

# Synthesis and Application of Methyl Methacrylate/Butyl Acrylate Copolymer Nanoemulsions as Efficient Retanning and Lubricating Agents for Chrome-Tanned Leather

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**ABSTRACT:** Two different nano-emulsions based on methyl methacrylate/butyl acrylate copolymers have been synthesized to be used as retanning and lubricating agents for chrome-tanned leather. The main difference and characteristics of the two prepared copolymers were studied. The nano particle size of the two copolymers was confirmed using transmission electron microscope (TEM). The influence of the prepared copolymers on chrome-tanned leather as retanning agents was investigated. The properties of the retanned leather, namely, physicomechanical properties as tensile strength, elongation at break and water absorption, were measured. Thermal gravimetric analysis (TGA) technique was used to examine the thermal stability of the retanned leather. Also, the texture of the grain surface and

fibers were inspected using scanning electron microscope (SEM). The retanned leather showed an improvement in its physicomechanical properties, as well as enhancement of its thermal stability as compared with the chrome-tanned leather. Furthermore, the retanned leather has uniform dye-stuff, softness, and firmness of grain. All these promising results provide evidence to the applicability of the prepared copolymer emulsions as efficient retanning and lubricating agents for chrome-tanned leather. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 3293–3301, 2012

**Key words:** retanning agent; lubricant; chrome-tanned leather; methyl methacrylate/butyl acrylate copolymers; nanoemulsion

## INTRODUCTION

Animal hides are transferred into leather by tanning process. There are many types of tanning and retanning agents. Chrome tanning is a well established industrial process used to produce high quality leather. However, chrome tan is the most widely used world wide because it accounts over 80% of the activities in the tanning industry used for the production of the great majority of leather.<sup>1,2</sup> Chrome-tanned leathers are characterized by their light weight and high tensile strength.<sup>3</sup> Also, it improves the physical and mechanical properties that give the leather its high quality.<sup>4</sup> This improvement is attributed to the crosslinks arising between chrome and polypeptide chains throughout coordination bonds with the amino acid side chains of the collagen fibers of the leather. On the other hand, chrome-tanned leathers have disadvantages such as lack of fullness and course nap especially in suede leather. Furthermore, chrome tannage generates byproduct wastes which contain chrome. Also, the

hexavalent chromium Cr(VI) was detected in some Egyptian tanneries in the wet finishing effluent, which considered as a toxic and polluting to the environment.<sup>5</sup> Because of these drawbacks, many of the researches have been carried out to reduce pollution by avoiding the application of chrome either totally or partially in the tanning industry. Today's most of retanning agents used are based on vegetable and phenolic synthetic/organic tanning materials.<sup>6,7</sup> On the other hand, many trials have been done to develop new retanning agents to improve the chrome-tanned leather properties based on acrylate polymer derivatives,<sup>8</sup> which are suitable for filling, softening, and even water proofing,<sup>9</sup> air permeability<sup>10,11</sup> or which combine all these properties. However, the majority of these researches focused on grafting of various monomers onto leather such as styrene<sup>12</sup> and acrylate monomer derivatives.<sup>13–15</sup> Unfortunately, from the environmental and economical point of view, most of monomers used in grafting process are costly in financial terms and dangerous in nature, in addition to the use of organic solvents as a medium for dissolving the monomers during the grafting process, which is not suitable for application in leather industry. For these reasons, the leather industry has issued laws and legislations for reagents used in leather industry must be safe and friendly to environment. So, it is better to use a

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prepared polymer emulsion using aqueous emulsion polymerization technique<sup>16</sup> for retanning of leather to avoid the toxicity of free monomers and to limit the use of organic solvents during the grafting process.

The present work aims to prepare eco-friendly to environment nano-emulsions based on methyl methacrylate/butyl acrylate copolymers. The prepared emulsions were used as retanning agents as well as to improve the undesirable properties of chrome-tanned leathers. This is assessed in terms of measurement of the physicochemical and thermal properties of chrome-tanned leather before and after retanning with the prepared emulsions. Also, the effect of the prepared retanning agents on color fastness, texture of grain and fibers of the retanned leather were examined.

## MATERIALS AND TECHNIQUES

### Materials

Methyl methacrylate (MMA), butyl acrylate (BuA), methacrylic acid (MAA), acrylic acid (AA) were supplied by Aldrich and distilled under reduced pressure before use. Potassium persulfate (initiator), nonyl phenol ethoxylate (Tergitol-NP9, nonionic surfactant), sodium lauryl sulfate (SLS, ionic surfactant), sodium bicarbonate, and ammonia solution (30% w/w) were supplied from Sigma chemicals. Sodium acetate, sodium chloride, and other chemicals for leather processing were used as received without further purification. Distilled water was used as dispersing medium for the prepared copolymer emulsions. Egyptian bovine hides were worked up in the tanning operation as usual in the conventional method by chrome tan (BCS).

