

Synthesis and Characterization of Nano Emulsions of Acrylate Copolymers as A Lubricant Agent

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Abstract

Two different micro-emulsions based on methyl meth acrylate / butyl acrylate copolymers have been synthesized to be used as retanning agents for chrome tanned leather. The main difference and characteristics of the two prepared copolymers were studied. The nano particle size of the two co-polymers was confirmed using transmission electron microscope (TEM). The characterization of the two prepared copolymers were investigated. The properties of the retanned leather, namely, physico-mechanical properties as water absorption, tear strength; tensile strength and elongation at break were measured. Thermal gravimetric analysis (TGA) technique was used to examine the thermal stability of the retanned leather. Texture of the grain surface and fibers were inspected using Scanning electron microscope (SEM). The retanned leather showed an improvement in its physico-mechanical properties, as well as enhancement of its thermal stability. Also, it has uniform dyestuff, softness and firmness grain. All these promising results provide evidence to the applicability of the prepared copolymer emulsions as efficient retanning agents.

Keywords: Micro-emulsions, Acrylate copolymers, Nano- Particles, Lubricant, Chrome tanned leather, Retanning agent, Scanning electron microscope, Thermal stability, Transmission electron microscope, Physico-mechanical properties, Color difference.

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INTRODUCTION

Raw hides and skins are transferred into leather by tanning process. There are many types of tanning and retanning agents. The most widely used one all over the world is chrome tan and is still the major tanning agent [1, 2]. It accounts over 80% of the activities in the tanning industry used for the production of the great majority of leather [1]. Chrome tanned leathers are characterized by their light weight and high tensile strength [3]. Chrome tan improves the physical and mechanical properties that give the leather its high quality [4]. This improvement is due to the cross-links between chrome and polypeptide chains throughout coordination bonds with the acidic amino acid side chains of the collagen. However, chrome tanned leathers have disadvantages such as lack of fullness and course nap especially in suede leather. Furthermore, chrome tanning generates byproducts wastes containing chrome which have adverse effects on the environment. In addition, hexavalent chromium was determined in mixture of Cr (III) and Cr (VI) in some Egyptians tanneries in wet finishing bath, which considered as a toxic and a pollutant to the environment [5].

Because of these drawbacks, numerous investigations are being currently carried out to reduce pollution by avoiding the application of chrome either totally or partially in the tanning industry. As a result, most retanning agents used are based on vegetable and phenolic synthetic/organic tanning materials [6, 7]. Recently, many trials have been done to develop new retanning agents to improve the chrome tanned leather properties based on acrylate polymer derivatives [8], which are suitable for filling, softening, and even water proofing [9], air permeability [10, 11] or which combine all these properties. However, the majority of these researches focused on grafting of various monomers onto leather such as styrene [12] and acrylate monomer derivatives [13-15].

From the environmental and economical point of view, it is urgent to diminish the using of monomers in grafting process. Because most of the monomers used in leather grafting are dangerous in nature and needs a special technique, which is not suitable for application in leather industry. The most suitable procedure must be applied in aqueous medium. Since,

the leather industry has brought forward requirements for reagents which be used in leather industry must be applied in aqueous medium, non-pollutant and give clear pore and fine grain of finished leather [16].

Thus, the present work was devoted to develop new acrylate copolymers nano-emulsion, which can be used as retanning agents and at the same time have lubricating ability as well as to improve the undesirable properties of chrome tanned leathers. The synthesis and applications of two nano-emulsions based on acrylate copolymers as well as the physico-mechanical properties, thermal stability, and color fastness measurements were studied. Also, the texture of grain and fibers of the retanned leather were examined.

MATERIALS AND TECHNIQUES

Raw Materials

- Methyl methacrylate (MMA), butyl acrylate (BuA), methacrylic acid (MAA) and acrylic acid (AA) were supplied by Aldrich and distilled under reduced pressure before use.
- Potassium persulphate (initiator), nonyl phenol ethoxylate (Tergitol-NP9, non-ionic surfactant), sodium lauryl sulphate (SLS) (ionic surfactant), sodium bicarbonate, ammonia solution (30%), were supplied from Sigma chemicals. Distilled water was used as dispersing medium.
- 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 without further purification.

Synthesis of Co-polymers

a- Pre-emulsion

Distilled water, part of the emulsifiers, (MMA) 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.

b- Seeded emulsion polymerization

Polymer lattices based on (MMA), (BuA) as well as (AA) and/or (MAA) were prepared by semi batch emulsion polymerization technique with solid content of 50%. Distilled water, residual emulsifiers, NaHCO_3 , part of initiator and part of pre-emulsion were added into the four-neck 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 an inert atmosphere of N_2 . When the reaction mixtures appeared blue and no evident 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 different compositions of polymer lattices is given in Table-1.

