NOVEL RETANNING AGENTS FOR CHROME TANNED LEATHER BASED ON EMULSION - NANO PARTICLES OF STYRENE / BUTYL ACRYLATE CO-POLYMERS

by

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ABSTRACT

The retanning process is a very important step in the leather manufacturing because it overcomes some of the disadvantages of chrome tannage. For this purpose, two different nano-emulsions of styrene/acrylate copolymers were prepared using seed emulsion polymerization technique. The main difference and characteristics of the two copolymer emulsions were studied. In addition, the morphology and the nano-particle size of the copolymer emulsions was proved by transmission electron microscope (TEM). The influence of the prepared copolymer emulsions as retanning agents for chrome tanned leather was also studied. The physico-mechanical properties of the retanned leather, namely, tensile strength, elongation at break and tear strength, were measured. Thermal stability and texture of grain surface and fibers of chrome tanned leather were examined using thermal gravimetric analysis (TGA) and scanning electron microscope (SEM), respectively. All these parameters were the main target of this work and used to evaluate the applicability of the copolymers as efficient retanning agents. The results showed an improvement in the physico-mechanical properties, softness, and firmness of grain as well as enhancement of in thermal stability upon retanning by the prepared copolymer emulsions.

RESUMEN

El proceso de recurtido es un paso muy importante en las operaciones de procesos húmedos en la fabricación del cuero, ya que puede superar algunas de las desventajas de la curtición al cromo. Con este fin, dos diferentes nano-emulsiones de los copolímeros estireno/acrilato fueron preparados, empleando la técnica de polimerización por emulsión, para su uso como agentes de recurtido. La principal diferencia en las características de los dos nano-copolímeros fue estudiada. El tamaño de la nano-partícula de los dos co-polímeros preparados se determinó por microscopía de transmisión electrónica (TEM) y la influencia sobre cuero curtido al cromo de los dos copolímeros preparados como agentes de recurtido fue estudiada. Las propiedades del cuero recurtido, es decir, resistencia a la tracción, elongación a la rotura y resistencia al desgarro, fueron medidas. La estabilidad térmica y la textura de la flor y de las fibras fueron examinadas usando análisis térmico gravimétrico (TGA) y microscopio electrónico de barrido (SEM), respectivamente. Todos estos parámetros fueron los principales objetivos de este trabajo y fueron empleados para evaluar la aplicabilidad de los copolímeros como agentes eficientes de recurtido. El cuero recurtido mostró una mejora en las propiedades mecánicas, nivelación del teñido, suavidad y firmeza de flor, así como la mejora en la estabilidad térmica.

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INTRODUCTION

In the past century, chrome tan was well known as the most commonly used tanning method for leather. It is still widely used as the main tanning agent[1] and it accounts over 80% of the activities in the tanning industry used for the production of the great majority of leather[2]. Chrome tanned leathers are characterized by their light weight and high tensile strength[3]. This can be attributed to that chrome makes cross-links with polypeptide chains through coordination bonds with the acidic amino groups in side chains of the collagen. The cross-links induce physical and mechanical properties that give the chrome tanned leather its high quality[4]. On the other hand, there are some disadvantages of chrome tanned leather, such as lack of fullness and course nap, especially in suede leather. In addition, hexavalent chromium Cr (VI) was determined in mixture with Cr (III) in some Egyptians tanneries in the wet finishing bath[5], which considered as a serious source of environmental pollution. Therefore, many retanning agents were developed to improve the chrome tanned leather properties and to limit the use of chrome in the retanning process. In general, most retanning agents are vegetable tan and phenolic synthetic/organic tanning materials. In the last decade, many trials have been done to use synthetic acrylate polymer derivatives as retanning agents 6 and they have been found suitable for filling, softening, and even water proofing[7] and air permeability[8,9], or a combination of these properties. Most of researches focused on grafting of different monomers onto the leather such as styrene[10] and acrylate derivatives[11-13]. But the grafting process needs a special procedure and precautions, which is not suitable for application in leather industry. Because most of monomers used in grafting of leather dissolve in organic solvent which is dangerous in nature and economically expensive. The most suitable procedure must be applied in aqueous medium. Thus, the leather industry has issued requirements for reagents used in retanning agent as follow: they must be non- polluting and must be applied in aqueous medium, and give clear pores and fine grain of finished leather[14].