### Synthesis of copolymer emulsions

The copolymer latexes based on MMA, BuA, AA, and/or MAA were prepared by semibatch emulsion polymerization technique with solid content of  $\approx 50\%$ . Typically, the copolymers synthesis has been carried in two steps; preemulsion step and seeded emulsion polymerization step. In the preemulsion step, 30% of distilled water, SLS emulsifier, and the monomers (MMA and BuA) were added into glass beaker and mixed for 30 min using high speed homogenizer. The acid monomers (AA or MAA) were added during continuous homogenization. In the seeded emulsion polymerization step, distilled water, NP9 emulsifier,  $\text{NaHCO}_3$ , 50% of the initiator, and 10% of the preemulsion were added into four-necked flask equipped with continuous stirring under reflux. The polymerization reaction was carried out at  $80^\circ\text{C}$  using thermo stated water bath for 30 min under inert  $\text{N}_2$  atmosphere. When the reaction mixtures appeared blue and no evident of back

**TABLE I**  
Recipe of Methyl Methacrylate/Butyl Acrylate Copolymer Emulsions

Ingredients (g)	Copolymer A	Copolymer B
Deionized water	50.4	50.4
Methyl methacrylate (MMA)	26.5	22.75
Butyl acrylate (BuA)	19	22.75
Acrylic acid (AA)	1.8	–
Methacrylic acid (MAA)	–	1.8
SLS emulsifier	2	2
Sodium bicarbonate	0.1	0.1
Potassium persulfate	0.2	0.2

flow existed in the reactor, the remaining preemulsion and initiator were step wise added into the reactor within 3 h. The recipe used for preparation of the copolymer latexes is given in Table I.

### Retanning of the chrome-tanned leather

The retanning process of the chrome-tanned leather samples was carried out through different treatment processes; they include:

#### Neutralization process

The pH of chrome-tanned hides was adjusted to be 5.5 using a solution containing 0.25% sodium acetate ( $\text{CH}_3\text{COONa}$ ) and 0.5% sodium bicarbonate ( $\text{NaHCO}_3$ ).

#### Retanning process

Based on the weight of the neutralized chrome-tanned leather, 8% w/w of the copolymer emulsions were prepared by dilution with water. Then, the leather samples were treated by these emulsions under continuous stirring for 3 h. Afterward, the leather samples were washed several times with water and left to dry at room temperature.

#### Dyeing process

After retanning process, the leather samples were subjected to dyeing using acidic type dye (5%).

### Characterization

#### FT-IR analysis

FT-IR analysis was performed to determine the functional groups and the chemical composition of the prepared copolymers using Jasco FT-IR-6100 spectrophotometer with resolution  $4\text{ cm}^{-1}$ .

#### Transmission electron microscope (TEM) examination

The nanosize and morphology of the copolymer emulsions were examined by transmission electron

microscopy (TEM) with JEM-200CX operating at 200 kV. The copolymer emulsions were diluted with distilled water by the ratio 1: 100 based on the solid copolymer, and then a drop of the diluted emulsion for each copolymer was deposited on the TEM grid, which covered with carbon film, and left to dry completely at room temperature.

#### Scanning electron microscope (SEM) examination

Circular shape leather specimens of 10-mm diameter were cut from the leather before and after retanning process. Then, the specimens were subjected to sputter coating (Edwards's model S 140A) with gold ions to have a conducting medium, followed by scanning with SEM, JEOL Model JSM-T20.

#### Thermal gravimetric analysis (TGA)

The thermal stability of the leather samples were examined using thermal gravimetric analysis (TGA) technique. Shimadzu TGA-50 apparatus was used to estimate the weight loss of the leather samples as a function of temperature.<sup>17,18</sup> Thermal degradation was studied by heating the samples from ambient temperature up to 750°C, with heating rate of 10°C min<sup>-1</sup> under inert N<sub>2</sub> atmosphere.

#### Mechanical properties

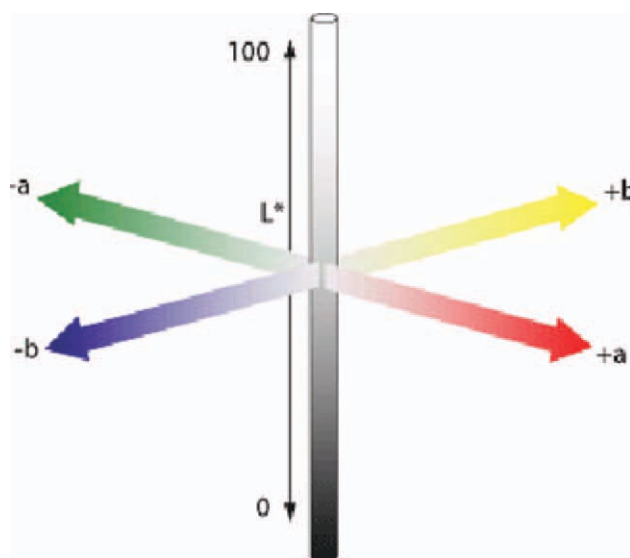
Dumbbell shaped leather specimens of 50-mm length and 4-mm neck width were prepared for measurement of the tensile strength and elongation at break. These tests were carried out using a Zwick-1425 tensile tester-25 at 25°C with a cross-head speed of 50 mm min<sup>-1</sup>. The test was carried out according to ASTM D 412.<sup>19</sup>