Sample Preparation

a- Neutralization process

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

b- Retanning process

Retanning process of the neutralized leather was carried out using 8% of the prepared copolymer emulsions. Then, the retanned leather was washed several times with water and left to dry in fresh air through hanging up at room temperature.

c- Dying process

Dying process was done on retanned leather with acidic type dye (5%).

Note: All chemical additives were calculated on the basis of leather weight (w/w).

Mechanical Properties

Dumbbell shaped leather specimens, of 50 mm length and 4mm (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^{-1} . The test was carried out according to ASTM D 412 [17].

Water Absorption

Discs of 70 mm diameter were cut from the leather samples, then tested with the Kubelka apparatus for their water absorption after 2 and 24 hours according to ES 123 [18]. The percentage of water absorption, i.e. the amount of water absorbed by the leather immersed in water for a given time was then calculated.

Color Measurements

The CIELAB coordinates were measured using Ultra Scan PRO Spectrophotometer with D65 illuminant at 10° standard observer. Leveling of the treated dyed leather samples were assessed by measuring the color difference calculated from the CIELAB coordinates bond ($L^*a^*b^*$) and the k/s values of the treated dyed leather relative with untreated one.

Scanning electron microscope examination (SEM)

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

Thermal Analysis

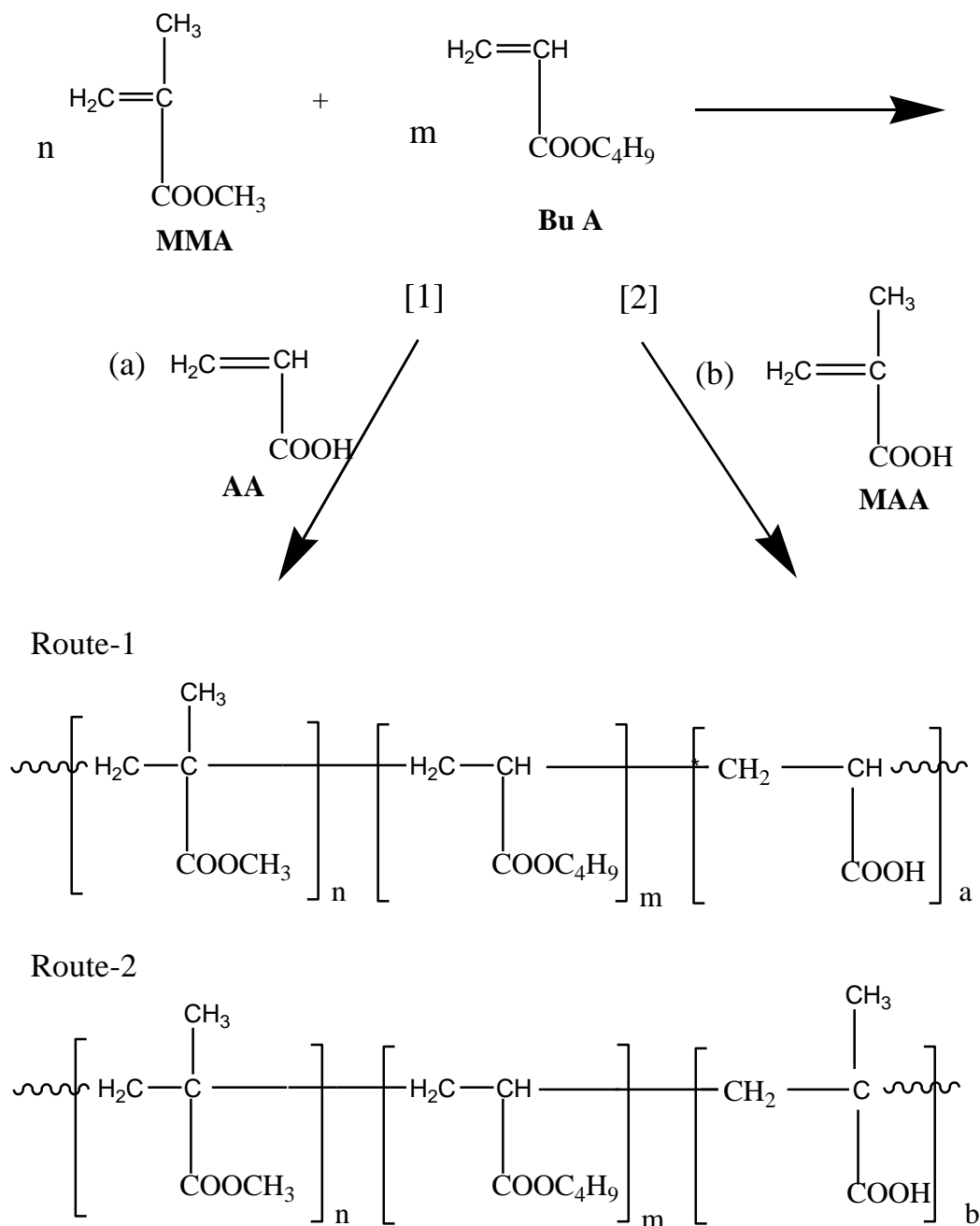
The thermal stability of the leather samples were examined using thermal gravimetric analysis

