Synthesis of Citric Acrylate Oligomer and Its *In-Situ* Reaction with Chrome Tanned Collagen (Hide Powder)

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Summary: The purpose of this study was to formulate the new combined system of acrylic and citric acids, which was prepared by free radical polymerization and esterification reaction at the same time to form citric-acrylate CAC oligomer. The presumable chemical structure of this oligomer and the reaction mechanism were investigated by different spectroscopic tools (^{1}H,^{13}C-NMR and ATR-IR), GPC and TGA/DTA. The effect as masking agent of the eco-friendly oligomer (CAC) in the chrome tanning of the collagen and the pickling of the hide was approached by the study of the hydrothermal and mechanical properties of *in-situ* treated/grafted chrome tanned collagen (hide powder) and pickled hide, respectively. The use of citric acrylate CAC oligomer instead of the traditional strong acids resulted in significant improvement in chrome exhaustion and physical properties of the leather.

Keywords: acrylic acid; citric acid; collagen; chrome tanning; grafting; pickled hide

Introduction

Leather making is constantly changing because it is expected to respond to the demands of the market place, and the environmental legislation[1]. The temperature of collagen denaturation (T_d) close to 35°C reaches 66°C in the mature skin. Tanning, by introducing cross-links, generally increases T_d, but its influence on the shrinkage behaviour varies with its nature and the kind of involved reactive groups[2]. The hydrothermal stability of collagen fibres is a particularly good measure of the strength or quality of skin, leather and parchment materials and the degree of their deterioration. The hydrothermal stability is characterized by a shrinkage of the material when heated in water at a defined temperature[3–5]. The swelling of the pickle under the action of acid (pickling) and salt addition is used to modifies the reactive acidic (–COOH) and basic (–NH_2) groups on the collagen[6]. Tanning is accompanied by introduction of additional cross-links into collagen, which bind the active groups of the tanning agents to functional groups of the protein[7,8]. The unique combination of properties that results from successful tanning obviously requires much more than the simple introduction of cross-links, probably the number, size and location of the cross links, as well as any change in the electrostatic charge and hydrophilic/hydrophobic character of the collagen, all play apart of determining the properties of the resultant leather[9]. The conventional chrome tanning gave ecological problems due to the enormous quantities of chrome containing solid waste (shavings and trimmings) waste water[10]. Synthetic tanning agents or syntans form a generic group of tanning agents, characterized as synthetic polymers or resins with chemically active groups capable of interacting with collagen typically via multiple hydrogen bonding[11–13]. The acrylic polymers used for impregnation, base coat and top coat[14] and the flexibility of acrylic polymers in general is unmatched among polymeric materials, in addition to flexibility, exceptional light fastness, absence of discoloration, pigment

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binding capacity, moulding ability, water resistance and compatibility with other synthetic resins are some of the striking operatives of acrylic emulsions which highly desirable for use in leather industry[15]. A new non formaldehyde durable press finishing system was developed based on the combination of citric acid and a terpolymer of maleic acid, acrylic acid and vinyl alcohol[16]. In this paper a similar approach was investigated by combining the positive aspects of citric acid with those of acrylic copolymers.

Experimental

Materials

i) Hide powder which provided by Merck with specific characteristics (pH 5.2–5.6, Cr_2O_3: below 0.9%, ignition residue: below 0.9%).

ii) Pickled hide was supplied by local tannery at Cairo. iii) Citric acid (99.5%) was provided by Biosar, s.d. Fine Chem. LTd.) Acrylic acid (99%) was provided by Merck.

The chemicals were used as received.

Methods

Synthesis of CAC Oligomer

7.2 g of acrylic acid (0.1 mol) was mixed dropwise with 19.2 g of citric acid (0.1 mol) at 65°C, for 3 hours in 200 ml distilled water in the presence of sodium bisulfite/potassium (1%) persulfate (1:2) as initiator. No further purification was performed.

Structure Characterization of the Synthesized CAC Oligomer Mixture

I) Spectroscopic techniques. ^1H, ^{13}C-NMR spectra were recorded by using a Varian Unity at 300 MHz. The IR spectra were recorded with a Perkin-Elmer Spectrum GX equipped with an ATR accessory with SeZn crystal. All ATR spectra were processed with the Spectrum software v. 3.2.

