

Graft Copolymerization of Methyl Methacrylate onto Gelatin Using $\text{KMnO}_4\text{-H}_2\text{SO}_4$ Redox System

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ABSTRACT: The graft copolymerization of methyl methacrylate onto gelatin was studied using $\text{KMnO}_4\text{-H}_2\text{SO}_4$ redox system. The maximum graft yield of 64.5% was obtained at the potassium permanganate concentration of 2.00×10^{-3} mol/L and the optimum temperature of 50°C. Activation energy was calculated as 18.6 kcal/mol at the temperature interval of 40–70°C. The results of the thermogravi-

metric analysis showed that the degradation temperature of gelatin increased as a result of grafting. Moreover, some changes in the properties of methyl methacrylate-grafted samples were also observed. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2836–2844, 2003

Key words: copolymerization; graft copolymer; density

INTRODUCTION

Graft copolymerization is one of the methods to improve the properties of the natural^{1–4} and synthetic polymers.^{5–8} When using graft copolymerization, it is a goal that the host polymer gains some of the desired properties of monomer(s) used for grafting.

Gelatin is one of the natural polymers that was attempted to be modified by the graft polymerization. Due to its unique properties gelatin is widely used in food, gummed tapes, adhesives, and as a colloid to prevent coalescence. Due to the various potential uses of gelatin, it is worthwhile to investigate its modification to develop new materials with improved properties.

Vinyl monomers such as methacrylonitrile,¹ acrylonitrile,^{1,4} methyl acrylate,⁹ butyl acrylate,¹⁰ and ethyl acrylate¹¹ can be grafted onto gelatin by various techniques. There are also some studies concerned with grafting methyl methacrylate (MMA) onto gelatin in the literature. Klasek et al.¹² used $\text{HSO}_3^- \text{-S}_2\text{O}_8^{2-}$ as initiator in the grafting of MMA. Stejskal et al.¹³ investigated the grafting of MMA onto gelatin using $(\text{NH}_4)_2\text{S}_2\text{O}_8$.

However, there is no detailed study in literature concerning the MMA grafting onto gelatin in aqueous media using $\text{KMnO}_4\text{-H}_2\text{SO}_4$ redox system. The present article discusses the grafting of MMA onto gelatin using this redox system. Besides the investigation of the effects of temperature, and the concentra-

tion of monomer, initiator, and acid on grafting, some properties of MMA grafted gelatin such as moisture regain, water uptake, and density were also investigated. Furthermore, the grafted gelatins were characterized using techniques such as thermogravimetric analysis and infrared (IR) spectroscopy.

EXPERIMENTAL

Materials

The granulated gelatin (molecular weight = 18,000 g/mol; Merck, Germany) was used as purchased. MMA (Merck) was washed with 5% NaOH three times, dried over CaCl_2 , and distilled under vacuum at 46°C. KMnO_4 (Merck) and the other chemicals were used as purchased without any further treatment.

Graft copolymerization

Gelatin (1.00 ± 0.01 g) was placed in a 50 mL polymerization tube and KMnO_4 at a suitable concentration dissolved in 5 mL H_2SO_4 solution (Merck, Germany) was added to it. The total volume was made up to 30 mL with 1.00×10^{-2} M H_2SO_4 solution prepared using distilled water. The mixture was then placed in a water bath (Lauda D40 S, Germany) and the temperature was controlled within $\pm 0.1^\circ\text{C}$. At the end of polymerization, the polymerization tube was taken from the water bath, 100 mL of acetone was added to it, and so the precipitated gross polymer was recovered by filtration.

Characterization

Isolation of grafted gelatin

Gross polymer contains ungrafted gelatin and homopolyMMA together with polyMMA grafted gela-

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tin. Selective solvent extraction technique was used to extract pure PMMA and ungrafted gelatin from that mixture.^{14,15} For the removal of ungrafted gelatin, gross polymer was decanted with boiling water by changing the washing water at least three times for 2 h. It was then Soxhlet-extracted with acetone for 1 h to remove homopolyMMA. The residue was assumed to be polyMMA grafted gelatin.

Apparent grafting was based upon the weight of initial gelatin (1.00 g):

$$\text{Apparent Grafting} = (w_g/w_i) \times 100 \quad (1)$$

where w_g and w_i denote the weights of the polyMMA grafted gelatin and initial gelatin, respectively. In the figures, G% stands for apparent grafting.

Hydrolysis of polyMMA grafted gelatin and molecular weight measurements

The grafted samples were hydrolyzed by refluxing them in 15 mL 6N HCl for 9 h.¹⁶ PolyMMA is resistive against hydrolysis with acids and shows its own IR spectrum after being treated with 6N HCl at 100–110°C for 9 h.¹⁷ After the hydrolysis the remaining polyMMA-grafted chains were filtered, washed, and weighted.