#### Water absorption measurement

The weight of water absorbed by the leather sample which immersed in water for a given time was determined (water absorption), and it was expressed in weight percentage (wt %). The water absorption test was carried out on circular shape leather specimens of 70-mm diameter which were cut from the leather samples, and then immersed in water for 2 and 24 h at room temperature according to Egyptian standard method ES-123.<sup>20</sup>

#### Color measurements

After dye finishing of the treated and untreated leather samples, their colors were measured using CIELAB method. The CIE organization (Commission Internationale de l'Eclairage) determined standard values that are used worldwide to measure color. The values used by CIE are called  $L^*$ ,  $a^*$ , and  $b^*$ . In this color space, any color can be identified accord-



**Figure 1** CIELAB coordinate system. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

ing to its position within three dimensional frameworks, as indicated in Figure 1. The  $L^*$  axis shows its lightness, the  $a^*$  axis its redness or greenness, and  $b^*$  axis its yellowness or blueness. This uniform system offers effective calculation of color and total color differences between sample and a reference one:  $\Delta L^*$ ,  $\Delta a^*$ ,  $\Delta b^*$ , and total difference  $\Delta E$ .

$$\text{where } \Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

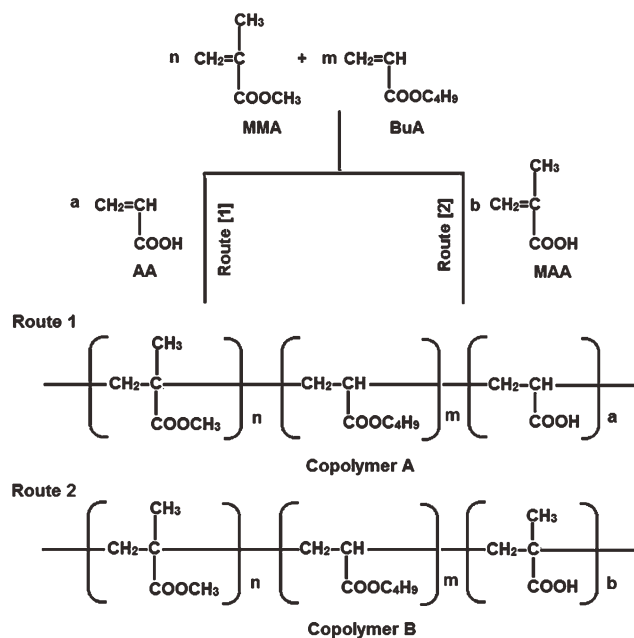
The CIELAB coordinates were measured using Ultra Scan PRO Spectrophotometer with D65 illuminant at 10° standard observer. Color of the retanned leather samples were assessed by measuring the total color difference between the dyed retanned leather and the dyed chrome-tanned leather.

## RESULTS AND DISCUSSION

### Characteristics of the prepared copolymer emulsions

Many trials were carried out to get the optimum formulation for preparing methyl methacrylate/butyl acrylate and carboxylic acid copolymer emulsions with stable properties for a period of 6 months. The optimum formulations of the prepared copolymer emulsions are represented in Table I. The prepared emulsions have high stability against salts and chemicals, and have high storage stability and low coagulum during preparation. Scheme 1 represents synthesis route of the two copolymer emulsions.

The physical, chemical, and mechanical properties of the prepared copolymer emulsions were



**Scheme 1** Synthesis routes of the two copolymer emulsions.

examined according to international standards as shown in Table II. The mechanical properties, namely, pencil hardness test, bending test, wet scrub, or washability test, and adhesion to different substrates were examined for the dry film of the copolymer emulsions.

### TEM of the prepared copolymer emulsions

The particle size and morphology of the prepared copolymer emulsions were examined using transmission electron microscope (Fig. 2). It is clearly seen from the figure that the particle size of the prepared latexes was about 90 nm for copolymer A, which prepared with high content of methyl methacrylate and acrylic acid, while the particle size of copolymer B was about 70 nm, which prepared from

