Styrene and Butyl Methacrylate Copolymers and Their Application in Leather Finishing

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ABSTRACT: Homopolymers and copolymers of styrene and butyl methacrylate were synthesized with different ratios by an emulsion polymerization technique with $K_2S_2O_8$/NaHSO$_3$ as the redox initiation system and sodium dodecyl sulfate as the emulsifier at $60°C$ for 3 h. The effects of different monomer ratios on the kinetics of emulsion polymerization and polymer viscosity were studied. These copolymers were applied to leather surfaces with a hand coater to a thickness of 18 μm. The effects of the coatings on the leather surfaces were evaluated through the measurement of physical and mechanical properties of coated and uncoated leather. IR spectra showed new bands characteristic of styrene and butyl methacrylate, which disappeared in the spectrum of uncoated leather. The physical and mechanical results showed that the water absorption content decreased with increasing styrene content, and the water vapor permeability of the coated leather was less than that of the uncoated leather; however, it was still in the acceptable range. The results indicated improvements in the tensile strength and elongation (%) for the coated leather with increases in the butyl methacrylate content. Thermogravimetric analysis showed characteristic improvements in the thermal stability of leather after the coating; its optimum stability was reached when the leather was coated with poly(styrene:butyl methacrylate) (1 : 1). Finally, scanning electron microscopy showed the full grain surface of the leather. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 1488–1495, 2009

Key words: electron microscopy; emulsion polymerization; films; FT-IR; polystyrene

INTRODUCTION

The leather industry is one of the oldest industries in the world. The process of leather manufacturing is a complex sequence of chemical reactions and mechanical processes used to convert hides and skins to stable finished leather. Among these, leather finishing is one of the most important stages, responsible for the enhancement of the appearance of leather, and it provides the performance characteristics expected of finished leather that are required for end users.

Leather finishes are divided according to the finishing techniques and finishing effects. Finishing techniques include spray rolling, coating, and dipping. Coatings impart flexibility, elongation, resistance to water, resistance to abrasion, and thermal stability to the finished leather.

The most common finishing materials are classified into two main groups: binders such as waxes, proteins, and synthetic polymers and additives such as pigments. The common synthetic binders in leather finishing are acrylates, butadienes, and polyurethanes.[1] The manufacturing processes for these products are quite different. Acrylates are produced by low-pressure polymerization, butadiene is produced by high-pressure polymerization, and polyurethane is produced by polyaddition.[2]

Acrylate binders are mainly dispersions of polyacrylic and polymethacrylic esters and are usually produced by radical-initiated emulsion polymerization.

The application of an acrylic emulsion as a topcoat system provides an excellent balance of safety, performance, and commerciality in comparison with other topcoat materials. Much research has been conducted to produce companion acrylic topcoat systems with additional benefits such as high temperature resistance, greater fullness, and smoothness.[3–5]

Finally, many polymer films are used in leather finishing to improve the tensile strength and elongation of coated leather.[6] Coatings impart high gloss as well as high wear resistance and also protect leather from the damage of weathering, affecting its water vapor permeability[7] and improving its thermal properties.[8,9]

The objective of this investigation was to synthesize polystyrene (PSty) and poly(butyl methacrylate) (PBMA), apply them in different ratios to leather surfaces, and then evaluate the coated leather mechanically, physically, and thermally and compare the results to those for uncoated leather.

EXPERIMENTAL

Materials

Dyed bovine leather was supplied by Hafez-Abaas Medium Tannery (Misr-Elkadima, Cairo, Egypt). Butyl methacrylate (BMA) and styrene (Sty) were provided by Merck-Schuchardt (Germany) and redistilled before use; potassium persulfate was supplied by Modern Laboratory Co. Sodium bisulfite was supplied by El-Naser Pharmaceutical Chemical Co. Sodium dodecyl sulfate was obtained from Merck-Schuchardt.

Methods

Emulsion polymerization

The following ingredients were mixed in a 250-mL, three-necked flask: water, the emulsifier, and the monomer. Finally, the initiator was dissolved in a small amount of water and added to the reactor under a nitrogen atmosphere. The reactions were run with mechanical stirring at 500 rpm for 3 h at 60°C.[10]

Monomer conversion

Samples with a certain volume of the reaction mixture were taken at various intervals and put on a glass watch. The reaction was stopped with a 7 ppm hydroquinone solution; then, the mixture was evaporated at room temperature and dried in an electric oven at 60–80°C until a constant weight was obtained.

Viscosity

The viscosity of the emulsion was determined according to ASTM D 4212 with a Zahn cup with an orifice diameter of 2.69 mm (Sheen Instrument, Ltd., United Kingdom).

