer morphology, such as void formation.[37] The greater freedom for chain movement is thus allowed for polymerization in the voids with minimum linkage to the PET chains. The plasticizing effect of the newly

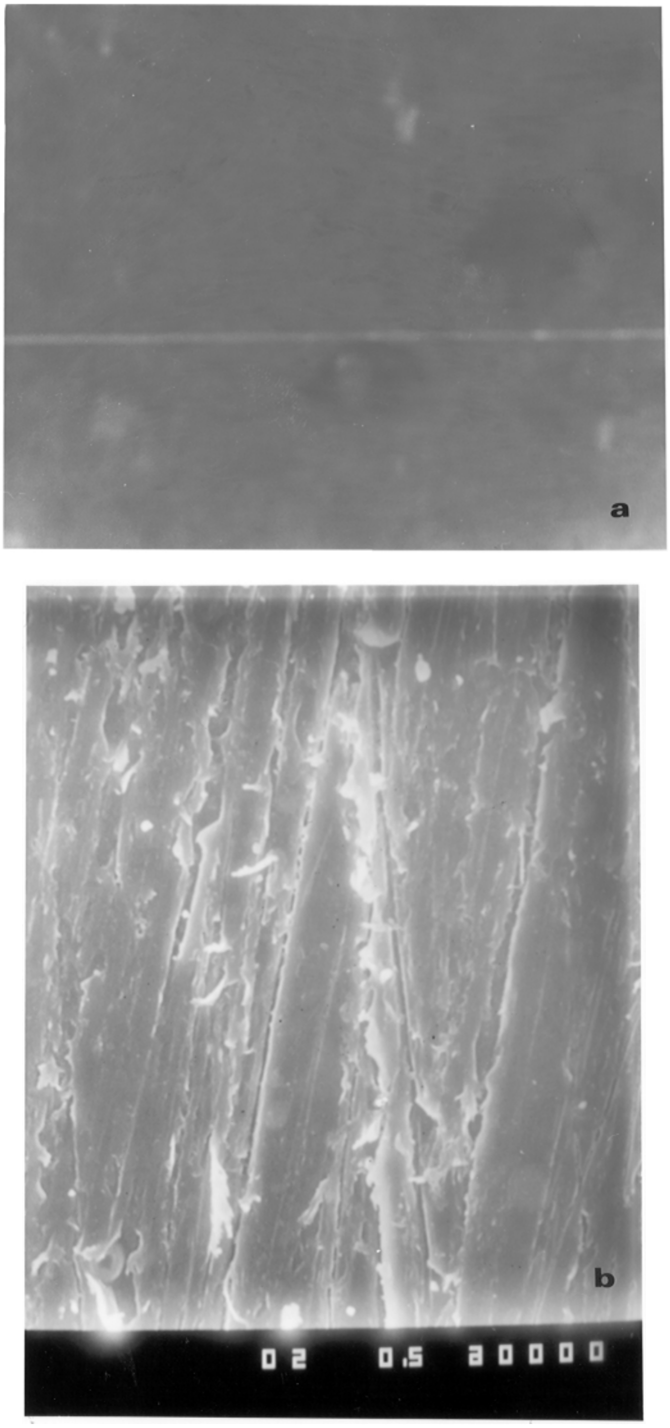

Figure 12. SEM micrographs obtained from (a) ungrafted and (b) HEMA-grafted PET films (500X).

Table 2. Mechanical Test Results of HEMA-Grafted PET Films

Grafting Yield (%)	Elongation* at Break (%)	Stress* at Break (kgf/cm^2)
0	40	740
25	46	1142
30	65	1336
34	76	2069
38	66	735
42	65	730

*The results are the average of two measurements.

polymerized molecules in the amorphous region may also contribute to the higher elongation at break. On the other hand, elongation at break showed a decrease after 34% HEMA grafting onto PET films. This may be attributed to the high penetration of monomer and the subsequent polymerization and/or crosslinking of monomer in the amorphous regions of the PET backbone, which may have contributed to the increase in rigidity of the PET matrix resulting in less extension at break.[10] Therefore, mechanical test results also indicate another proof of grafting.

CONCLUSION

This study relates the graft copolymerization of HEMA onto DMSO pretreated PET films using BP initiator. The following conclusions were drawn from the experimental results.

The optimum conditions of grafting were found to be temperature of 85°C, time of 4 hours, HEMA and BP concentrations of 0.5 M and 2.2×10^{-2} M, respectively.

The inclusion of BP or HEMA in PET films before the copolymerization process enhanced the grafting yield.

The order of grafting with respect to HEMA and BP was found to be as 0.4 and the activation energy as 20 kcal/mol.

Intrinsic viscosity and water absorption capacity of the HEMA-grafted PET films increased with increasing grating yield.

ACKNOWLEDGMENT

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