(TGA) technique. Shimadzu TGA-50 apparatus was used to estimate the weight loss of the leather samples as a function of temperature [19, 20]. Thermal degradation was studied by heating the samples from ambient temperature up to 1000°C.

RESULTS AND DISCUSSION

Characteristics of the prepared copolymers

Stable micro-emulsions against salts, chemicals with high storage stability and low coagulum during preparation were the main demand in production of methyl meth acrylate /butyl acrylate carboxylic acid emulsion. Many trials were carried out to get the optimum formulation for preparing methyl methacrylate /butyl acrylate and carboxylic acid with stable properties for a period of six month. Equation No. (1) represent the reaction of the two monomers.



Equation-1: Synthesis routes of monomers to form two Co-polymers

Different surfactant systems were also examined as well as the initiator to get the optimum

formulas. Table-1 represents the optimum formulations of the prepared emulsions.

Table-1: Recipe of optimum methyl meth acrylate /butyl acrylate emulsion co-polymers containing different ratios of methyl methacrylate, butyl acrylate, acrylic acid or meth acrylic acid

Ingredients (gm)	A	B
Methyl meth acrylate	29	25
Butyl acrylate	21	25
Acrylic acid	2	-
Meth acrylic acid	--	2
Acrylamide	1	1
<i>The emulsion recipe contain H₂O (54)gm, Potassium per sulfate (0.2) gm, NP30 (0.5) gm, Texapone K12 P (2.2) gm and Sodium bicarbonate (0.1) gm.</i>		

The physical, chemical as well as mechanical properties of the prepared copolymer emulsions were examined according to international standard as shown in Table-2. Also, pencil hardness test, bending test,

washability of the film and adhesion to different substrate were examined to dried film and recorded in Table-2.

Table-2: Characteristics of the prepared two copolymer emulsions

Properties	Standard	Value	
	ASTM	A	B
pH [17]		8.2	8.1
Solids by weight, (%)	D 2369.	48.1	48.5
Conversion, (%) [17]		99.5	99.1
Wet coagulum 100 mesh, (g/l) [18]		1.3	1.6
Particle size, (nm)	TEM	99	73
Brookfield Viscosity RV #50 rpm, (cps)	D 2196	60000	40000
Surface Tension, (dynes/cm)	FTMS 2141	47.1	46.7
Chemical Stability	D 1308	Excellent	Excellent
Stability Against CaCl ₂	D 3912	Pass	Pass
Freeze Thaw -15°C, (cycles)	D 2243	4	5
Pencil Hardness test	D 3363	HB	3B
Bending test	D 522	Pass	Pass
Washability (Cycle)	D 3450	>6000	>6000
Adhesion to PVC sheet	D 3359	Gt ₀	Gt ₀
Adhesion to metal	D 3359	Gt ₀	Gt ₀

TEM of the Prepared Emulsion Co-Polymers

Figures 1 & 2 show the transmission electron microscope of the prepared emulsion lattices. It is clearly seen from the figures that, the particle size of the prepared lattices was about 90 nm for copolymer (A) which prepared with high content of methyl meth

acrylate and acrylic acid while the particle size of copolymer (B) was about 70 nm which prepared from high content of butyl acrylate and meth acrylic acid. Also, the TEM figures represent that the prepared lattices have homo dispersed nano-particles with core-shell structure.

