Grafting Emulsion Polymerization of Glycidyl Methacrylate onto Leather by Chemical Initiation Systems

K. A. Shaffei,[1] A. B. Moustafa,[2] W. S. Mohamed[2]

[1]*Department of Polymer Chemistry, Helwan University, Ain Helwan, Cairo, Egypt*
[2]*Depatment of Polymers and Pigments, National Research Centre*

ABSTRACT: The kinetics of the grafting polymerization of glycidyl methacrylate (GMA) onto leather were studied with chemical initiation systems. The results showed that the rate of grafting of GMA onto leather was dependent on different rates in the chemical initiation systems; for ammonium persulfate (AmPS)/acetone sodium bisulfite (ASBS), potassium persulfate (PPS)/ASBS, and sodium persulfate (SPS)/ASBS, the powers were 1.06, 0.48, and 0.43 and 0.63, 0.46, and 0.43, respectively, with respect to the concentration of the emulsifier sodium dodecyl sulfate, whereas the powers were 1.41, 0.70, and 0.81, respectively, with respect to the monomer concentration. The apparent activation energy was calculated for each initiation system and was found to be 180.8, 361.63, and 542.45 kcal for the AmPS/ASBS, PPS/ASBS, and SPS/ASBS systems, respectively. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 3923–3931, 2008

Key words: activation energy; hardness; kinetics (polym.)

INTRODUCTION

A variety of polymerized monomers grafted onto natural and synthetic polymers have been successfully developed, but grafting by free-radical polymerization is a widely used method that can be created with a chemical initiation system.[1–10]

Musina et al.[11] found an anomalous effect of a copper and hydrogen peroxide compound in oxidation–reduction on the graft polymerization rate of glycidyl methacrylate (GMA). The graft polymerization in the presence of an oxidation–reduction system was characterized by a high rate, and the conversion of the monomer occurred without homopolymer formation.

Arimas et al.[12] improved the quality of leather for shoes by using a GMA and methacrylate copolymer finishing agent developed for combination with microparticle collagen under roller coating conditions.

Iwakura et al.[13] examined the tensile strength (TS), elongation, and elastic recovery of cellulose fibers grafted with GMA. They found that denier and recovery increased with an increase in the grafting content, but the TS and elongation decreased.

The grafting of acrylate monomers onto collagenous or soluble collagenous substrates, leather, and hide powder has been discussed previously.[14,15] Grafting polymerization has been initiated by differ-ent initiation systems, including Ce(IV) ions,[16] potassium permanganate,[7] and potassium persulfate (PPS),[17] as well as redox system such as PPS/ascorbic acid[18] and persulfate/bisulfite redox systems.[19,20] The improvement of the properties of leather can be accomplished with different techniques; one of them is the grafting emulsion polymerization of a monomer onto leather by chemical and radiation initiators.[21,22] However, the second one is performed with a latex polymer as a finishing agent to modify different leather properties, such as the blustering agent,[23] water resistance,[24] and quality of the leather.[25,26]

The aim of this work was to choose a suitable polymer and apply it as a grafting material to leather with the aim of adding some good properties to the leather without the loss of any of its initial properties. That is why we chose poly(glycidyl methacrylate) (PGMA).

EXPERIMENTAL

Materials

Leather

Chrome-tanned cow leather, supplied by 6-October Tanner (Misr, Cairo, Egypt), was selected for this investigation. The leather was washed with water, drained, and finally neutralized.

Neutralization

The neutralization process was designed to remove the free acids present in the mineral-tanned leather

or those that formed during leather storage. The leather pieces were washed with water for about 30 min in a drum. The water was then drained off, 1% calcium formate was added to the water and followed by sodium bicarbonate, and the drum was left for 40 min.

The neutralized leather pieces were washed with water for about 10 min and dried between 2 pieces of filter paper. The neutralization processes facilitated penetration of the monomer; in addition, the grains were made smoother and remained firm.

The leather samples were cut into the desired shapes (5 cm × 1 cm dumbbell-shaped strips with a narrow neck 4 mm wide); some of these pieces were used as blanks, and the others were used for grafting.

Chemicals

Monomer

Merck (Schuchardt Germany) provided GMA, which was redistilled before use and stored at $-20°C$.

Initiators

PPS, ammonium persulfate (AmPS), and sodium persulfate (SPS) were supplied by Merck. Sodium bisulfite was a product of El-Naser Pharmaceutical Chemical Co. (Cairo, Egypt).

Emulsifier

Sodium dodecyl sulfate (SDS) was obtained from El-Naser Pharmaceutical Chemical.

Other substances

Merck supplied butanol, toluene, and acetone.
Ferrous ammonium sulfate (FAS) was supplied by BDH Co. (England), along with distilled water.

