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Novel tanning agent based on silica-nanocomposite emulsion polymers

Abstract

Purpose – The research reported in this paper was devoted to application of the emulsion polymer of poly(methyl methacrylate-co-butyl acrylate) prepared with *in situ* nano-silica as a novel tanning agent of hide to partly or totally replace chrome salt and to improve physical, thermal and mechanical properties of the tanned leather as well as to reduce the environmental impact of chrome tanning effluent.

Design/methodology/approach – 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, 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 tanned leather are discussed.

Findings – It was found that the viscosity, the particle size, and the solid content of the prepared polymers increased as the content of the nano-silica increased while gloss and drying time of the resulting polymer film decreased. Tanning buffalo hide by Polymer F (containing a high content of nano-silica) gave desirable properties in terms of tensile strength, thermal stability as well as shrinkage temperature.

Research limitations/implications – This paper discusses the preparation and the characterisation of emulsion polymers with *in situ* nano-silica and their application in tanning process to enhance and improve the leather quality as well as reduce the use of chrome tanning materials and consequently chrome tanning waste.

Practical implications – The tanned leather showed an improvement of physico-mechanical properties, as well as enhancement of thermal stability. Furthermore, the tanned leather has uniform colour, softness, and firmness of grain. All these promising results provide evidence to support the applicability of the prepared copolymer/nano-silica emulsions as an efficient tanning agent that also provides lubricating properties for leather.

Originality/value – Since May 2015, REACH Annex XVII restricts Cr(VI) in leather articles or leather parts of articles that come into contact with skin to a concentration of less than 3 mg/kg. Cases of discovery of Cr(VI) in leather articles have been reported by the European rapid alert system on dangerous consumer products (RAPEX). The emulsion poly(methyl methacrylate-co-butyl acrylate) with *in situ* nano-silica that has been developed via the study reported in this paper is one of the better technologies for the reduction of chromium ratio used in tanning industry.

Keywords: Butyl acrylate, Chrome tanning, Chromium uptake, Core-shell, De-pickled hide, Emulsion polymer, Methyl methacrylate, Nano-silica

Introduction

Emulsion polymerisation systems are widely used in the manufacture of a wide range of polymers used in many applications including adhesives, binders, paints (used for nonwoven fabrics), additives (used for textiles, paper and construction materials), impact modifiers (applicable for plastic matrices and diagnostic tests), and drug delivery systems. The market demand for unique polymers with special design to address environmental concerns and governmental regulations (*e.g.* substitution of waterborne products for solvent based systems) has promoted the development of this branch of polymer science. (Mojgan *et al.*, 2014; Abd El-Wahab *et al.*, 2018, 2019; El-sherief *et al.*, 2017; *Ahmed et al.*, 2017).

However, many emulsion polymers exhibit poor water/solvent-resistance and poor hardness (Zou *et al.*, 2007; Ge *et al.*, 2005). One of the methods to improve such properties is to combine emulsion polymers with inorganic nanometre materials to form organic/inorganic composite coatings (Tamai and Watanabe, 2006; Abd El-Shafey *et al.*, 2015).

The field of inorganic-organic nanocomposites is growing rapidly because such hybrid materials can possess combined desirable properties of both the incorporated inorganic materials and the base polymers. Among all hybrid materials, nanocapsules are especially interesting, due to their capability of creating a diverse range of new materials for a wide range of different applications (Ghosh *et al.*, 2006).

A wide variety of colloidal inorganic materials have been used in polymer nanocomposites including silica (Zou *et al.*, 2008), titanium dioxide (Caris *et al.*, 1989), copper oxide (Huang *et al.*, 1995), magnetic oxide (Li and Sun, 1995), aluminium hydroxide (Oyama *et al.*, 1993), silver (Yazdimamaghani *et al.*, 2011), clay (Huang *et al.*, 2001) and carbon black (Bakhshaee *et al.*, 1985). Among them, silica is the most studied material, because the 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. Uniform dispersion of nano-silica in polymers can improve the strength, the abrasion-resistance, the aging-resistance and the climate-resistance of the polymer too. Indeed, such nano-silica – polymer composites have been used as thermal insulators, bioactive supports, next-generation exterior facade paints and scratch-resistant transparent coatings (Tamai and Watanabe, 2006), polymer light-emitting diodes and molecular imprinting, plastics, rubbers, coatings, drug delivery systems and general composite materials (Yazdimamaghani *et al.*, 2011).

Such nanocomposite particles are commonly produced by incorporation of colloidal silica in heterogeneous polymerisations, such as emulsion, dispersion and suspension (Schmid *et al.*, 2006; Sondi *et al.*, 2000; Percy *et al.*, 2004). Although all of these methods have been reported to produce fine nanocomposites, in order to prepare organic-inorganic nano-hybrids, emulsion polymerisation is the especially preferred route to produce nanocomposites based on acrylic or styrenic polymers. This is mainly due to its ease of processability and the possibility to distribute nanoparticles of low concentrations into nanoscale-independent matrices (Mizutani *et al.*, 2005; Kimura *et al.*, 2006). Therefore, the work reported in this paper was devoted to exploring the application of emulsion polymerised organic-inorganic nanohybrids for use in leather industry as tanning agents (modifying agent).

Over several decades, leather technology literature has been dominated by ways to reduce the environmental impact of leather production. Hides are natural proteins which are easily attack by organisms and prone to putrefaction. Tanning operation is one of the more important steps for leather industry, in which protein of raw hide is transformed into a stable fibre structure (leather). There are many types of tanning agents, the more widely employed is the chrome tan (Hauber and German, 1999). Chrome tanning has proven to be an effective method of tanning and is employed in tanneries worldwide. It is used for the production of the great majority of various types of leathers such as upper, garments and other light leathers (EL-Shahat and Kamal, 2019). Chrome tanning affords the tanned leather better characters than other tanning agents including high thermal stability, light weight and high strength properties (Bieniewics, 1983; Srearam and Ramasami, 2003). However, despite the many advantages offered by chrome tanning, there is a worldwide interest in containing the environmental impacts caused by chrome tanning waste. Therefore, there is a growing demand for eco-benign tanning systems owing to stringent environmental regulations. The work that is reported in this paper aimed to develop acrylic co-polymers nano-silica emulsions as an efficient leather tanning agent in order to prevent the creation of chrome tanning waste negating the need for the treatment of chrome tanning waste.

Experimental

Materials

Materials that were employed in the study reported here included the following.

- Butyl acrylate (BA) and methyl methacrylate (MMA) were supplied by Sigma Aldrich and distilled at low pressure before use and stored at -20°C.
- Potassium persulphate (KPS), sodium bicarbonate, ammonium hydroxide (NH_4OH), ethanol, methacrylic acid (MAA) and acrylamide (AMM), all of which Fine Chemicals grade, were supplied by Sigma Chemicals.
- Sodium dodecyl benzene sulphonate (SDBS) was supplied by Across Chemical and was used as an anionic surfactant.
- Distilled water was used to prepare aqueous solutions where required.
- Modified alcohol ether phosphate (Maxemul 6112, supplied by Croda Coatings and Polymers) was used as an anionic reactive surfactant.
- Polyethylene oxide and alkenyl functionality (Maxemul 5011, also supplied by Croda Coatings and Polymers) was used as a non-ionic reactive surfactant.
- Coatosil VX 193 (vinyl trimethoxy silane) supplied by Momentive Performance Materials.
- Egyptian buffalo hides.

Experimental methods

Emulsion polymerisation

Preparation of in situ nano-silica/methyl methacrylate/butyl acrylate co-polymer emulsion (Li *et al.*, 2013)

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 (Li *et al.*, 2013). Vinyl trimethoxy silane (Coatosil VX 193) (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. Ammonium hydroxide solution (NH_4OH) (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 trimethoxy silane), anionic reactive surfactant and NH_4OH. 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, 2% for polymer C, 3% for Polymer D, 4% for Polymer E, and 5% for Polymer F) 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_2O, 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_2O) 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 and 3g acrylamide 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.