II) Gel permeation chromatography (GPC) measurements were obtained with a Techno Service, Jasco GP, under the following condition: ultrahydrogel linear 2×30 cm Column; eluent: 0.8 ml/min $LiNO_3$ 0.1 M; refractive index detector; pullulan as standard, temperature 35°C.

III) Thermogravimetric analysis was performed with a Mettler Toledo Stare System mod. 822e instrument equipped with a Stare software and liquid nitrogen cooling. Each sample were analyzed in the 30°–600°C temperature range under nitrogen atmosphere (60 ml/min), with scan rate of 10.0°C/min.

Uses of the Synthesized CAC Oligomer

I) Treatment of hide powder. 2 ml of sodium hydrogen phosphate was added to 5 g of hide powder for 10 min, followed by 5 g of CAC for 30 min, at 40°C, dried at 80°C for 15 min then washed by distilled water for 5 min and then filtered.

II) Treatment of pickled hide. 5% of CAC and 1% of sodium hypophosphite and 1.5% sodium chloride were added to the pickled hide at 35°C for 30 min (liquor ratio 1:10).

III) Microemulsion grafting copolymerization by using AIBN[17,18]: A mixture of 5 g of hide powder and 2.5 g of sodium dodecyl sulphate (SDS) in 100 ml distilled water and the required amount of 2,2-azo-bis-isobutyrronitrile (0.096 g) in 50 ml of 2-butanone was added in a flask equipped with stirrer, thermometer, condenser and nitrogen inlet at 70°C for a period 1 hour, so as to enable the complete dispersion of initiator as micro globules in aqueous medium stabilized by the surfactant (SDS)-cosurfactant (2-butanon) system. 5.28 g (0.1 mol) of the synthesized CAC oligomer was dissolved in 50 ml mixed solvent of distilled water and methanol and was added dropwise to the microemulsion solution. The copolymerization reaction was completed in 4 hours, after that, the contents were filtered and washed by distilled water, then dried in vacuum at 40°C. The homopolymer was removed from the grafted hide powder by exhaustive soxhlet extraction with absolute methanol for 18 hours.

IV) CAC as pretanning agent: Pickled hide samples were impregnated in float 100% water containing 35% of sodium chloride, 1% of sodium lauryl sulfate and different concentrations of CAC (1%, 2%, 3%, 4% and 5%, respectively) at 35°C for 40 min. The treated samples were washed with CO_2 –free distilled water, followed by 6% addition of basic chromium sulfate (33%basic) to each treated pickled hide sample at 35°C over night. After that 1% of formic acid was added as masking agent and stirred for 30 min.

V) CAC as masking agent: Pickled hide samples were impregnated in float 100% add 6% of basic chromium sulfate (33% basic) and 35% of sodium chloride at 35°C overnight. After that, different concentrations of CAC (1%, 3%, 5% and 8%, respectively) were added to each sample and stirred for 40 min.

VI) CAC as retanning agent: Pickled hide samples were tanned with 6% of basic chromium sulfate (33%basic) in the presence of 35% of sodium chloride at 35°C overnight, then different concentrations of CAC (2%, 4%, 6% and 8%, respectively) were added to each sample.

Measurements

I) Shrinkage Temperature[19,20]: All samples under investigation were measured according to the official methods of analysis IUP16 (International Union Commission Testing for Physical properties of leather).

II) Mechanical Properties (tensile strength and elongation)[21]. All samples under investigation were analyzed according to DIN (Deutsches Institute Fuer Normung e.v.)

Results and Discussion

The final chemical structure of acrylic/citric mixture was formulated according to scheme 1, and confirmed by different spectroscopic tools.

In the ^{1}H-NMR spectra of CAC oligomer, diagnostic peaks at 2.72 (d), 2.9 (d), 2.48 (t), 3.7(t), and 4.2–4.35(m) ppm which correspond to $–CH_2$ (citric acid), $–CH_2$ (citric acid), $–CH_2$, $–CH_2–C{=}O$ and $CH_2{=}CH$ groups, respectively, were observed.

In the ^{13}C-NMR spectra of CAC oligomer, the following signals at 35, 38, 42, 45, 59, 62, 73, 173, 178 and 179 ppm which correspond to the C-atoms in the functional groups of the proposed structure (Scheme 1) were observed.

