



## Retanning agent for chrome tanned leather based on modern technique of emulsion polymers



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### Abstract

Retanning process aims at filling up of the meatuses of the already tanned leather through the incorporation of vegetable or synthetic tannins or polymer (resins) with the aim of giving more fullness and improving to the final product. So using of the emulsion polymer of poly(methyl methacrylate-co-butyl acrylate) prepared with in situ nano-silica as a modern retanning agent of chrome tanned leather to totally replace chrome salt and to enhance physical, thermal shrinkage, and mechanical properties of the final tanned leather as well as to reduce the environmental impact of chrome tanning effluent. Polymer/nano-silica hybrid emulsions were prepared via in situ seed emulsion polymerisation. The prepared polymers were characterised for solid content, molecular weight, viscosity, drying time, minimum film-forming temperature (MFFT) and microstructures (via TEM). The mechanical, shrinkage, thermal and surface morphological (by SEM) properties of the treated samples were also investigated. The influences of the increase in the content of organic nano-silica on the properties of the retanned leather are discussed.

**Keywords:** butyl acrylate, Methyl methacrylate, emulsion polymer, reactive surfactants, nanosilica, core-shell, retanning agent, chromium uptake, chrome tanned leather.

### 1. Introduction

Leather production usually involves three distinct phases: preparation (in the beamhouse); tanning (in the tanyard); and finishing, including dyeing and surface treatment. In the tanning process, animal hides and skins are treated to remove hair and non-structured proteins and fats, leaving an essentially pure collagen matrix. The hides are then preserved by impregnation with tanning agents<sup>(1)</sup>. A wide range of processes and chemicals, including chrome salts, is used in the tanning and finishing processes (WORLD BANK GROUP July 1998). Generally, the tanning and finishing process consists of<sup>(2)</sup>:

- 1- Soaking and washing to remove salt, restore the moisture content of the hides, and remove any foreign material such as dirt and manure.
- 2- Liming to open up the collagen structure by removing interstitial material.
- 3- Fleshing to remove excess tissue from the interior of the hide
- 4- Dehairing or dewooling to remove hair or wool by mechanical or chemical means.
- 5- Bating and pickling to delime the skins and condition the hides to receive the tanning agents.
- 6- Tanning to stabilize the hide material and impart basic properties to the hides.

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- 7- Retanning, dyeing, and fat-liquoring to impart special properties to the leather, increase penetration of tanning solution, replenish oils in the hides, and impart color to the leather.
- 8- Finishing to attain final product specifications.

Retanning process is one step of wet-finishing operations and is very important operation which overcomes the disadvantages of chrome tan <sup>(3)</sup>.

Therefore, many retanning agents were developed to improve the chrome tanned leather properties. In general, the most retanning agents are vegetable tan and phenolic synthetic/organic tanning materials. In addition, many trials of Acrylate polymers derivatives to be used as retanning agents which are suitable for filling, softening, and even water proofing <sup>(4)</sup>, air permeability or which combine all these properties. Many researches focused on grafting of different monomers onto the leather such as styrene <sup>(5)</sup> and acrylate derivatives <sup>(6)</sup>

Therefore, work that is reported in this paper aimed to develop acrylic co-polymers nano-silica emulsions as an efficient leather retanning agent in order to prevent the creation of chrome tanning waste negating the need for the treatment of chrome tanning waste. Addition of filler to polymers affects matrix structure and hence affects final material properties. Organic/inorganic nano-composites, because of their attractive mechanical, thermal, optical, electrical, and magnetic properties, are used for different purpose in electronics, paints and coatings, adhesive industry, medicine, etc. <sup>(7)</sup>. These unique properties are achieved because of the effect of nano-sized filler and are greatly influenced by dispersion of the filler in polymer matrix <sup>(8,9)</sup>.

Such nanocomposite particles are commonly produced by incorporation of colloidal silica in heterogeneous polymerizations, such as emulsion, dispersion and suspension <sup>(10)</sup>. Although all of these methods have been reported to produce fine nanocomposites, in order to prepare organic-inorganic nano-hybrids, emulsion polymerization is the especially preferred route to produce nanocomposites based on acrylic or styrenic polymers <sup>(11, 12)</sup>. This is mainly due to its ease of process ability and the possibility to distribute nanoparticles nanoparticles of low concentrations into nanoscale-independent matrices <sup>(13, 14)</sup>.

Encapsulation of silica nano-filler with polymer, i.e. encapsulation efficiency depends on (a) nature of inorganic particle (silane grafting density), concentration and size of silica nano-filler, (b) use of high hydrophilic monomers and (c) nature and concentration of monomer, initiator, and emulsifier in polymerization. Depending on the above factors various morphologies such as core-shell, daisy like, petal like, raspberry like, and multilayered morphology were obtained <sup>(7,8)</sup>.

Hybrid structures of silica and polymer have excellent physical reinforcement, high thermal resistance, high flexibility, high gas permeability and low surface energy, due to the incorporation of silica <sup>(15)</sup>.