In this work, it is of interest to develop novel retanning agents to overcome the disadvantages of chrome tanned leather. For this purpose, nano-emulsions of styrene/butyl acrylate copolymers are prepared using seed emulsion polymerization technique. The prepared polymer emulsions were applied as retanning agents for chrome tanned leather. The effect of the copolymer emulsion on the mechanical properties, thermal stability, dyeability in terms of color measurements, and on the texture of grain and fibers of the retanned leather were studied.

MATERIALS AND TECHNIQUES

Raw materials

- The monomers, styrene (St), butyl acrylate (BuA), methacrylic acids (MAA) and acrylic acid (AA), were supplied by Aldrich Company and distilled under reduced pressure before use.
- Potassium persulphate (initiator), nonionic emulsifier nonyl phenyl ethoxylated (NP9), and anionic emulsifier sodium lauryl sulphate (SLS), sodium bicarbonate, and ammonia solution (30%) were supplied from Sigma chemicals.
- Distilled water was used as dispersing medium for all the prepared emulsions.
- Egyptian bovine hides were worked up in the tanning operation as usual in the conventional method by chrome tan (BCS).
- Sodium acetate, sodium chloride and other chemicals for leather processing were used as received without further purification.

Pre-emulsion

Distilled water, emulsifiers and monomers (St and BuA) were added into the flask equipped with high speed homogenizer for 30 min (in three time portions). The acid monomer (AA and/or MAA) is added during continuous homogenization.

Seeded emulsion polymerization

PPolymer emulsions based on St and BuA as well as AA and/or MAA were prepared by semi batch emulsion polymerization technique with solid content ≈ 50%. Distilled water, residual emulsifiers, $NaHCO_3$, part of initiator and part of the pre-emulsion were added into four-necked flask equipped with continuous stirring under reflux. The polymerization reaction was carried out at 80°C using thermo stated water bath for 30 min under inert N_2 atmosphere. When the reaction mixtures appeared blue and no evidence of back flow existed in the reactor, the remaining pre-emulsion and initiator were step wise added into the reactor within 3 h. The recipe used for preparation of the copolymer emulsions is given in Table (I).

Sample preparation

a- Neutralization process

The pH of chrome tanned hides was adjusted to be 5.5 using solutions of 0.25% sodium acetate (CH_3COONa) and 0.5% sodium bicarbonate ($NaHCO_3$).

b- Retanning process

The neutralized leather was retanned with 8% by weight of each of the prepared copolymer emulsions. Then, the retanned leather was washed with water and left to dry in fresh air by hanging at room temperature.

c- Dying process

In this process, the retanned leather samples were subjected to dyeing using acidic type dye (5%).

Transmission electron microscope (TEM) examination

The nano-size and morphology of the copolymer emulsions were examined by transmission electron microscopy (TEM) with JEM-200CX operating at 200 kV. TEM samples were prepared by deposition of a drop of diluted emulsion for each copolymer onto the TEM grid which covered with carbon film, and then it was left for evaporating the solvent completely at room temperature.

Mechanical properties

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

Stitch tear (single hole)

Rectangular shape (5×10 cm) leather samples were prepared. A hole (1×10 mm) was punched on the long axis of the leather specimens. The stitch tear was then measured and calculated from the load required to tear the leather specimen from a steel rode passing through the hole of the specimen. The test was carried out according to the Egyptian standard ES-123.

Color measurements

After dyeing of the retanned and chrome tanned 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. These values are called L*, a* and b*. In this color space, any color can be identified according to its position within three dimensional frameworks. The L* axis shows its lightness; the a* axis its redness or greenness, and b* axis its yellowness or blueness. The CIELAB coordinates (L*a*b*) were measured using Ultra Scan PRO Spectrophotometer with D65 illuminant at 10o standard observer. Color fastness of the treated dyed leather samples were assessed by measuring the color difference, calculated from the CIELAB coordinates (L*a*b*) and the k/s values, between the treated dyed leather and the untreated one.