Preparation of the sodium bisulfite adducts

Acetone sodium bisulfite (ASBS) was prepared by the addition of acetone to a supersaturated solution of sodium bisulfite (SBS) in water (ca. 25 g of SBS in 200 mL of water); the product, obtained by filtration, was purified with ethanol, dried *in vacuo* at a low temperature, and kept in dark bottles.[27]

Chemical grafting method

GMA monomer was added to a conical flask containing an emulsifier solution, toluene, butanol, and leather according to the recipe given in Table I. The flask components were mechanically stirred at 200

TABLE I
Components Used in the Chemical Grafting Polymerization

Component	Amount	Function
Leather	Constant	Substrate
AmPS	Variable	Initiator
PPS	Variable	Initiator
SPS	Variable	Initiator
ASBS	Variable	Initiator
GMA	Variable	Monomer
SDS	Variable	Emulsifier
Water	Variable	Medium
Butanol	Constant	Comedium
Toluene	Constant	Comedium
FAS	Constant	Inhibition of the homopolymer formation

rpm for 30 min; ferrous ammonium sulfate and the initiator were added to the flask, and the graft polymerization was continued for 150 min at the desired temperature. The homopolymer was extracted from the grafted leather by Soxhlet extraction with toluene until a constant weight of the leather was obtained.

The grafting yield was calculated according to the following equation:

$$\text{Grafting yield} = (w_2 - w_1)/w_1 \times 100$$

where w_2 is the weight of the grafted leather and w_1 is the weight of the ungrafted leather.

Determination of the rate of grafting

The rate of grafting polymerization (R_G) was determined with the following equation:

$$R_G = P/mtV \text{ (mol I/s)}$$

where m is the molecular weight of the monomer, V is the volume of the aqueous phase (L), t is the time (s), and P is the weight of the polymer grafted onto the leather divided by the molecular weight of the monomer.

Determination of the water absorption

The test for the determination of the water absorption capacity was based on the immersion of circle specimens into water for different times (15 min, 2 h, and 24 h) at room temperature. The water absorption capacity (ω) was determined with the following relationship:[25]

$$\omega = (W - W_o)/W_o \times 100$$

where W is the weight of the grafted leather after immersion in water and W_o is the weight of the grafted leather.
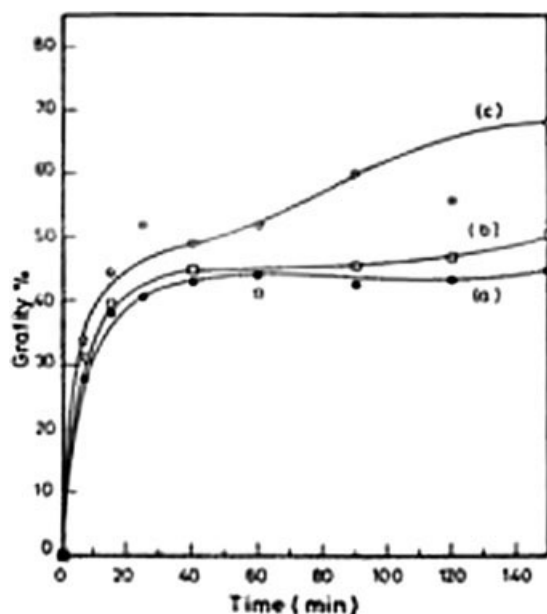
Figure 1 Grafting percentage/time dependence on the initiator concentration of AmPS/ASBS with [SDS] = 2.87 × 10^{-2} mol/L, [GMA] = 0.35 mol/L, temperature = 50°C, and [AmPS/ASBS] = (a) 0.5 × 10^{-2}/1.0 × 10^{-2}, (b) 1.0 × 10^{-2}/2.0 × 10^{-2}, and (c) 1.5 × 10^{-2}/3.0 × 10^{-2} mol/L.

Instrumental analyses

Scanning electron microscopy

A JEOL (Japan) JSM-400 scanning microscope was used for microscopy at the National Research Centre of Dokki, Giza, Egypt.

Mechanical properties

Dumbbell-shaped specimens (5 cm × 1 cm with a neck 4 mm wide) were used for the measurement of the ultimate TS and elongation at break.

These tests were carried out with an Instron model 1195 machine (Germany) according to the standard method at the Polymer Department of the National Research Centre of Dokki, Giza, Egypt; the crosshead speed was 50 mm/min.

Hardness

Grafted and ungrafted samples were measured with a Harterpufer model 53505 Shore A apparatus according to ASTM D 2240 at the Polymer Department of the National Research Centre of Egypt.

RESULTS AND DISCUSSION

Effect of the initiator type and concentration on the rate of grafting

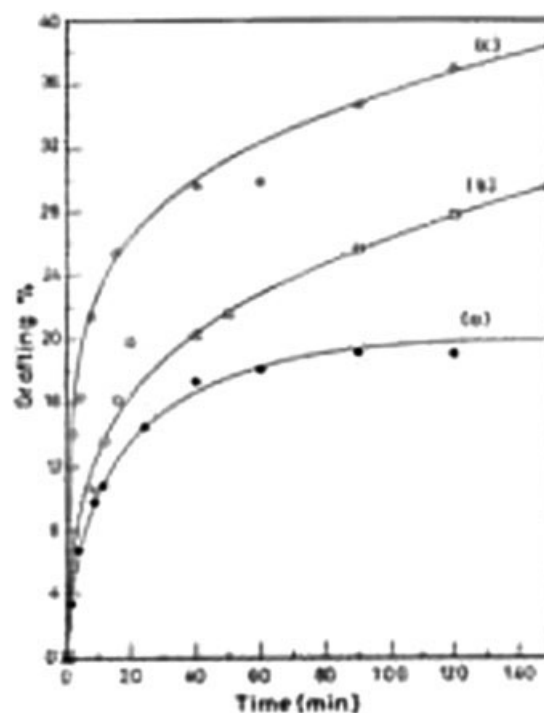The rate of grafting of GMA onto chrome-tanned leather with different developed redox initiator sys-