(Take in Scheme 1)

(Take in Figure 1)

(Take in Figure 2)

Preparation of leather

The raw hide selected for the study was the commercially available Egyptian buffalo hide. The samples were worked up following the typical beam house operations. Slow additions of each of the reagents (*e.g.* lactic acid, sodium sulphide, lime, sodium chloride, soda ash, and bactericide etc.) were carried out and all percentages of reagents were calculated on the dry weight of the pickled hide. (Abd El-Monem *et al.*, 2017).

Tanning process

The pH of the pickled hide that was used in each tanning process was adjusted to pH2.5. Then, the hide was treated with 10% NaCl for 30 minutes as the de-pickle stage. The de-pickled pelt samples were modified with chromium sulphate and the prepared polymers as tanning agents. This means that the tanning process was carried out using chromium sulphate followed by the prepared polymers according to the proportions in specific formulations.

Rectangular leather samples having the dimensions of 20 × 30 cm^2 were taken. These rectangular samples were then neutralised and re-tanned following the same procedure given above. All concentrations were calculated as wt/(wt of shaved chrome tanned leather).

Testing and analysis

Morphological study (*Groves, 1978*)

The microstructure 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.

Fourier transform infrared (*FTIR*)

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

Determination of molecular weight (*Malihi et al., 1984*)

A small amount of the sample (0.01 gm) was dissolved in 2ml of THF solvent. The solution was filtered using a 0.45μm 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 5μm, 3 columns of pore type 100, 104, 105 Å 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 g/mol.

Analysis of the surface morphology of the leather samples (*EL-Shahat et al., 2012*)

The surface morphology of the leather samples was analysed using a 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.

Analysis of mechanical properties

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.

Measurement of thermal properties (*EL-Shahat, 2012*)

The thermogravimetric analysis (TGA) measurements for the obtained samples were carried out at temperature ranging from 50°C to 1100°C under nitrogen atmosphere at a heating rate of 10°C/min using a Shimadzu TGA-50 instrument.

***Measurement of shrinkage temperature* (*EL-Shahat, 2012*)**

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 the Egyptian Specifications.

Results and discussion

This research aimed to use emulsion polymer-silica composites consisting of poly(methyl methacrylate-co-butyl acrylate) and nano-silica, to partially or totally replace chrome salt, for tanning buffalo hide, with a view to improving physical, thermal, and mechanical properties of the tanned buffalo leather as well as to reduce the environmental impact of chrome tanning waste.

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 and acrylamide as binder, potassium persulphate as initiator and Maxemul 6112 and Maxemul 5011 as reactive surfactants, as shown above for six polymer-nano-silica composites prepared, namely Polymer Composites A – F.

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.

(Take in Table I)

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 4% (E). 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 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 viscosity of the co-polymers increased as the concentration of nano-silica increased due to the improved gel content of latex co-polymers.

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 (Dashtizadeh *et al.*, 2011).

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.

(Take in Table II)

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 3. The FTIR spectra showed the effective modification of the silica surface with acrylic copolymer. The spectra shown in Figure 3 exhibited a number of characteristic spectral bands, such as: the peaks at 1140 and 473 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 cm^{-1} is ascribed to the stretching vibration of Si–O. The broad band around 3480 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 cm^{-1}. However, the peaks that appeared at 1740 and 1440 cm^{-1}, respectively, referred to the stretching vibration of carbonyl group and the bending vibration peak of C-H in acrylic copolymer. In addition $-CH_3$ and $-CH_2$ absorbance peaks for the copolymer around 2900 to 3100 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 cm^{-1}, indicating that approximately all of the silica nanoparticles had been covered by the polymer (Yazdimamaghani *et al.*, 2013). The absorption spectrum of nano-silica, pure copolymer (A) and the copolymer (F) nanocomposite proved that nano-silica were successfully bounded and covered with the copolymer.

(Take in Figure 3)

Microstructure of the prepared polymers

The TEM images of pure emulsion polymer (A) and its polymer/nano-silica emulsions (B-F) are shown in Figures 4. TEM images of pure emulsion polymer (A) shows uniform and mono-dispersed particles in the range of 220 nm.

(Take in Figure 4)

It is clear that the total particle sizes of nano-silica/methyl methacrylate/butyl acrylate copolymer emulsions of Composites B, C, D, E and F increased gradually as the concentration of nano-silica increased and were found to be 270, 290, 310, 400 and 480 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.

Nano-silica/methyl methacrylate/butyl acrylate co-polymer emulsion as tanning agent for buffalo hide

Pickled hide was treated with sodium formate and sodium chloride to adjust the pH through its thickness as well as to eliminate the acid and salts. This process (de-pickling) is a very important process to prevent the acid or salt hydrolysis of protein fibres. The de-pickled pelt samples were modified with the prepared polymers as tanning agent.

The tanning process of buffalo hides was performed as follows:

a. Treatment of pickled hide with 10% NaCl, as de-pickle agent, for 30 minutes.
b. The de-pickled pelt was tanned by 1%, 2% and 3% of BCS (basic chromium sulphate) respectively, followed by 2%, 4% and 6% of different types of polymers for each percentage of chrome, respectively.

Characteristics of the tanned leather

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

Mechanical properties

Mechanical properties is one of the more important criteria to give an indication of tanning actions and provide a basis for evaluation of tanned leather properties (Virgilijus *et al.*, 2010). The mechanical properties of interest include the tensile strength and elongation at break. Relevant tensile strength and elongation at break results are shown in Figures 5 and 6. It can be seen from Figures 5 and 6 that, in general, strength properties of leather by the prepared polymers improved well over untreated one. This may be due to the good adhesion of the polymer/nano-silica to hide fibre of the leather and also due to the filling of voids and pores with active sites of the leather by the nano-silica (amino and carboxylic terminal groups) (EL-Shahat *et al.*, 2011, 2012).

(Take in Figure 5)

Tensile strength

Figure 5-a shows the tensile strength of tanned samples with 1% chrome followed by nano-silica-polymer composites at 2, 4 and 6% dosing levels, respectively. It was observed from Figure 5-a that samples treated with Polymer F at 4% dosing level helped achieve the greatest tensile strength. Figure 5-c shows the tensile strength of the leather samples tanned with 3% chrome and different types of polymers (2, 4 and 6% dosages). It can be seen from Figure 5-c that Polymer F also helped achieve a greater tensile strength (at 4% dose) comparing with other polymers. It is also clear from Figure 5-c that, at a dosing level of 6% Polymer F, tensile strength was lowered, which may be due to the increased polymer content leading to low exhaustion of chrome in the tanning process.

Figure 5-b illustrates tensile strength of the leather samples tanned with 2% chrome and different types of polymer-nano-silica composites at dosages of 2, 4 and 6%, respectively. It is clear from Figure 5-b that Polymer F at 6% concentration achieved a better tensile strength compared with other polymers. This means that Polymer F was the best one amongst the used polymers and the most suitable content was 4% and over to give an unfavourable effect with tensile strength with 1% and 3% chrome, Figure 5 (a &c), and 6% with 2% chrome, Figure 5 (b). In general, tensile strength of the treated samples was improved and tensile strength increased with the increase in the concentration of nano-silica within the composites. This may be due to the filling effect of nano-silica.

Elongation at break

Figures 6 show that the elongation at break of the leather samples treated with 1% chrome decreased with increasing content of nano-silica-polymer composites (Figure 6-a), while the decreases for the cases of 2% and 3% chrome treatments were less significant (Figures 6-b and 6-c). Such a phenomenon is likely an indication of the reinforcement of the strength and integrity of the tanned leather due to the presence of nano-silica-polymer matrix.

(Take in Figure 6)

It was noticed from Figure 6-a that, Polymer A achieved good elongation at break, comparing with the other polymers used with 1% chrome. However, the elongation at break of tanned leather was improved by Polymer A at 4% dose. The undesirable effect of elongation at break for Polymers B-F is due to the presence of nano-silica build-up, with the elongation at break decreasing with increasing nano-silica percent. It can also be seen, from Figure 6-b, that Polymer A achieved good elongation at break, at 2% and 4% concentrations while Polymer B achieved good elongation at 6% concentration comparing with the other polymers. Figure 6-c shows elongation at break of the leather samples tanned with 3% chrome and different types of polymers at dosages 2%, 4% and 6%, respectively. It can be seen, from Figure 6-c that Polymer B achieved good elongation at break at dosing levels of 2% and 4%, and Polymer A achieved a good elongation at break at a dosing level of 6%.