The initial gelatin weight of 1.00 g was taken as the basis of the calculation of the graft yield. However, because the washing process with water removes the ungrafted gelatin, the amount of gelatin in the grafted samples decreases. 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_g) was determined by subtracting the weight of polyMMA (w_m) obtained after the hydrolysis from the weight of the polyMMA-grafted gelatin (w_g). True grafting, based upon the amount of gelatin involved with grafting, was calculated from the relation:

$$\text{True Grafting} = (w_m/w_a) \times 100 \quad (2)$$

The molecular weight of the grafted polyMMA branches was determined by viscosimetric measurements at 25°C, based upon the relation¹⁸ $[\eta] = 7.5 \times 10^{-5} Mw^{0.70}$. A 0.5% solution of the polymer in acetone was used in the measurements.

IR spectra

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

Thermogravimetric analysis

The thermogravimetric analysis was performed using a Rheometric Scientific 1000+ Model thermal analyzer. The samples were heated up to 600°C starting from the room temperature with a heating rate of 10°C/min in a 200 mL/min N₂ atmosphere.

Density measurements

The densities of the samples were determined at 23°C using the density gradient tube prepared by carbon tetrachloride and xylene. The levels of the glass floats (made by Davenport Ltd., the density of which is known within 1/10,000) and the samples were determined with the help of a cathetometer (within a sensitivity of ±0.01 mm).

Moisture regain

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

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 filter paper. The water uptake of the grafted samples was determined from the weights of the dry and the wet samples.

RESULTS AND DISCUSSION

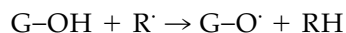
KMnO₄, which was used as initiator in our study, forms MnO₂ in acidic medium. As a result of the reaction between MnO₂ and acid, primary radical species form in the polymerization medium. The types of radical species depend on the nature of the acid used.¹⁹ For example, H₂SO₄ and MnO₂ react to form sulfate ion:



Other free radical species such as hydroxyl radicals may also be formed:



These radical species produce active centers onto gelatin chains by the abstraction of hydrogen atoms from the hydroxyl groups of the gelatin:



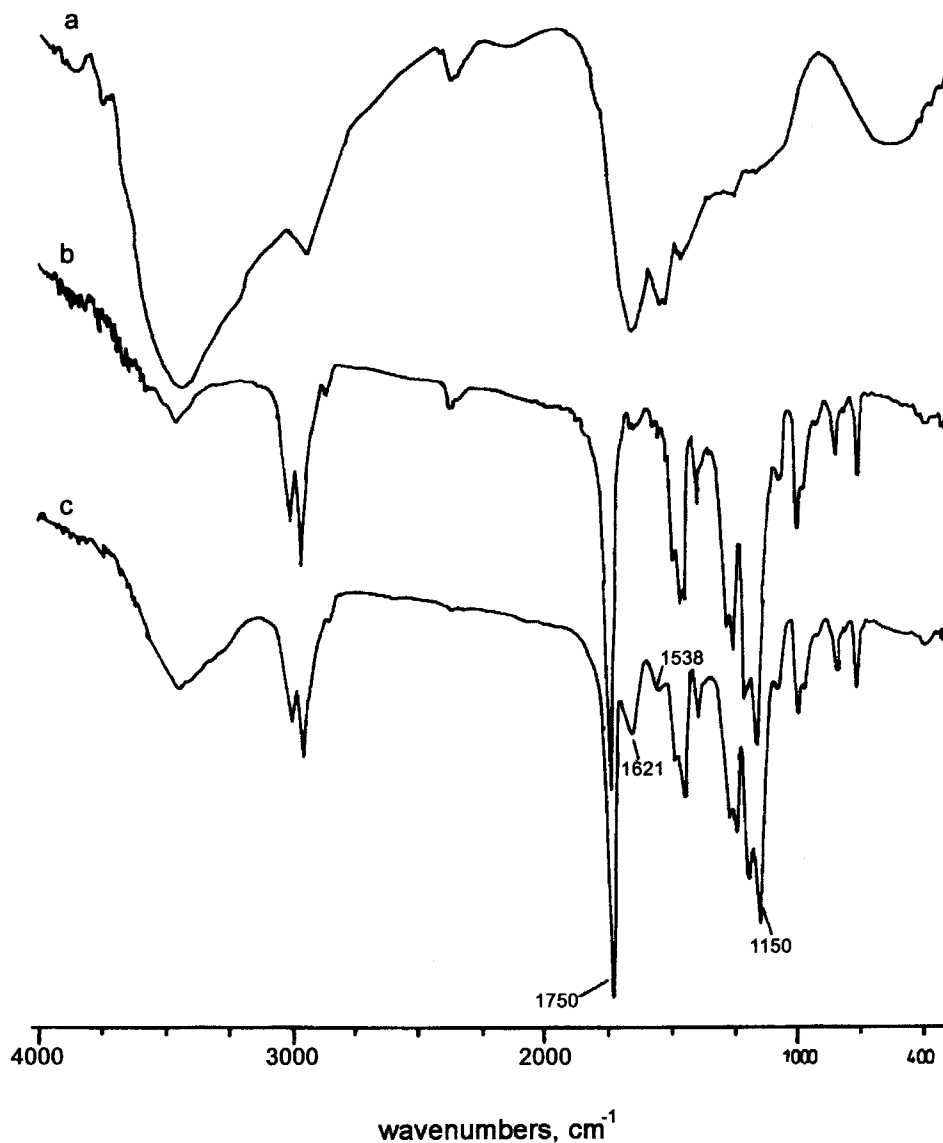


Figure 1 The FTIR spectra of (a) pure gelatin, (b) pure polyMMA, and (c) %64.5 polyMMA-grafted gelatin.

where R' is SO_4^- or OH .