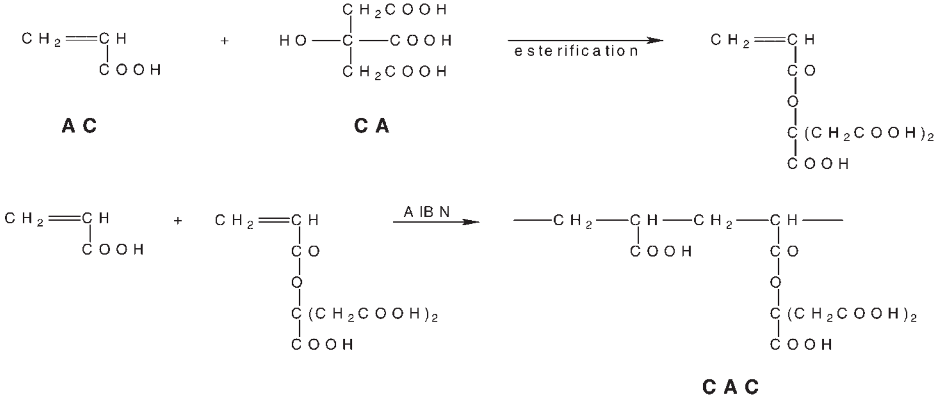
In the ATR-IR spectra of CAC oligomer (Fig. 1), the characteristic peaks at 3433, 2967, 2621, 1720, 1648, 1638, 1400 and 1223 cm^{-1} corresponding to –OH (stretching), –OH (bending), $–CH_2$, $–C{=}O$, –CO (ester), $CH_2{=}CH–C{=}O$ (denoting acetyl group beside the carbonyl group) were observed.

From the GPC analysis the formation of CAC oligomeric species was proposed with a polydispersity of about 1.04 and a number average molecular weight $\overline{M_n}$ of about 2250. According to the above characterization the most probable reaction pathway to obtain CAC seems to proceed firstly by esterification of the acrylic acid via ester linkage, followed by free radical copolymerization up to low molecular weight oligomers (Scheme 1)[22].

The C=C double bonds observed experimentally are not here indicated and are probably associated to terminal unsaturated units.

In both ATR-IR spectra reported in Fig. 2 of the untreated hide powder (blank, black line) and the grafted one (red line), the primary bands of collagen due to the peptide bond vibrations[23], amide I, II and III centred at 1654, 1631 and 1238 cm^{-1}, respectively, were observed. The spectra of the grafted hide powder showed that, both characteristic bands at 1654 and 1238 cm^{-1} were disappeared and new other bands at 1233 and 1203 cm^{-1} were formed. This may be due to in-situ grafting reaction; the formation of oligomers can affect the amide I and III bands more than the amide II.

Also, the disappearing of the peaks at 1515 and 3280 cm^{-1} corresponding to the bending and stretching respectively of the amino group in free form can be related to the in-situ reaction of the carbonyl group of



Scheme 1.
Presumable main structure of the CAC oligomer.

the acrylic acid to form amide cross-linking. It is well known that the –NH stretching absorption takes place at the region (3500–3000 cm^{-1}), and the frequency of its vibration decreases and its intensity increases if the –NH group participates in hydrogen bonding. It can be concluded that, the free amino groups of the collagen were considered to be a potential site for the in-situ reaction with CAC.

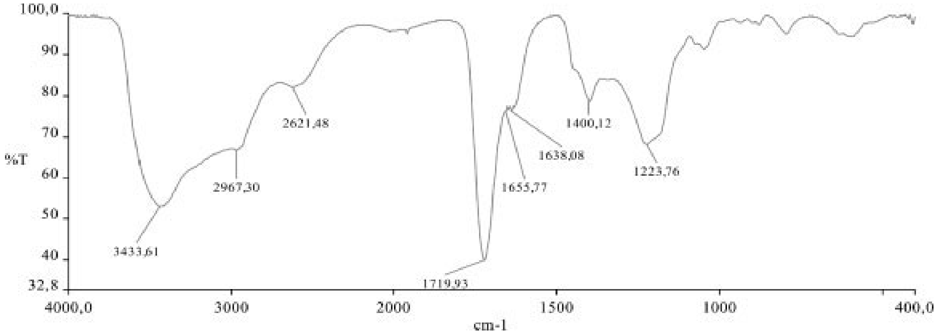


Figure 1.
ATR-IR spectrum of CAC oligomer.