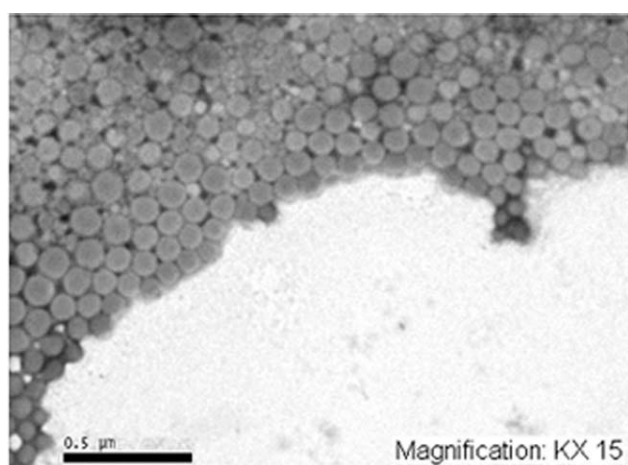
high content of butyl acrylate and methacrylic acid. Also, it is clear that the prepared latexes have poly-dispersed nanoparticles with core-shell structure. The core consists of the hydrophobic BuA/MMA copolymer and the shell consists of the hydrophilic PMAA and/or PAA. As reported earlier, the hydrophobic/hydrophilic character of the monomer(s) used in emulsion polymerization has a decisive influence on the particles morphology. According to some authors, macromolecules with an increase in hydrophilicity facilitate carboxyl ionization, resulting in higher particle swelling (increase in viscosity), and particles with high contents of AA and/or MAA being completely solubilized.<sup>21</sup> Carboxylic acid monomers are often used to improve the mechanical, freeze-thaw, and dyeability of the prepared polymers. Regardless of they are often completely soluble in water, they will still distribute to varying extents into the organic phase depending on their relative hydrophobicity. Recently, it was reported that the rate of copolymerization of itaconic acid (IA), acrylic acid (AA), and methacrylic acid (MAA) with butyl acrylate (BuA) in separate reactions was found to increase in the order  $IA < AA < MAA$ , i.e., the rate increases as the hydrophobicity of the monomer increases.<sup>22</sup> The copolymerization of BuA with AA (acidic portion) tends to produce significant amounts of water-soluble polymer, and that portion of the copolymer is usually located near to the outer surface of the latex particles. In the case of MAA, a significantly less water soluble polymer was formed, and the MAA portion in the copolymer is somewhat more dispersed within the latex particles.

### FT-IR analysis of the prepared emulsion copolymers

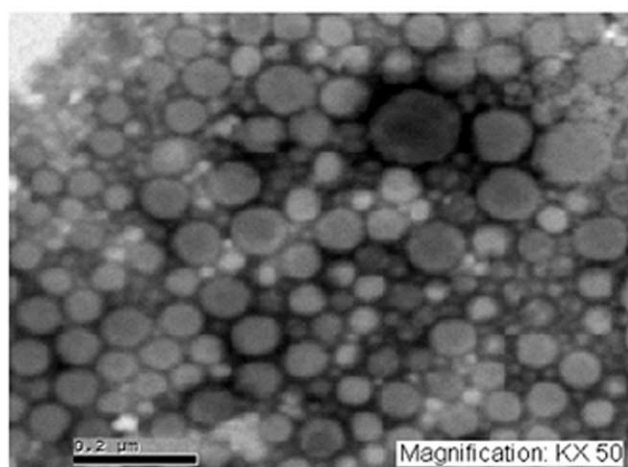
FT-IR spectra of the prepared copolymer emulsions (A and B) were illustrated in Figure 3. It is clear

**TABLE II**  
Characteristics of the Prepared Copolymer Emulsions

Property	Value		
	Copolymer A	Copolymer B	ASTM standard
pH	8.2	8.1	—
Solids by weight (%)	48.1	48.5	D 2369
Polymer conversion (%)	99.5	99.1	—
Particle size (nm)	99	73	—
Brookfield viscosity RV no. 50 rpm, (cPs)	60,000	40,000	D 2196
Chemical stability	Excellent	Excellent	D 1308
Stability against CaCl <sub>2</sub>	Pass	Pass	D 3912
Freeze thaw at -15°C, (cycles)	4	5	D 2243
Hardness (pencil) test	HB	3B	D 3363
Bending (cylindrical mandrel) test	Pass	Pass	D 522
Wet scrub-washability (cycles)	>6000	>6000	D 3450
Adhesion to PVC sheet	G <sub>t0</sub>	G <sub>t0</sub>	D 3359
Adhesion to metal	G <sub>t0</sub>	G <sub>t0</sub>	D 3359



Copolymer A



Copolymer B

Figure 2 TEM of the prepared copolymer emulsions.

from the IR spectra that both copolymers have similar molecular structure. The IR spectra show characteristic bands at 2950 and 2873  $\text{cm}^{-1}$  due to C—H stretching vibrations of  $\text{CH}_3$  and  $\text{CH}_2$  groups, respectively. Also, a sharp peak appeared at 1728  $\text{cm}^{-1}$  due to C=O of the carboxylate groups. Furthermore, characteristic bands appeared at 1169 and 967  $\text{cm}^{-1}$  due to C—O vibrations of ester groups.