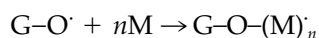
Gelatin macroradicals may also occur by the following reactions:



or



Once the gelatin macroradicals are produced, the monomer molecules add rapidly to it to give a graft polymer:



Termination of the grafting may take place in one of the chain transfer or combination reactions involving the growing grafted chain radical.¹⁴

Evidence of grafting

FTIR spectra

IR spectra of the pure gelatin, pure MMA, and 64.5% polyMMA-grafted gelatin are shown in Figure 1(a), 1(b), and 1(c), respectively. The spectrum of polyMMA-grafted gelatin displays bands at 1621 and 1538 cm^{-1} due to the amide groups upon the pure gelatin, as well as bands at 1750 and 1150 cm^{-1} coming from the carboxyl groups of pure polyMMA.

Hydrolysis of polyMMA-grafted gelatin results in degradation of gelatin backbone and facilitates the liber-

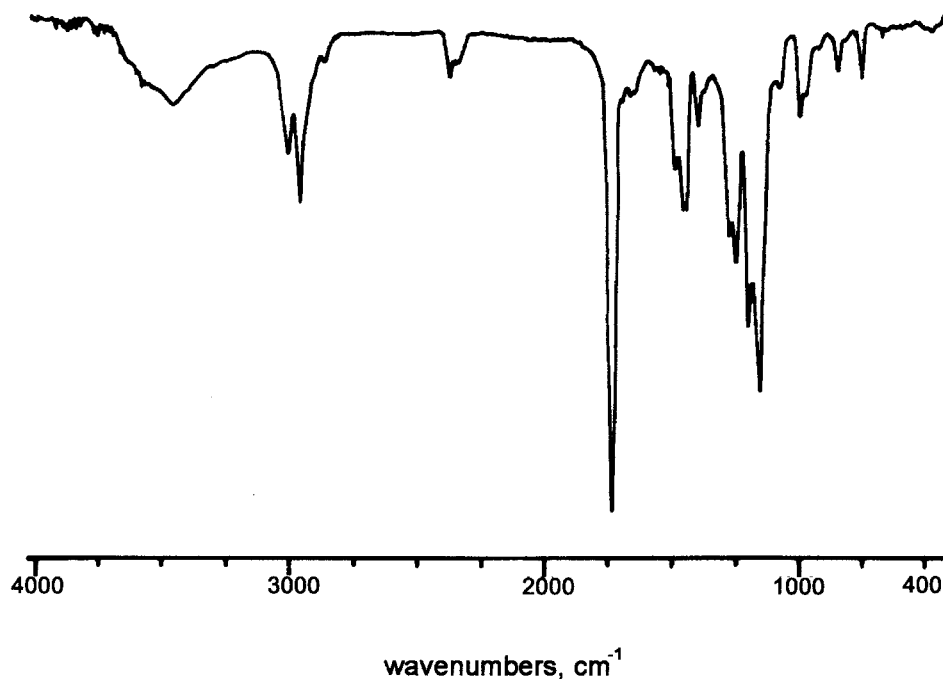


Figure 2 The FTIR spectra of polyMMA branches separated after hydrolysis of polyMMA-grafted gelatin.

ation of polyMMA. The hydrolysis process is not detrimental for polyMMA at our experimental conditions.¹³ The FTIR spectra of polyMMA obtained after the hydrolysis are given in Figure 2. Figure 2 displays characteristic bands similar to those in Figure 1(b) for pure polyMMA. This similarity proves the existence of polyMMA in the graft copolymer structure. The weight of 0.390 g sample of polyMMA-grafted gelatin decreased to 0.236 g after hydrolysis, which also indicates the existence of the gelatin in polyMMA-grafted gelatin.

Treatment of isolated grafts with ninhydrin reagent

Grafting can be verified by detection of amino acid end groups in the remaining solution by treatment with ninhydrin reagent after the hydrolysis of polyMMA-grafted gelatin.¹¹ The characteristic blue color associated with the presence of amino acids after this procedure was observed.