Thermal analysis

Thermal gravimetric analysis of the leather samples was carried out using Shimadzu TGA-50 apparatus to estimate the weight loss of the leather samples as a function of temperature[15,16]. Thermal degradation was studied by heating the samples from ambient temperature up to 800°C, with heating rate of 10°C/min under Nitrogen atmosphere.

Scanning electron microscope (SEM) examination

Circular shape leather samples, of 10 mm diameter, were prepared. These samples were subjected to sputter coating (Edwards's model S 140A) with gold ions to have a conducting medium. The sputter coated samples were scanned with JEOL Model JSM-T20 SEM.

Results and Discussion

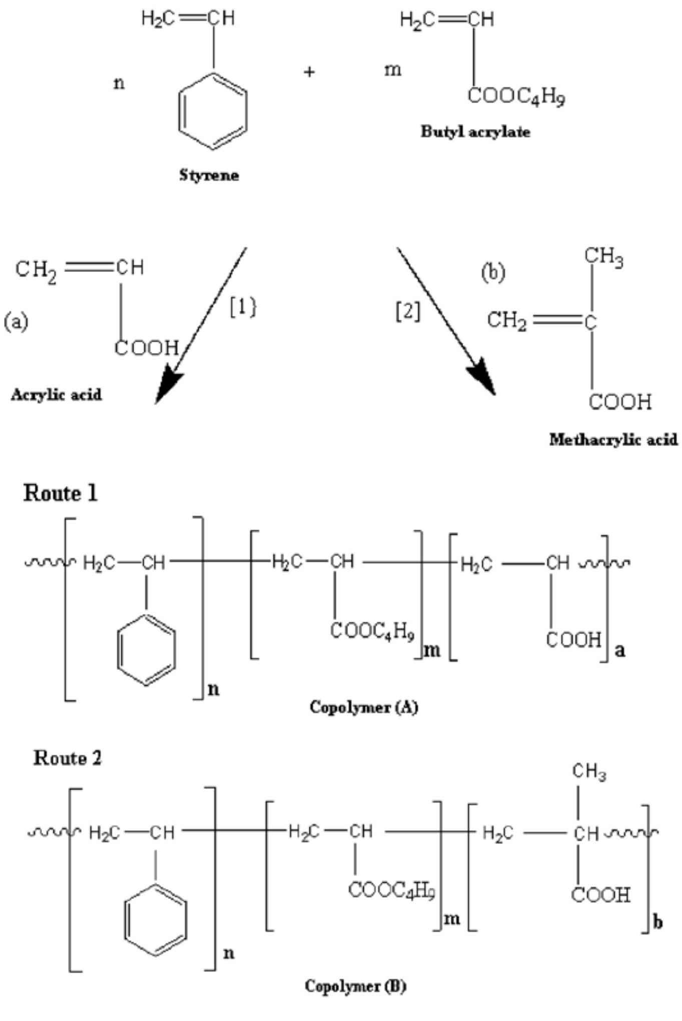
Characteristics of the prepared copolymer latexes

Styrene/ butyl acrylate/ carboxylic acid copolymer emulsions were successfully prepared using seed emulsion polymerization technique. The prepared emulsions have low coagulum during preparation, have stability against salts and chemicals, and have high storage stability for a period of six months. The optimum formulations of the prepared copolymer

TABLE 1
Recipe of styrene / butyl acrylate co-polymer emulsions

Ingredients (gm)	Co-polymer (A)	Co-polymer (B)
Styrene	30	23
Butyl acrylate	20	27
Acrylic acid	2	—
Methacrylic acid	—	2

The emulsion recipe contain H_2O (44) gm, Potassium per sulfate (0.2) gm, NP9 (0.4) gm, Sodium lauryl sulfate (1.8) gm and Sodium bicarbonate (0.1) gm.