### Scanning electron microscope (SEM)

SEM is a useful technique for evaluating the effect of various treatments on the skin. Thus, it is used to assess the penetration of the copolymer emulsions through the leather surface into the hierarchy of its structure. Thus, a morphological study was carried out for the chrome-tanned leather and compared with the retanned leather by the two prepared copolymer emulsions. As shown in Figures 4 and 5, scan micrographs of the grain surface (100 $\times$ ) and

the cross section (1000 $\times$ ) of the skin were carried out to show the effect of the prepared copolymers on the grain surface and fiber bundles as retanning agents.

From the cross section micrographs [Fig. 5(a–c)], it is clear that the chrome-tanned leather fibers were completely separated from each other, but in the case of retanned leather, fibers aggregates could be noticed. These aggregates refer to the coating or deposition of copolymers on leather fibers during their interaction with the leather fiber active centers. While, the empty parts of leather surface were filled up upon treating with the copolymer emulsions [Fig. 4(b–c)] when compared with the untreated leather [Fig. 4(a)]. On the other hand, a modified handling of the retanned leather samples was noticed, because they have more softness and flexibility than the chrome-tanned leather. These results indicate the significant lubrication of fiber bundles and the fine grain surface of leather upon retanning with the two copolymer emulsions. Also, the filling of the grain layer improve buffability for uses as corrected grain leather and it has no side effect on the grain surface with respect to finishing.

### Thermal study (TGA)

It was proved by thermogravimetric analysis (TGA) that the treatment of chrome-tanned leather by the prepared copolymer emulsions was successful. As shown in Figure 6, the TGA thermogram of chrome-tanned leather [Fig. 6(a)] shows two main inflections, which proved by DTA. The first inflection appeared at 75.9 $^{\circ}\text{C}$ , which corresponds to 10% weight loss in the leather sample due to the release of humidity entrapped by leather fibers. Then, the leather sample started to decompose at 268 $^{\circ}\text{C}$  to reach at 309.87 $^{\circ}\text{C}$ ,

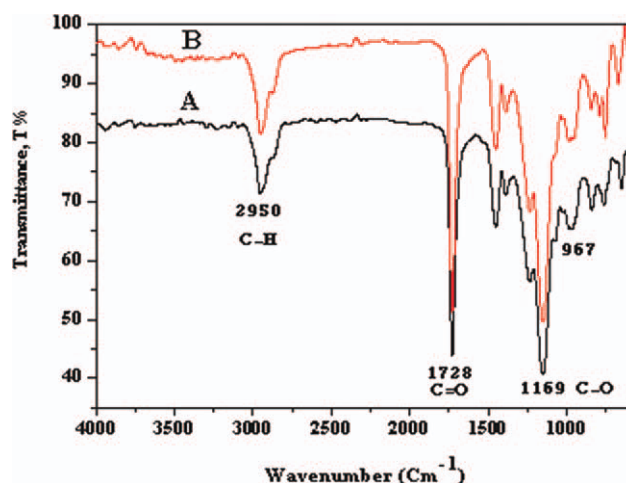
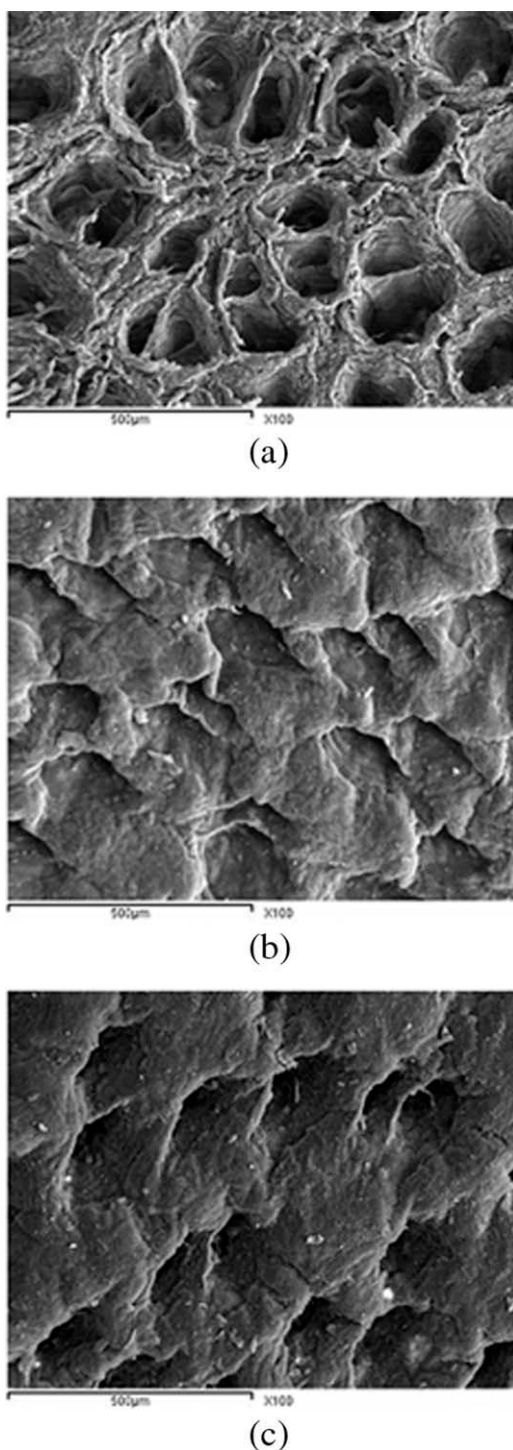