## 2. Experimental

### 2.1. Materials

Butyl acrylate (BA), methyl methacrylate (MMA), and Methacrylic acid (MAA) were supplied by Sigma Aldrich and distilled at reduced pressure before use and stored at -20°C. Ammonium per sulphate (APS), ethanol, sodium acetate, sodium dodecyl benzene sulphonate (SDBS), and trimethyl amine, all of which Fine Chemicals grade, were supplied by Across Chemicals. Modified alcohol ether phosphate (Maxemul 6112) as anionic reactive surfactant, Polyethylene oxide and alkenyl functionality (Maxemul 5011) as nonaionic reactive surfactant, supplied by Croda Coatings and Polymers) were used as reactive surfactants. Silquest A-151NT (vinyl triethoxy silane) supplied by Momentive Performance Materials. Distilled water was used to prepare aqueous solutions where required. Egyptian buffalo chrome tanned leather.

### 2.2. Experimental methods

#### *Emulsion polymerisation*

#### *Preparation of in situ nano-silica/methyl methacrylate/butyl acrylate co-polymer emulsion* <sup>(16)</sup>

The nano-silica/methyl methacrylate/butyl acrylate co-polymer emulsions were synthesised through a three--steps route, according to the following methods.

#### Synthesis of dispersed nano-silica

Dispersed nano-silica was synthesised via a sol-gel technique in an aqueous solution according to <sup>(17)</sup>.

Vinyl triethoxy silane (Silquest A-151NT) (5.4 g) and sodium dodecyl benzene sulphonate (SDBS) (0.063g) were dropped into 50 mL of deionised water under vigorous mechanical stirring until the formation of a uniform emulsion. Trimethyl amine solution (1 mL, 25%) was added drop-wise to the prepared emulsion, and the reaction mixture was kept at ambient temperature for 48 hours.

At the end of the reaction, the resulting dispersion was centrifuged at a speed of 5000 rpm for 5 minutes, and the obtained precipitate was washed using deionised water followed with ethanol. Repeated centrifugation was carried out to remove free monomer (vinyl triethoxy silane), anionic surfactant and trimethyl amine. Finally, white powder was obtained after drying at 45°C for 3 hours under vacuum.

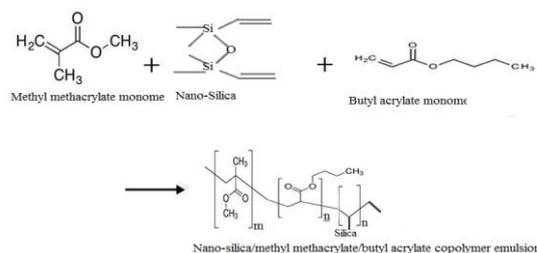
#### The seeding stage

The emulsion polymerisation was carried out in a 500 mL four neck flask which was equipped with an inlet for nitrogen gas, reflux condenser, thermocouple, Teflon-steel mechanical stirrer and feeding inlets. The process was started with a seed polymerisation as follows. The calculated amount of nano-silica in grammes (0% for polymer A, 1% for polymer B, 3% for polymer C, and 5% for Polymer D) and 2.4 g Maxemul 5011 were dispersed in 52 g water having 10% of pre-emulsified mixture of monomers containing 90 g BA, 60 g MMA, 41 g H<sub>2</sub>O, and 6.6 g Maxemul 6112) and gently stirred for 15 minutes followed by sonication (Hielscher, UP200S) in an ice bath for 20 minutes. The mixture was then poured into a reactor containing buffer solution while stirring (80 rpm). When the water temperature reached 80°C, calculated amount of potassium persulphate (KPS) solution (0.36 g dissolved in 10 g H<sub>2</sub>O) was added dropwise into the reactor and the mixture left to stand for 30 minutes to create the seeding system.

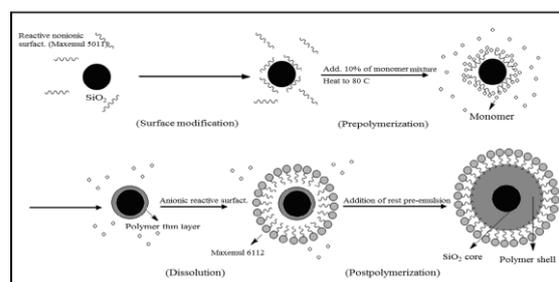
#### The feeding stage

The feeding stage of the polymerisation was conducted as described as follows. The remaining potassium persulphate solution (0.24 KPS dissolved in 50g distilled water) and a pre-emulsified mixture containing 3g methacrylic acid were mixed using a dual syringe pump within 4 hours to obtain the nano-silica/methyl methacrylate/butyl acrylate composite emulsion. The mixture was cooled to 40°C and the

pH was adjusted to pH8. See (schemes 1, 2).



**Scheme 1** Preparation of nano-silica/methyl methacrylate/butyl acrylate copolymer emulsion.



**Scheme 2** Mechanism of the formation process of nanosilica particles with the acrylic copolymer by in situ emulsion polymerization using reactive surfactants.

### 2.3. Preparation of leather

#### - Neutralization process

The pH of chrome tanned leather was adjusted to be 5.5 using 0.25% sodium acetate (CH<sub>3</sub>COONa) and 0.5% sodium bicarbonate (NaHCO<sub>3</sub>).

#### - Retanning process

The retanning process is performed to improve the leather characteristics and the re-wetting properties (e.g. the presence of liquid, such as water, into hides, skins or dried leather) of the hides necessary to facilitate and optimize the subsequent dyeing process. The retanning process was carried out using (2%, 4%, and 6%) of different types of polymers. Then, the retanned leather was washed with water and left to dry in fresh air by hanging at room temperature.