Scheme (1): Synthesis routs of the two co-polymer emulsions

TABLE 2
Characteristics of the prepared two copolymer emulsions

Properties	Standard	Value	
	ASTM	Co-polymer (A)	Co-polymer (B)
pH (17)		8.2	8.1
Solids by weight, (%)	D 2369	49.1	49.8
Conversion, (%) (17)		99.8	99.8
Wet coagulum 100 mesh, (g/l) (18)		1.1	1.2
Particle size, (nm)	TEM	93	63
Brookfield Viscosity RV #50 rpm, (cps)	D 2196	50000	40000
Surface Tension, (dynes/cm)	FTMS 2141	47.3	46.2
Chemical Stability	D 1308	Excellent	Excellent
Stability Against $CaCl_2$	D 3912	Pass	Pass
Freeze Thaw -15°C pH 9.0, (cycles)	D 2243	4	5
Pencil Hardness test	D 3363	HB	2B
Bending test	D 522	Pass	Pass
Washability (Cycle)	D 3450	>5000	>5000
Adhesion to PVC sheet	D 3359	Gt_0	Gt_0
Adhesion to metal	D 3359	Gt_0	Gt_0

emulsions are represented in Table (1). The synthesis routs of the two copolymer emulsions are shown in Scheme.

As shown in Table (2), the physical, chemical as well as mechanical properties of the prepared copolymer emulsions were examined according to international standards. The physico-mechanical properties including pencil hardness, bending (flexibility), washability, and the adhesion of dry films of copolymer emulsions to different substrates were examined.

Figures 1 and 2 show the TEM of the prepared copolymer emulsions. It is clear from figures that the particle size of the prepared latexes was ≈ 100 nm for copolymer (A) which was prepared with high content of styrene and acrylic acid; while the particle size of copolymer (B) was ≈ 65 nm which was prepared from high content of butyl acrylate and methacrylic acid.

Also, it is clear from the figures that the copolymer emulsions have homo dispersed particles with core-shell morphology. The core represents the hydrophobic monomers (styrene and butyl acrylate) and the shell represents the hydrophilic monomer carboxylic acid (acrylic acid or methacrylic acid). In a previous work, it has been reported that the hydrophobic/hydrophilic character of the monomer(s) used in emulsion polymerization has a crucial influence on the particle morphology. It was found that, macromolecules with increase in their hydrophilicity facilitate carboxyl ionization, which result in a higher particle swelling (increase in viscosity), while particles with high contents of acrylic acid (AA) and/or methacrylic acid (MAA) are being completely solubilized (19). Usually, carboxylic acid monomers are added to improve the mechanical properties, freeze-thaw stability, and dyeability of the polymer latexes. Carboxylic acid monomers are often completely soluble in water; however, they will still distribute to varying extents into the organic phase depending on their relative hydrophobicity. The most frequently studied acid monomers copolymerized with styrene are itaconic acid (IA), acrylic acid (AA) and methacrylic acid (MAA). The rate of copolymerization of IA, AA and MAA with styrene in separate reactions was found to increase as follow: IA < AA < MAA. i.e., the rate increased as the hydrophobicity of the monomer increased (20). The use of AA tends to produce significant amounts of water-soluble polymer, and this acidic portion of the copolymer is usually located near to the outer surface of the latexes particles. While, in the case of MAA, there is a significantly less water-soluble polymer formed and the MAA portion in the copolymer is somewhat more evenly dispersed within the particle.