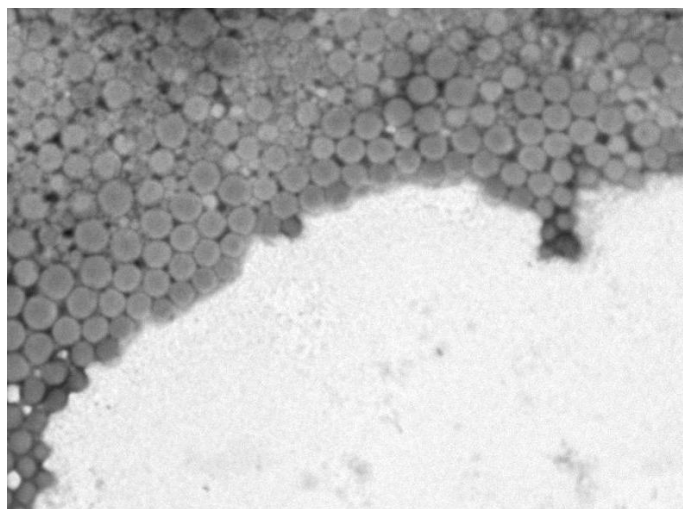


Fig-1: TEM of the emulsion co-polymer (A)

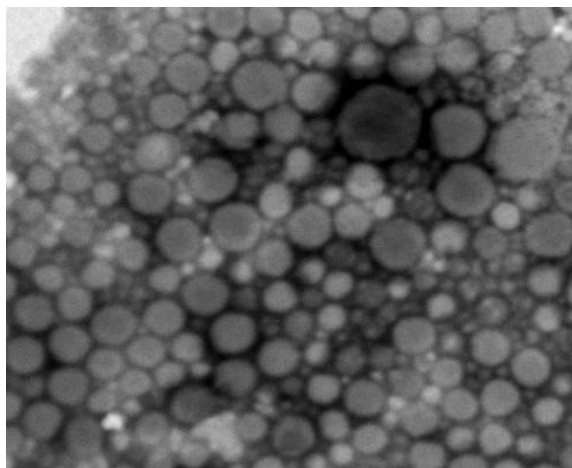


Fig-2: TEM of the emulsion co-polymer (B)

The core consists of BuA/MMA copolymer and the shell consists of the carboxylic acid. It has also been reported that the hydrophobic/hydrophilic character of the monomer(s) used in emulsion polymerization has a decisive influence on particle morphology: according to some authors, macromolecules with an increase in hydrophilicity facilitate carboxyl ionization, resulting in higher particle swelling (increase in viscosity), particles with high contents of AA and/or MAA being completely solubilized [21]. Carboxylic acids monomers are often used to improve the mechanical, freeze-thaw, and dyability of the prepared polymers. Carboxylic acid monomers are often completely soluble in water; however, they will still distribute to vary extents into the organic phase depending on their relative hydrophobicity.

The rate of copolymerization of (IA), (AA) and MAA with butyl acrylate in separate reactions was found to increase in the order (IA) < (AA) < (MAA), i.e. the rate increased as the hydrophobicity of the monomer increase [22]. The use of AA tends to produce significant amounts of water-soluble polymer, and that portion of the acid copolymer that is in the particles is usually located near the outer surface of the lattices particles. With MAA, there is significantly less water-soluble polymer formed and the MAA copolymer in the particle is somewhat more evenly dispersed within the particle.

FT-IR Analysis

In order to elucidate the molecular structure of the studied samples FT-IR is utilized. Figure-1 illustrates the spectra of co-polymer (A) low viscous and Co-polymer (B) high viscous FT-IR transmittance bands in the range of 4000 to 570 Cm^{-1} , Figure-3.