It can concluded from Figure 5 that, Polymer F is the best one in its beneficial effect on tensile strength at 4% concentration (with 1and 3% chrome) and 6% with 3% chrome. From Figure 6, it can be seen that Polymers A and B had greater beneficial effects on elongation at break.

***Thermal Study* (*TGA*)**

The TGA curves of the leather samples tanned by the prepared polymers are shown in Figure 7 and the relevant weight loss data are provided in Table III. The TGA analysis show that, the decomposition temperature of the polymer/inorganic nano-silica tanned leather is higher than those of the chrome tanned 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 tanned 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 inorganic nano-silica brings about multiple weak 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 (EL-Shahat *et al.*, 2012). These results indicate that polymer/inorganic nano-silica fills up the voids in the leather and lubricates the leather fibres, which leads to enhanced thermal stability.

(Take in Figure 7)

(Take in Table III)

Generally, polymer/inorganic nano-silica usually exhibits enhanced thermal stability. TGA curves of leather tanned with different dosages of nano-silica can be seen in Figure 7. 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 non-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).

Surface morphology by scanning electron microscope (SEM)

The surface morphological study of the leather samples tanned with Polymers A, B, C, D, E and F was carried out in comparison 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 tanned leather samples were performed in order to gain an insight to the effect of the prepared nano-silica/polymers on fibre bundles as tanning agents.

(Take in Figure 8)

(Take in Figure 9)

SEM (×100 and ×200) of the cross-section of the leather treated with polymers were carried out to show the effect of the prepared polymers on the fibre bundles as tanning agents (Figures 8 and 9). It can be observed from Figures 8 and 9 that, SEM of the cross section of the leather fibres tanned by polymers showed separated fibres (tanning effect). But, as can be seen from Figure 9, the fibre bundles has smooth, firm fibre grain and improved handle than fibres in Figure 8. This may be due to fibres shown in Figure 8 having been treated with a smaller amount of nano-silica than fibres shown in Figure 9. This means that, fibres aggregate which are likely due to nano-silica composites of Polymer F having a greater penetration than Polymer B into the leather surface and fibre matrix and function like a plasticiser. The leather tanned by polymers gave better grain smoothness and filling. On the other hand, a modified handling and soft fibres of the tanned leather samples were noticed, because they have high flexibility and greater softness. The filling of the grain layer improves buff ability for uses as corrected grain leather.

Shrinkage temperature

One of the more important characters which indicate the desirable effect of the tanning action is the shrinkage temperature (TS). Due to this, the shrinkage temperature remains as important index, which reflects the quantity of new bonds formed in collagen and the quality of tanning and the tanned leather. 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 tanning 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 tanning materials with chrome agent for tanning can the required thermal stability achieved (Gangopadhyay *et al.,* 2000; Fathima *et al.*, 2004; Tao-Tao *et al.,* 2009).

For that reason, this work combined different nano-silica-polymer composites with chrome agents. Figure 10 show shrinkage temperature of the leather samples tanned with chrome (3%) followed by each of the different types of prepared nano-silica-polymer composites. It can be seen, from Figure 10, that the leather samples tanned with 3% chrome followed by 4% nano-silica-polymer composite F possessed more desirable shrinkage temperature (117°C) than do other samples, followed by Polymer E (115°C) and Polymer D (111°C), all of which above the TS achieved with chrome agent (100°C). This once more confirms the proposition that tanning complexes are somewhat linked to the collagen active sites. Such rises in shrinkage temperature of these tanned leather samples indicated the positive effects of nano-silica-polymer composites as a good tanning agents.

(Take in Figure 10)

Conclusions

It can be concluded from the results obtained through the work that, the characteristics of the tanned leather had been improved in the following respects:

- The use of nano-silica methyl methacrylate/butyl acrylate copolymer as a tanning agent in tanning industry allowed a significant reduction in the quantity of chromium sulphate required, which is very important from an environmental stand point.
- The chrome-free tanning method based on nano-silica-polymer composites improved the main characteristics of the tanned leather such as thermal stability, shrinkage temperature and acceptable texture, as well as tensile strength.
- The aesthetic properties of the treated leather have been improved.
- The strength properties of leather are important in deciding about quality of manufactured leather. The best tensile strength and elongation at break were obtained by tanning the leather with Polymer F, due to the high content of nano-silica and plasticisation effect respectively.
- Leather shrinkage temperature increased when the leather was tanned using Polymers F, D and E, as a result of the linkage formed between the polymers and the collagen active sites.
- A high proportion of nano-silica in the polymer matrix helped enhance the thermal stability of the treated leather.

References

Abd El-Monem, F., Ahmed, I.H., EL-Shahat, H.A.N., Abd El-Wahab, H. and Nasser, A.M. (2017), “Nano-emulsion an efficient pre-tanning agent for buffalo hide”, *Arabian Journal of Chemistry*, Vol. 10, pp. S3861–9.

Abd El-Shafey, I.A., Ahmed, I.H., El-Masry, A.M. and Saleh, H.A. (2015), "Effect of changing mass ratio of styrene/butyl acrylate on the behavior of nano organo-silica in poly(styrene-co-butyl acrylate) emulsion core-shell", *Journal of Engineering and Applied Sciences*, Vol. 10 No. 14, pp. 6127-34.

Abd El-Wahab, H., Attia, M., Hassan, W.A. and Nasser, A.M. (2018), "Preparation and characterization of nano-copolymers (styrene/2-Ethyl Hexyl Acrylate) based on two different surfactants and use it as a binder for surface coatings", *Nanoscience & Nanotechnology: An Indian Journal*, Vol. 12 No. 2, pp. 1-17.

Abd El-Wahab, H., Hassan, W.A., Nasser, A.M. and Elsayed, S.S. (2019), "Effect of different surfactant monomers on alkali soluble emulsion polymer as a binder for water base printing inks", *Egypt J. Chem.*, Vol. 62 No. 1, pp. 63-76.

Ahmed, G.S., Nasser, A.M., Abd El-Wahab, H., Abd El-Fattah, M. and Abdelzaher, E.A.M. (2017), "Improving of reclaimed asphalt pavement using vinyl acetate butyl acrylate polymer", *Global Journal of Engineering Science and Researches*, Vol. 4 No. 10, pp. 1-13.

Bakhshaee, M., Pethrick, R.A., Rashid, H. and Sherrington, D.C. (1985), "Encapsulation of carbon black in suspension polymerised copolymers", *Polym. Commun.*, Vol. 26 No. 11, pp. 185–92.

Bieniewics, K. (1983), *Physical Chemistry and Leather Making*, R.E. Malabar, Florida, Chapter 4.

Caris, C.H.M., van Elven, L.P.M., van Herk, A.M. and German, A.L. (1989), "Polymerisation of MMA at the surface of inorganic submicron particles", *Br. Polym. J.*, Vol. 21 No. 2, pp. 133–40.

Dashtizadeh, A., Abdouss, M., Mahdavi, H. and Khorassani, M. (2011), "Acrylic coatings exhibiting improved hardness, solvent resistance and glossiness by using silica nano composites", *Applied Surface Science*, Vol. 257 No. 6, pp. 2118–25.

EL-Shahat, H.A.N., Ahmed, I.H. and Mahmoud, M.E. (2011), "Novel Retanning agents for chrome tanned leather based on emulsion–nano particles of styrene/butyl acrylate copolymers", *Journal of American Leather Chemical Association*, Vol. 106, pp. 241-8.

EL-Shahat, H.A.N. and Kamal, A.E. (2019), "High exhaustion of chrome tan, enhancement of leather properties and reduction of chrome tanning effluent impact", *Egypt. J. Chem.*, Vol. 62 No. 3, pp. 415-28.

El-Shahat, H.A.N., Mohamed, M.E. and Ahmed, I.H. (2012), "Retanning agents for chrome tanned leather based on emulsion nano-particles of styrene/butyl acrylate copolymers", *New York Science Journal*, Vol. 3 No. 11, pp. 13-21.