Mechanical properties

Tensile properties of the leather have great consideration in the evaluation of leather products. The mechanical properties include measurement of the tensile strength, elongation at break, and tear strength. The average value of five tests for each leather sample was calculated and listed in Table (3). Generally, it is clear from Table (3) that the mechanical properties of chrome tanned leather improved upon retannig with the two prepared

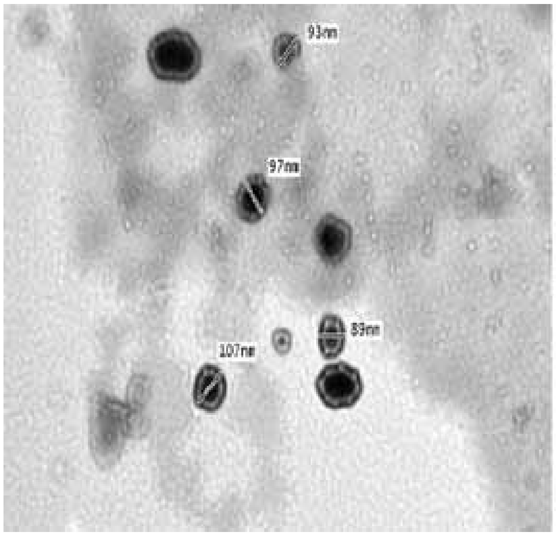


Figure (1): TEM of co-polymer (A) emulsion.

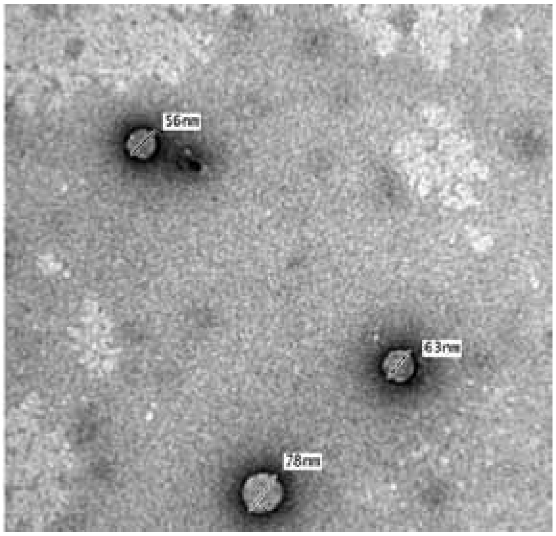


Figure (2): TEM of co-polymer (B) emulsion.

copolymer emulsions. This may be attributed to the good adhesion of the copolymer on the fiber of the leather beside to the filling of grain layer of the leather. Also, it was noticed that, copolymer (B) improves the tensile strength, elongation at break, and tear strength of the leather when compared with copolymer (A). This can be attributed to the more lubrication effect of copolymer (B) which has higher ratio of the soft butyl acrylate monomer than styrene. Furthermore, copolymer (B) has smaller particle size, as compared with copolymer (A) and in turn, the interaction between the leather fibers and copolymer B will be more than copolymer (A).

Color measurements

Color fastness of the treated dyed leather samples was assessed by measuring the color difference between the CIELAB coordinates (L*a*b*) and the k/s values of the treated dyed leather and the untreated dyed one (Table 4).

The results listed in Table (4) showed that the color of the treated samples with copolymer (B) is characterized by a slight decrease in lightness (L*), and in redness (+ a*). Also, the treated samples with copolymer (A) have slight decrease in lightness and a decrease in yellowness (+ b*) as compared with the chrome tanned leather (Blank). Generally, it can be concluded that the treatment of chrome tanned leather with copolymer (B) is preferable than that of using copolymer (A). In general, acrylate polymers in most cases can affect the brightness of the dyed leather[21]. In the present work we used acrylate copolymers with styrene in different ratios to study the suitable ratio which can overcome the disadvantage of acrylate one. The colorimetric data of the sample treated with copolymer (B) remains slightly unchanged relative to the untreated (blank) sample and also showed greater uniformity across the leather surface. This means that the copolymer (B) does not affect the color shade of the dyed leather, when using the dyes chosen in this study.

