

Graft Copolymerization of Methyl Methacrylate upon Gelatin Initiated by Benzoyl Peroxide in Aqueous Medium

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ABSTRACT: The graft copolymerization of methyl methacrylate upon gelatin was studied using benzoyl peroxide as an organic initiator in aqueous medium. The grafting reactions were carried out within the 65–90°C temperature range, and the effect of monomer and initiator concentrations on the graft yield were also investigated. The maximum graft yield was obtained at a benzoyl peroxide concentration of 0.20×10^{-2} mol/L and the optimum temperature was 80°C. Thermogravimetric analysis showed that the thermal stability of gelatin increased as a result of grafting. Further, such changes in the properties of methyl methacrylate-grafted gelatin as density, moisture regain, and water uptake were also determined. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 1547–1556, 1999

Key words: gelatin; grafting; methyl methacrylate; benzoyl peroxide

INTRODUCTION

One of the ways to improve the properties of the natural^{1–4} and synthetic^{5–8} polymers and to give them new properties is graft copolymerization. Using graft copolymerization, the aim is that the host polymer gains some of the desired properties of the monomer(s) used for grafting. The grafting of vinyl monomers upon the natural polymers such as starch,^{1,4,9} cellulose,^{2,10} and wool^{3,11} is of great importance to develop new materials combining the properties of both natural and synthetic polymers.¹²

Gelatin is a mixture of high molecular weight and water-soluble proteins and it gels at temperatures lower than 30–40°C. Due to its unique

properties, it is used widely in food, gummed tapes, and adhesives and as a colloid to prevent coalescence. Because of various potential uses of gelatin, it is worthwhile to investigate its modification to develop new materials with improved properties. Among the monomers grafted upon gelatin for its modification are methyl methacrylate,^{12–15} methyl acrylate,¹⁶ acrylonitrile,¹⁷ butyl acrylate,^{18–21} and ethyl acrylate.^{15,18,22,23}

The graft copolymerization was generally carried out by chemical means. There is very little work on the radiation-induced grafting of vinyl monomers upon gelatin.²⁴ The initiators used in the chemical grafting are generally redox initiators such as potassium persulfate,^{18,20,21} ceric ammonium nitrate,²⁵ and ammonium persulfate.¹² There is no detailed report on the use of an organic initiator such as benzoyl peroxide for grafting of methyl methacrylate upon gelatin in the literature. This study was directed to carry out the grafting of methyl methacrylate upon gelatin using benzoyl peroxide in an aqueous me-

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dium and to investigate the effects of the factors such as temperature and monomer and initiator concentration. The properties of grafted gelatin such as density and moisture regain were also examined.

EXPERIMENTAL

Materials

The granulated gelatin (Merck, Germany; molecular weight = 18,000 g/mol) was used as purchased. Methyl methacrylate (MMA; Merck, Germany) was washed with 5% NaOH three times, dried over CaCl₂, and distilled under a vacuum at 46°C. Benzoyl peroxide (Bz₂O₂; Merck, Germany) was recrystallized twice from the methanol and chloroform mixture.

Graft Copolymerization

Gelatin (1.00 ± 0.01 g) was placed in a 50-mL polymerization tube and Bz₂O₂, at a suitable concentration dissolved in 1 mL acetone, was added to it. The total volume was made up to 20 mL with distilled water after the addition of the monomer and the mixture was vigorously mixed. The mixture was then placed in a water bath (Lauda D40 S, Germany) adjusted to the polymerization temperature. At the end of polymerization, the polymerization tube was taken from the water bath and 50 mL of acetone was added and kept overnight. The gross polymer was recovered by filtration.

Characterization

Isolation of Grafted PolyMMA

The gross polymer is a mixture of ungrafted gelatin, homopolyMMA, and polyMMA-grafted gelatin. The isolation method employed was selective solvent extraction based upon the difference in the solubility of polyMMA-grafted gelatin and homopolymers (ungrafted gelatin and homopolyMMA). This is the principal method used in graft copolymerization studies to separate the homopolymer of the grafted monomer and the host polymer.^{15,17,24}

The gross polymer was treated by boiling water by changing the washing water at least three times for 2 h in order to remove ungrafted gelatin and then was refluxed with acetone for 2 h

to remove the homopolyMMA. The resulting polyMMA-grafted gelatin was dried and weighted.