### 2.4. Testing and analysis

#### a. Morphological study<sup>(18,19)</sup>

The morphology of the polymer particles prepared was examined using Transmission Electron Microscopy (TEM). For the present work, the use of cryo-TEM was required because of the low glass

transition temperature of the prepared polymer. To perform cryo-TEM analysis, the latex was diluted with distilled water. A drop of the diluted latex was placed on a carbon-coated grid and dried in a dissector. Then, 1–2 drops of a 0.8 wt% aqueous solution of phosphotungstic acid (PTA) was used to stain the particles.

**b. Fourier transform infrared (FTIR)<sup>(7,20)</sup>**

FTIR measurement were taken in the range 4000–500  $\text{cm}^{-1}$  at room temperature using a Thermo Nicolet Avatar 370 spectrometer.

**c. Determination of molecular weight<sup>(21)</sup>**

A small amount of the sample (0.01 gm) was dissolved in 2ml of THF solvent. The solution was filtered using a 0.45  $\mu\text{m}$  pore-size filter for the determination of molecular weight using an Agilent 1100 series gel permeation chromatography analyser (GPC). For the analyses, a refractive index detector was employed, as well as polymethyl methacrylate standard of particle size 5  $\mu\text{m}$ , 3 columns of pore type 100, 104, 105  $\text{\AA}$  in sequence each having a diameter of 7.5 and a length of 300 mm that covered the molecular weight ranging from 1,000 to 4,000,000 daltons.

**d. Analysis of mechanical properties<sup>(22)</sup>**

The tensile strength and the elongation at break properties of the dumbbell shaped leather samples were measured according to ASTM D 412, using a Ziwick tensile testing machine, at a crosshead speed of 200 mm/min. The average value of the mechanical properties was calculated from at least five repeated analyses.

**e. Measurement of thermal properties<sup>(3, 23)</sup>**

The thermogravimetric analysis (TGA) measurements for the obtained grafted samples were carried out at temperature ranging from 50°C to 700°C under nitrogen atmosphere at a heating rate of 10°C/min using a Shimadzu TGA-50 instrument.

**f. Analysis of the surface morphology of the leather samples<sup>(24)</sup>**

The surface morphology of the leather samples was analysed using JEOL Model JSM-T20 Scanning Electron Microscope (SEM). Specimens were cut

from the samples to be studied. Specimen was circular in shape having a 10 mm diameter. Each specimen was sputter coated with gold using an Edwards Model S 140A sputter coater.

**g. Measurement of shrinkage temperature<sup>(25)</sup>**

Shrinkage occurs when leather is exposed to excessive heat. The shrinkage temperature is defined as one at which a significant shrinkage of leather occurs. An increase in the shrinkage temperature of a tanned hide indicates desired effect of tanning agent. In the study reported here, the shrinkage temperature of leather samples was measured according to the conventional method and Egyptian Specification.

### 3. Results and discussion

The emulsion copolymerisation of poly (methyl methacrylate-co-butyl acrylate) with *in situ* nano-silica was carried out at different concentration ratios of nano-silica in the presence of methacrylic acid as binder, ammonium persulphate as initiator and Maxemul 6112 and Maxemul 5011 as reactive surfactants, as shown above for four polymer-nano-silica composites prepared, namely Polymer Composites A – D.

#### 3.1. Characteristics of the nano-silica/methyl methacrylate/butyl acrylate co-polymer emulsion composites

The prepared polymer-silica emulsion composites were characterised for solid content, M.wt, viscosity, drying time, MFFT (Minimum Film Forming Temperature), and particle morphology (by TEM). The mechanical properties of the prepared leather samples were also examined to study the characteristics of the polymer. The physical, chemical as well as mechanical properties of the prepared polymer emulsions were examined according to international standard and the results are represented in Table I.

**Table I Characteristics of the prepared copolymers emulsion**

Properties	Standard	Value			
		A	B	C	D
pH		8.4	8.6	8.5	8.3
Solid Content (%)	D4139	50.00	49.65	50.54	49.13
Drying time (seconds) at 23°C		85	75	65	57
(Minimum Film Forming Temperature) MFFT (°C)	D2354	16	16	18	18
Particle size (nm)	TEM	130	280	317	450
Brookfield Viscosity RVT #50 rpm (cPs)	D2196 – 99	6150	7650	9100	9700
Gloss at (60°)	D523	133	85	66	54

Based on the results shown in Table I, it can be seen that, as the concentration of nano-silica increased, the solid content increased until the concentration of the nano-silica reached 3% (C). This may be due to the decrease in the conversion of the monomers to form polymer out of the micelles as a result of the increase in the concentration of nano-silica. The viscosity of the co-polymers increased as the concentration of nano-silica increased due to the improved gel content of latex co-polymers.

The increase of nano-silica caused a decrease in the drying time of nano-silica/polymer emulsion samples. This can be attributed to the increase of modulus due to the presence of the silica nano-particles. The minimum film forming temperature (MFFT) was recorded as 16-18 °C, which is due to the hydrophobic nature of the monomer and the absence of external of coalescing agent.

The gloss values decreased in all nano-silica/methyl methacrylate/butyl acrylate co-polymer emulsion films. This is due to the nano-silica particles tending to accumulate and coagulate near the latex surfaces, forming loose and granular particles. Consequently, the gloss values of the resulting composition films decreased as a result of

the increased light diffraction from the film surface with increasing nano-silica content<sup>(7, 26)</sup>.