Thermal stability study (TGA)

As shown in Figures (3 a, b and c), the TGA and Dr-TGA curves show that the decomposition temperature of retanned

TABLE 3
Physico-mechanical properties of leather samples

Leather type Property	Chrome tanned (Blank)	Re-tanned by co-polymer (A)	Re-tanned by co-polymer (B)
Tensile strength, (M Pa)	21.3	25.6	28.9
Elongation at break, (%)	71.20	111.50	123.25
Tear strength, Kg/Cm	75.50	87.06	94.04

TABLE 4
Color measurements of the treated leather samples in comparison with the untreated one

Type of leather sample	L*	a*	b*	*k/s*
Chrome tanned (Blank)	43.99	12.80	30.16	*9.77*
Re-tanned by co-polymer (A)	40.42	11.53	22.22	*8.70*
Re-tanned by co-polymer (B)	42.17	11.00	23.68	8.49

TABLE 5
Weight loss measurements of chrome tanned leather and retanned leather by the two co-polymers (A & B)

Temperature, °C	Weight loss, (%)		
	Chrome tanned leather	Chrome/ co-polymer (A)	Chrome/ co-polymer (B)
70	12.8	9.1	9.6
310	32.9	27.6	24.3
390	45.8	31.5	32.5
750	96	95.2	85.9

leather by the two copolymers is higher than that of chrome tanned leather one. Thus, the thermal stability of the chrome tanned leather increases upon treatment with the prepared copolymer emulsions. Table (5) illustrate the weight loss measurements chrome tanned leather and the reatnned leather by copolymers A and B.

This improvement in thermal stability can be attributed to the formation of polymer – collagen composite. This can be explained by the multiple weak hydrogen bonds between the numerous carbonyl groups (C=O) of the copolymers and the countless hydrogen atoms of (NH) peptide groups of leather fibers, which support the junction between the grain and the corium.

Scanning electron microscope (SEM)

SEM can be used to assess the penetration of the copolymer through the leather and into the hierarchy of the leather structure and thus it is a useful technique for evaluating the effects of various treatments on the skin. As shown in Figures (4 and 5), a morphological study was carried out for the chrome tanned leather in comparison with retanned leather by the two copolymers (A&B). SEM of the grain surface (×50) and the cross-section of the (×1000) of the skin with and without copolymers were carried out to show the effect of the prepared copolymers on the grain and fiber bundles as retanning agents.

From the cross section micrographs in (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, fiber 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. 4b-c) when compared with the untreated leather (Fig. 4a). On the other hand, a modified handling of the retanned leather samples was noticed, because