tems, which consisted of PPS, AmPS, and SPS as oxidizing agents and ASBS as a reducing agent, at 50°C was studied. The grafting percentage/time plots of these data are presented in Figures 1–3. It is evident that, regardless of the initiation system used, the
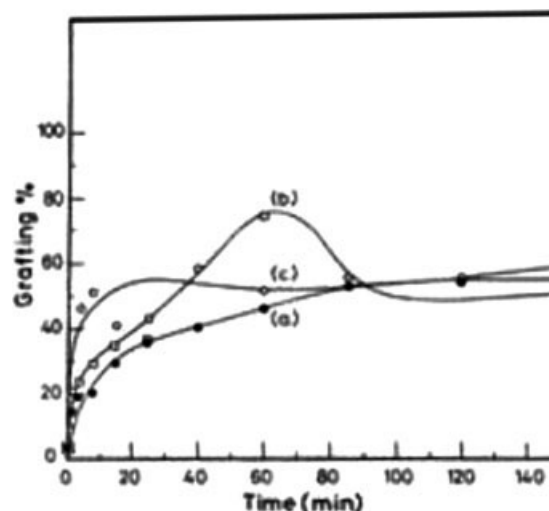

Figure 2 Grafting percentage/time dependence on the initiator concentration of PPS/ASBS with [SDS] = 2.87 × 10^{-2} mol/L, [GMA] = 0.35 mol/L, temperature = 50°C, and [PPS/ASBS] = (a) 0.5 × 10^{-2}/1.0 × 10^{-2}, (b) 1.0 × 10^{-2}/2.0 × 10^{-2}, and (c) 1.5 × 10^{-2}/3.0 × 10^{-2} mol/L.

Figure 3 Grafting percentage/time dependence on the initiator concentration of SPS/ASBS with [SDS] = 2.87 × 10^{-2} mol/L, [GMA] = 0.35 mol/L, temperature = 50°C, and [SPS/ASBS] = (a) 0.5 × 10^{-2}/1.0 × 10^{-2}, (b) 1.0 × 10^{-2}/2.0 × 10^{-2}, and (c) 1.5 × 10^{-2}/3.0 × 10^{-2} mol/L.
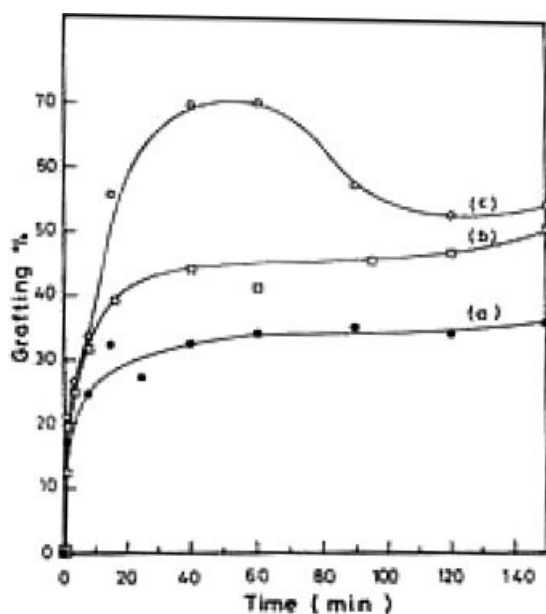
Figure 4 Grafting percentage/time dependence on the emulsifier concentration with [AmPS/ASBS] = $1.0 \times 10^{-2}/2.0 \times 10^{-2}$ mol/L, [GMA] = 0.35 mol/L, temperature = 50°C, and [SDS] = (a) 1.43×10^{-2}, (b) 2.87×10^{-2}, and (c) 4.31×10^{-2} mol/L.

grafting percentage increased as the initiator concentration increased, and the magnitude of the grafting obtained with the AmPS/ASBS initiation system was considerably higher than that obtained with the other systems. This system reached the saturation level of grafting onto leather. Considering the rates of grafting for the three types of initiation systems, we found that the rate of grafting increased with increasing initiator concentration, and the AmPS/ASBS system had higher grafting rate values than the other two systems; this was due to the weaker basicity of the medium as it is well known that this reaction is inhibited by the addition of a few drops of a sodium hydroxide solution and is activated in an acidic medium.[28]

The calculated powers of the developed redox pair initiation systems with respect to the rate of grafting were found to be 1.06, 0.48, and 0.43 for the AmPS/ASBS, PPS/ASBS, and SPS/ASBS systems, respectively. These power values reflected the difference between the activity of the oxidizing agents with respect to (1) the rate of initiator decomposition, the decomposition products (i.e., free radicals), and their ability to attack the chrome-tanned leather to form leather macroradicals, (2) the location and position of the free-radical sites on the leather backbone, (3) the availability of leather macroradicals to capture the double bonds of ethyl acrylate molecules to initiate grafting, (4) the rate of propagation of the graft, which was governed by the conditions used for each initiator and the availability of monomer

molecules in the proximity of the leather molecules under these conditions, and (5) the rate of termination, for which an abundance of free radicals seemed to play a key role.