The percent graft yield ($G\%$) based upon the initial amount of gelatin was calculated from the weight of initial gelatin (w_i) (1.00 g) and polyMMA-grafted gelatin (w_g) as follows:

$$G\% = (w_g/w_i) \times 100$$

Hydrolysis of PolyMMA-Grafted Gelatin

The grafted samples were hydrolyzed by refluxing in 15 mL 6N HCl for 9 h.²⁶ PolyMMA is resistive against hydrolysis with acids and shows its own infrared spectrum after being treated with 6N HCl at 100–110°C for 9 h.²⁷ The remaining polyMMA-grafted chains were filtered.

The initial gelatin weight of 1.00 g was taken as a basis in the calculation of the graft yield. However, since the washing process with water removes the ungrafted gelatin, the amount of gelatin in the grafted samples will decrease. Therefore, the calculations based upon the initially taken gelatin do not give a graft yield of the amount of gelatin actually taking place in the grafting process.

For some samples, the graft yield based upon the amount of gelatin involved in the grafting process was determined by hydrolysis. PolyMMA-grafted samples freed from ungrafted gelatin and homopolyMMA were weighted and hydrolyzed as outlined above. The weight of gelatin involved with the grafting (w_a) was determined by subtracting the weight of polyMMA (w_m) obtained after the hydrolysis from the weight of the polyMMA-grafted gelatin (w_g). The graft yield based upon the amount of gelatin involved with grafting ($RG\%$) was calculated from the relation

$$RG\% = (w_m/w_a) \times 100$$

Molecular Weight Measurements

The molecular weight of the grafted polyMMA branches was determined by viscosimetric measurements at 25°C, based upon the relation²⁸ $[\eta] = 7.5 \times 10^{-5} M_v^{0.70}$. A 0.5% solution of the polymer in acetone was used in the measurements.

IR Spectra

The infrared spectra of the samples were taken with MATTSON 1000 Model FTIR spectrophotometer using KBr pellets.

Thermogravimetric Analysis

The thermogravimetric analysis was carried out in a nitrogen atmosphere with a flow rate of 200 mL/min using a LINSEIS 81 Model thermal analyzer. The samples were heated to 600°C at a rate of 10°C/min starting from the room temperature.

Density Measurements

The apparent densities of the samples were measured at 23°C with a density gradient column detailed previously.⁸

Moisture Regain

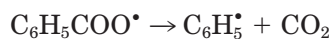
The weighted dry samples were placed in a desiccator over water (100% humidity) and kept at 25°C for 24 h, closing the cap of the desiccator. The moisture-regain values of the samples were calculated from their dry and conditioned weights.

Water Uptake

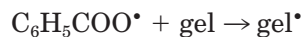
The dry samples were weighted and kept in water for 2 h at room temperature. The wet weights were determined after sandwiching the samples between the filter paper 10 times. The water uptake of the grafted samples was determined from the weights of the dry and the wet samples.

RESULTS AND DISCUSSION

Chemical grafting involves the formation of active centers upon the gelatin backbone. Once these centers are formed, polymer chains start to grow on them, resulting in branches. Bz₂O₂ undergoes thermal dissociation as



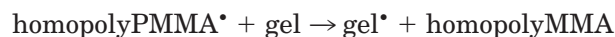
The C₆H₅COO[•] and C₆H₅[•] radicals formed in the polymerization medium may initiate the production of gelatin radicals (gel[•]):



Also, the C₆H₅COO[•] and C₆H₅[•] radicals may initiate the homopolymerization of MMA:



If an organic initiator such as Bz₂O₂ is used in the aqueous media, the chain-transfer reactions also play an important role. It was reported that grafting was due to the backbone radical formed by the chain-transfer reactions in the grafting of wool by azobisisobutyronitrile.²⁹ Bz₂O₂ is thought to be dissolvable in the oil phase of monomer, so the primary radicals may readily add to the monomer to initiate the homopolymerization.²⁶ The chain-transfer reaction between the growing polyMMA chains and the gelatin which forms active sites upon gelatin is

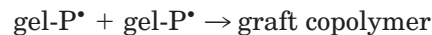
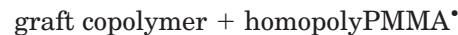


Once the gelatin radicals are produced, the monomer adds to it to give a graft polymer:



where gel-P[•] is the growing gelatin graft polymer.