Coating process

Leather samples were coated with the prepared polymers to a film thickness of 18 μm with a K hand coater from RK Print Coat Instrument, Ltd. (United Kingdom).

Spectrophotometry analysis

Fourier transform infrared (FTIR) spectra were taken with a Nexus 670 FTIR spectrophotometer (Nicolet,

United States) over the range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1}; the KBr disk technique was applied.

Scanning electron microscopy (SEM)

Samples (1 cm^2) were subjected to sputter coating of gold ions, which acted as a conducting medium during scanning with a JEOL (Japan) JXA-840A scanning microscope.

Thermogravimetric analysis (TGA)

Thermal analysis was studied with a PerkinElmer thermogravimetric analyzer (rate = 10°C/min) from room temperature to 500°C at the National Research Center of Egypt.

Determination of water absorption

The test for the determination of the water absorption capacity was based on the immersion of circular specimens with a diameter of 2.5 cm into water for different time intervals (15 min, 30 min, 1 h, 2 h, 3 h, 4 h, 5 h, and 24 h) at room temperature. The immersed samples were removed from water, and excess water was wiped off with filter paper and then weighed.

The water absorption capacity (ω) was determined with the following relationship:[11]

$$\omega(\%) = [(W - W_0)/W_0] \times 100$$

where W is the weight of wet coated leather after immersion in H_2O and W_0 is the weight of dry coated leather.

Water vapor permeability

Circle-shaped specimens with a diameter of 5.5 cm were used for the measurement of the water vapor permeability. This was carried out with a Herfeld instrument for 72 h according to standard method 122/2002 (last updated in August 2005) for physical tests of leather from the Egyptian Organization for Standardization and Quality.

Mechanical properties

Dumbbell-shaped specimens (5 × 1 cm^2 with a 4-mm-wide neck) were used for the measurement of the tensile strength and elongation at break (%).

These tests were carried out with an Instron model 1195 machine according to standard methods at the Polymer Department of the National Research

TABLE I
Polymerization of Sty and BMA at Different Ratios and Their Viscosities

Monomers	Sty : BMA (mol/L)	Viscosity (cP)
Sty	2.22	10
4 : 1 Sty : BMA	1.78 : 0.33	10
3 : 2 Sty : BMA	1.33 : 0.56	11
1 : 1 Sty : BMA	1.1 : 0.81	13
2 : 3 Sty : BMA	0.89 : 0.98	14
1 : 4 Sty : BMA	0.44 : 1.3	15
BMA	1.63	15

TABLE II
Monomer Conversion (%) with Time

Sty : BMA ratio	Monomer conversion (%)				
	10 min	20 min	30 min	60 min	150 min
5 : 0	10.32	13.00	27.12	76.8	86.4
4 : 1	13.79	26.23	42.09	68.88	79.3
3 : 2	14.26	24.95	35.65	67.72	81.98
2.5 : 2.5	26.65	43.87	67.65	75.00	80.36
2 : 3	28.8	41.2	60.4	75.00	79.3
1 : 4	28.08	50.4	66.96	75.00	82.8
0 : 5	44.46	54.39	73.22	81.00	84.98

RESULTS AND DISCUSSION

Preparation of the polymer emulsions

The polymerizations of Sty and BMA and their copolymerization were carried out with $K_2S_2O_8$ (0.0937 g)/$NaHSO_3$ (0.0676 g) as a redox initiation system and sodium dodecyl sulfate (0.03 g) as an emulsifier at 60°C for 3 h in 50 mL of water. Viscosities of different polymers were measured, and the results were presented in Table I.

Table I shows that the viscosity of the polymers increased with increasing BMA content, and this was due to the higher solubility of BMA (0.6 g/ 100 mL)[12] versus that of Sty (0.03 g/100 mL),[13] which promoted the formation of new particles; the formation of more particles led to increased viscosity, so with an increase in the BMA content, the viscosity increased.