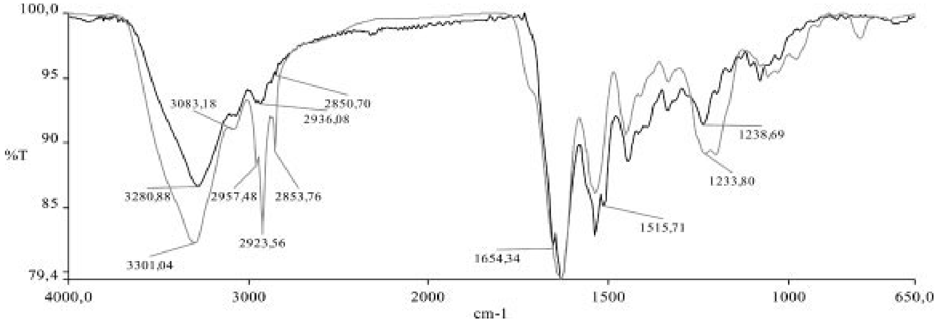


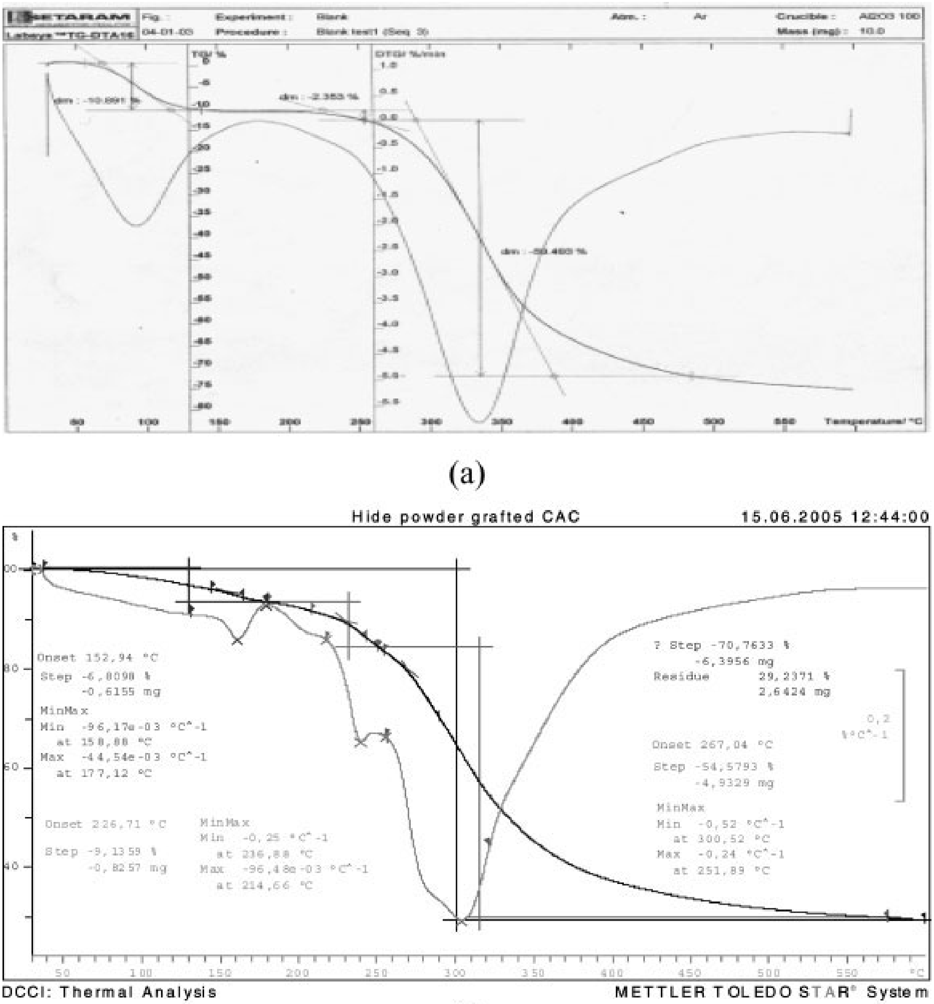
Figure 2.
ATR-IR spectrum of hide powder (red line) and grafted hide powder (black line)with (CAC).

Table 1.
Effect of CAC oligomer on thermal stability of the pickled hide.