Termination of the polymerization process may take place in one of the chain-transfer or combination reactions involving the growing chain radical given below^{17,19}:



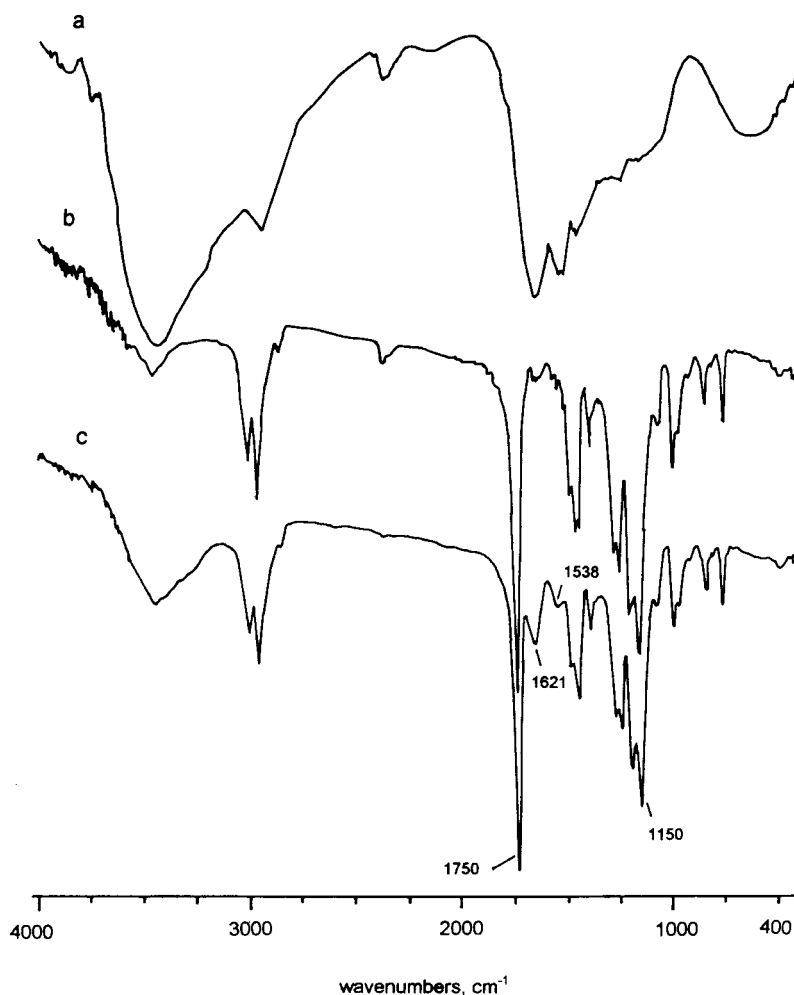


Figure 1 FTIR spectra of (a) pure gelatin, (b) pure polyMMA, and (c) 131.7% polyMMA-grafted gelatin.

The grafting was verified by the IR spectra of the grafted polymers.^{23,24,30} Figure 1(a–c) shows the IR spectra of the pure gelatin, homopolyMMA, and 131.7% polyMMA-grafted gelatin, respectively. The spectrum of polyMMA-grafted gelatin displays the band at 1621 and 1538 cm^{-1} due to the amide groups upon gelatin as well as the bands at 1750 and 1150 cm^{-1} coming from the carbonyl groups of pure polyMMA.