EL-Shahat, H.A.N., Othman, O., Kottab, A. and Ibrahim, M. I. (2012), "Molecular spectroscopic studies for suggested mechanistic of chrome tan", *J. of Spectrochimica Acta Part A: Molecular and Bimolecular Spectroscopy*, Vol. 88, pp. 171-6.

El-Sherif, H.M., Nasser, A.M., Ahmed, I.H., Abd El-Wahab, H., Ghazy, M.B.M. and ElSayed, A.E. (2017), "Nano emulsion binders for paper coating synthesis and application", *J. of Macromolecular Science PAC*, Vol. 54 No. 5 pp. 271-87.

Fathima, N.N., Saravanabhavan, S., Rao, J.R. and Nair, B.U. (2004), "An eco-benign tanning system using aluminium, tannic acid and silica combination", *J. of the American Leather Chemists Association,* Vol. 99 No. 2, pp. 73–81.

Gangopadhyay, S., Lahiri, S. and Gangopadhyay, P.K. (2000), "Chrome-free tannage by sequential treatment with synthetic resins and aluminium or titanium", *J. the Society of Leather Technologists and Chemists*, Vol. 84 No. 2, pp. 88–93.

Ge, X.W., Zou, M.X., Huang, F.Z., Nie, J. and Zhang, Z.C. (2005), "Preparation and characterization of polysiloxane-polyacrylate composite lattices and their film properties", *Polym. Int.*, Vol. 54 No. 1, pp. 861-9.

Ghosh, S.K. (2006), *Functional Coatings*, WILEY-VCH Verlag GmbH & Co., KGaA: Weinheim, Germany.

Groves, M.J., Ed., (1978), *Particle Size Analysis*, Heyden, London, pp. 77-100.

Hauber, C. and Germann, H.P. (1999) "Investigations on a possible formation and avoidance of chromate in leather", *J. of World Leather*, Vol. 12 No. 6, pp. 73–80.

Huang, C., Partch, R.E. and Matijevic, E. (1995), "Coating of uniform inorganic particles with polymers: II. Polyaniline on copper oxide", *J. Colloid Interface Sci.*, Vol. 170 No. 5, pp. 275–83.

Huang, X. and Brittain, W.J. (2001), "Synthesis and characterization of PMMA nanocomposites by suspension and emulsion polymerisation", *Macromolecules*, Vol. 34 No. 10, pp. 3255–60.

Kimura, Y., Mizutani, T., Arai, K. and Miyamoto, M. (2006), "Application of silica-containing nano-composite emulsion to wall paint: A new environmentally safe paint of high performance", *Prog. Org. Coat.*, Vol. 55 No. 3, pp. 276–83.

Li, J., Chen, L., Li, X., Zhang, Z. and Jiao, C. (2013), "Preparation and characterization of a novel nanocomposite particles via in situ emulsion polymerization of vinyl functionalized silica nanoparticles and vinyl acetate", *J. Sol-Gel Science and Technology*, Vol. 68 No. 1, pp. 54–9.

Li, X. and Sun, Z. (1995), "Synthesis of magnetic polymer microspheres and application for immobilization of proteinase of balillus sublitis", *J. Appl. Polym. Sci.,* Vol. 58 No. 10, pp. 1991–7.

Malihi, F.B., Kuo, C.-Y. and Provder, T. (1984), "Development in plastic technology", *J. Appl. Polym. Sci.*, Vol. 29 No. 3, p. 925.

Mizutani, T., Arai, K., Miyamoto, M. and Kimura, Y. (2005), "Preparation of spherical nanocomposites consisting of silica core and polyacrylate shell by emulsion polymerisation", *J. Appl. Polym. Sci.*, Vol. 99 No. 3, pp. 659–69.

Mojgan, M., Amir, H.M. and Mehrnaz, L. (2014), "Emulsion polymerisation and encapsulation of micro and nanoparticles within polymer droplets", *Journal of Chemistry (Iran Polymer & Petrochemical Institute)*, Vol. 9 No. 4, pp. 229-66.

Oyama, H.T., Sprycha, R., Xie, Y., Partch, R.E. and Matijevic, E. (1993) "Coating of uniform inorganic particles with polymers", *J. Colloid Interface Sci.*, Vol. 160 No. 2, pp. 298–303.

Percy, M.J., Amalvy, J.I., Randall, D.P. and Armes, S.P. (2004), "Synthesis of vinyl polymer-silica colloidal nanocomposites prepared using commercial alcoholic silica sols", *Langmuir*, Vol. 20 No. 6, pp. 2184–90.

Schmid, A., Fujii, S. and Armes, S.P. (2006), "Polystyrene-silica nanocomposite particles via alcoholic dispersion polymerisation using a cationic azo initiator", *Langmuir*, Vol. 22 No. 11, pp. 4923–7.

Sondi, I., Fedynshyn, T.H., Sinta, R. and Matijevic, E. (2000), "Encapsulation of nanosized silica by in situ polymerisation of tert-butyl acrylate monomer", *Langmuir,* Vol. 16 No. 23, pp. 9031–4.

Srearam, K.J. and Ramasami, T. (2003), "Sustaining tanning process through conservation, recovery and better utilization of chromium", *Resour. Conserv. Recycl.*, Vol. 38 No. 3, pp. 185–212.

Tamai, T. and Watanabe, M. (2006), "Acrylic polymer/silica hybrids prepared by emulsifier-free emulsion polymerisation and sol-gel process", *J. Poly. Sci., Part A: Polym Chem.*, Vol. 44 No. 1, pp. 273- 80.

Tao-Tao, Q., Xue-Chuan, W., Long-Fang, R. and Yong-Qiang, R. (2009), "Zirconium-oxalizidine combination tannage for sheep garment leather", *J. of the Society of Leather Technologists and Chemists,* Vol. 93 No. 4, pp. 35–9.

Virgilijus, V., Justa, S. and Kęstutis, B. (2010), "Estimation of chrome-free tanning method suitability in conformity with physical and chemical properties of leather", *J. Materials Science (MEDŽIAGOTYRA)*, Vol. 16 No. 4, pp. 330–6.

Yazdimamaghani, M., Pishvaei, M. and Kaffashi, B. (2011), "Synthesis of latex based antibacterial acrylate polymer/nanosilver via in situ miniemulsion polymerisation", *Macromol. Res.*, Vol. 19 No. 3, pp. 243–9.

Yazdimamaghani, M., Pourvvala, T., Motamedi, E., Fathi, B., Vashaee, D. and Tayebi, L. (2013), "Synthesis and characterization of encapsulated nano-silica particles with an acrylic copolymer by in Situ emulsion polymerisation using thermoresponsive nonionic surfactant", *Materials Journal*, Vol. 6 No. 9, pp. 3727-41.

Zou, H., Wu, S. and Shen, J. (2008), "Polymer/silica nanocomposites: Preparation, characterization, properties, and applications", *Chem. Rev.*, Vol. 108 No. 9, pp. 3893–957.

Zou, M.X., Zhao, Q.C., Nie, J. and Zhang, Z.C. (2007), "Preparation and characterization of polysiloxane polyacrylates composite lattices by two seeded emulsion polymerisation and their film properties", *J. Appl. Poly. Sci.*, Vo. 103 No. 3, pp. 1406-11.