Characterization of the polymers: monomer conversion (%)

The monomer conversion (%) was measured as follows: samples were taken from the reaction mixtures at different time intervals, evaporated at room temperature, and then dried in an electric oven until a constant weight was obtained. The results are shown in Table II.
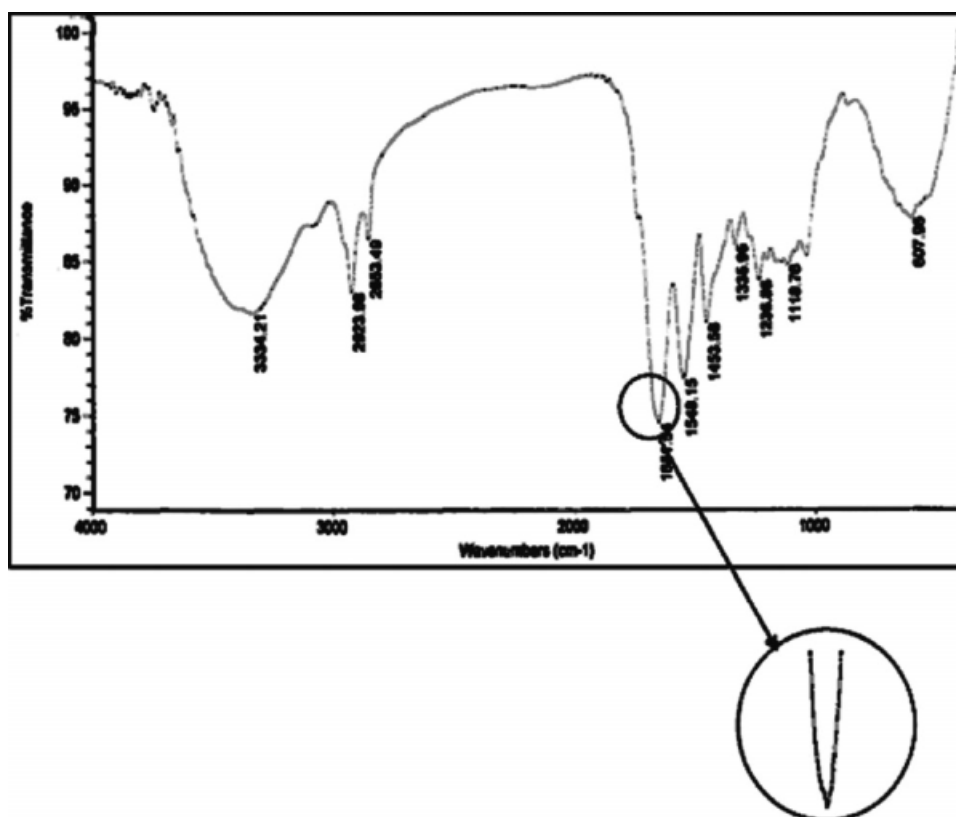

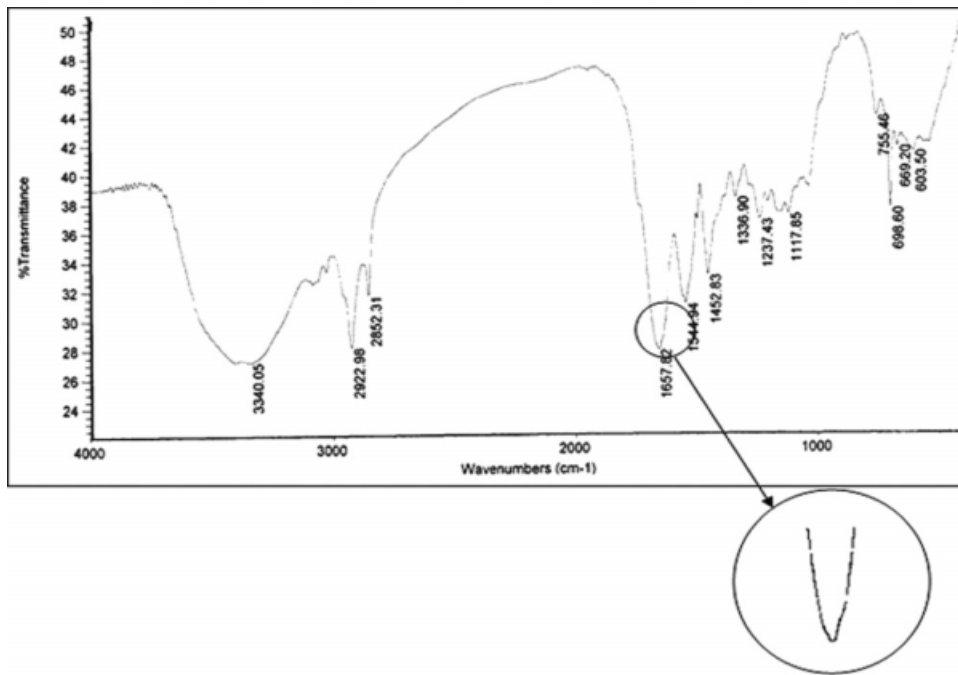**Figure 1** IR chart of uncoated leather (blank).

Figure 2 IR chart of coated leather with PSty.