Influence of reaction parameters

Reaction time and temperature

Variation of graft yield with temperature was studied within the temperature range of 30–70°C and the experimental data obtained are shown in Figure 3. Graft yield reached a maximum value of 64.5% at 50°C and then showed a decrease to 50.0% at 70°C. An induction period of 30, 10, and 5 min was observed at lower temperatures used, namely 30, 40, and 50°C. Because termination reactions predominate, the graft yield decreases at higher temperatures.²⁰

The initial rates of grafting (R_g) calculated for the experimental temperatures are given in Table I. Figure 4 was plotted using the data given in Table I. The

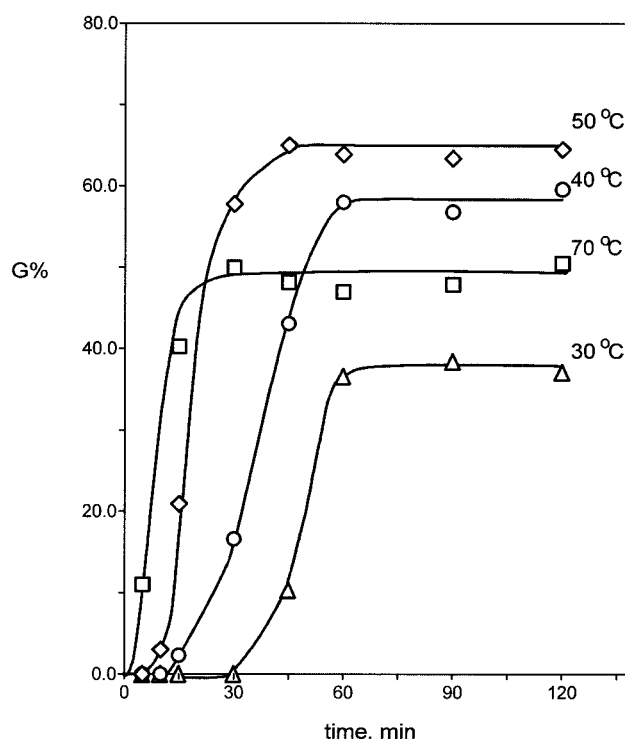


Figure 3 Change of the graft yield with temperature and the polymerization time: gelatin concentration = 1.85×10^{-3} mol/L, KMnO_4 concentration = 2.00×10^{-3} mol/L, MMA concentration = 0.25 mol/L, H_2SO_4 concentration = 1.00×10^{-2} mol/L.

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

Temperature (°C)	$R_g \times 10^3$ (mol L ⁻¹ s ⁻¹)	$1/T \times 10^3$	$\log R_g + 4$
40	0.85	3.195	0.930
50	7.74	3.096	1.888
60	8.22	3.003	1.915
70	1.49	2.911	2.174

^a Gelatin concentration = 1.85×10^{-3} mol/L, KMnO_4 concentration = 2.00×10^{-3} mol/L, MMA concentration = 0.25 mol/L, H_2SO_4 concentration = 1.00×10^{-2} mol/L, time = 15 min.

slope of $\log R_g$ versus $1/T$ graph showed that the overall activation energy for grafting within the temperature range of 40–70°C is 18.6 kcal/mol.

Concentration of initiator

To investigate the effects of initiator concentration on the graft yield, the temperature and the concentration of gelatin and MMA were kept unchanged, and KMnO_4 concentration was increased from 0.50×10^{-3} mol/L to 12.00×10^{-3} mol/L. The results are given in Figure 5. As shown in Figure 5, the maximum graft yield (64.5%) was obtained at the initiator concentration of 2.00×10^{-3} . A rapid increase in graft yield was observed up to this optimum initiator concentration and the graft yield decreased after this point. Higher concentration of KMnO_4 causes acceleration of the termination reactions and this leads to the decrease in the graft yield.²¹

Concentration of monomer

Experimental results obtained at the different concentrations of MMA are shown in Figure 6. It was ob-

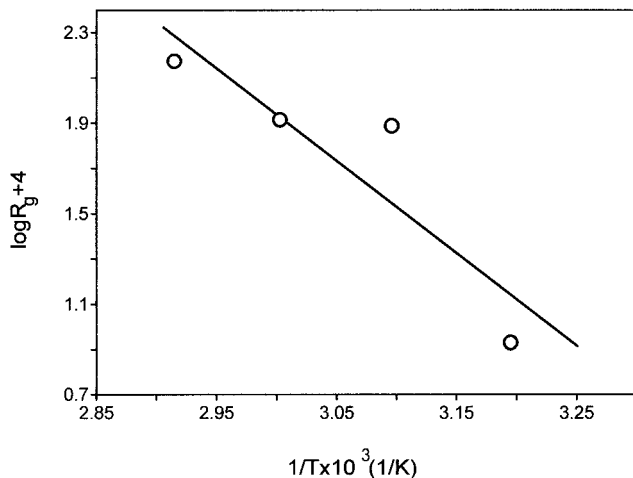


Figure 4 $1/T$ versus $\log R_g$ plot for grafting of MMA onto gelatin using KMnO_4 .