Table I Characteristics of the prepared copolymers emulsion

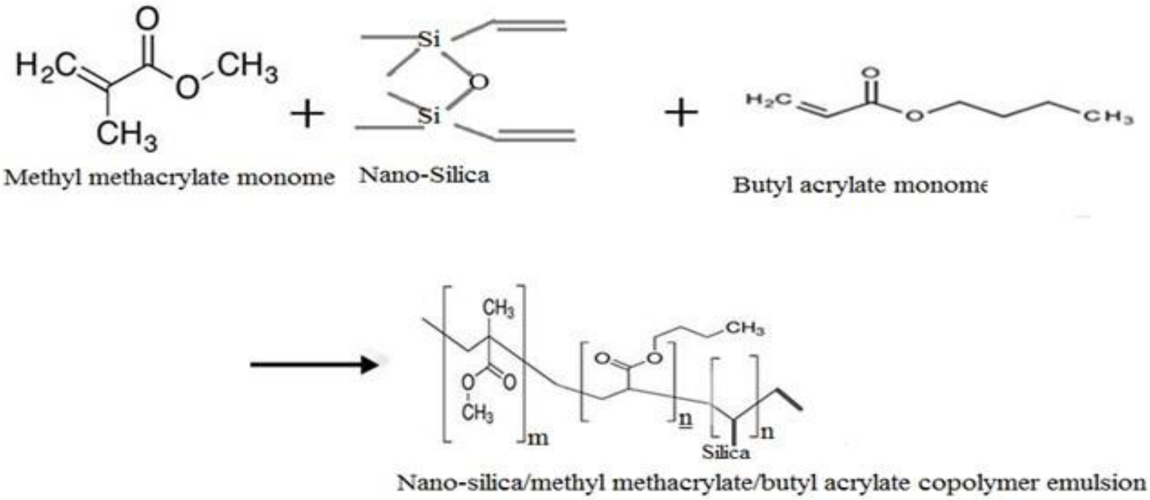
Properties	**Standard** (ASTM)	**Value**					
		Polymers					
		A	B	C	D	E	F
pH		8.3	8.2	8.3	8.1	8.0	8.1
Solid Content (%)	D4139	50.1	49.6	50.7	51.5	52.0	51.1
Conversion (%)		100	99.4	99.3	98.5	98.0	96.1
Drying time (seconds) at 23°C		85	75	70	65	64	57
(Minimum Film Forming Temperature) MFFT (^{O}C)	D2354	16	16	18	18	18	18
Particle size (nm)	TEM	220	270	290	310	400	480
Brookfield Viscosity RVT #50 rpm (cPs)	D2196 – 99	6350	7500	7650	9050	9200	9350
Gloss	D523	87	74	66	60	58	51

Table II Effect of nano-silica on the molecular weight and its distribution

Polymer	**M_n^a (g /mol)**	**M_w^a (g /mol)**	**Polydispersity (Mw/Mn)**
A	1.744×10^5	6.977×10^5	4.00
B	1.605×10^5	5.840×10^5	3.63
C	1.127×10^5	4.309×10^5	3.82
F	1.303×10^5	5.765×10^5	4.42

Table III Thermal gravimetric analysis (TGA) of tanned leather

Temp. (°C)	Weight loss (%)					
	Leather tanned with 3% Cr/4% Polymer A	Leather tanned with 3% Cr/4% Polymer B	Leather tanned with 3% Cr/4% Polymer C	Leather tanned with 3% Cr/4% Polymer D	Leather tanned with 3% Cr/4% Polymer E	Leather tanned with 3% Cr/4% Polymer F
100	27.956	7.608	25.263	12.903	13.333	1.750
300	46.236	14.130	31.578	31.720	27.778	27.956
500	67.741	30.434	65.263	54.838	44.454	38.709
700	94.623	53.260	71.578	71.397	72.233	60.215
900	97.849	91.304	93.684	93.225	92.220	78.494
1000	98.924	95.652	94.993	94.912	94.455	94.623



Schema 1 Preparation of nano-silica/methyl methacrylate/butyl acrylate copolymer emulsion

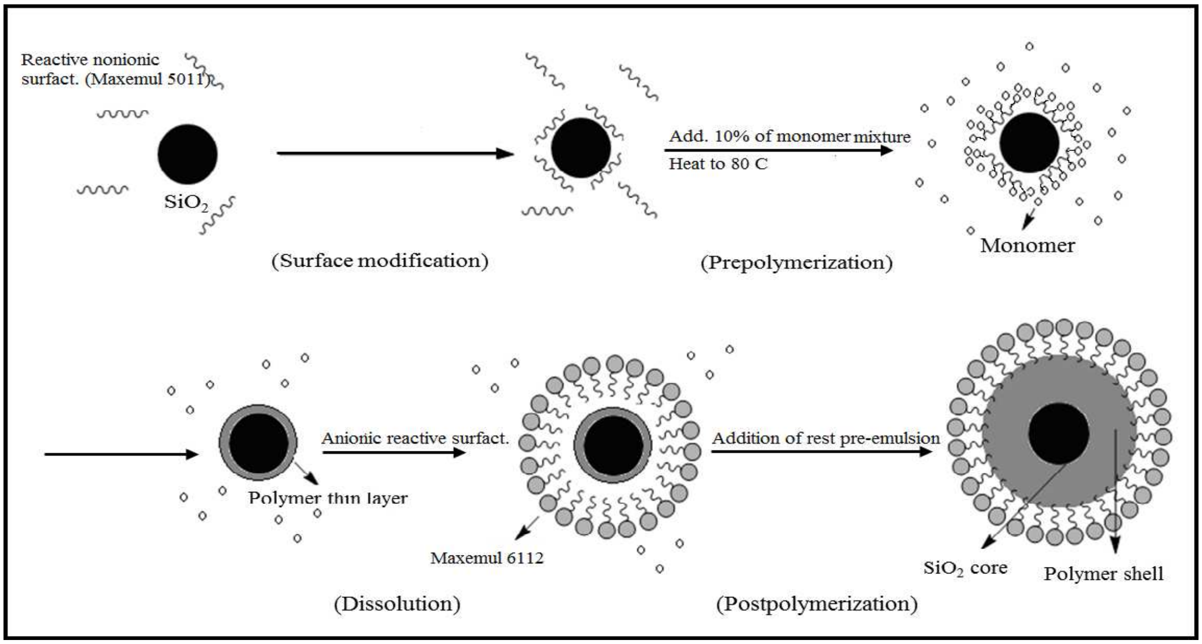


Figure 1 Schematic mechanism of the formation process of nanosilica particles with the acrylic copolymer by *in situ* emulsion polymerisation using reactive non-ionic surfactant