There was an obvious increase in the monomer conversion (%) with time. After about 150 min, the rate of conversion tended to be steady, and this could be attributed to the consumption of monomers with time during the reaction. From Table II, it can be noted that the conversion rate increased with increasing BMA content, and this can be attributed to the higher water solubility and propagation rate. The results were compared with the literature: the Fineman–Ross method yielded reactivity ratios of 0.17 ± 0.02 and 0.60 ± 0.02 for the copolymerization of Sty and BMA, respectively.[14]
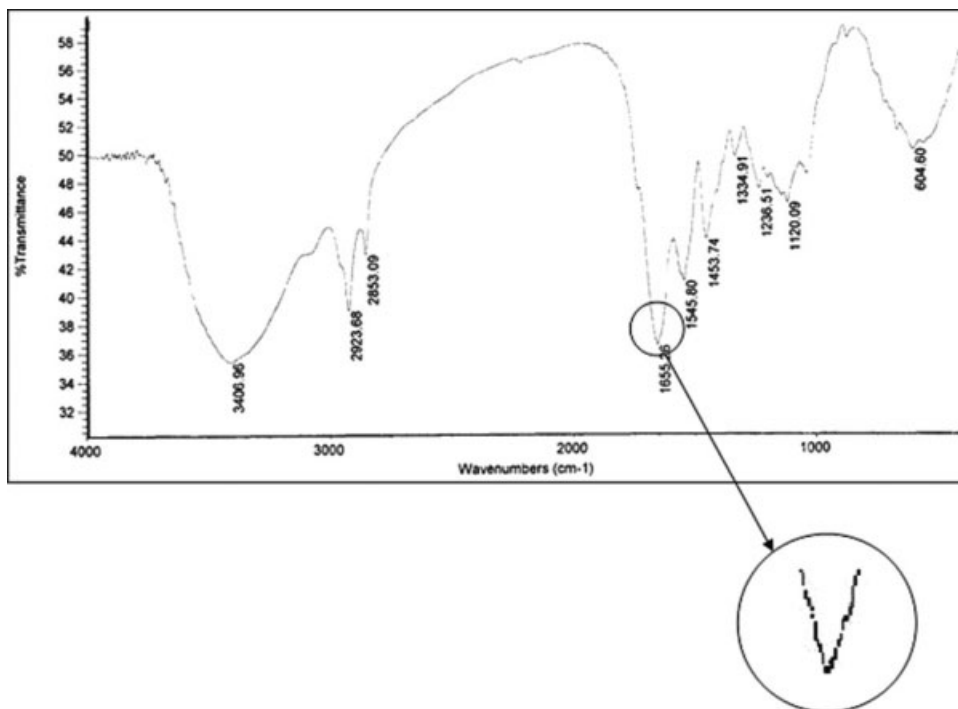

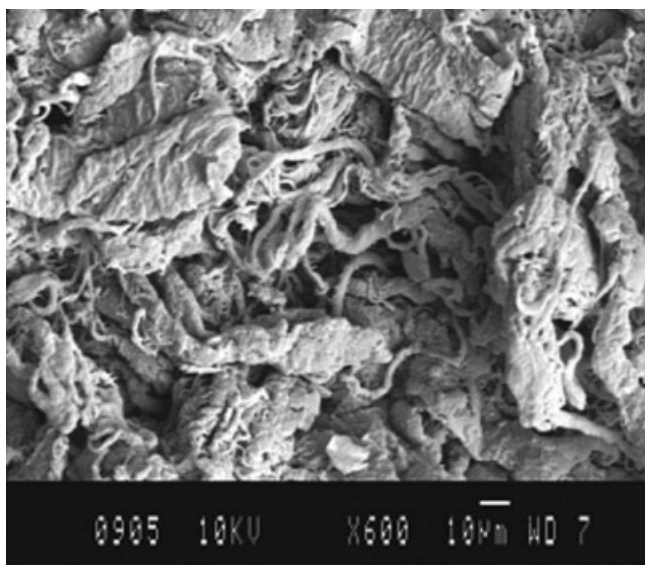
Figure 3 IR chart of coated leather with PBMA.

Figure 4 SEM of uncoated leather.

Evaluation of the coated leather

IR spectra of the coated leather

From Figures 1–3, a broad band in the range of 3300–3440 cm^{-1} was assigned to the OH group of carboxylic acid of leather, and the band in the range of 2920–2925 cm^{-1} was related to aromatic $=$C$-$H stretching in both the leather and polymer chain. Another band in the range of 2852–2855 cm^{-1} could be attributed to $-$C$-$H of both the leather and polymer, and the band in the range of 1544–1556 cm^{-1} was related to N$-$H bending of the amide group of leather.