Influence of Reaction Parameters

Reaction Time and Temperature

The change of the graft yield with time and temperature is shown in Figure 2. An induction period of 30 and 15 min was observed at the lowest

temperatures used, namely, 65 and 70°C. The graft yield was found to increase with increase in the polymerization time and then remained more or less constant (saturation graft yield) (except 65°C). The increase in graft yield with time is accounted for by increase in the number of grafting sites on the gelatin chains in the initial stages of the polymerization. Longer reaction periods have little effect on the graft yield since the number of active sites remains almost constant with increasing reaction time and, hence, there is no further change in the graft yield.¹²

The grafting rate increased in parallel with the temperature. However, the saturation graft yield increased up to an optimum temperature of 80°C (58.0%) and then showed a decrease to 47.0% at 90°C. The increase in temperature increases the

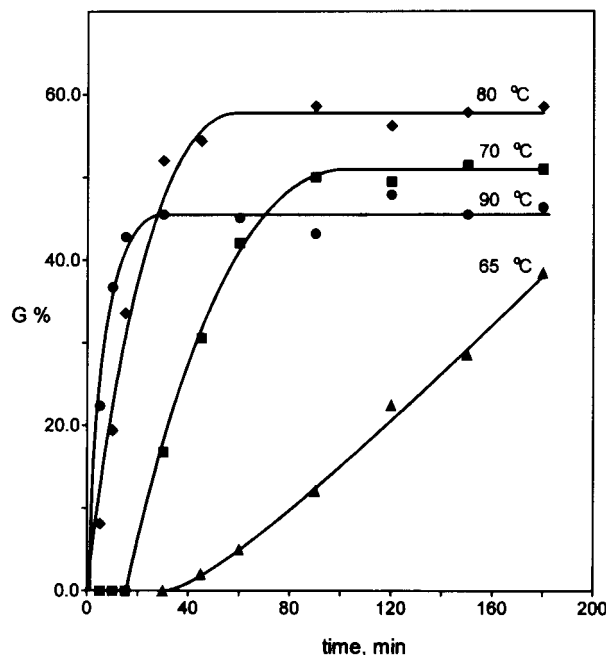


Figure 2 Change of the graft yield with temperature and the polymerization time: Bz_2O_2 concentration = 0.20×10^{-2} mol/L; time = 180 min; MMA concentration = 0.37 mol/L.

dissociation rate of the initiator and the mobility of the monomer, polymer, and molecular species present in the medium. The rates of initiation, propagation, and termination reactions also increase with the increasing temperature. However, termination reactions predominate at higher temperatures, which explains the decrease of the graft yield after a certain temperature (90°C at our experimental conditions). The saturation graft yield at 90°C is decreased to 15 min due to the rapid consumption of the monomer due to the high rate of the homopolymerization reactions. This behavior observed at the saturation graft yield is typical for many grafting systems.^{7,11,15}

The initial rates of grafting (R_g) calculated for the experimental temperatures are given in Table I. The slope of $\log R_g$ versus $1/T$ graph shows that the overall activation energy for grafting is 8.66 kcal/mol within the 70–90°C temperature range (Fig. 3).

Concentration of Initiator

The effect of the initiator concentration was investigated by keeping the concentration of MMA

Table I Values of the Initial Rates of Grafting (R_g) at Various Temperatures^a

Temperature (°C)	$R_g \times 10^5$ mol L ⁻¹ s ⁻¹	$1/T \times 10^3$ (°C)	$\log R_g + 5$
70	8.490	2.915	0.9284
80	14.316	2.833	1.1558
90	16.980	2.755	1.2299

^a Bz_2O_2 concentration = 0.20×10^{-2} mol/L; MMA concentration = 0.37 mol/L.

at 0.37 mol/L, the temperature at 80°C, and the polymerization time at 2 h. Figure 4 shows the results obtained by changing the Bz_2O_2 concentration between 0.19×10^{-3} and 0.10×10^{-1} mol/L.

The highest grafting yield (58.0%) was obtained at an initiator concentration of 0.20×10^{-2} mol/L. The grafting yield, which showed a rapid increase up to this optimum initiator concentration, decreased, although not very significantly, after this value.