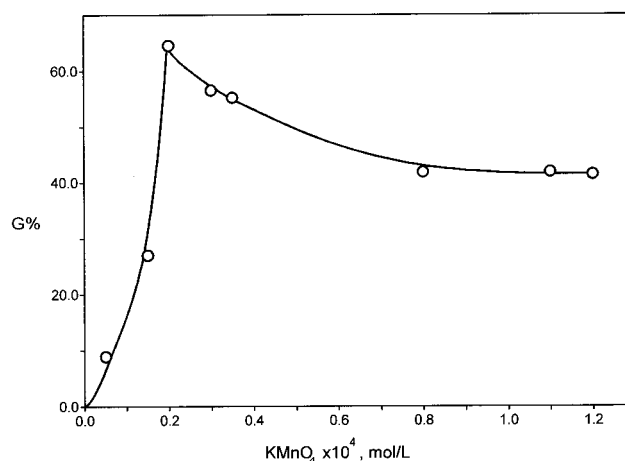


Figure 5 Change of the graft yield with initiator concentration: temperature = 50°C, time = 120 min, MMA concentration = 0.25 mol/L, gelatin concentration = 1.85×10^{-3} mol/L, H_2SO_4 concentration = 1.00×10^{-2} mol/L.

served that the graft yield increased up to a monomer concentration of 0.37 mol/L and then decreased. The highest graft yield was found to be 64.5% at 0.25 mol/L MMA concentration.

The induction period was decreased with the increasing monomer concentration. For the monomer

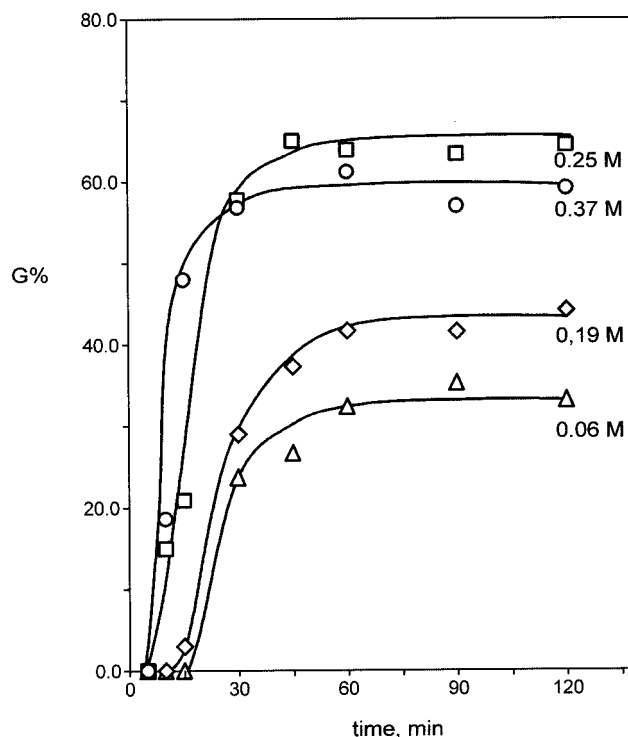


Figure 6 Change of the graft yield with monomer concentration: temperature = 50°C, KMnO_4 concentration = 2.00×10^{-3} mol/L, time = 120 min, gelatin concentration = 1.85×10^{-3} mol/L, H_2SO_4 concentration = 1.00×10^{-2} mol/L. MMA concentration: Δ = 0.06 mol/L; \diamond = 0.19 mol/L; \square = 0.25 mol/L; \circ = 0.37 mol/L.

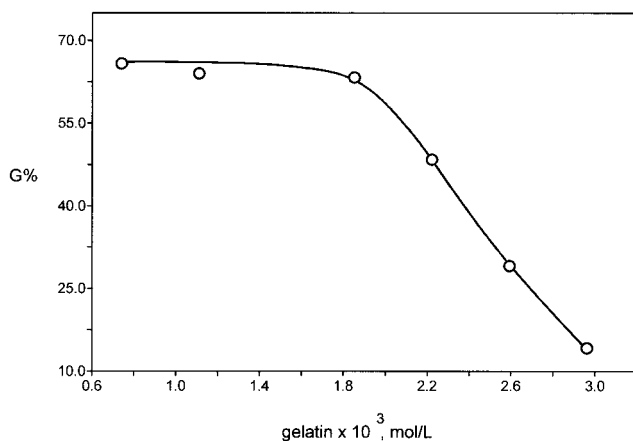


Figure 7 Change of the graft yield with gelatin concentration: MMA concentration = 0.25 mol/L, KMnO_4 concentration = 2.00×10^{-3} mol/L, H_2SO_4 concentration = 1.00×10^{-2} mol/L, time = 120 min, temperature = 50°C.

concentrations of 0.06, 0.19, 0.25, and 0.37 mol/L MMA grafting was not observed within the first 15, 10, and 5 min for the last two samples, respectively.