Effect of the emulsifier concentration on the rate of grafting

The relationship between the rates of grafting of GMA onto leather with various concentrations of SDS as an emulsifier for different redox systems at 50°C was studied and is illustrated in Figures 4–6. The obtained data showed that the rate of grafting of GMA increased with an increasing emulsifier concentration in the presence of all redox initiation systems used. This can be attributed to the fact that an emulsifier plays an important role in increasing the swellability of leather; consequently, more facilitation and penetration of free radicals inside the leather take place. The emulsifier powers were found to be 0.63, 0.46, and 0.43 for the AmPS/ASBS, PPS/ASBS, and SPS/ASBS systems, respectively; the AmPS/ASBS system had the highest value.

The developed redox initiation systems not only initiated the graft polymerization but also worked as coemulsifiers with SDS, which increased the emulsification of the GMA monomer to form a homogeneous, miscible solution suitable for carrying out grafting polymerization.
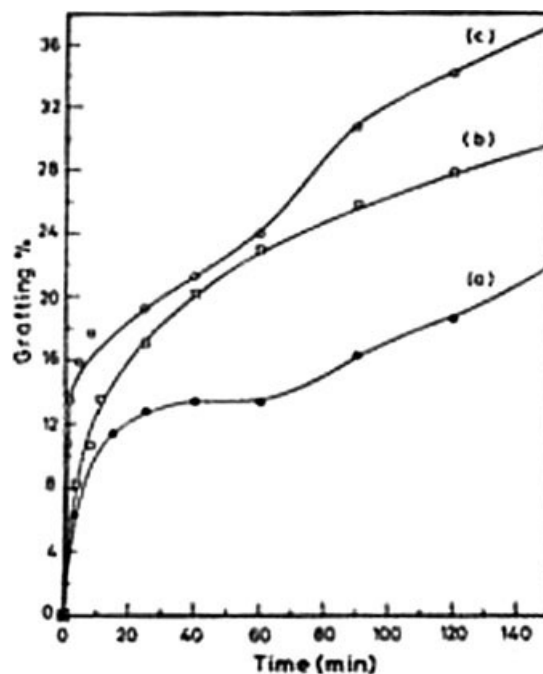

Figure 5 Grafting percentage/time dependence on the emulsifier concentration with [PPS/ASBS] = $1.0 \times 10^{-2}/2.0 \times 10^{-2}$ mol/L, [GMA] = 0.35 mol/L, temperature = 50°C, and [SDS] = (a) 1.43×10^{-2}, (b) 2.87×10^{-2}, and (c) 4.31×10^{-2} mol/L.

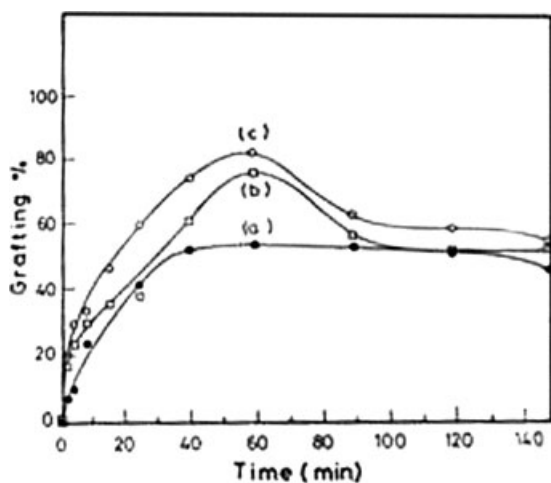**Figure 6** Grafting percentage/time dependence on the emulsifier concentration with [SPS/ASBS] = 1.0×10^{-2}/ 2.0×10^{-2} mol/L, [GMA] = 0.35 mol/L, temperature = 50°C, and [SDS] = (a) 1.43×10^{-2}, (b) 2.87×10^{-2}, and (c) 4.31×10^{-2} mol/L.