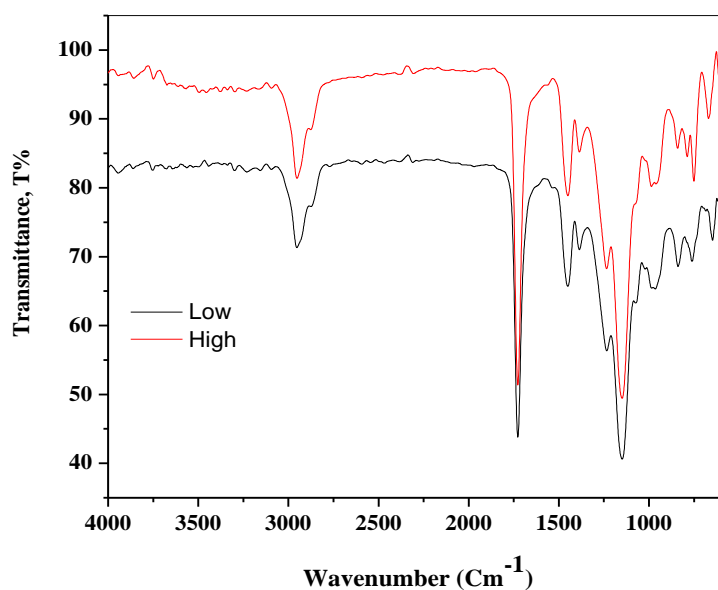


Fig-3: FT-IR spectra of two Co-polymers

As a general remark both polymers indicate a similar molecular structure. The transmittance of high viscous sample is higher than the lower viscous sample. The spectra could be assigned as; characteristics bands at 2950 and 2873 cm^{-1} are attributed to C-H stretching vibrations. The strong peak at 1728 cm^{-1} is assigned to free carboxylic group and the bands at 1451 cm^{-1} , 831 cm^{-1} corresponding to C-H & CH₂ bending vibration respectively. Also, the spectra show stretching bands at 1384 cm^{-1} , 1233 cm^{-1} and 1150 cm^{-1} which are corresponding to splitting CH₃ umbrella mode. But the bands at 1069 cm^{-1} and 967 cm^{-1} are corresponding to C-C-O finger print. Only one difference could be found if we compare the spectra of the two polymers. The high viscous co-polymer shows a band at 794 cm^{-1} due to the C-H angular deformation of anomeric carbon.

Mechanical Properties of Treated Leather

The mechanical characters including the measurement of tensile strength and elongation at break have been given the greatest consideration in the evaluation of leather. These tests were carried out according to the Egyptian standard method (ES-123) and official methods, and the average value of at least five replicates was taken for each item. It was revealed from Figure 3 & 4 that, an improvement in the mechanical properties of treated leather by two copolymers than untreated one this may be due to the good adhesion effect of the copolymer and at the same time good lubrication on the fiber of the leather and also due to the filling of grain layer.