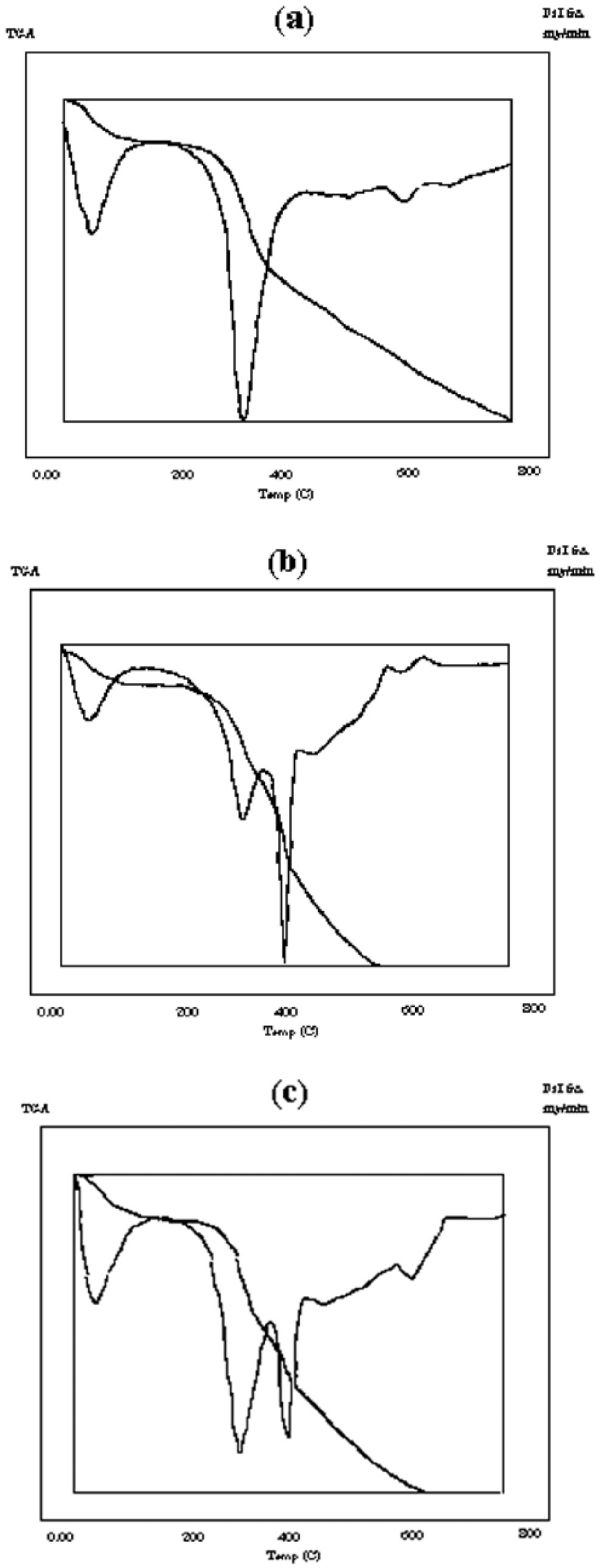


Fig. (5): TGA and Dr-TGA of chrome tanned leather (a), retanned leather by copolymer (A) (b), and retanned leather by copolymer (B) (c).

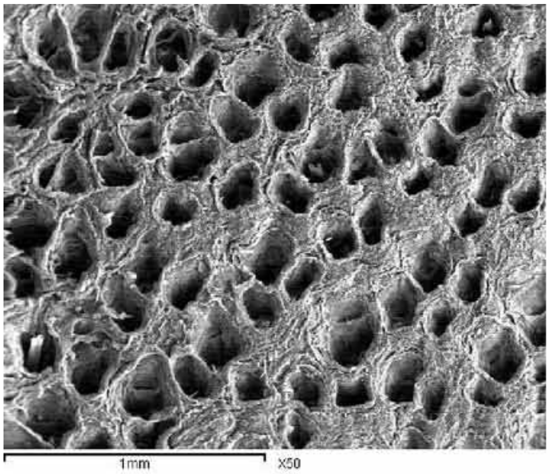


Figure 4a: SEM of grain surface of chrome tanned leather.

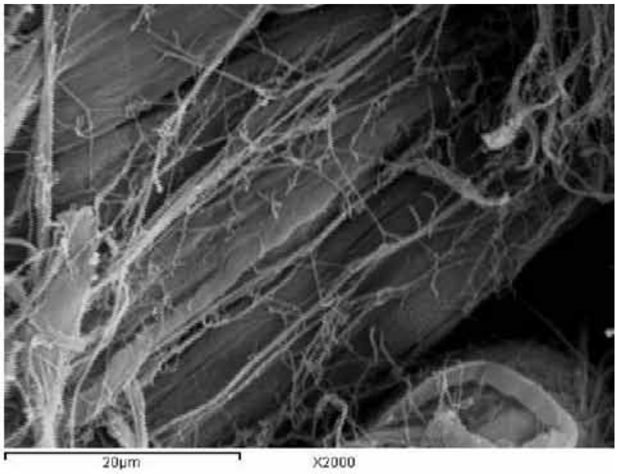


Figure 5a: SEM of fiber bundles of chrome tanned leather.

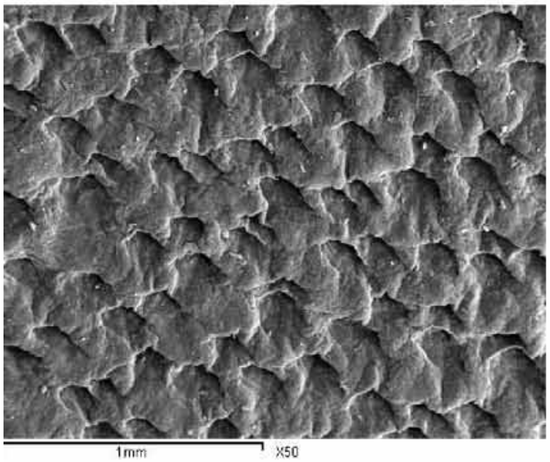


Figure 4b: SEM of grain surface of chrome tanned leather retanned by copolymer (A).