In the range of 1640–1671 cm^{-1}, there was a band resulting from the $-$C$=$O group of both the amide group of leather and the carbonyl group of BMA. The sharp band at 1651 cm^{-1} for the blank (split in coated leather with PBMA or its copolymers with
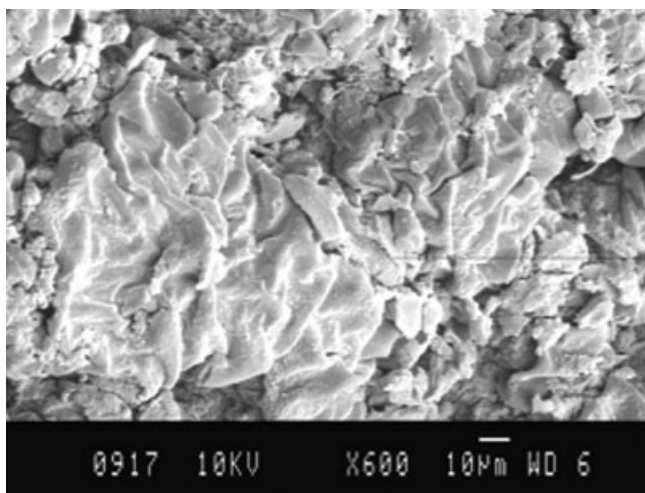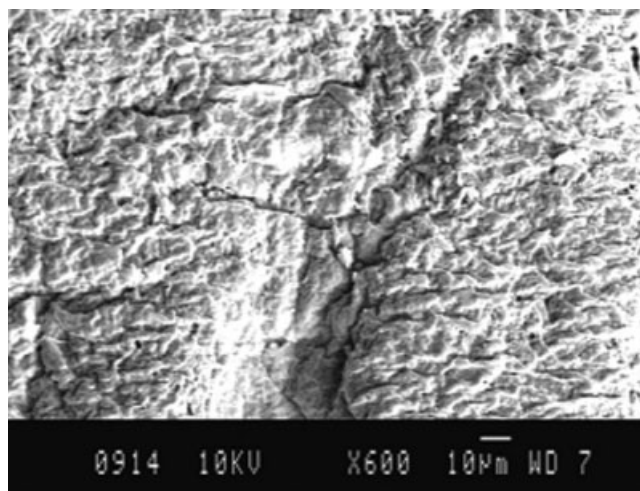

Figure 6 SEM of coated leather with P(Sty : BMA) (4 : 1).

Sty) could be attributed to overlapping between the carbonyl group of leather and carbonyl of BMA. The weak bands in the range of 1300–1000 cm^{-1} were related to C$-$O stretching characteristics for esters.

Finally, the spectra exhibited two strong absorption bands at 698.60 and 755.46 cm^{-1} characteristic of monosubstituted aromatic rings (Sty).[15–17]

SEM

SEM showed that the grain surface of leather (i.e., the surface exposed when the epidermis is removed during manufacturing) was covered with a layer of nonfibrous material.[18] SEM of leather grain before and after coating showed significant effects of the prepared polymer on the leather grain versus the uncoated leather.

Figures 4–11 present SEM images for blank leather and leather coated with PSty, P(Sty : BMA) (4 : 1),
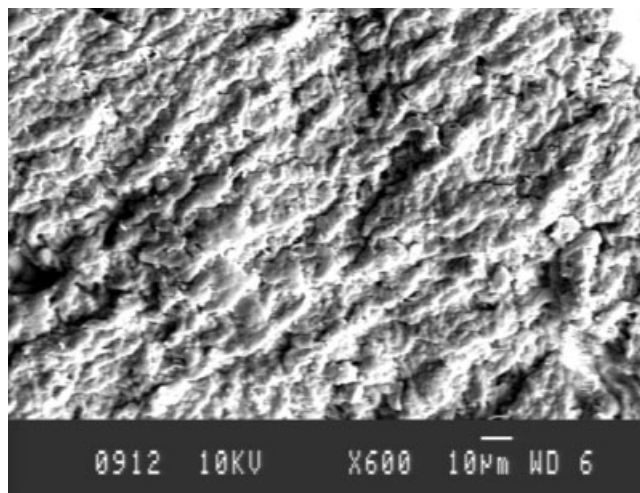

Figure 5 SEM of coated leather with PSty.