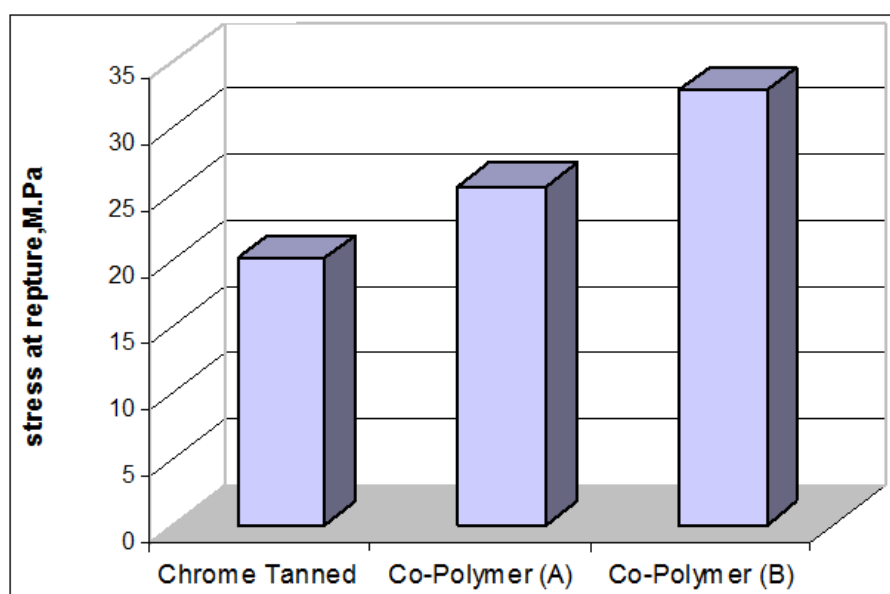


Fig-3: Influence of the prepared two co-polymers on tensile strength

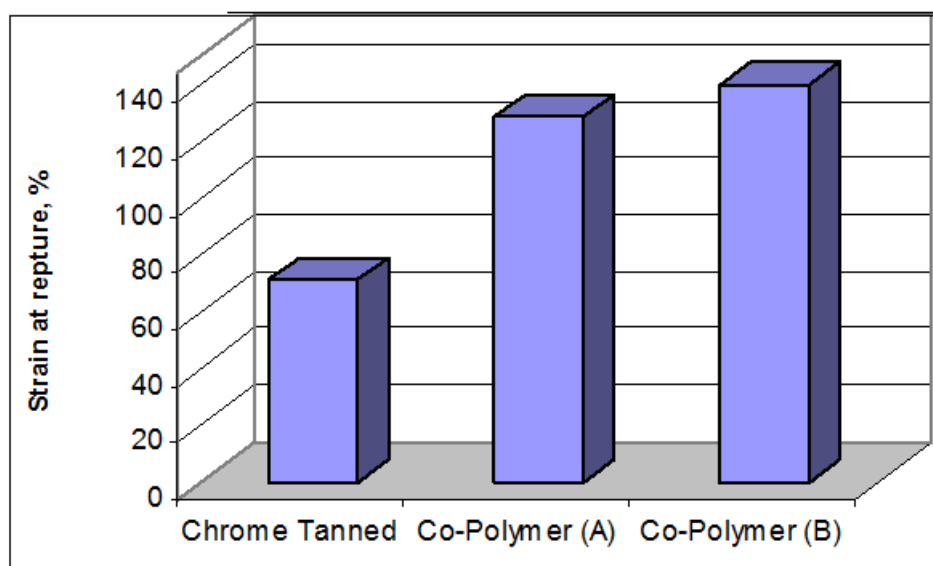


Fig-4: Influence of the prepared two co-polymers on elongation at break

It was also noticed that the copolymer (B) improve the elongation comparing with copolymer (A). However, the tensile strength was improved by copolymer (B) than copolymer (A). This can be attributed to the lubricating effect of copolymer (B) (higher ratio of acrylate which had elastic properties than methyl acrylate and also had smaller particle size compare with copolymer (A).

Water Absorption

It is obviously important that leather should be resistant to water absorption, as wet shoes are uncomfortable, especially in winter, for insulating efficiency leather for shoes should be made highly

water-resistance. The leather samples, after treatment with the investigated retanning agents showed different behaviour towards water absorption after periods of 2 and/or 24 hours, using Kubelka's Method [18].

The incorporation of the prepared two copolymers showed a remarkable decrease of the water absorption of the resulting leather compared with chrome tanned one. Also it was noticed that, the value of water absorption of the treated leather by two copolymers can be arranged as follows: high viscous > low viscous. The percentages of water absorption after 24 hours were higher than the percentages after 2 hours; the results are shown in Table-3.

Table-3: Water absorption of Re - tanned leather samples

Water absorption vs. treatments	Water absorption at 2 hours	Water absorption at 24 hours
Blank	112.8	137.4
Co-polymer (A)	99.5	105.5
Co-polymer (B)	75.57	100.1

In general, the lubrication of the leather fibers by incorporation of lubricant polymers during retanning process should lead to decrease in the percentage of water absorption because polymers contains a predominate portion of long chain hydrocarbons (hydrophobic part) [23, 24].

Color Measurements

Leveling of the treated dyed leather samples was evaluated by measuring the color difference calculated from the CIELAB coordinates bond ($L^*a^*b^*$) and the k/s values and the average color difference (ΔE) by comparing the change in color between the treated samples relative to the untreated one Table-4.

Table-4: Color measurements of the treated leather samples in comparison with the untreated one

Type of Sample	L^*	a^*	b^*	ΔE	k/s
Without treatment (Blank)	35.83	37.61	19.02	blank	11.04
Leather retanned by Copolymer (A)	35.17	36.35	18.65	1.46	11.04
Leather retanned by Copolymer (B)	36.14	36.84	18.86	0.88	10.36

Where,

L^* : Lightness,

a^* : Redness,

b^* : yellowness,

ΔE : Color difference

The colorimetric data was evaluated from k/s and reflectance measurements converted to L^* , a^* , b^* values using the CIELAB system. The results listed in Table-4 showed that, the color build-up of the treated samples with copolymer (A) is characterized by a non significant decrease in lightness (L^*), while the treated samples with copolymer (B) produced a significant change in lightness. Also, the k/s , a^* and b^* values of dyed treated leather samples are similar for both two treatment of two co-polymers. The further means of illustrating the color change makes use of the color difference (ΔE , calculated from the CIE $L^* a^* b^*$ coordinates) between the dyed sample between the dyed sample, which treated with copolymer (A and B). The average color difference shows good leveling properties. The results also indicate that the treatment

with copolymer (B) is slightly better than that treated with copolymer (A) and also greater uniform across leather surface.

Thermal Study (TGA)

The TGA curve, Figure (5), shows that the decomposition temperature of the copolymer- retanned leather is higher than that of chrome tanned leather. Thus, the incorporation of the co-polymer (s) into chrome tanned leather increases its thermal stability, which can be attributed to the formation of co-polymer - collagen composite. This composite can be brought about multiple weak hydrogen bonding between the numerous carbonyl groups ($C=O$) of the co-polymers and the countless hydrogen atoms of (NH) peptide groups, which support the junction between the grain and corium, and at the same time the pendant carboxyl groups of polymers are reacted with available chromium complex. Thus, the copolymers will undergo physical bonding with the fiber active centers and fill up the empty parts of leather and deposited inside the leather and fixed to the leather fiber.