Samples	Shrinkage Temp(°C)
Untreated pickled hide	69
Treated pickled hide	63
Treated pickled hide*	74

* Pickled hide was treated with Polyacrylic acid (PAA)

The influence of the treatment with CAC oligomer on the thermal stability of the pickled hide is reported in Table 1. It seems that the shrinkage temperature of the treated pickled hide was slightly altered relative to the untreated one. On the other side, the thermal stability of the treated pickled hide with polyacrylic acid was higher than that of the untreated and CAC treated pickled hide. This may be due to the presence of high/low molecular weight compounds into the network of the polypeptide chains of collagen. CAC oligomer has low molecular weight in compared with polyacrylic acid (PAA), and can be used in the pretanning step without any



(a)

(b)

Figure 3.
TGA/DTA diagram of :(a) hide powder Blank; (b) grafted hide powder with CAC.

Table 2.
Effect of CAC oligomer as pretanning agent on the mechanical properties of chrome tanned leather.

CAC oligomer Conc (%)	Tensile Strength N/mm^2	Elongation at Break (%)
1	11.3	58.2
3	12.5	58.9
5	12.5	59.0
8	12.4	60.0

Table 3.
Effect of CAC oligomer as masking agent on the mechanical properties of chrome tanned leather.

CAC oligomer Conc (%)	Tensile Strength N/mm^2	Elongation at Break (%)
1	12.0	52.0
3	12.9	52.8
5	13.0	53.0
8	13.0	53.3

harmful effect on the fiber of the pickled hide.

The first derivatives of the TGA curves are shown in Figs. 3-a and 3-b. The results show that, in the case of the untreated hide powder, the first step occurs at 90°C which is attributed to the loss of adsorbed water (11%), while in case of the grafted hide powder, the loss (7%) occurs at 152°C. The dehydration of the grafted hide powder takes place at 226°C and 267°C and both of hygroscopes and water were highly lost (9 and 55%) in comparison with the untreated hide powder (3%). Between 267°C and 335°C bound water (co-ordination water) was lost. Stabilisation of the collagen takes place through electrostatic and hydrophobic interactions, so hydrogen bonded water plays an important part in the stabilisation of the molecule. At low moisture content, one single endothermic peak was detected which corresponds to the denaturation process of leather and the evaporation of water was detected, on the other side. At higher moisture, two endothermic peaks were detected, the first one corresponding to denaturation and the second one to evaporation of water.

Tables 2 and 3 show the effect of CAC oligomer as pretanning and masking agents on the mechanical properties of the pickled hide, respectively. Both tensile strength and elongation at break were slightly altered when the concentration of CAC oligomer was increased.

Table 4 shows the effect of CAC oligomer as retanning agent on the mechanical properties of the chrome tanned leather relative to basic aluminum sulphate. The data show that, 5% CAC gives the same effect in compared with 8% basic aluminum sulphate. The chrome exhaustion during chrome tanning of pickled hide was increased with increasing CAC concentration, while the thermal stability of the chrome tanned collagen was levelled off with increasing CAC concentration (Fig. 4). This may be due to the effect of the low pH, at high CAC concentration, on the rate of the chromium complex formation between polypeptide chains of the collagen in the pickled hide.

The effect of CAC oligomer as pretanning agent on both thermal stability and chrome exhaustion of the pickled hide is also observed. At 4% CAC (Fig. 5), the optimum chrome exhaustion can be achieved while the thermal stability was slightly altered with increasing CAC concentration. This means that the suitable pH of the pickled hide which gives the suitable condition for tanning process is below 4-5.

The CAC oligomer as retanning agent affects thermal stability of chrome tanned leather relative to the traditional retanning agents. Indeed (Fig. 6), the thermal stability of CAC retanned leather was increased with increasing CAC concentration and the optimum shrinkage temperature was done at 4–5% CAC. In case of aluminum

Table 4.
Effect of CAC oligomer as retanning agent on the mechanical properties of chrome tanned leather.