Concentration of gelatin

Figure 7 presents the results of the experiments that were performed at different gelatin concentrations. It was found that the higher graft yields were obtained at lower gelatin concentrations. This can be explained by the fact that at higher gelatin concentration more active sites are formed upon the gelatin backbone. These active sites may interact with each other and lead to termination of side chains.²

Concentration of acid

For the investigation of the effect of acid concentration on the graft yield, grafting experiments were carried out with various concentrations of H_2SO_4 , HNO_3 , and HCl while other conditions were kept unchanged. Figure 8 shows the experimental results. The graft yield increased up to a critical acid concentration for acids examined and then decreased. Decrease in the graft yield at higher acid concentrations can be explained by the hydrolysis and decomposition of the gelatin because of the acids.²²

Properties of polyMMA-grafted gelatin

Table II shows the apparent graft yield and true graft yield values, which are based on the initial amount of the gelatin and the amount of gelatin involved with grafting, respectively. The true graft yield values show a trend similar to the apparent graft yield values, which are based on the initial amount of gelatin. For instance, the apparent graft yield was found as 37.1%

at 30°C, and then increased to 50.0% at 70°C. Similarly, the true graft yield value of 100.0% at 30°C was increased to 128.8% at 70°C.

Molecular weight of the polyMMA side chains

Gelatin is easily hydrolyzed to amino acids and grafted polymer can be isolated. In Table III, molecular weights of the polyMMA side chains are given for various experimental conditions. The molecular weights of all side chains of polyMMA appear to be in the range of 10^6 .

It was observed that the molecular weight of the polyMMA chains decreased with the increasing temperature and initiator concentration. As mentioned in our previous work, the increase in temperature and initiator concentration increases the free radical concentration in the polymerization media.¹⁴ Free radicals interact directly with the gelatin backbone and create a higher number of active sites suitable for grafting. An increase in the number of active sites on the backbone and a higher rate of chain transfer reactions results in graft chains of lower molecular weight. Moreover, the chain transfer reactions, which take place during the polymerization process, are also effective in reducing the molecular weight. It was also observed that the molecular weight of the side chains and graft yield showed an increase up to a critical value of monomer concentration and then started to decrease.

The molecular weight of side chains increased with reaction time. However, insignificant change in molecular weight was observed with the three acids used at the same concentration.

Density

Effect of MMA grafting on the density of gelatin is given in Table IV. The density of gelatin decreases

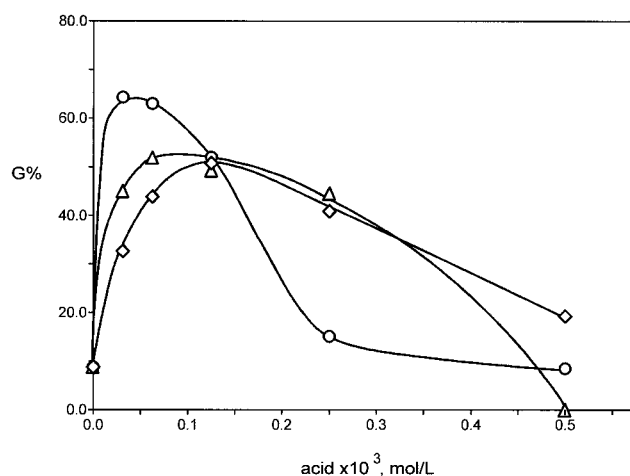


Figure 8 Change of the graft yield with acid concentration: Δ = HNO_3 , \diamond = HCl , \circ = H_2SO_4 , gelatin concentration = 2.78×10^{-3} mol/L, KMnO_4 concentration = 2.00×10^{-3} mol/L, MMA concentration = 0.31 mol/L, time = 120 min, temperature = 50°C.

TABLE II
Change of Apparent Grafting (G%) and True Grafting with Time, Temperature, and Concentrations of Initiator, MMA, and Acid

Experimental conditions	Apparent grafting (%)	True grafting (%)
Time ^a (min)		
45	65.0	153.2
60	63.9	182.4
120	64.5	175.0
Temperature ^b (°C)		
30	37.1	100.0
50	57.8	186.8
70	50.0	128.8
Concentration of KMnO ₄ ^c (mol/L)		
2.00 × 10 ⁻³	64.5	175.0
2.50 × 10 ⁻³	55.7	217.8
3.00 × 10 ⁻³	56.5	228.8
3.50 × 10 ⁻³	55.2	202.8
Concentration of MMA ^d (mol/L)		
0.19	41.7	138.5
0.25	64.5	175.0
0.37	49.7	81.5
Concentration of acid ^e (mol/L)		
3.13 × 10 ⁻³ HNO ₃	45.0	83.2
3.13 × 10 ⁻³ H ₂ SO ₄	64.3	84.2
3.13 × 10 ⁻³ HCl	32.7	109.3

^a Gelatin concentration = 1.85 × 10⁻³ mol/L, KMnO₄ concentration = 2.00 × 10⁻³ mol/L, MMA concentration = 0.25 mol/L, H₂SO₄ concentration = 1.00 × 10⁻² mol/L, temperature = 50°C.