Effect of the monomer concentration on the rate of grafting

Figures 7–9 show the effect of the GMA monomer concentration on the rate of grafting with different initiation systems at 50°C. It is obvious that, regard-
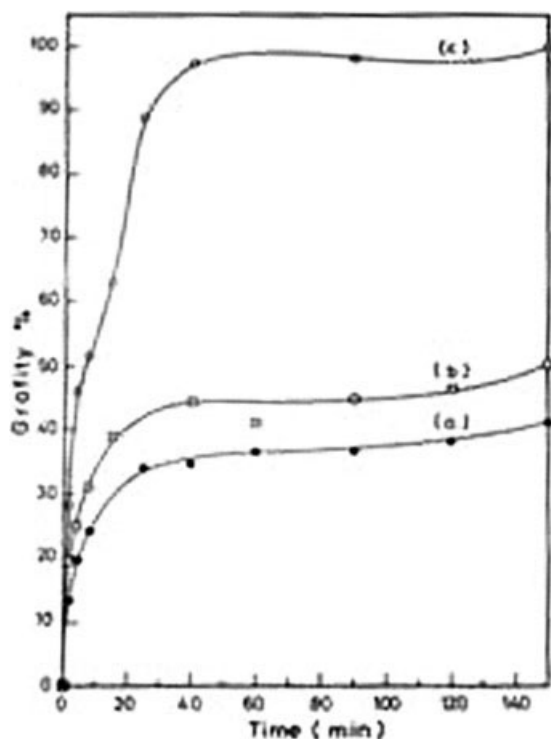

Figure 7 Grafting percentage/time dependence on the GMA monomer concentration with [AmPS/ASBS] = 1.0×10^{-2}/2.0×10^{-2} mol/L, [SDS] = 2.87×10^{-2} mol/L, temperature = 50°C, and [GMA] = (a) 0.175, (b) 0.35, and (c) 0.7 mol/L.
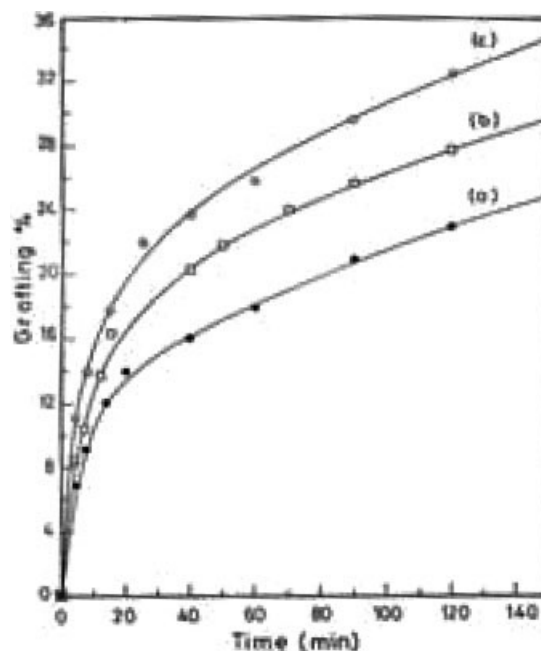

Figure 8 Grafting percentage/time dependence on the GMA monomer concentration with [PPS/ASBS] = 1.0×10^{-2}/2.0×10^{-2} mol/L, [SDS] = 2.87×10^{-2} mol/L, temperature = 50°C, and [GMA] = (a) 0.175, (b) 0.35, and (c) 0.7 mol/L.

less of the type of initiation system, the grafting percentage increased with the time and monomer concentration within the range studied. This may be due to the fact that, at a higher monomer concentration, more growing polymer chains were available near the collagen matrix and were mainly used for grafting polymerization. Another probable explanation could be associated with the greater availability of monomer molecules at higher GMA concentrations in the proximity of leather. It is understandable that the active centers on leather, that is, leather macroradicals, are immobile. Hence, their reaction with a monomer would essentially depend on the availability of the latter in the vicinity of leather macroradicals. The grafting rate of polymerization of GMA onto leather, for different redox initiation systems, increased with an increasing monomer concentration within the range studied (from 1 to 150 min) as it is well known that the rate of reaction is directly proportional to the monomer concentration.

The powers were found to be 1.41, 0.70, and 0.81 for the AmPS/ASBS, PPS/ASBS, and SPS/ASBS systems, respectively, and this indicated that the AmPS/ASBS system had a higher value than the other two systems.

Effect of the temperature on the rate of grafting

The effect of temperature on the rate of grafting of GMA onto leather at constant concentrations of the
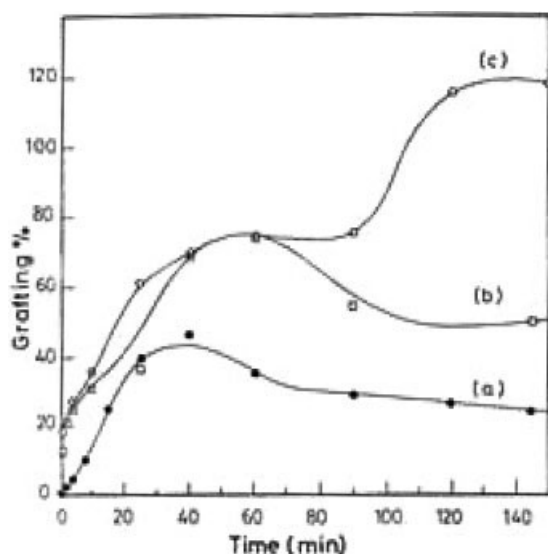
Figure 9 Grafting percentage/time dependence on the GMA monomer concentration with [SPS/ASBS] = 1.0 × 10^{-2}/2.0 × 10^{-2} mol/L, [SDS] = 2.87 × 10^{-2} mol/L, temperature = 50°C, and [GMA] = (a) 0.175, (b) 0.35, and (c) 0.7 mol/L.