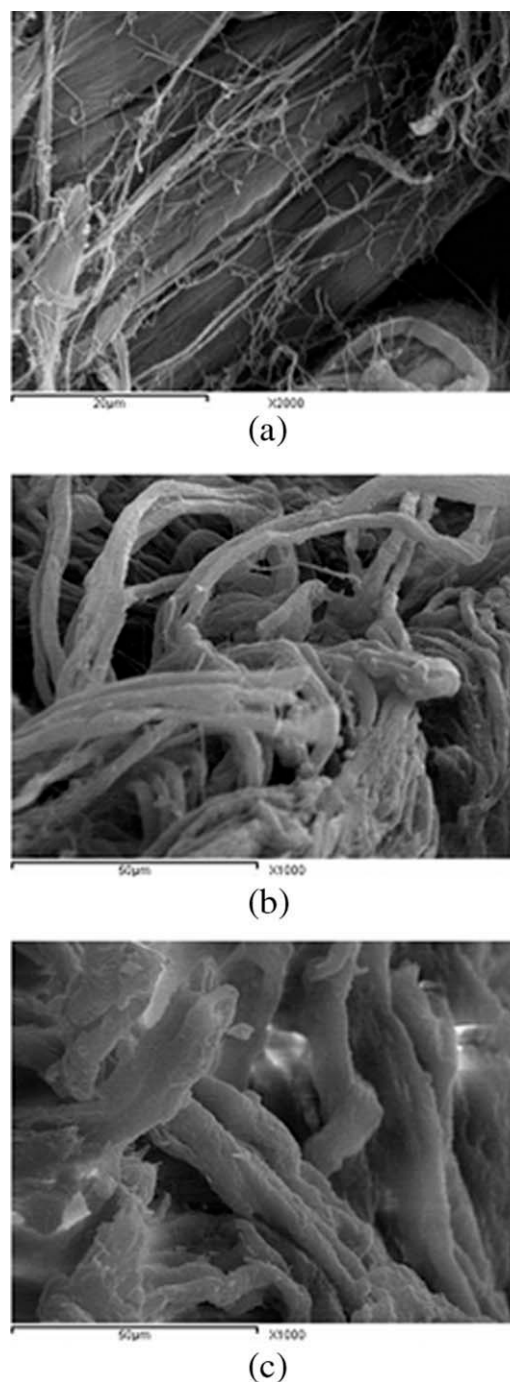
Figure 3 FT-IR spectra of copolymers A and B. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



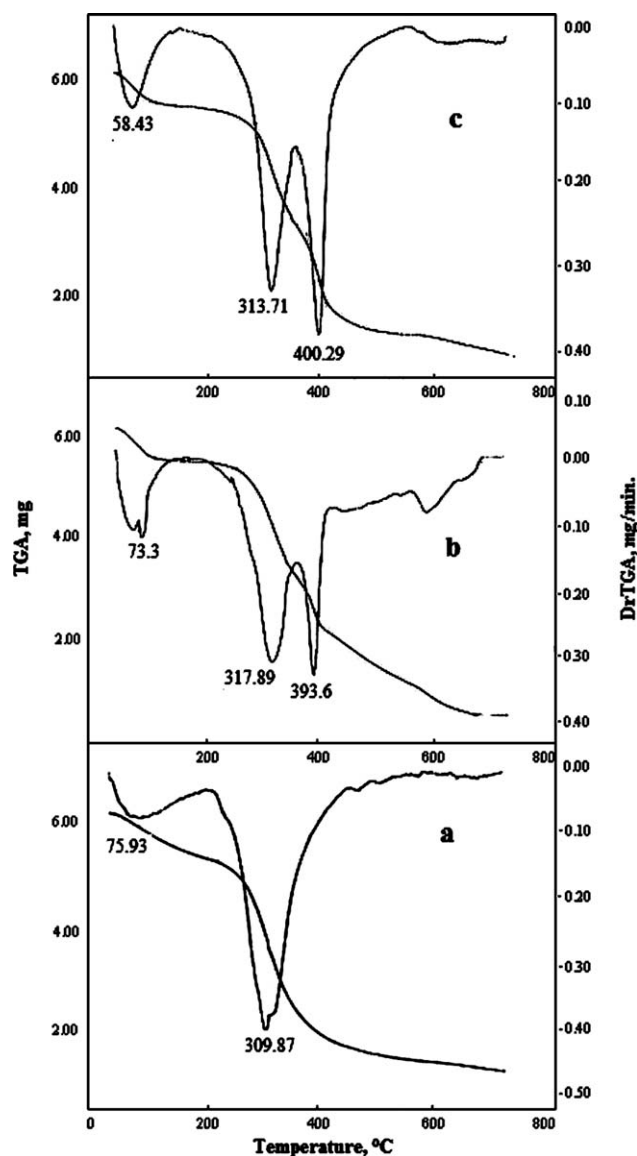
**Figure 4** (a) SEM of grain surface of chrome-tanned leather. (b) SEM of grain surface of chrome-tanned leather retanned by copolymer (A). (c) SEM of grain surface of chrome-tanned leather retanned by copolymer (B).