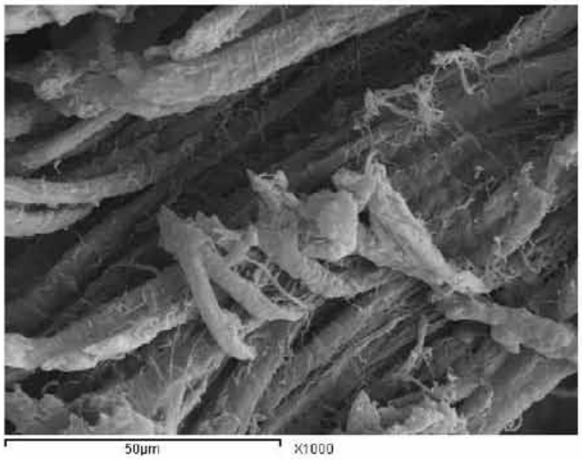


Figure 5b: SEM of fiber bundles of chrome tanned leather retanned by copolymer (A).

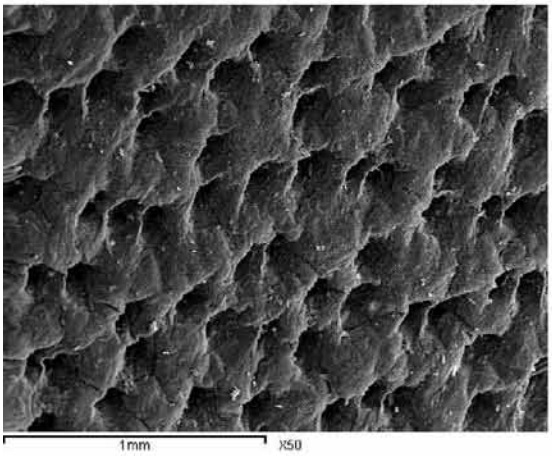


Figure 4c: SEM of grain surface of chrome tanned leather retanned by copolymer (B).

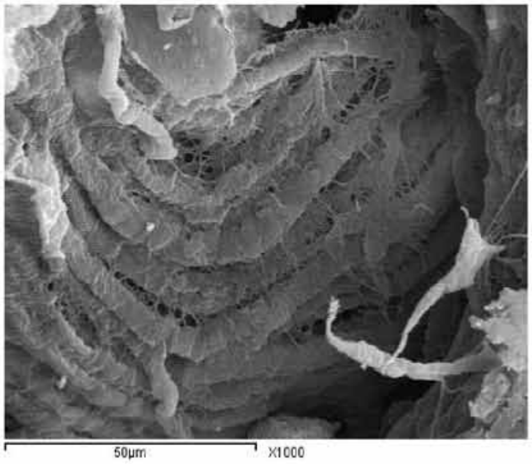


Figure 5c: SEM of fiber bundles of chrome tanned leather retanned by copolymer (B).

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.

Conclusions

The aforementioned results indicate that eco-friendly and efficient retanning agents based on styrene/ butyl acrylate copolymer latexes were successfully prepared using seed emulsion polymerization technique. The characteristics of the finished leather were improved in the following aspects:

1. The fullness and tight of grain obtained were due to the filling action of the copolymer nano- particles.
2. The elongation of the retanned leather decreased by increasing the styrene monomer content with respect to the butyl acrylate due to its crystallinity.
3. Improvement of the softness and mechanical properties of the retanned leather which refers to the lubrication effect of the copolymer.
4. No side effect was noticed on uniform dyestuff especially with respect to copolymer (B).
5. Enhancement of the thermal stability of leather upon retanning by the prepared copolymer emulsions.
6. The prepared copolymer emulsions can be used as retanning agents who limit the use of chrom as a retanning agent, and consequently decrease the pollution.

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