CAC oligomer Conc (%)	Tensile Strength N/mm^2	Elongation At Break (%)
1	12.0	60.0
3	12.5	60.0
5	13.8	62.0
8	13.0	62.2
2% Al	11.5	60.2
8% Al	13.2	63.0

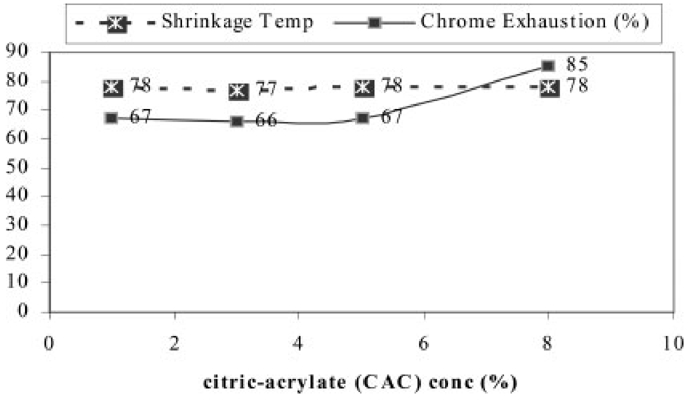


Figure 4.
Effect of CAC oligomer as masking agent on chrome tanning of leather.

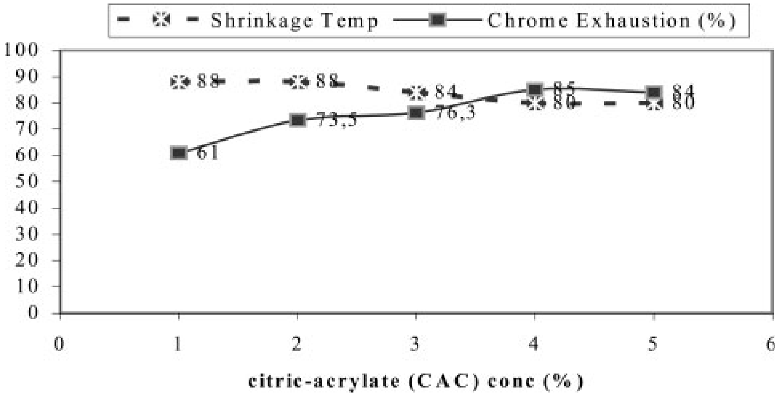


Figure 5.
Effect of CAC oligomer as pretanning on pickled hide.

retanned leather, the optimum shrinkage temperature was obtained at 6–8% basic aluminum sulfate.

Also, thermal stability and chrome exhaustion percentage were affected by CAC oligomer during chrome tanning of the pickled hide. Both shrinkage temperature and chrome exhaustion were gradually decreased with increasing CAC concentration (Fig. 7) and the optimum CAC

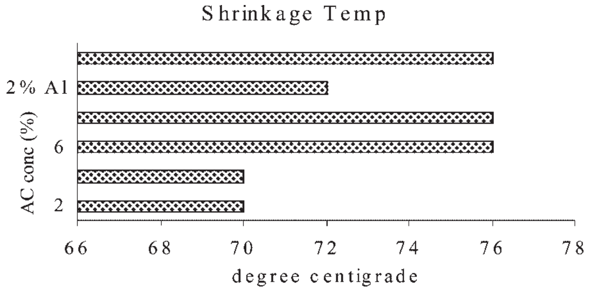


Figure 6.
Effect of CAC oligomer as retanning on chrome tanned leather. Al = Basic Aluminium Sulphate.

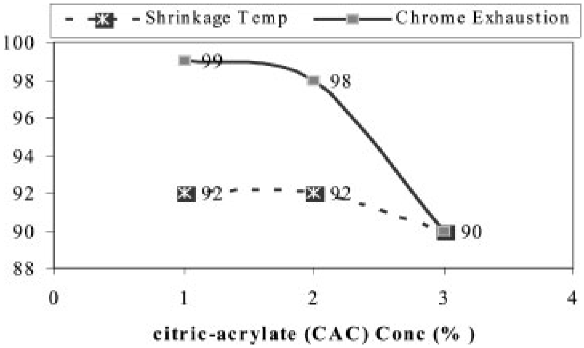


Figure 7.
Effect of CAC oligomer as exhausting agent chrome tanning of leather.

concentration is 1%, due probably to the highly acidic medium of the chrome tanning bath.

Conclusions

In the presence of citric acid the free radical polymerization of acrylic acid proceeds via formation of citric acrylate oligomer with low molecular weight (M_w 2250), relative to the polyacrylic acid. This oligomer can be used for surface modification of the chrome tanned collagen and also in the pickling process of the leather industry, instead of harmful strong acids such as sulfuric, hydrochloric and formic acid, which resulted in significant improvement in chrome exhaustion and physical properties. This new oligomer can also decrease corrosion and microbial growth in compared with the above traditional strong acids.

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