The increase in the initiator concentration increases the dissociation rate of Bz_2O_2 and therefore increases the free-radical concentration ($\text{C}_6\text{H}_5\text{COO}^\bullet$ and $\text{C}_6\text{H}_5^\bullet$) in the polymerization me-

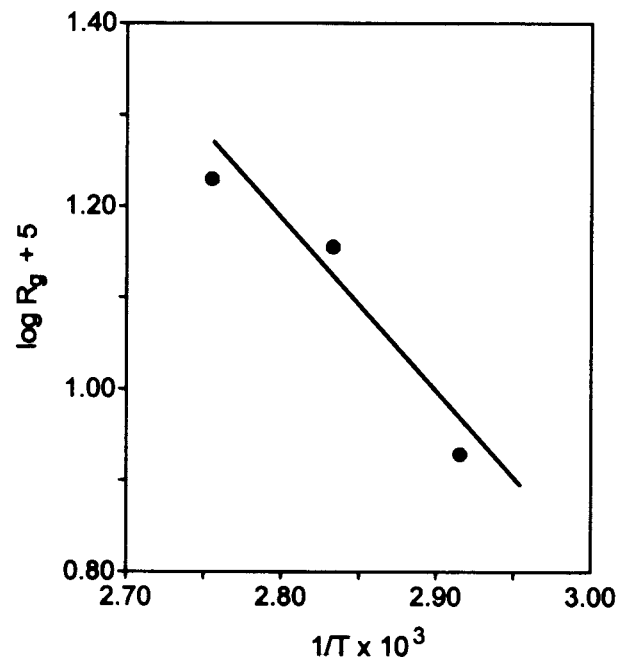


Figure 3 $1/T$ versus $\log R_g$ plot for grafting of MMA upon gelatin using Bz_2O_2 .

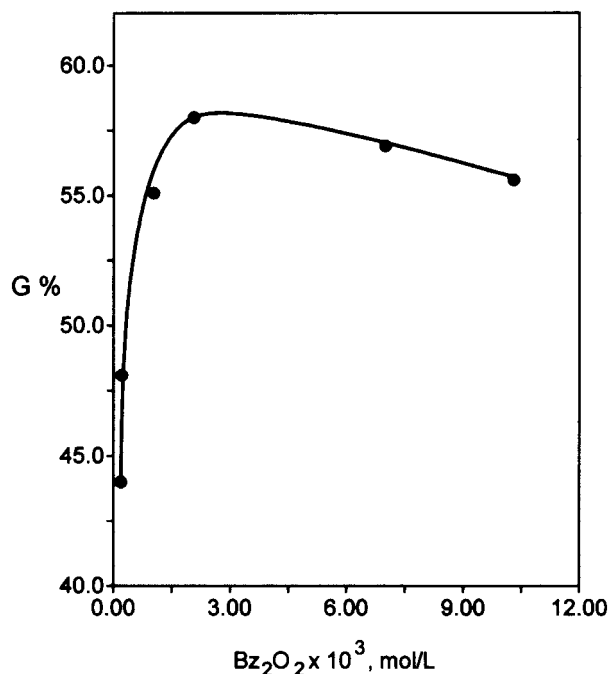


Figure 4 Change of the graft yield with initiator concentration: temperature = 80°C; time = 2 h; MMA concentration = 0.37 mol/L.

dium. The free radicals take place in many reactions in the graft-copolymerization media. They can directly interact with the gelatin backbone and form active sites. They can also initiate the homopolymerization of MMA. The active homopolyMMA chains may give chain-transfer reactions with the gelatin backbone and create active sites upon it, which, consequently, increases the graft yield.

Further increase in the concentration of Bz_2O_2 (over 0.20×10^{-2} mol/L) results in the enumeration of the number of primary radicals, gelatin radicals, and growing macroradicals of side chains which may interact with each other, causing termination and thus reducing the graft yield.^{18,20,30}

Concentration of Monomer

The effect of the monomer concentration was investigated by changing the MMA concentration from 0.20 to 0.80 mol/L and the results are plotted in Figure 5. Both the grafting rate and the saturation graft yield were observed to increase with increasing monomer concentration. The saturation graft yield increased from 25.0% at an MMA concentration of 0.20 mol/L to 128.0% at an MMA

concentration of 0.80 mol/L. There was an induction period of 10 min at an MMA concentration of 0.20 mol/L.