Figure 11 Grafting percentage/time dependence on the temperature with [PPS/ASBS] = 1.0 × 10^{-2}/2.0 × 10^{-2} mol/L, [GMA] = 0.35 mol/L, [SDS] = 2.87 × 10^{-2} mol/L, and temperature = (a) 40, (b) 50, and (c) 60°C.

initiator, emulsifier, and monomer with different types of developed redox initiation systems is illustrated in Figures 10–12. It is evident that, regardless of the initiator type, the rate of grafting of GMA increased with increasing temperature, and the AmPS/ASBS system had a higher value than the other two studied systems.
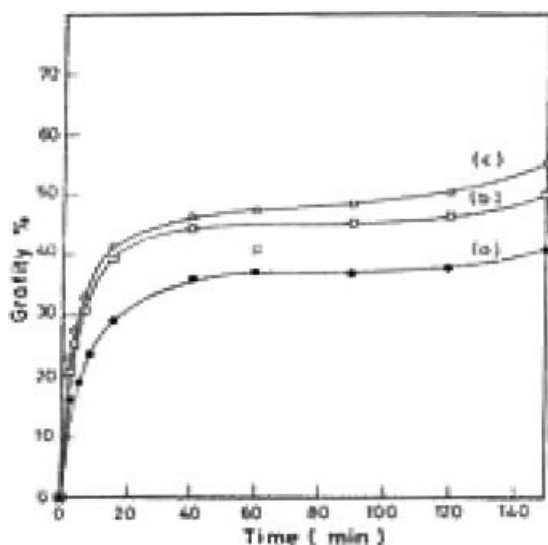
The apparent activation energy was calculated for each initiation system and was found to be 180.8, 361.63, and 542.45 kcal for the AmPS/ASBS, PPS/ASBS, and SPS/ASBS systems, respectively. The lower activation energy of the AmPS/ASBS system indicated the higher activity of that redox initiation system.

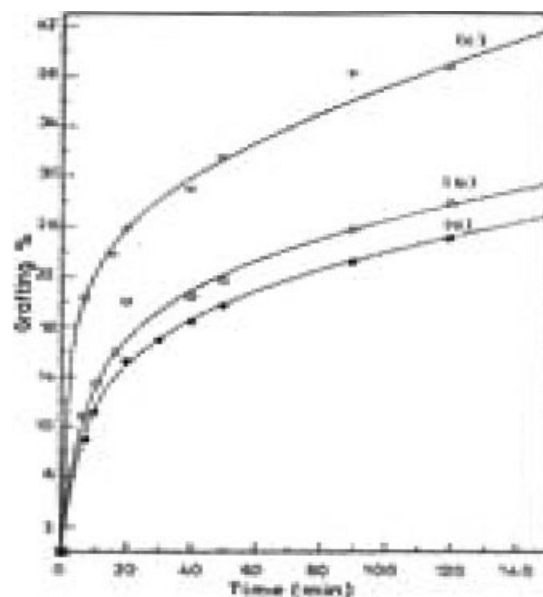In our studies, the proposed rate equation of the grafting emulsion polymerization of acrylate mono-

Figure 10 Grafting percentage/time dependence on the temperature with [AmPS/ASBS] = 1.0 × 10^{-2}/2.0 × 10^{-2} mol/L, [GMA] = 0.35 mol/L, [SDS] = 2.87 × 10^{-2} mol/L, and temperature = (a) 40, (b) 50, and (c) 60°C.

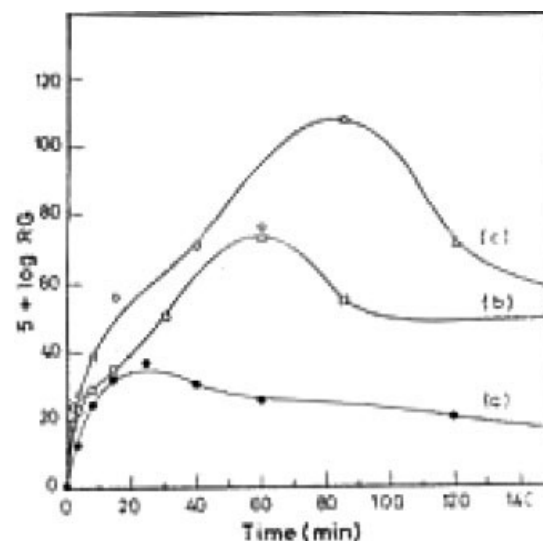**Figure 12** Grafting percentage/time dependence on the temperature with [SPS/ASBS] = 1.0 × 10^{-2}/2.0 × 10^{-2} mol/L, [GMA] = 0.35 mol/L, [SDS] = 2.87 × 10^{-2} mol/L, and temperature = (a) 40, (b) 50, and (c) 60°C.