which corresponding to the decomposition temperature of chrome-tanned leather<sup>23</sup> with weight loss of 54.75%. On the other hand, the retanned leather by copolymer A [Fig. 6(b)] has initial weight loss of 11% around 73.3°C due to the release of humidity in the leather fibers. The main decomposition takes

place in two steps starting from 277°C, where a gradual decomposition of the retanned leather began; the first inflection occurred at 317.89°C with weight loss 38% and the last inflection appeared at 393.52°C with weight loss 19%. A similar trend was noticed with respect to the retanned leather by copolymer B [Fig. 6(c)]; a moderate inflection occurred at 58.3°C at which 9.5% weight loss in leather



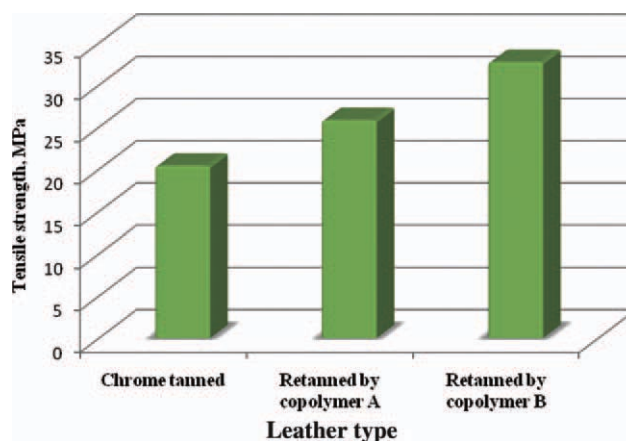
**Figure 5** (a) SEM of fiber bundles of chrome-tanned leather. (b) SEM of fiber bundles of chrome-tanned leather retanned by copolymer (A). (c) SEM of fiber bundles of chrome-tanned leather retanned by copolymer (B).



**Figure 6** TGA and DTA thermograms of (a) chrome-tanned leather, (b) retanned leather by copolymer A, and (c) retanned leather by copolymer B.

sample was detected due to moisture loss, then the leather sample was stable up to 285°C where a gradual decomposition started. By increasing the temperature, two large inflections appeared; one inflection appeared at 313.71°C with weight loss 33%, and the other one appeared at 400.29°C with weight loss 30.3%.

From the aforementioned results, it is clear that the decomposition temperature of the chrome-tanned leather increased upon treating with the prepared copolymer emulsions, especially with copolymer B. This improvement could be attributed to the formation of copolymer–collagen composite through the multiple hydrogen bonding between the numerous carbonyl groups (C=O) of the copolymers and the countless hydrogen atoms of (NH) peptide

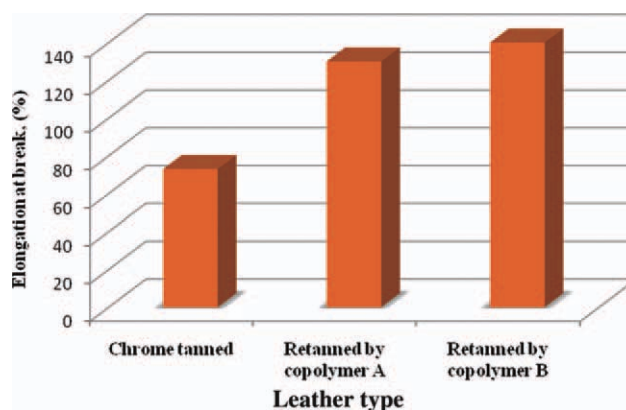


**Figure 7** Influence of the prepared copolymers on tensile strength of the retanned leather. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

groups, which support the junction between the grain and corium. At the same time, the pendant carboxyl groups of copolymers enhance the reaction with the available chromium complexes within the chrome-tanned leather.