The increase in the monomer concentration increases the chance of the active sites upon gelatin chains and the growing polyMMA side chains to find and add monomer molecules. Since the increase in the monomer concentration increases the viscosity of the medium, the diffusion of the chains becomes highly difficult. This, in turn, reduces the termination of side PMMA chains and leads to a higher graft yield.

Properties of PolyMMA-Grafted Gelatin

The graft-yield values calculated as regards the amount of gelatin involved with grafting and the graft yields calculated for 1.00 g of the initial gelatin were compared in Table II for some experimental conditions. The graft yields calculated as regards the amount of gelatin involved with grafting showed a similar behavior with those obtained based upon 1.00 g of the initial gelatin. For instance, while the graft yield of 40.0% calculated as regards the amount of initial gelatin at 65°C increased to 53.8% at 80°C, the graft yield calculated on the basis of the gelatin involved with

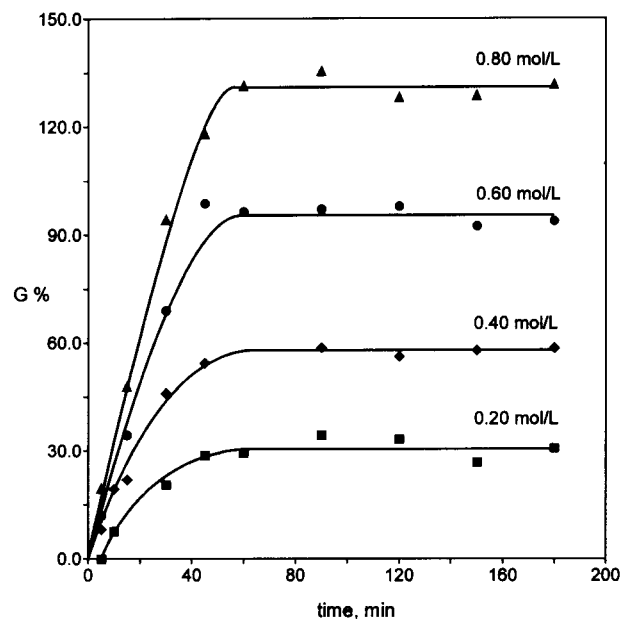


Figure 5 Change of the graft yield with monomer concentration: Temperature = 80°C; Bz_2O_2 concentration = 0.20×10^{-2} mol/L; time = 180 min.

Table II Change of Graft Yield with Time, Temperature, and Initiator Concentration Based upon the Initial Amount Gelatin ($G\%$) and the Amount of Gelatin Involved with Grafting ($RG\%$)

Experimental Conditions	$G\%$ (According to Initial Amount of Gelatin)	$RG\%$ (According to Amount of Gelatin Involved with Grafting)
Time ^a (min)		
10	38.5	71.8
15	46.9	76.5
90	64.2	78.6
Temperature ^b (°C)		
65	40.0	76.0
80	53.8	83.7
90	48.4	81.2
Concentration of Bz_2O_2 ^c (mol/L)		
0.10×10^{-2}	53.1	85.2
0.20×10^{-2}	56.2	87.4
0.20×10^{-1}	46.4	84.9

^a Bz_2O_2 concentration = 0.20×10^{-2} mol/L; MMA concentration = 0.37 mol/L; temperature = 80°C.

^b Bz_2O_2 concentration = 0.20×10^{-2} mol/L; time = 180 min; MMA concentration = 0.37 mol/L.

^c MMA concentration = 0.37 mol/L; time = 180 min; temperature = 80°C.

grafting showed an increase from 76.0 to 83.7% in the same temperature range.

Also, the graft yields computed based upon the initial amount of gelatin showed a similar decreasing trend with the graft yield calculated for the amount of gelatin involved with grafting after an optimum temperature (80°C) and initiator concentration (0.20×10^{-2} mol/L).