#### A. Molecular weight and molecular weight distribution

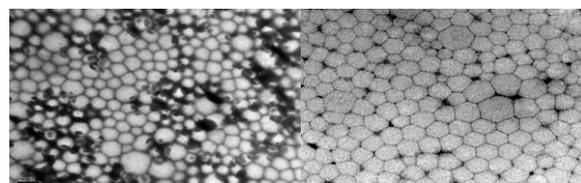
The molecular weight and its distribution are listed in Table II. It is clear, from Table II, that there is a significant influence of nano-silica on the molecular weight of the prepared nano-silica/methyl methacrylate/butyl acrylate co-polymer emulsion. The number-average molecular weight ( $M_n$ ) and the weight-average molecular weight ( $M_w$ ) are not in the same values for these samples. In addition to the nano-silica amount, low molecular weight molecules may be formed during the polymerisation process such as dimer, trimer and oligomer which are calculated in case of  $M_w$  measurement. It can also be seen that the polydispersity increased with increasing amount of nano-silica in the polymer matrix.

**Table II** Effect of nanosilica on the molecular weight and its distribution

Polymer	$M_n^a$ (g/mol)	$M_w^a$ (g/mol)	Polydispersity ( $M_w/M_n$ )
A	$1.343 \times 10^5$	$5.723 \times 10^5$	4.26
B	$1.555 \times 10^5$	$5.450 \times 10^5$	3.50
C	$1.352 \times 10^5$	$4.981 \times 10^5$	3.68
D	$1.244 \times 10^5$	$5.801 \times 10^5$	4.66

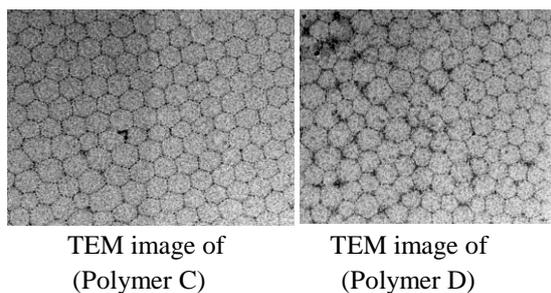
#### B. Microstructure of the prepared polymers

The TEM images of pure emulsion polymer (A) and its polymer/nano-silica emulsions (B-D) are shown in Figures 1. TEM images of pure emulsion polymer (A) shows uniform and mono-dispersed particles in the range of 130 nm.



TEM image of (Polymer A)

TEM image of (Polymer B)



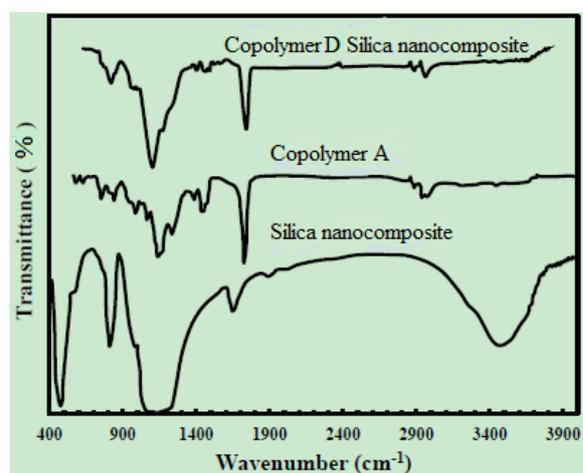
**Figure 1** TEM images of prepared polymers

It is clear that the total particle sizes of nano-silica/methyl methacrylate/butyl acrylate copolymer emulsions of Composites B, C, and D increased gradually as the concentration of nano-silica increased and were found to be 280, 317, and 450 nm, respectively. This may be due to the new physical bonding instead of the chemical one established between the nano-silica particles and the polymer matrix as the concentration of nano-silica increased, which led to greater extents of aggregation (7).

### C. FTIR spectra of nano-silica/methyl methacrylate/butyl acrylate copolymer emulsion film

The FTIR spectra of pure emulsion and its nano-silica/methyl methacrylate/butyl acrylate co-polymer emulsion films are shown in Figure 2. The FTIR spectra showed the effective modification of the silica surface with acrylic copolymer. The spectra shown in Figure 2 exhibited a number of characteristic spectral bands, such as: the peaks at 1140 and 473  $\text{cm}^{-1}$  due to the asymmetric stretching vibration, symmetric stretching vibration and bending vibration of Si–O–Si, respectively, which are the specific bands of the nano-silica. The peak at 960  $\text{cm}^{-1}$  is ascribed to the stretching vibration of Si–O. The broad band around 3480  $\text{cm}^{-1}$  can be attributed to absorbed water. In the silica nanoparticles, the tether between the silica and the polyacrylate chains caused the band absorptions corresponding to the C–OH and C–O–C groups of the polyacrylate chains, which are significantly overlapped with the Si–O–Si group of the silica, as shown in the spectral range of 1000–1400  $\text{cm}^{-1}$ . However, the peaks that appeared at 1740 and 1440  $\text{cm}^{-1}$ , respectively, referred to the stretching vibration of carbonyl group and the bending vibration peak of C–H in acrylic copolymer.

In addition –CH<sub>3</sub> and –CH<sub>2</sub> absorbance peaks for the copolymer around 2900 to 3100  $\text{cm}^{-1}$  are observed for both the neat copolymer and the prepared nanocomposite. The FTIR spectrum showed a decrease in the adsorption band intensity at 3480  $\text{cm}^{-1}$ , indicating that approximately all of the silica nanoparticles had been covered by the polymer (15). The absorption spectrum of nano-silica, pure copolymer (A) and the copolymer (D) nanocomposite proved that nano-silica were successfully bounded and covered with the copolymer.