TABLE II
Variation of the Water Absorption and Mechanical Properties with the Graft Yield
(GY) Percentage for Leather Grafted with GMA Monomer

GY (%)	Water absorption (%)			Mechanical properties		
	30 min	60 min	120 min	TS (kg/c)	$E\%$	Hardness (Shore)
0.0	78.0	80.0	83.0	6.72	15.30	95
26	69.43	70.05	71.23	7.60	22.00	92
32	63.31	66.48	70.29	8.25	24.74	86
34	61.61	65.19	68.26	10.70	34.98	84
36	61.12	64.65	66.25	13.66	39.77	83
43	57.11	59.87	61.58	16.84	43.23	81
52	50.65	53.98	56.39	19.94	53.19	76
61	41.02	48.37	53.51	23.05	57.84	75

mers onto leather is as follows:

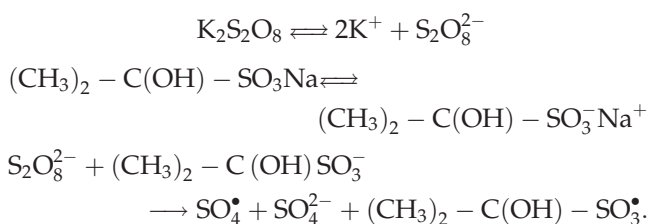$$R_G \alpha [I]^X [E]^Y [M]^Z \qquad (1)$$

where [I], [E], and [M] are the initiator, emulsifier, and monomer concentrations, respectively. The calculated values of X were found to be 1.06, 0.48, and 0.43, Y was equal to 0.63, 0.46, and 0.43, and Z was equal to 1.41, 0.70, and 0.81 for the following developed redox pair initiation systems: AmPS/ASBS, PPS/ASBS, and SPS/ASBS, respectively.

From the previous results, it can be concluded that the developed redox initiation system AmPS/ASBS played a more important role in the grafting emulsion polymerization of the GMA monomer onto leather than the other two studied systems.
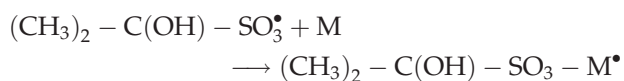
Most likely, the lower decomposition temperature of AmPS as well as the evaluation of the ammonium ion as ammonia, causing less basicity for the reaction medium, created a suitable environment for more free-radical formation to initiate grafting.

The suggested equations of the grafting process can be represented as follows.
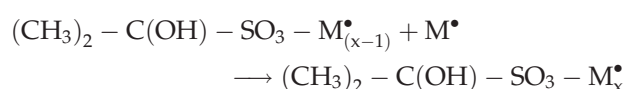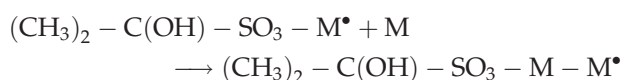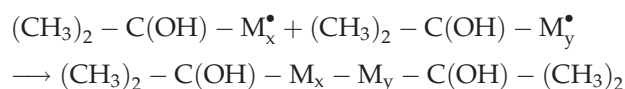
Polymerization reaction mechanism:

$$K_2S_2O_8 \rightleftharpoons 2K^+ + S_2O_8^{2-}$$

$$(CH_3)_2 - C(OH) - SO_3Na \rightleftharpoons$$
$$(CH_3)_2 - C(OH) - SO_3^- Na^+$$

$$S_2O_8^{2-} + (CH_3)_2 - C(OH)SO_3^-$$
$$\longrightarrow SO_4^\bullet + SO_4^{2-} + (CH_3)_2 - C(OH) - SO_3^\bullet.$$

Initiation:

$$(CH_3)_2 - C(OH) - SO_3^\bullet + M$$
$$\longrightarrow (CH_3)_2 - C(OH) - SO_3 - M^\bullet$$

Propagation:

$$(CH_3)_2 - C(OH) - SO_3 - M^\bullet + M$$
$$\longrightarrow (CH_3)_2 - C(OH) - SO_3 - M - M^\bullet$$

$$(CH_3)_2 - C(OH) - SO_3 - M^\bullet_{(x-1)} + M^\bullet$$
$$\longrightarrow (CH_3)_2 - C(OH) - SO_3 - M^\bullet_x$$

Termination:

$$(CH_3)_2 - C(OH) - M^\bullet_x + (CH_3)_2 - C(OH) - M^\bullet_y$$
$$\longrightarrow (CH_3)_2 - C(OH) - M_x - M_y - C(OH) - (CH_3)_2$$

Mechanical properties

Because of the importance of physical and mechanical properties in practical applications, some of the mechanical properties—TS, elongation percentage ($E\%$), and hardness—were measured for the leather grafted with PGMA with different grafting percentages and for ungrafted leather.

As shown in Table II, both TS and $E\%$ increased with an increase in the grafting percentage and also improved in comparison with those of the ungrafted leather.

On the other hand, the hardness was also measured for the grafted and ungrafted leather, and Table II shows that the hardness decreased as the grafting percentage increased, and the hardness of the grafted leather was lower than that of the ungrafted leather.