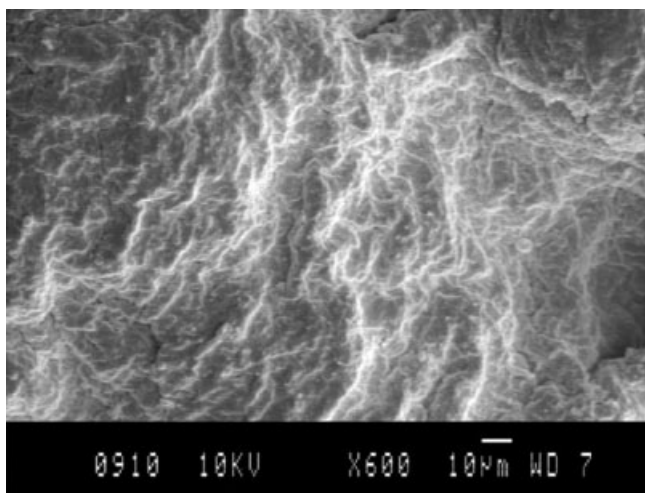**Figure 7** SEM of coated leather with P(Sty : BMA) (3 : 2).

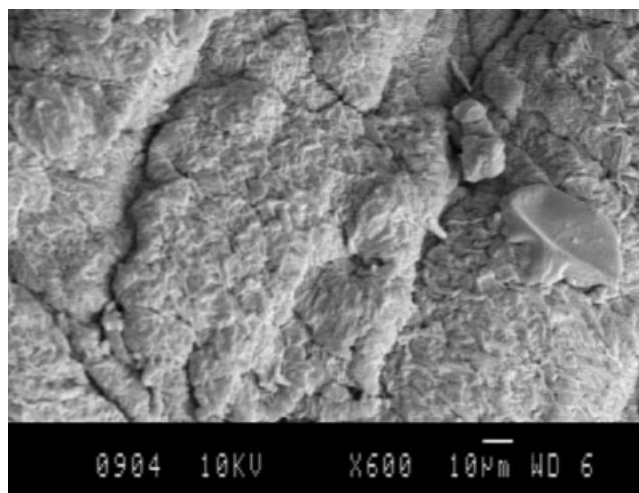**Figure 8** SEM of coated leather with P(Sty : BMA) (1 : 1).

Figure 10 SEM of coated leather with P(Sty : BMA) (1 : 4).

P(Sty : BMA) (3 : 2), P(Sty : BMA) (1 : 1), P(Sty : BMA) (2 : 3), P(Sty : BMA) (1 : 4), and PBMA, respectively.

Figure 4 shows the presence of uncoated grain composed of interwoven collagen fibers and hair follicles at a high magnification, whereas in the coated leather samples shown in Figures 5–11, the pores were coated with the prepared polymers, and this confirmed the coating process. However, there were still small pores left after the coating process, and these pores gave the leather the chance to breath and help in the transfer of water vapor. Also, the pore filling, regularity, and softness of the coating film increased with increasing BMA content because of the low glass-transition temperature (T_g) of PBMA, which made the formed film softer and more elastic. In contrast, a rigid film formed with PSty.
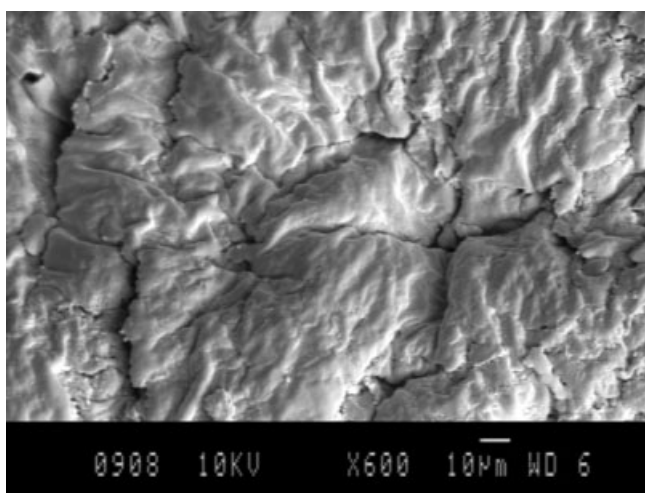
Effect of the coating layer on the water absorption content

The effects of PSty, PBMA, and their different ratios in the copolymers on the water absorption of the coated leather are shown in Figure 12. An increasing time of immersion in water for both coated and uncoated leather samples caused an increase in the water absorption percentage.[19,20]

All the coated samples had more water resistance than the blank ones because of the pores filling through the coating layer with the different polymers, especially those with a higher ratio of Sty with its hydrophobic character.