**Figure 2** FTIR spectra of pure emulsion and its nano-silica/ methyl methacrylate/butyl acrylate co-polymer emulsion film

### 3.2. Nano-silica/methyl methacrylate/butyl acrylate co-polymer emulsion as retanning agent for chrome tanned leather

The retanning process of chrome tanned leather was performed as follows:

- Treatment of chrome tanned leather with (0.25%) sodium acetate and (0.5) sodium bicarbonate for 30 minutes to adjust the pH5.5.
- The retanning process was carried out on the treated leather with (2%, 4%, and 6%) of different types of emulsion polymers and with basic chromium sulphate (BCS) solution.
- Then, the retanned leather was washed with water and left to dry in fresh air by hanging at room temperature.

### 3.3. Characteristics of the tanned leather

The leather samples retanned using the prepared polymers were characterised for the following parameters.

#### a) Mechanical properties

Mechanical properties have generally been given the greatest consideration in the evaluation of leather. The mechanical characters include the measurement of the tensile strength and elongation at break. These characters were carried out according to the Egyptian standard method (ES – 123) and official methods. Figure (3, 4) showed, in general, strength properties of leather by the prepared polymers improved well over untreated leather one. This may be due to the good adhesion effect of the polymer / nano-silica on the fiber of the leather and also due to the filling of grain layer<sup>(25, 27)</sup>.

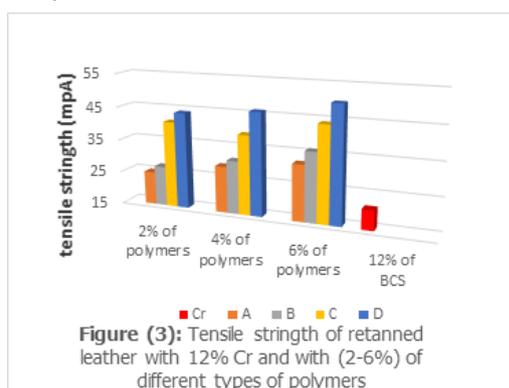
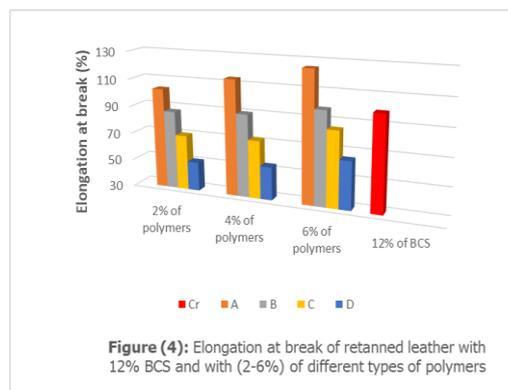


Figure 3 illustrates tensile strength of the leather samples retanned with 12% of basic chromium sulphate (BCS) solution and with different types of polymer-nano-silica composites at dosages of 2, 4 and 6%, respectively. It is clear from Figure 3 that an improvement in the tensile strength properties of treated leather samples by Polymers than sample treated with basic chromium sulphate (BCS) solution, it was also noticed that the tensile strength increased gradually for the samples treated with the polymers B, C, and D comparing with polymer A due to the filling effect of nano-silica.



It was noticed from Figure 4 that, Polymer A achieved good elongation at break, comparing with the other polymers and with BCS. The undesirable effect of elongation at break for Polymers B-D is due to the presence of nano-silica build-up, with the elongation at break decreasing with increasing nano-silica percent.

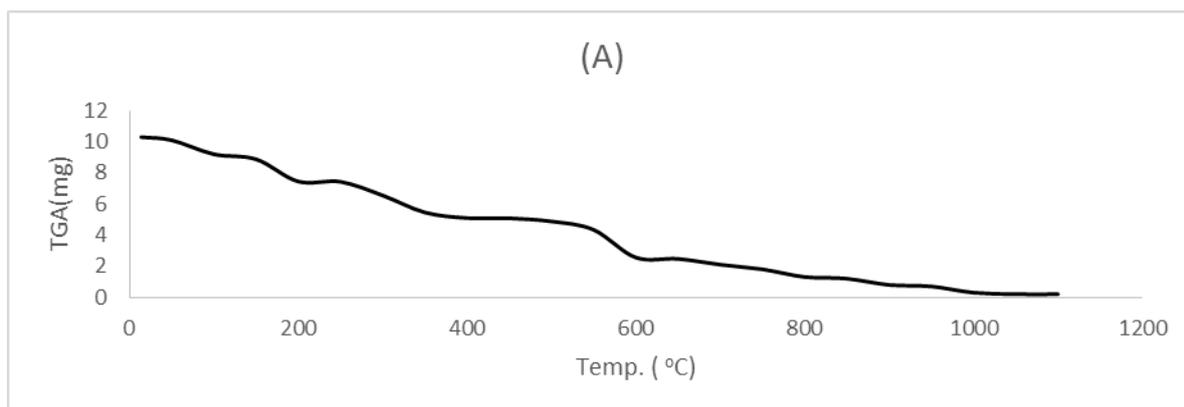
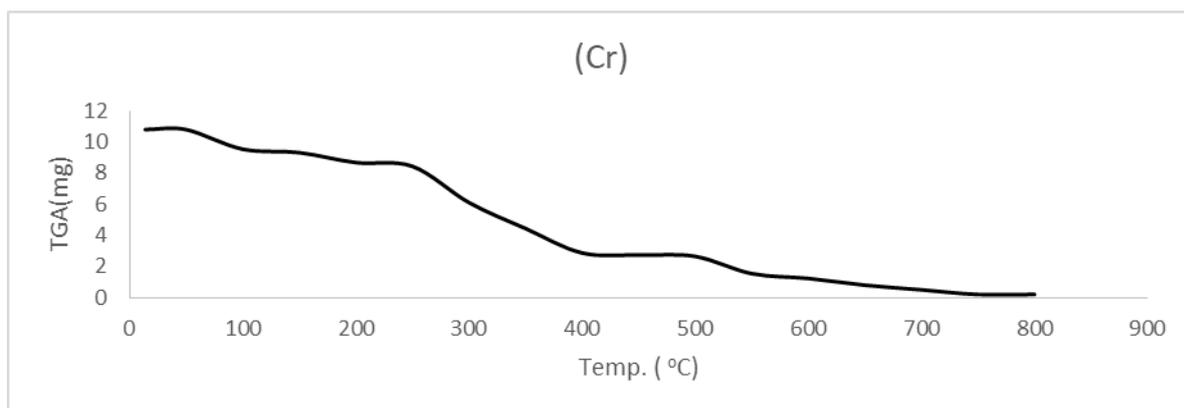
In general, it can be concluded from Figure 3 that, Polymer D is the best one in its beneficial effect on tensile strength. From Figure 4, it can be seen that Polymers A had greater beneficial effects on elongation at break.