From the properties of the leather grafted with PGMA, we found that these properties added some good qualities to the leather, such as softness, and this resulted in better TS and less hardness. All these properties are desirable in the leather industry.

Effect of grafting on the water absorption of the leather

It is important for leather to be more resistant to water absorption, so many methods have been directed to increase the water resistance of leather.[27]

Grafting with various synthetic polymers is beneficial in increasing the water repellence of leather.

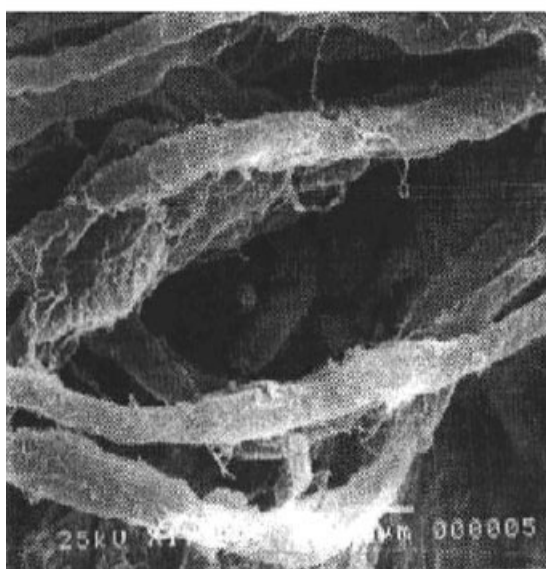From Table II, it can be concluded that the water absorption decreased with an increase in grafted

Figure 13 Scanning electron microscopy images of ungrafted leather: (top) 500 and (bottom) 1500×.

GMA, whereas the mechanical properties increased, and the hardness decreased; these new properties were good additions to the leather sample. Therefore, a remarkable decrease in the water absorption of leather is a good and favorable property that we try to attain.

Scanning electron microscopy

A morphological study was carried out for some selected samples of unmodified leather and PGMA-grafted leather. From the micrographs in Figures 13 and 14, it is clear that the unmodified leather fibers were completely separated from one another, but in the case of grafted leather fibers, aggregates of PGMA could be noticed, which are good evidence

for the formation of PGMA grafted onto the leather surface.

Proof of grafting by Soxhlet extraction

The grafting process was ensured by the subjection of the leather samples after removal from the reaction medium to Soxhlet extraction for a suitable time to remove any homopolymer; then, the samples were washed quite well with the solvent and weighed.

The increase in the weight of the leather samples after being washed thoroughly with water and the solvent proved that grafting took place in our samples.

Initiation system

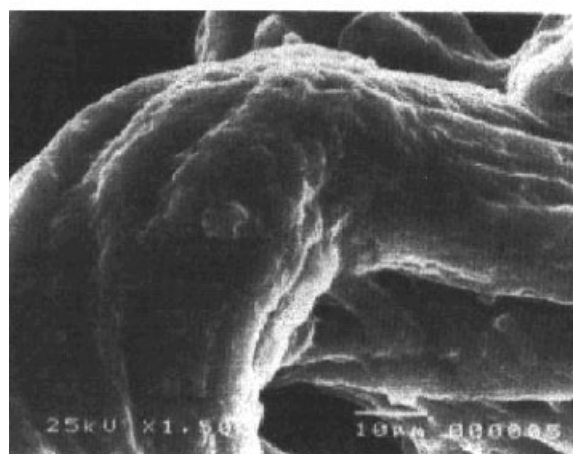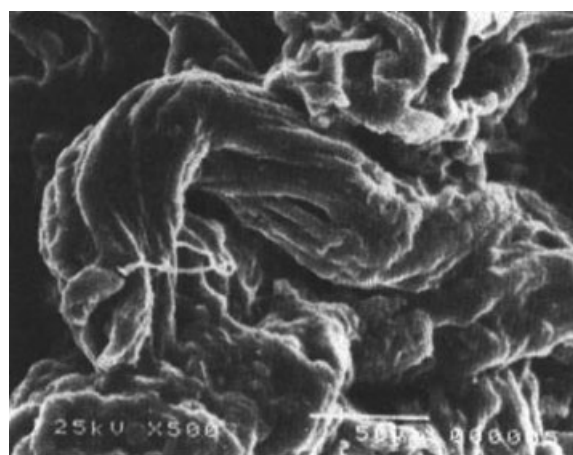We chose this initiation system because we found in our previous work that this system needs less energy

Figure 14 Scanning electron microscopy images of grafted leather with GMA monomer, SDS emulsifier, and AmPS/ASBS initiator at 60°C: (top) 500 and (bottom) 1500×.

to produce the radicals responsible for the polymerization reaction.

CONCLUSIONS

The grafting emulsion polymerization of GMA onto leather with our selected chemical initiation system both improved the physicomechanical properties of the leather and decreased the hardness and water absorbance; these properties are favored by the leather industry.

The AmPS/ASBS system was found to be a better system for increasing the rate of grafting copolymerization of GMA onto leather, and this system also improved emulsification more than any other system.

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