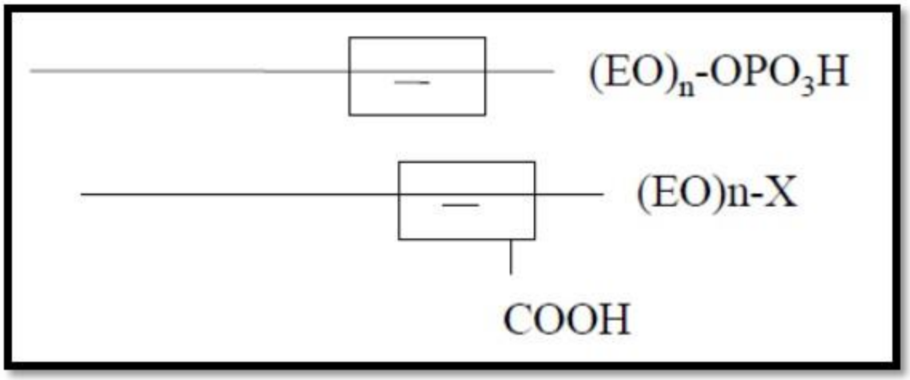


Figure 2 Structures of reactive surfactants

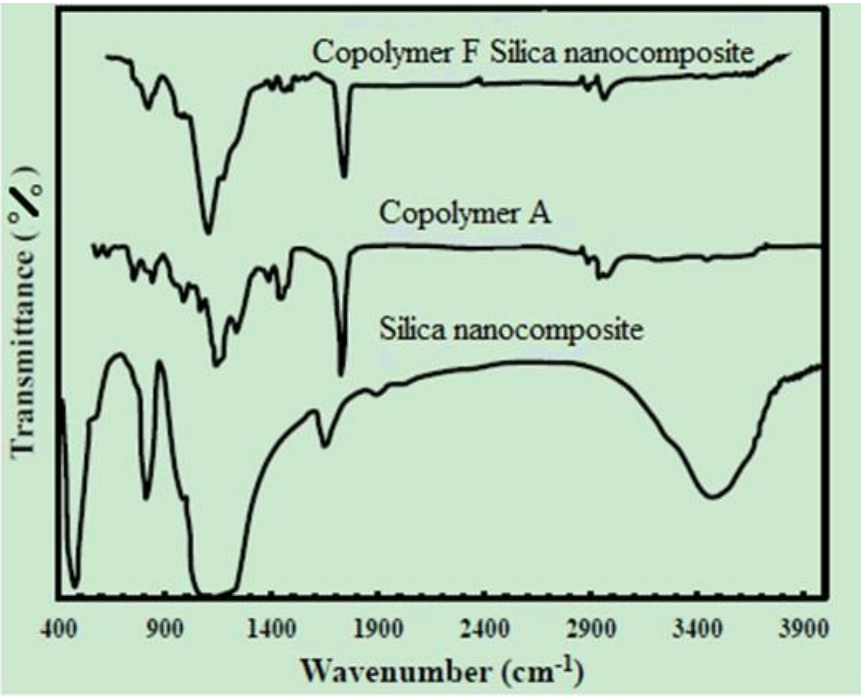
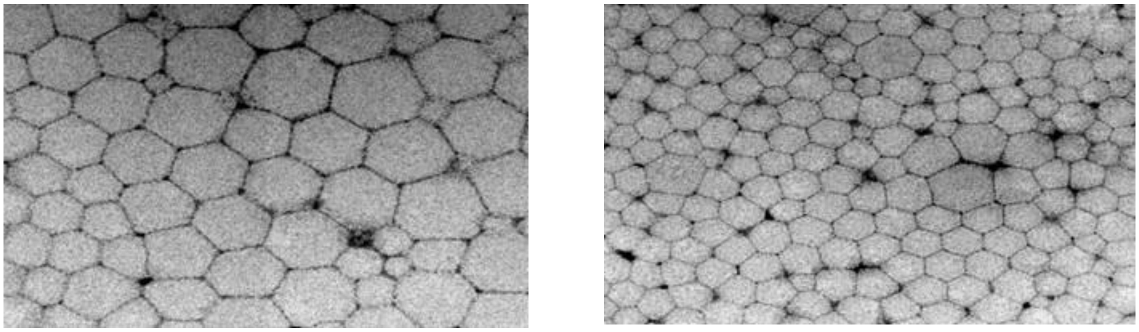
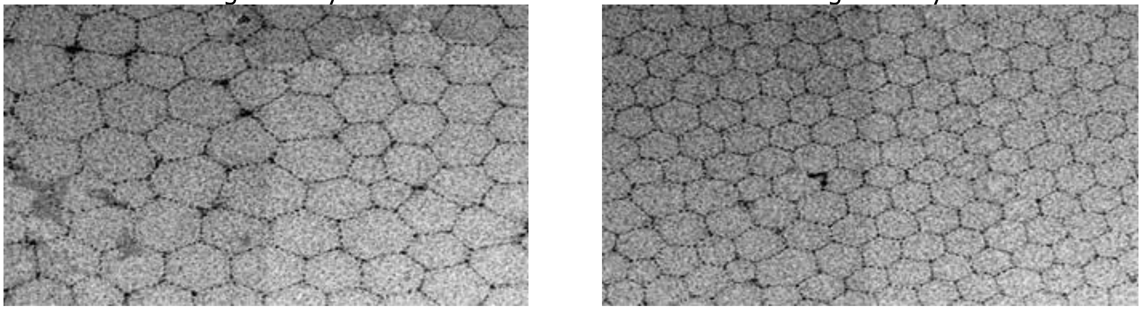


Figure 3 FTIR spectra of pure emulsion and its nano-silica/ methyl methacrylate/butyl acrylate co-polymer emulsion film



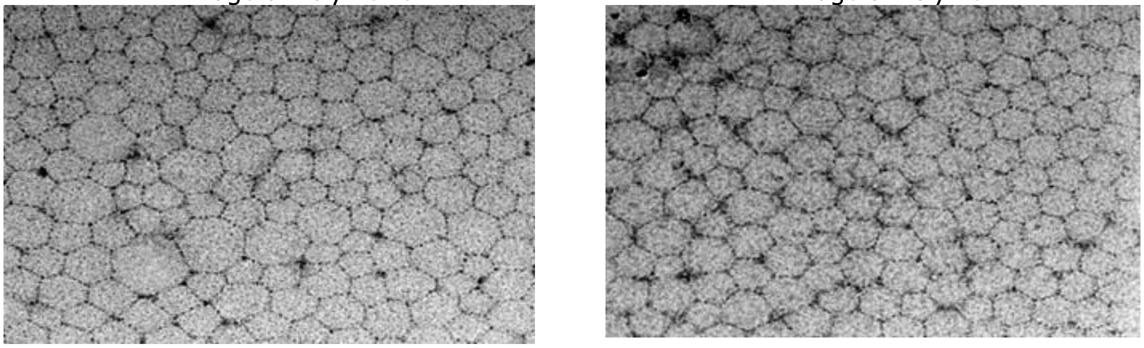
TEM image of Polymer A

TEM image of Polymer B



TEM image of Polymer C

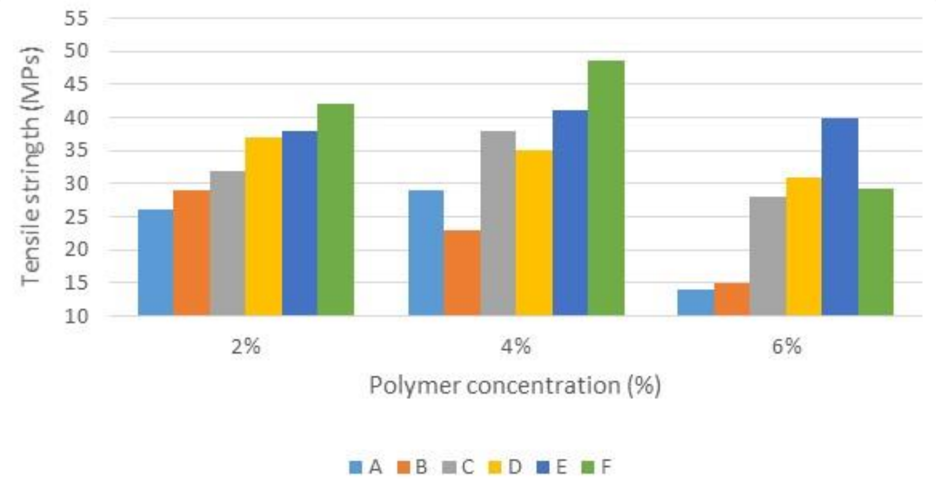
TEM image of Polymer D



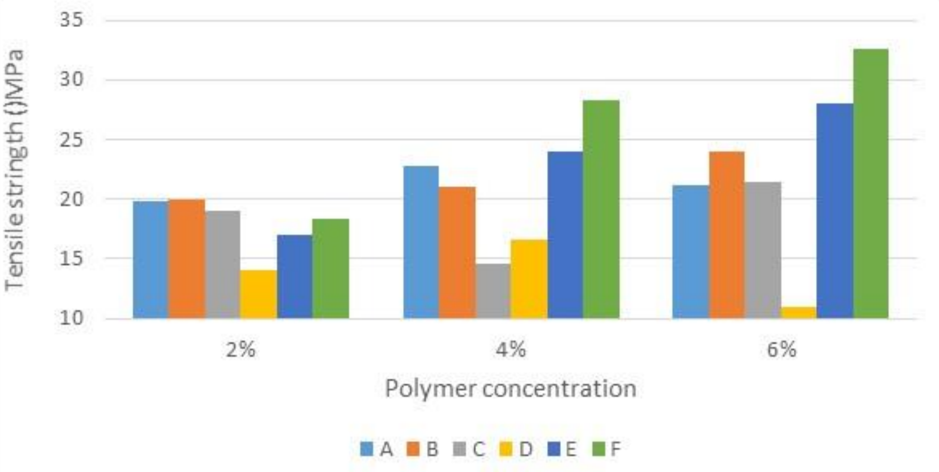
TEM image of Polymer E

TEM image of Polymer F

Figure 4 TEM images of the prepared polymers


55
50
45
40
35
30
25
20
15
10
Tensile stringth (MPs)
2%
4%
6%
Polymer concentration (%)
A B C D E F

(a)


35
30
25
20
15
10
Tensile stringth ()MPa
2%
4%
6%
Polymer concentration
A B C D E F

(b)