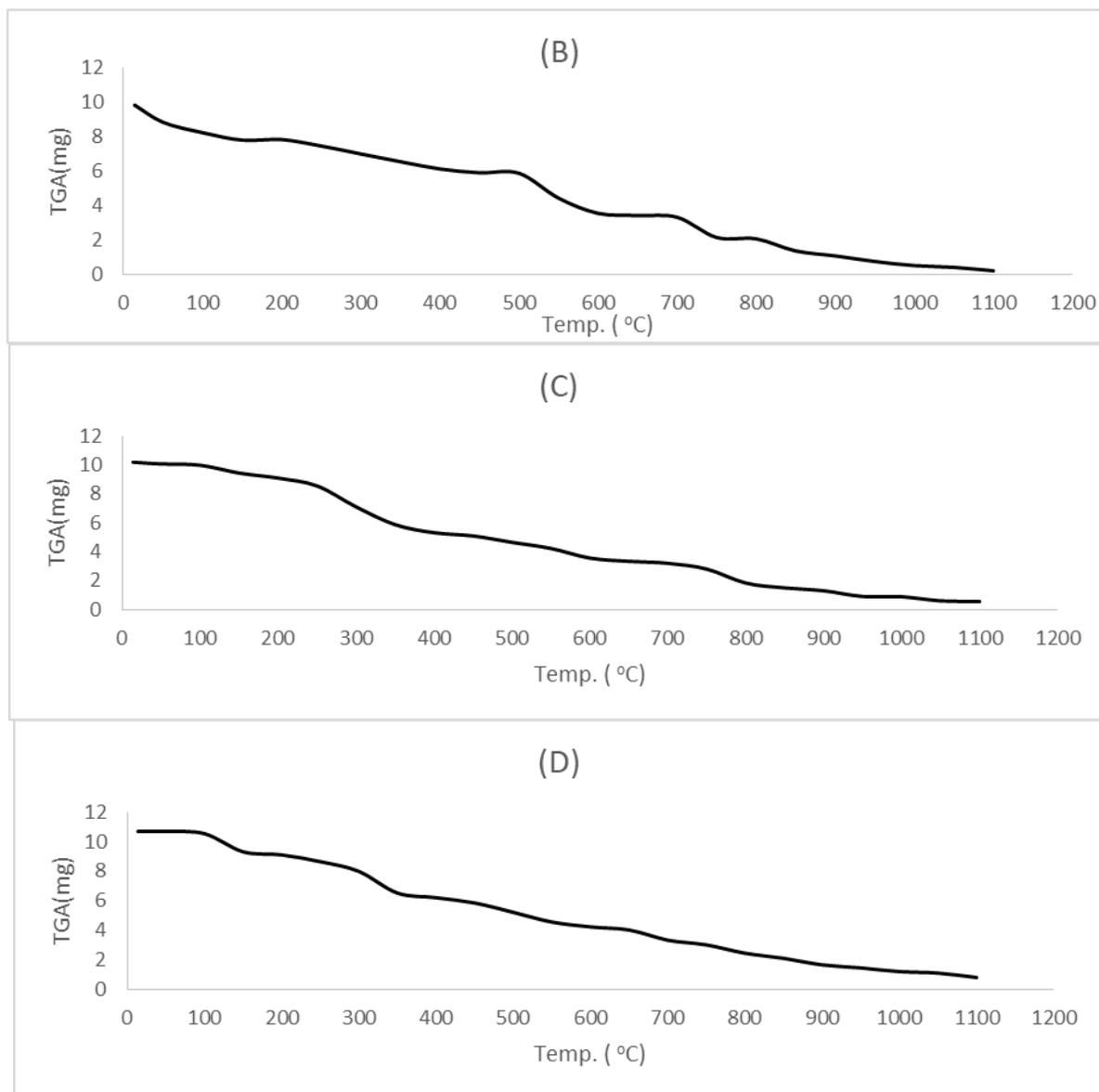
#### b) Thermal Study (TGA)