^b Gelatin concentration = 1.85 × 10⁻³ mol/L, KMnO₄ concentration = 2.00 × 10⁻³ mol/L, MMA concentration = 0.25 mol/L, H₂SO₄ concentration = 1.00 × 10⁻² mol/L.

^c Gelatin concentration = 1.85 × 10⁻³ mol/L, MMA concentration = 0.25 mol/L, H₂SO₄ concentration = 1.00 × 10⁻² mol/L, time = 120 min, temperature = 50°C.

^d Gelatin concentration = 1.85 × 10⁻³ mol/L, KMnO₄ concentration = 2.00 × 10⁻³ mol/L, H₂SO₄ concentration = 1.00 × 10⁻² mol/L, time = 120 min, temperature = 50°C.

^e Gelatin concentration = 2.78 × 10⁻³ mol/L, KMnO₄ concentration = 2.00 × 10⁻³ mol/L, MMA concentration = 0.31 mol/L, time = 120 min, temperature = 50°C.

with grafting. The density of ungrafted gelatin was 1.1610 g/cm³, but it was found to decrease to 0.9203 g/cm³ for 41.6% polyMMA-grafted samples. The grafting process makes the gelatin chains in solid form fall apart by inserting new polyMMA chains, which brings about an increase in volume. Additionally, inserting new polyMMA chains reduces the ability of gelatin to make hydrogen bonds, which prevents the packing of the chains in regular form, which causes an increase in volume. Because the increase in volume dominates the increase in the weight, the density of polyMMA-grafted gelatin decreases with grafting.⁵

Moisture regain and water uptake

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

TABLE III
Effect of the Temperature, Time, and Concentrations of Initiator, Monomer, and Acid on the Molecular Weight (*M_w*) of PolyMMA Branches

Experimental conditions	Apparent grafting (%)	<i>M_w</i> × 10 ⁶
Temperature ^a (°C)		
30	37.1	1.720
50	57.8	1.520
70	50.0	1.130
Concentration of KMnO ₄ ^b (mol/L)		
2.00 × 10 ⁻³	64.5	1.990
2.50 × 10 ⁻³	55.7	1.730
3.00 × 10 ⁻³	56.5	1.190
3.50 × 10 ⁻³	55.2	0.460
Time ^c (min)		
45	65.0	0.720
60	63.9	1.260
120	64.5	1.990
Concentration of MMA ^d (mol/L)		
0.187	41.7	0.890
0.249	64.5	1.990
0.374	49.7	0.950
Concentration of acid ^e (mol/L)		
3.13 × 10 ⁻³ HNO ₃	45.0	1.110
3.13 × 10 ⁻³ H ₂ SO ₄	64.3	1.060
3.13 × 10 ⁻³ HCl	32.7	0.980

^a Gelatin concentration = 1.85 × 10⁻³ mol/L, KMnO₄ concentration = 2.00 × 10⁻³ mol/L, MMA concentration = 0.25 mol/L, H₂SO₄ concentration = 1.00 × 10⁻² mol/L.

^b Gelatin concentration = 1.85 × 10⁻³ mol/L, MMA concentration = 0.25 mol/L, H₂SO₄ concentration = 1.00 × 10⁻² mol/L, time = 120 min, temperature = 50°C.

^c Gelatin concentration = 1.85 × 10⁻³ mol/L, KMnO₄ concentration = 2.00 × 10⁻³ mol/L, MMA concentration = 0.25 mol/L, H₂SO₄ concentration = 1.00 × 10⁻² mol/L, temperature = 50°C.

^d Gelatin concentration = 1.85 × 10⁻³ mol/L, KMnO₄ concentration = 2.00 × 10⁻³ mol/L, H₂SO₄ concentration = 1.00 × 10⁻² mol/L, temperature = 50°C.

^e Gelatin concentration = 2.78 × 10⁻³ mol/L, KMnO₄ concentration = 2.00 × 10⁻³ mol/L, MMA concentration = 0.31 mol/L, time = 120 min, temperature = 50°C.

the moisture regain and water uptake values of the polyMMA-grafted gelatin.

Moisture regain values of the materials are closely related with their structures. Those materials that contain hydrophilic groups such as —OH in their structure have higher moisture regain values. The decrease in moisture regain value is a result of the hydrophobic character of the MMA.

TABLE IV
Effect of MMA Grafting on the Density of Gelatin

Apparent grafting (%)	Density (g/cm ³)
Ungrafted	1.1610
2.3	0.9932
9.2	0.9361
21.5	0.9336
41.6	0.9203

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

Apparent grafting (%)	Moisture regain (%)	Water uptake (%)
Ungrafted	60.0	87.9
8.2	32.3	78.6
21.5	24.7	75.7
41.7	23.3	65.1
49.7	21.3	60.4

The grafting process may also cause the formation of a crosslinked structure that prevents the inserting of water molecules into the structure. As a result of this

structural change, water uptake values of polyMMA-grafted gelatin decrease.