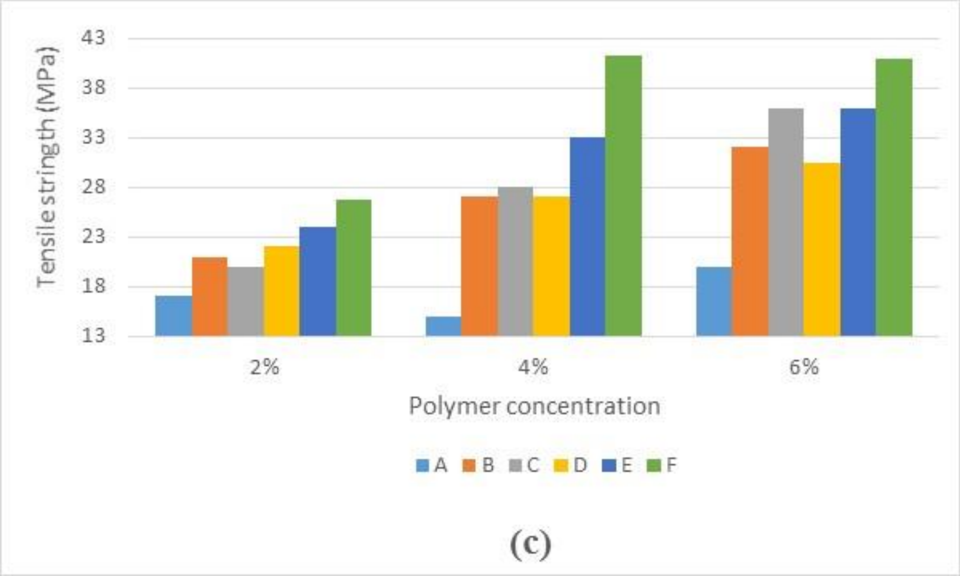
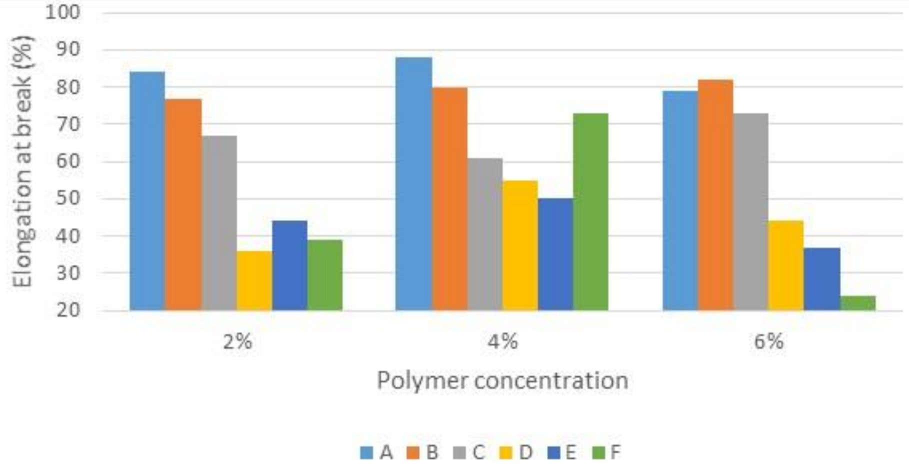
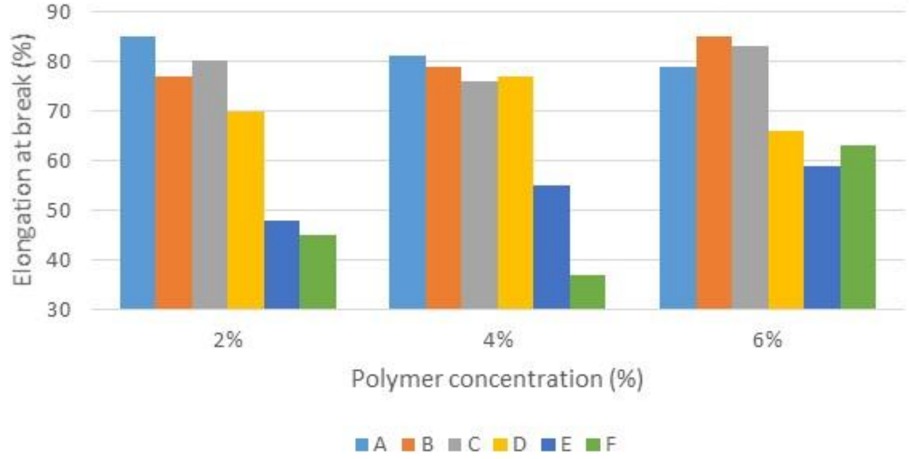


Figure 5 Tensile strength of leather tanned with (a) 1% chrome; (b) 2% chrome; and (c) 3% chrome followed by different types of polymers at different concentrations


100
90
80
70
60
50
40
30
20
Elongation at break (%)
2%
4%
6%
Polymer concentration
A
B
C
D
E
F

(a)


90
80
70
60
50
40
30
Elongation at break (%)
2%
4%
6%
Polymer concentration (%)
A
B
C
D
E
F

(b)

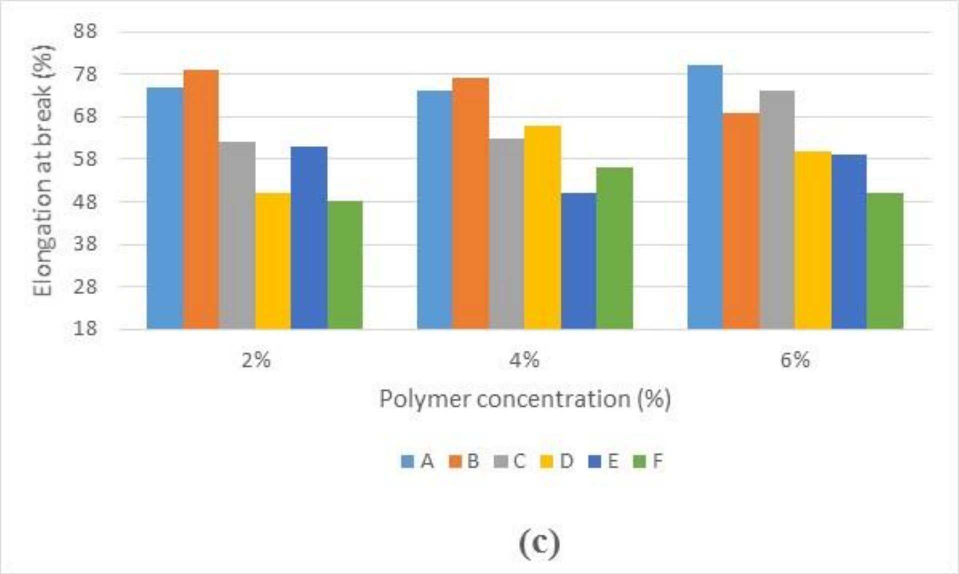
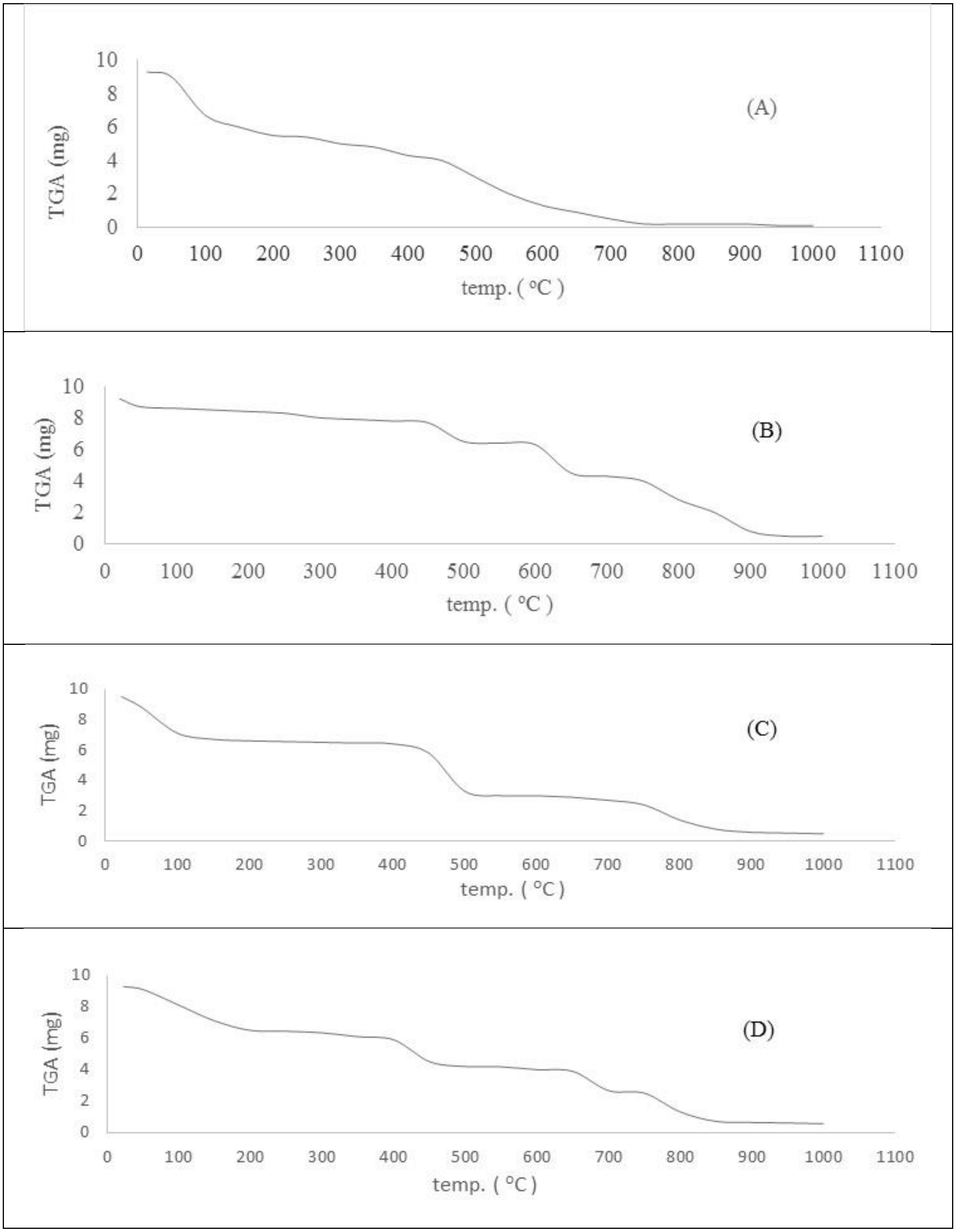