A calculation based upon Table II shows that the mass contribution of polyMMA in the polyMMA-grafted gelatin is higher than that of pure gelatin. The calculations made for each experiment based upon the hydrolysis data the amount of polyMMA entering to the structure of the copolymer for each initial 1.00 g of gelatin varied from 2.54 g (71.8% for the amount of gelatin involved with grafting) to 6.91 g (87.4% for the amount of gelatin involved with grafting).

Molecular Weight of the PolyMMA Side Chains

The use of gelatin in grafting offers an attractive possibility of subsequent hydrolysis of gelatin chains. This enables one to destroy the gelatin backbone and isolate the polymer branches grafted onto the gelatin. Table III tabulates the molecular weights of the polyMMA side chains isolated from the gelatin samples, grafted with varying amounts of polyMMA, by hydrolysis. The molecular weights of all side chains of polyMMA appears to be in the range of 10^6 .

The molecular weight of the polyMMA chains decreases with temperature and initiator concentration. Similar behavior was observed in the grafting of acrylonitrile using potassium persulfate.¹⁸ The increase in temperature and the initiator concentration increases the free-radical concentration in the polymerization media. The free radicals interact directly with the gelatin backbone and create a higher number of active sites suitable for grafting. The number of active sites

Table III Effect of Temperature and Initiator Concentration on Molecular Weight (M_v) of PolyMMA Branches

Experimental Conditions	$G\%$	$M_v \times 10^6$
Temperature ^a (°C)		
65	50.8	1.500
80	48.5	0.977
90	48.4	0.748
Concentration of Bz_2O_2 ^b (mol/L)		
0.10×10^{-2}	53.1	1.315
0.20×10^{-2}	56.2	1.161
0.20×10^{-1}	46.4	0.350

^a Bz_2O_2 concentration = 0.20×10^{-2} mol/L; time = 180 min; MMA concentration = 0.37 mol/L.

^b MMA concentration = 0.37 mol/L; time = 180 min; temperature = 80°C.

Table IV Effect of MMA Grafting on the Apparent Density of Gelatin

G%	Apparent Density (g/cm ³)
Ungrafted	1.1610
19.4	0.9456
30.6	0.9125
40.0	0.8089
51.5	0.7313
58.5	0.7187
78.9	0.5990
98.8	0.5777
118.2	0.5546
131.7	0.4924

formed by the transfer reactions also increases. This decreases the number of monomer molecules per side chain at a constant monomer concentration and the molecular weight of the polyMMA side chains.

Density

The apparent densities of the ungrafted gelatin and gelatin grafted with various ratios are given in Table IV. Grafting has a decreasing effect on the apparent density of the gelatin. While the density of ungrafted gelatin was 1.1610 g/cm³, this value decreased to 0.9456 g/cm³ for 19.4% polyMMA-grafted and 0.4924 g/cm³ for 131.7% polyMMA-grafted gelatin.

The weight of the polymer chains increases with grafting of MMA upon the gelatin. However, the grafting process makes the polymer chains fall apart by inserting new polyMMA chains and causes an increase in volume. Another factor which causes the increase in volume is that the inserting of new polyMMA side chains decreases the ability of gelatin to make hydrogen bonds. This prevents the packaging of the chains in a regular manner. These two causes make the increase in volume dominate the increase in weight and decrease the density.

Moisture Regain and Water Uptake

The moisture-regain and water-uptake values of polyMMA-grafted gelatin are listed in Table V. It is observed that the grafting process decreases both the moisture-regain and water-uptake values.

The decrease in moisture regain can be attributed to the hydrophobic character of the polyMMA side chains and decrease in the number of hydrophilic groups on the gelatin as a result of grafting process. Both effects lessen the moisture regain. The decrease in water uptake can be explained by the fact that the grafting process causes the formation of a crosslinked structure to a certain extent, which prevents the inserting of water molecules into the structure.

Thermogravimetric Analysis

Figure 6 shows thermograms of the ungrafted and polyMMA-grafted gelatin together. The weight loss of the pure gelatin started at 302.7°C and reached to a value of 56.8% at 600°C. The weight loss which took place in a wide temperature range in 12.0% polyMMA-grafted gelatin reached a value of 83.3% at 600°C. Two staged thermograms for higher grafted gelatin were observed. For instance, in 118.2% polyMMA-grafted gelatin, there were two weight-loss points at 369.4 and 394.4°C. The total weight loss for this sample was 89.4% at 600°C.