Thermogravimetric analysis

In Figure 9, thermograms of the pure gelatin, pure polyMMA, and polyMMA-grafted gelatin are shown. The weight loss of the pure gelatin reached 76.09% at 600°C. At the same temperature, weight loss of 22.2% polyMMA-grafted sample was 83.50%, but for the 64.5% grafted sample it was 88.00%.

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

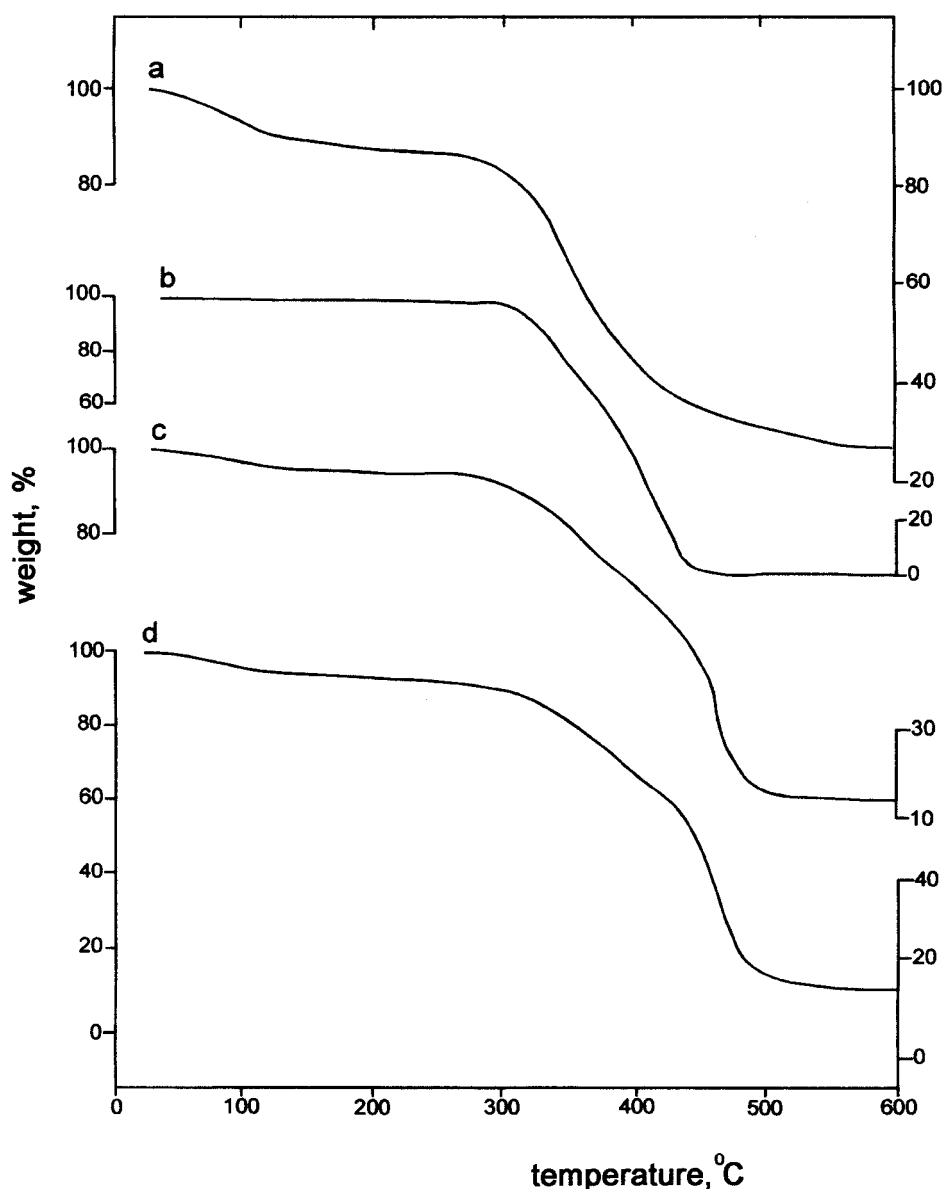


Figure 9 TGA curves of (a) pure gelatin, (b) pure PMMA, (c) 22.2% polyMMA-grafted gelatin, and (d) 64.5% polyMMA-grafted gelatin obtained in nitrogen atmosphere at a heating rate of 10°C/min.

to the anhydride formed by the neighboring ester moiety of the MMA.

CONCLUSIONS

This study shows that MMA can be grafted onto gelatin using H_2SO_4 - KMnO_4 redox system. The highest graft yield (64.5%) was obtained with the initiator and monomer concentrations of 2.00×10^{-2} mol/L and 0.25 mol/L at 50°C , respectively. It was observed that grafting has a marked effect on some properties of gelatin such as density, moisture regain, and water uptake. Increasing graft yield resulted in decrease of density, moisture regain, and water uptake capacity of gelatin. Besides, decomposition temperature of the copolymers increased with the increasing graft yield.

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