The TGA curves of the leather samples retanned by the prepared polymers are shown in Figure 5 and the relevant weight loss data are provided in Table III. The TGA analysis illustrate that, the decomposition temperature of the polymer/inorganic nano-silica retanned leather is higher than those of the chrome retanned leather samples. Thus, it would appear that the incorporation and interaction of the polymer/inorganic nano-silica into leather increases the thermal stability of the polymer leather over that of the chrome retanned leather. Such an improvement in thermal stability can be attributed to gap-filling and the formation of polymer – collagen composite. Thus, the gap-filling by the nano-silica brings about multiple hydrogen bonding between the numerous carbonyl groups (C=O) and the active sites of the polymers having a large number of hydrogen atoms in (NH) peptide groups, which supports of the junction between the grain and corium<sup>(3,6,22)</sup>. These results indicate that polymer/inorganic nano-silica fills up the empty parts of leather and lubricates the leather fibres.

**Table III** Thermal gravimetric analysis (TGA) of retanned leather

Temp. (°C)	Weight loss (%)				
	Retanned leather by 12% Cr	Retanned leather by 6% polymer A	Retanned leather by 6% polymer B	Retanned leather by 6% polymer C	Retanned leather by 6% polymer D
100	11.66	10.67	16.32	2.05	1.40
300	43.42	36.40	28.87	30.29	25.32
500	75.46	52.62	40.30	54.41	51.21
700	95.37	79.61	66.32	68.62	68.87
900	98.14	92.23	89.18	87.52	84.48
1000	99	97.08	94.89	91.37	88.78





**Figure 5** TGA of retanned leather with 12% chrome and with 6% of different types of Polymers

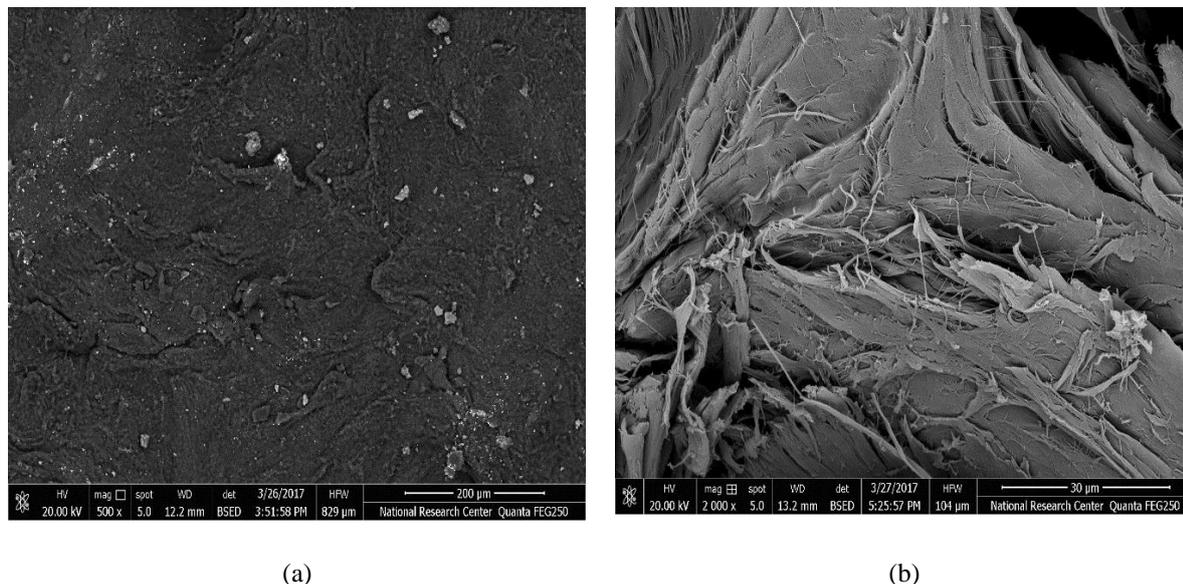
TGA curves of leather retanned with different dosages of nano-silica can be seen in Figure 5. Relevant thermal stability data are shown in Table III, which show that the thermal stability for all samples tanned with polymers containing nano-silica had increased against free-nano-silica containing emulsion (A). This confirms that the introduction of silica enhanced the thermal stability of leather. Moreover, mass fraction of the residual increased with the increase of the content of nano-silica. This is due to the high thermal stability of nano-silica in monomer phase or polysiloxane (polymer phase).