Effects of different coating agents on the water vapor permeability of leather

From Table III, we find that all coated samples with PSty and PBMA and their different copolymers had
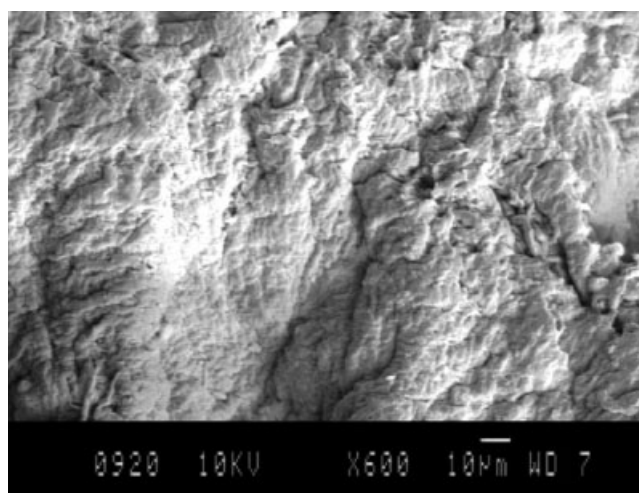

Figure 9 SEM of coated leather with P(Sty : BMA) (2 : 3).

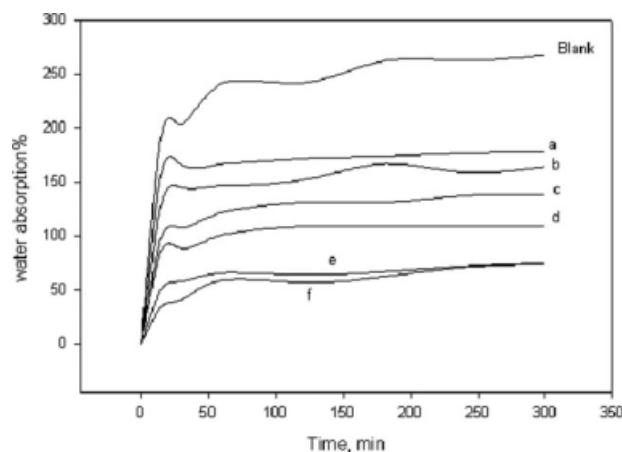**Figure 11** SEM of coated leather with PBMA.

Figure 12 Relation between the water absorption (%) and different leather coatings: (a) PBMA, (b) P(Sty : BMA) (1 : 4), (c) P(Sty : BMA) (2 : 3), (d) P(Sty : BMA) (1 : 1), (e) P(Sty : BMA) (3 : 2), (f) P(Sty : BMA) (4 : 1), and (g) PSty.

less water vapor permeability than the blank; this feature was due to the coating layer. However, the results still satisfy standard method 122/2002 (last updated in August 2005) for physical tests of leather from the Egyptian Organization for Standardization and Quality.

Effects of different coating agents on the mechanical properties of leather

From Table IV, it is obvious that coating agents filled up the empty hide parts, resulting in more strength for leather fibers. The leather samples coated with PSty had a lower tensile strength than the blank one because of the hard film formed by PSty. However, with increasing BMA content, the tensile strength of the samples increased and reached the maximum for samples coated with PBMA; this was due to the low T_g value of BMA, which was equal to 20°C;[21] this made the film very soft. Therefore, it filled the pores well and reinforced the fibers. On the contrary, a high T_g value of the Sty monomer (95°C)[22] would mostly produce a brittle film. The results are in

TABLE III
Relation Between the Type of Leather Coating and Water Vapor Permeability

Coated leather sample	Water vapor permeability (mg/1000 mm²)
Blank	497.5
PSty	356.93
P(Sty : BMA) (4 : 1)	386.7
P(Sty : BMA) (3 : 2)	400.3
P(Sty : BMA) (1 : 1)	377.4
P(Sty : BMA) (2 : 3)	400.9
P(Sty : BMA) (1 : 4)	373.7
PBMA	398.5

TABLE IV
Relation Between the Type of Leather Coating and the Tensile Strength and Elongation (%)

Coated leather sample	Tensile strength (kg/cm²)	Elongation (%) at break
Blank	141.6	95
PSty	128	103
P(Sty : BMA) (4 : 1)	141.2	114
P(Sty : BMA) (3 : 2)	145	122
P(Sty : BMA) (1 : 1)	153	126
P(Sty : BMA) (2 : 3)	213	135
P(Sty : BMA) (1 : 4)	223	147
PBMA	234	155

good agreement with what is reported in the literature.[6]

TGA of coated leather

TGA is a thermoanalytical technique that follows the change in weight of a material as a function of temperature. The weight changes (as small as a decrease of a few milligrams) can be determined as the sample is heated from room temperature to a certain specific temperature.[23–25]

The response to thermal treatment depends on the structure and morphology at all steps forming the polymerization and coating process.