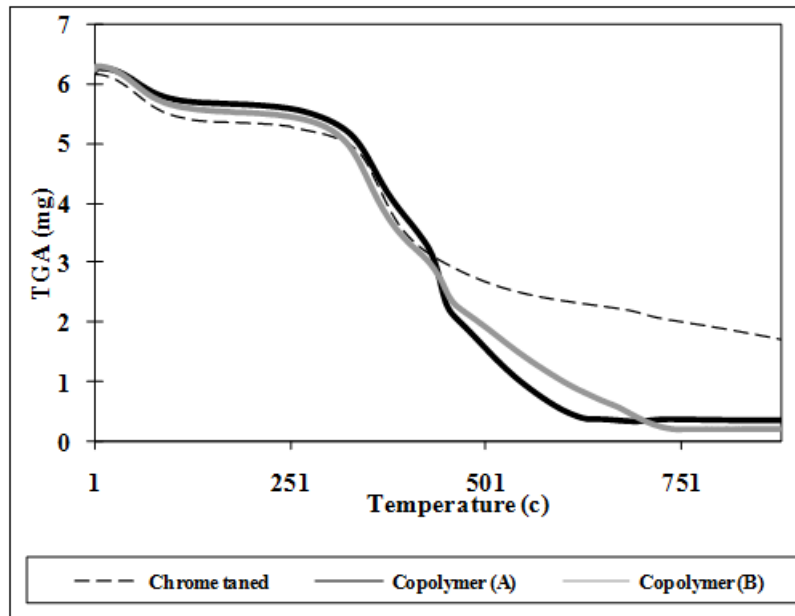


Fig-5: TGA of chrome tanned and retained leather by copolymer (A & B)

Scanning electron microscope (SEM)

A morphological study was carried out for the chrome tanned leather in comparison with retained leather by the two co-polymers (A & B). SEM of the grain surface ($\times 50$) and the cross-section ($\times 1000$) 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 (Fig 6, 7 & 8). SEM can be used to assess the penetration of the copolymer through the leather and into the hierarchy of the structure and is thus a useful technique for evaluating the effects of various treatments on the skin.

From the cross section micrographs in (Fig 9, 10 & 11), it is clear that the chrome tanned leather fibers were completely separated from each other, but

in the case of retained leather, fibers aggregates could be noticed. In addition, SEM of the cross section of the leather fibers before and after retanning by the two copolymers showed a significant lubrication of fiber bundles (Fig 9, 10 & 11) and fine surface grain (Fig-7). It was observed that the SEM of the samples retanned by copolymer (B) has a smooth fiber, firmness grain and modified handle, which are good evidence for the penetration and lubrication of two co-polymers onto the leather fibers and grain surface. At the same time, the co-polymers don't have any ill-effect on the grain surface with respect to finishing. The treated chrome tanned leather by the two copolymers gives better grain smoothness, soft fibers, filling and modified handle. The filling of the grain layer improve buff ability for uses as corrected grain leather.

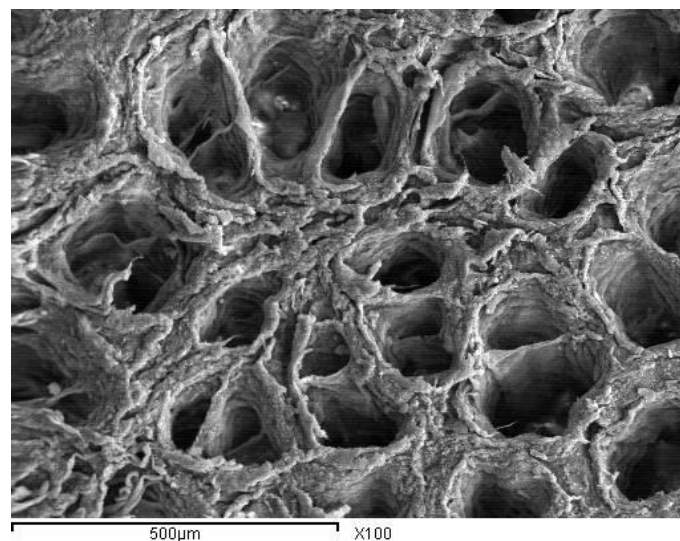


Fig-6: SEM of grain surface of chrome tanned leather

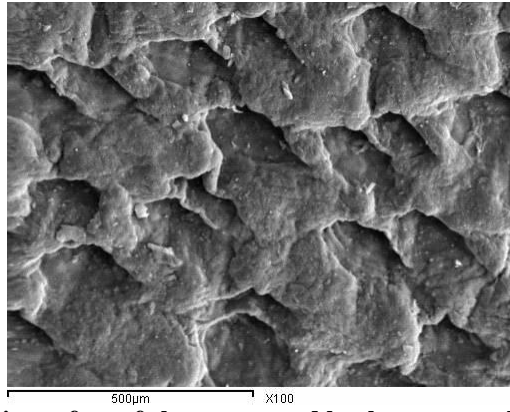


Fig-7: SEM of grain surface of chrome tanned leather retained by co-polymer (A)