At higher graft yield values, the decomposition temperature of polyMMA-grafted gelatin samples was observed to increase. The increase in thermal stability up to 600°C in polyMMA-grafted gelatin may be due to the late decomposition of polyMMA, thus increasing the overall thermal stability of the grafted samples.

CONCLUSIONS

In this study, it was shown that MMA can be grafted upon gelatin using Bz₂O₂ as an organic initiator in aqueous medium. The optimum tem-

Table V Effect of MMA Grafting on the Moisture Regain and Water Uptake of Gelatin

G%	Moisture Regain (%)	Water Uptake (%)
Ungrafted	60.0	87.8
8.1	46.6	74.1
30.6	38.8	68.9
40.0	36.4	71.4
118.2	6.5	45.8
131.7	3.8	30.0

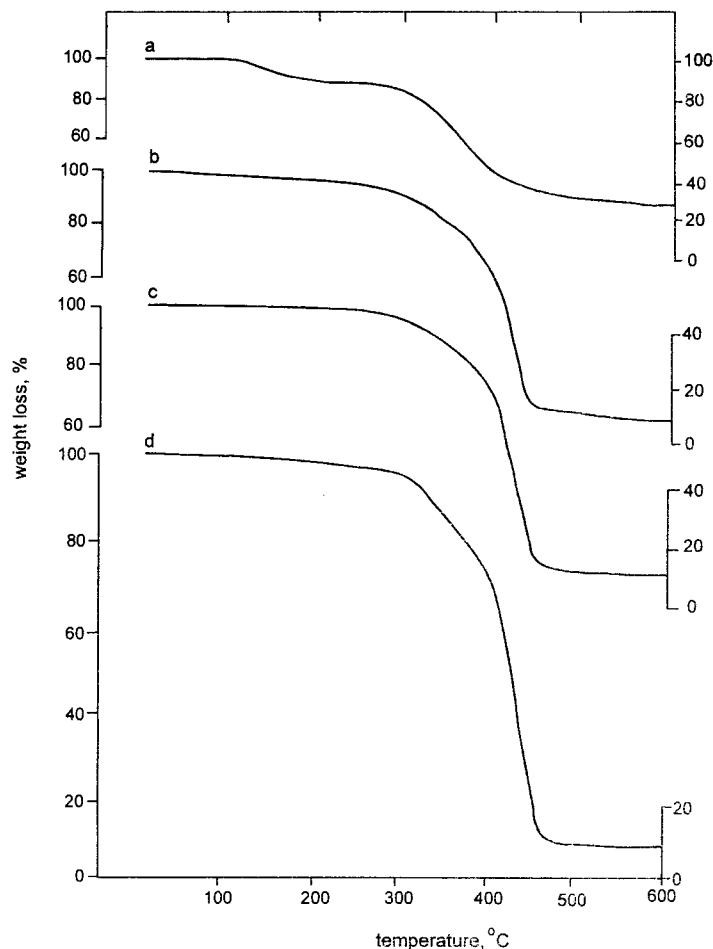


Figure 6 TGA curves of (a) pure gelatin, (b) 12.0% polyMMA-grafted gelatin, (c) 56.2% polyMMA-grafted gelatin, and (d) 118.2% polyMMA-grafted gelatin obtained in nitrogen atmosphere at heating rate of 10°C/min.

perature and initiator concentration are 80°C and 0.20×10^{-2} mol/L, respectively, to obtain a higher graft yield. No optimum value for the monomer concentration and the graft yield was observed to increase with the monomer concentration in the experiments carried out in a concentration range of 0.20 and 0.80 mol/L. The grafting process was observed to have a marked effect upon the moisture-regain and water-up-take values of the gelatin. A significant decrease in both these parameters after grafting was observed. Finally, the thermal stability of the gelatin was found to increase after being grafted with polyMMA.

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