#### c) Surface morphology by scanning electron microscope (SEM)

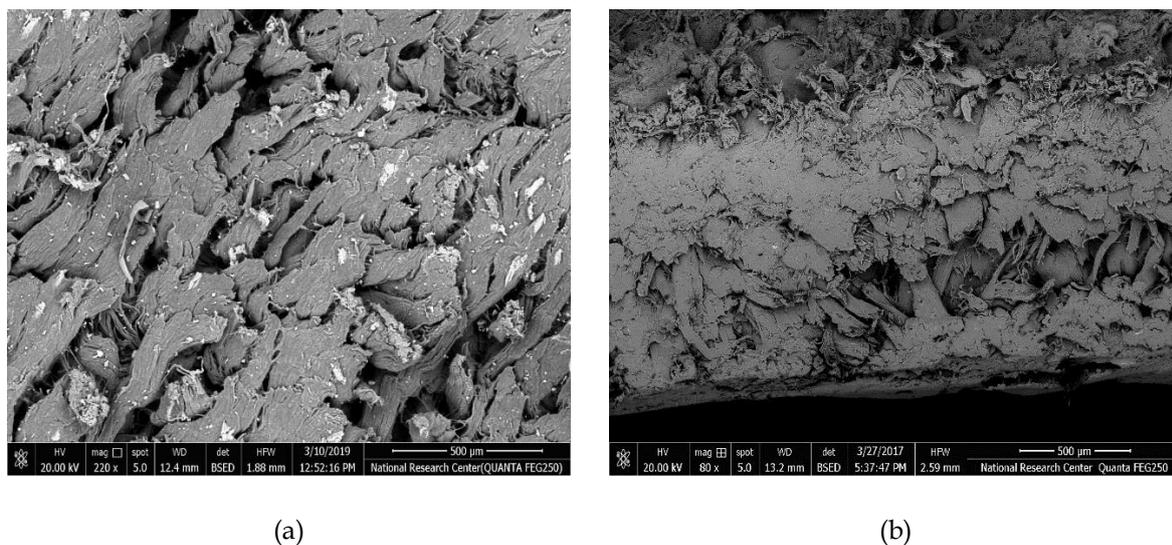
A morphological study was carried out for the chrome tanned leather samples in comparison with retanned leather by four Polymers A, B, C, and D was using SEM. In particular, SEM was employed to assess the penetration of the nano-silica-polymer composites through the leather and into the hierarchy of the structure and is thus a useful technique for evaluating the effects of various treatments on the skin. Thus, SEM analyses of the retanned leather

samples were performed in order to gain an insight to the effect of the prepared nano-silica/polymers on

fiber bundles as tanning agents.



**Figure 6** SEM of grain surface (a) and cross section (b) of retanned leather with 6% polymer B



**Figure 7** SEM of grain surface (a) and cross section (b) of tanned leather with 6% polymer D

It was observed from figures 6&7 (a) that, the SEM of the samples retanned by copolymers have a smooth fiber, firmness grain and modified handle, which are good evidence for the penetration and lubrication of polymers onto the leather fibers and grain surface. At the same time, the polymers don't have any ill-effect on the grain surface with respect

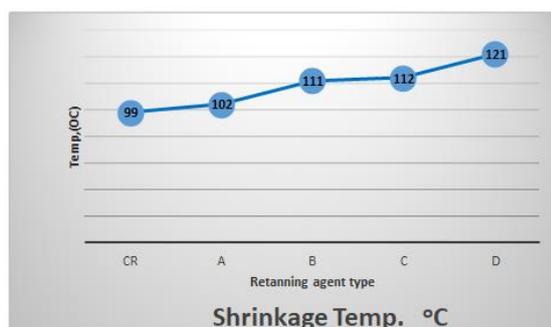
to finishing. The treated chrome tanned leather by polymers gives better grain smoothness, soft fibers, filling and modified handle. The filling of the grain layer improve buff ability for uses as corrected grain leather.

It can be obvious from figures 6&7 (b) that, SEM of the cross section of the leather fibres

retanned by polymers showed separated fibres (tanning effect). But, as can be seen from Figure 7, the fibre bundles has smooth, firm fibre grain and improved handle than fibres in Figure 6. This may be due to fibres shown in Figure 6 having been treated with a smaller amount of nano-silica than fibres shown in Figure 7. This means that, fibres aggregate which are likely due to nano-silica composites of Polymer D having a greater penetration than Polymer B into the leather surface and fibre matrix and function like a plasticiser.

#### d) Shrinkage temperature

One of the more important characters which indicate the desirable effect of the tanning action is the shrinkage temperature (TS). Commonly, leather makers require the shrinkage temperature of leather to be greater than 100 °C for the tanned leather to be used for shoes, garments etc. Such a shrinkage temperature can be achieved when chrome compounds are use in tanning process. On the other hand, the achievement of such a shrinkage temperature using chrome-free retanning materials is more complicated due to different crosslinking abilities of various tanning materials with the active sites of fibres. Only by combining different chrome-free retanning materials with chrome agent for tanning can the required thermal stability achieved<sup>(28-30)</sup>.



**Figure 8** Shrinkage temperatures for the retanned leather

Figure 8 illustrate that, the leather samples retanned with nano-silica-polymer composites D possessed more desirable shrinkage temperature (121°C) than do other samples, followed by Polymer C (112°C) and Polymer B (111°C), all of which above the TS achieved with chrome agent (99°C). Such rises in shrinkage temperature of these retanned leather samples indicated the positive effects of nano-silica-polymer composites as a good retanning agents.

#### 4. Conclusion

The obtained results of this work indicated that, the characters of the retanned leather is improved in the following respects:

- The visual properties of treated leather through fullness and tight grain were modified due to the filling action of nano- silica/copolymer.
- The Polymer A improved the elongation at break when applied as retanning agent as a result of its plasticisation effect and the absence of rigid nanosilica.
- The strength properties of leather are important in deciding about quality of manufactured leather. The best tensile strength were obtained by retanning the leather with Polymer D, due to the high content of nano-silica.
- Leather shrinkage temperature increased when the leather was retanned using Polymers D, C, and B, as a result of the linkage formed between the polymers and the collagen active sites.

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