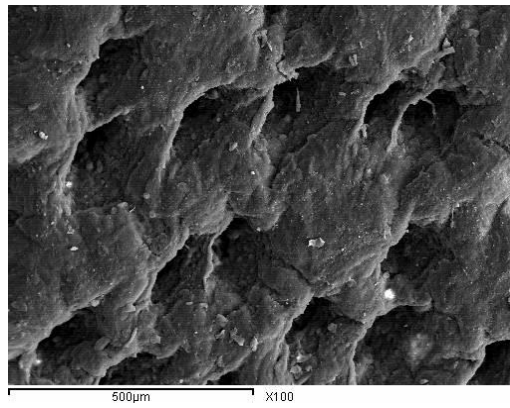


Fig-8: SEM of grain surface of chrome tanned leather retained by co-polymer (B)

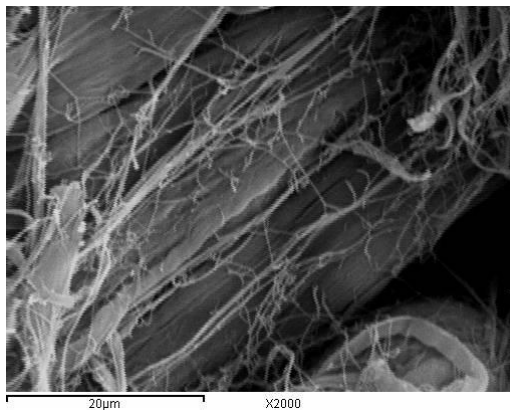


Fig-9: SEM of fiber bundles of chrome tanned leather

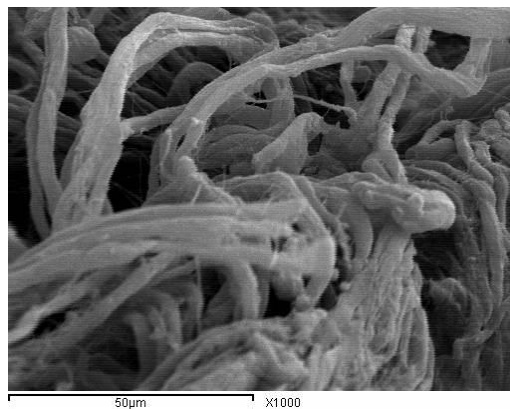


Fig-10: SEM of fiber bundles of chrome tanned leather retained by co-polymer (A)

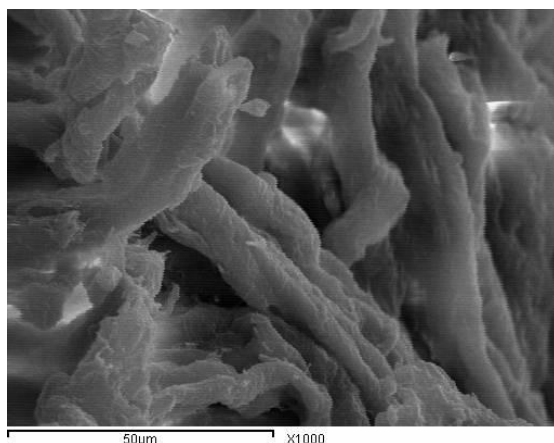


Fig-11: SEM of fiber bundles of chrome tanned leather retained by co-polymer (B)

CONCLUSIONS

The results of this work indicated that the application of the prepared two copolymers has retanning and lubricating effect combined in one product. The character of the finished leather reveals that, the tanners are enabling to use these new developed copolymers as lubricant syntans. The improved characters are in the following respects:

- The water absorption of the modified leather samples was reduced, without hindering the finishing process.
- The prepared two nano-emulsion copolymers have not side effect on uniform dyestuff especially with respect to copolymer (B).
- Fullness and tight grain obtained due to the filling action of nano-particles copolymer.
- Softness and improving the mechanical properties depend upon its lubrication.
- Enhancement the thermal stability of treated leather.
- The mechanical properties (tensile strength and elongation at break) were markedly improved as the introduction of co-polymers.

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