It was proved by TGA that the leather coated with the prepared copolymers achieved increased thermal stability with respect to the blank leather; this is shown in Figure 13. The leather samples had an initial weight loss of ≈ 10% at temperatures between 50 and 100°C because of the release of water
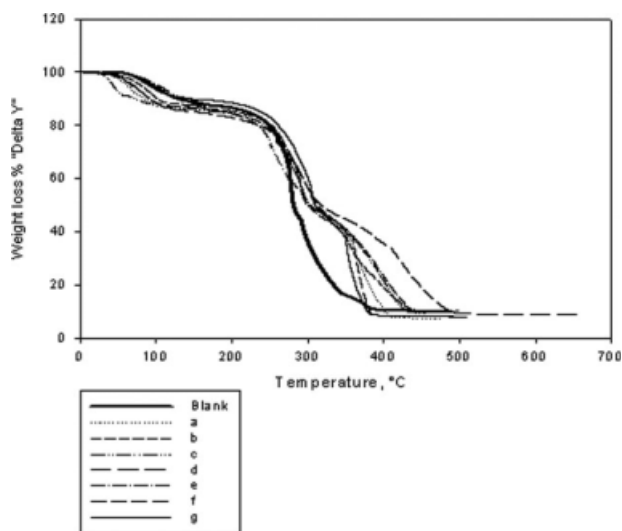

Figure 13 TG curves for uncoated and coated leather samples: (a) PBMA, (b) P(Sty : BMA) (1 : 4), (c) P(Sty : BMA) (2 : 3), (d) P(Sty : BMA) (1 : 1), (e) P(Sty : BMA) (3 : 2), (f) P(Sty : BMA) (4 : 1), and (g) PSty.

included in the leather fibers. After this process, the leather fiber was approximately stable up to 250°C, at which gradual decomposition began to take place, and two inflections were observed. From Figure 13, it can be observed that at the first inflection at 250–320°C, there was a loss of nearly 40 wt % that resulted from the burning of hydrocarbon chains of the polymers and leather (CO, CO_2, CH, CH_2, and NH_3).[26] The second inflection at 320–500°C included the degradation of the polymer. It can be noted that all the coated samples needed a higher degradation temperature than the blank one. This improvement in the thermal stability of the coated leather could be attributed to crosslinking between the polymer coating and hide collagen chain through hydrogen bonding. Coats containing Sty caused more thermal stability because of the resonating properties of the benzene ring, which exhibited higher thermal stability. At temperatures above 500°C, the residue ash formation was about 12% of the initial weight.

CONCLUSIONS

Homopolymers and copolymers of Sty and BMA were synthesized by emulsion polymerization with different ratios with $K_2S_2O_8$ and $NaHSO_3$ as the redox initiation system and sodium dodecyl sulfate as the emulsifier at 60°C for 3 h. The relation between the monomer ratios and the kinetics of the emulsion polymerization and polymer viscosity was studied: the monomer conversion and viscosity increased with increasing BMA content. The prepared polymers were applied to leather surfaces as coating agents.

The coated leather was evaluated through physical and mechanical measurements. IR spectra of the coated leather exhibited new bands characteristic of Sty and BMA. SEM images of leather grain before and after coating showed significant effects of the prepared polymer on the leather grain compared with the uncoated one. The regularity and softness of the coated film increased with increasing BMA content because of the soft and elastic film formed by PBMA. Improvements in the tensile strength and elongation (%) for leather coated with PBMA were due to the soft elastic film formed by PBMA as a result of its low T_g value (20°C).

TGA showed characteristic improvements in the thermal stability of leather after coating due to crosslinking between the polymer and leather. All the coated samples had less water absorption than the uncoated sample, the lowest occurring for the leather sample coated with PSty and the highest for the leather sample coated with PBMA (85 and 197%, respectively, versus 269.9% for the blank one). However, all coated samples with PSty and PBMA and their various copolymers had less water vapor permeability less than the blank one, and this feature

was due to the coating effect; it was still in the accepted range.

The obtained results showed some advantages in mechanical properties and some disadvantages concerning water absorption with a minor effect on water vapor permeability, which agreed with literature data.[6,7]

The test results clearly showed that the application of P(Sty : BMA) (1 : 1), among other selected copolymers, succeeded in achieving satisfactory mechanical properties with an accepted range of water vapor permeability. Also, the thermal stability reached its optimum; the P(Sty : BMA) (1 : 1) copolymer is suggested as a coating that can be used in the leather industry.

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