### Mechanical properties

The mechanical properties, including the measurement of tensile strength and elongation at break, have been carried out for the chrome-tanned leather before and after treating with the copolymer emulsions. The average value of at least five replicates was taken for each item. Figures 7 and 8 show the improvement in the physicochemical properties of the chrome-tanned leather upon treating with the two copolymers as compared with the untreated one. This may be attributed to the good interaction between the fibers of the leather and the treating copolymers, and in turn the good filling of grain



**Figure 8** Influence of the prepared copolymers on elongation of the retanned leather. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

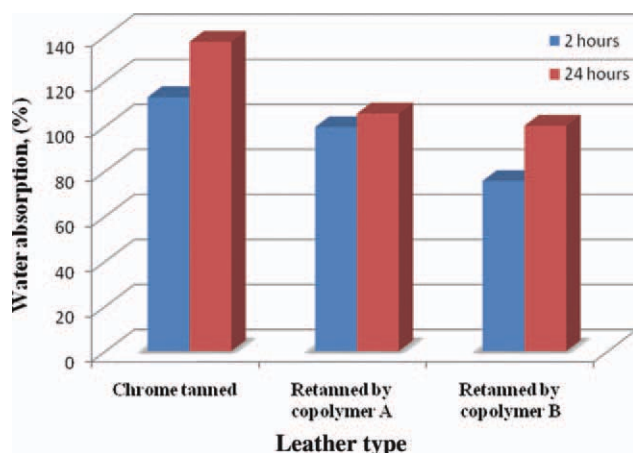
**TABLE III**  
Water Absorption (%) of the Retanned Leathers

Leather sample	Time of immersion (h)	
	2	24
Chrome tanned (blank)	112.8	137.4
Retanned by copolymer (A)	99.5	105.5
Retanned by copolymer (B)	75.57	100.1

layer, as proved by SEM measurement. Also, it was noticed that the leather treated by copolymer (B) showed better improvement in the tensile strength and elongation at break than treated by copolymer (A). This can be attributed to the lubricating effect of copolymer (B), which contain higher ratio of the soft butyl acrylate monomer than copolymer (A), and also copolymer B has smaller particle size as compared with copolymer (A).

### Water absorption

Water resistance of leather is one of the most important properties that the leather must have. For example, it is known that wet shoes are uncomfortable, especially in winter, thus it is important to make leather with high water insulating efficiency. The effect of the prepared retanning agents on water insulating efficiency of the leather samples was investigated, and the values of water absorption of retanned leather after periods of 2 and 24 h were listed in Table III. The results showed a remarkable decrease in water absorption of the retanned leather as compared with chrome-tanned one. Also it was noticed that, the value of water absorption of the treated leather by the two copolymers can be arranged as follows: copolymer A > copolymer B, which means that the leather retanned by copolymer B has higher water-insulation efficiency than that retanned by copolymer A. This can be explained as,



**Figure 9** Effect of copolymers as retanning agents on water absorption of leather. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**TABLE IV**  
Color Measurements of the Dyed Retanned Leathers

Leather sample	$L^*$	$a^*$	$b^*$	$\Delta E$
Chrome tanned (blank)	35.83	37.61	19.02	Blank
Retanned by copolymer (A)	35.17	36.35	18.65	1.46
Retanned by copolymer (B)	36.14	36.84	18.86	0.88

copolymer (B) contains higher ratio of the hydrophobic butyl acrylate monomer than copolymer (A) which increase its water repelling efficiency and in turn decrease the water absorption of leather as shown in Figure 9. This result is in agreement with researches published before,<sup>24,25</sup> which indicated that the lubrication of the leather fibers using lubricant polymers during retanning process lead to decrease in the percentage of water absorption because polymers contain a predominate portion of long hydrophobic chain.

### Color measurements

The effect of the prepared copolymer emulsions on the color fastness of the dyed leather samples was evaluated by measuring the total color difference ( $\Delta E$ ) between the dyed retanned leather and the dyed chrome-tanned leather samples. The results listed in Table IV showed that, the color build-up of the treated samples with copolymer (A) is characterized by a very slight decrease in lightness ( $L^*$ ) when compared with the dyed chrome-tanned leather samples. Also, the  $a^*$  and  $b^*$  values of dyed retanned leather are slightly lower than that of the dyed chrome-tanned leather sample (blank). Furthermore, the low average color difference ( $\Delta E$ ) indicates that there is no remarkable change in color fastness of the leather upon retanning with the prepared emulsions, especially, upon treatment with copolymer B ( $\Delta E = 0.88$ ) which is better than that treated with copolymer A ( $\Delta E = 1.46$ ).

### CONCLUSIONS

The aforementioned results indicated that eco-friendly to environment nanoemulsions based on methyl methacrylate/butyl acrylate copolymers were successfully prepared. The synthesized copolymers were used as efficient retanning agents for chrome-tanned leather. These copolymer emulsions markedly improved the mechanical properties, water insulating efficiency, and thermal stability of the treated leather. Also, there is no remarkable change in color fastness of the leather upon retanning with the prepared emulsions. Furthermore, they confer softness and flexibility in leather handling, especially on using copolymer B, which contain higher butyl acrylate (soft) monomer content than copolymer A. This means that the prepared copolymer emulsions



have retanning and lubricating effect combined in one product, which enables for the tanners to use these new developed copolymers as lubricant syntans. In addition, the prepared copolymers can be used as safe alternatives for chrome tan in retanning process.

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