Figure 6 Elongation at break of leather tanned with (a) 1% chrome; (b) 2% chrome; and (c) 3% chrome followed by different types of polymers at different concentrations


(A)
TGA (mg)
0
2
4
6
8
10
0 100 200 300 400 500 600 700 800 900 1000 1100
temp. (°C)
(B)
TGA (mg)
0
2
4
6
8
10
0 100 200 300 400 500 600 700 800 900 1000 1100
temp. (°C)
(C)
TGA (mg)
0
2
4
6
8
10
0 100 200 300 400 500 600 700 800 900 1000 1100
temp. (°C)
(D)
TGA (mg)
0
2
4
6
8
10
0 100 200 300 400 500 600 700 800 900 1000 1100
temp. (°C)

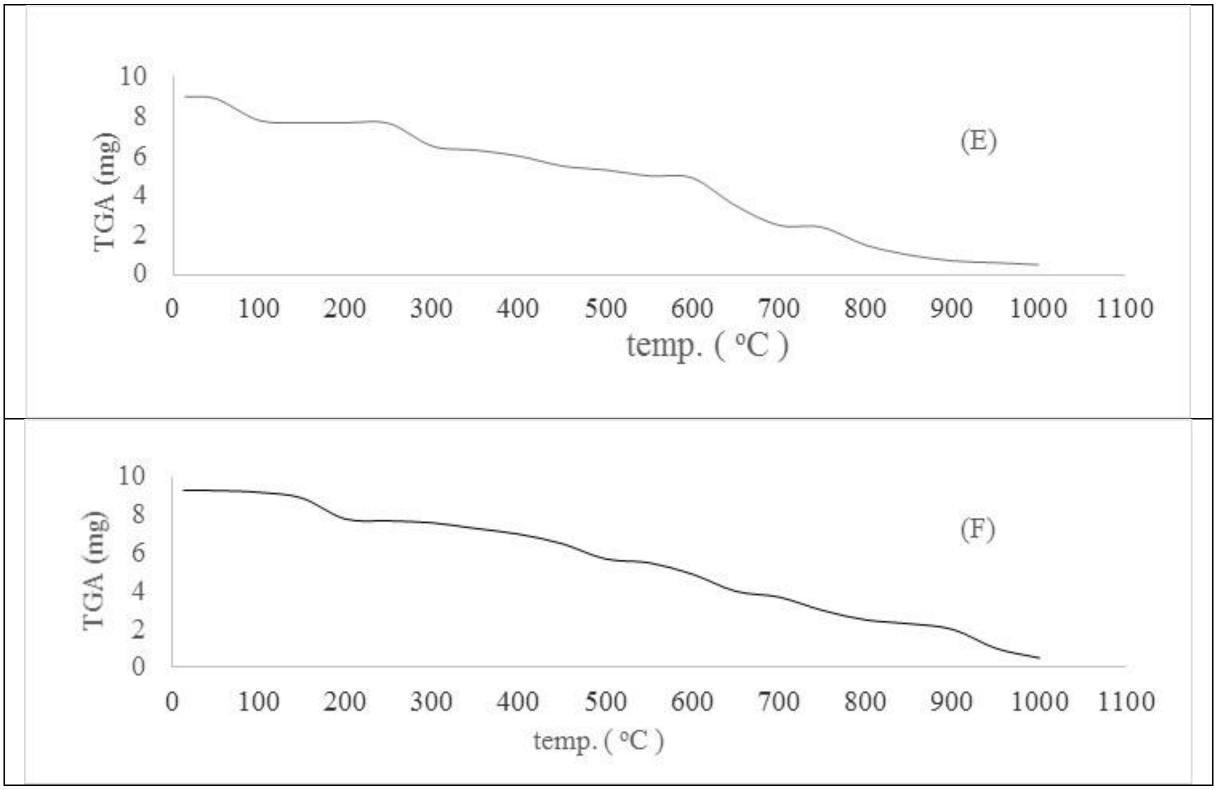
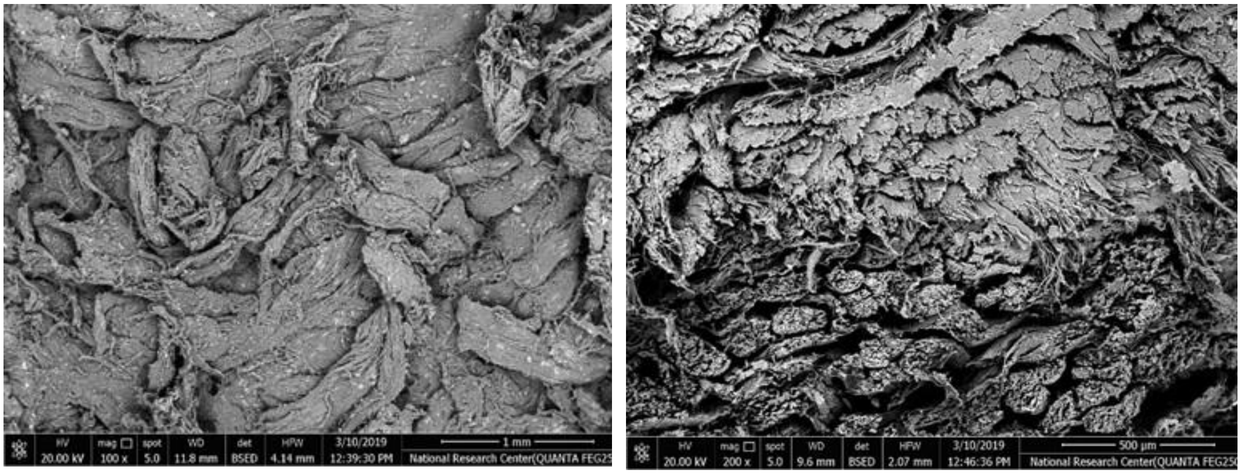
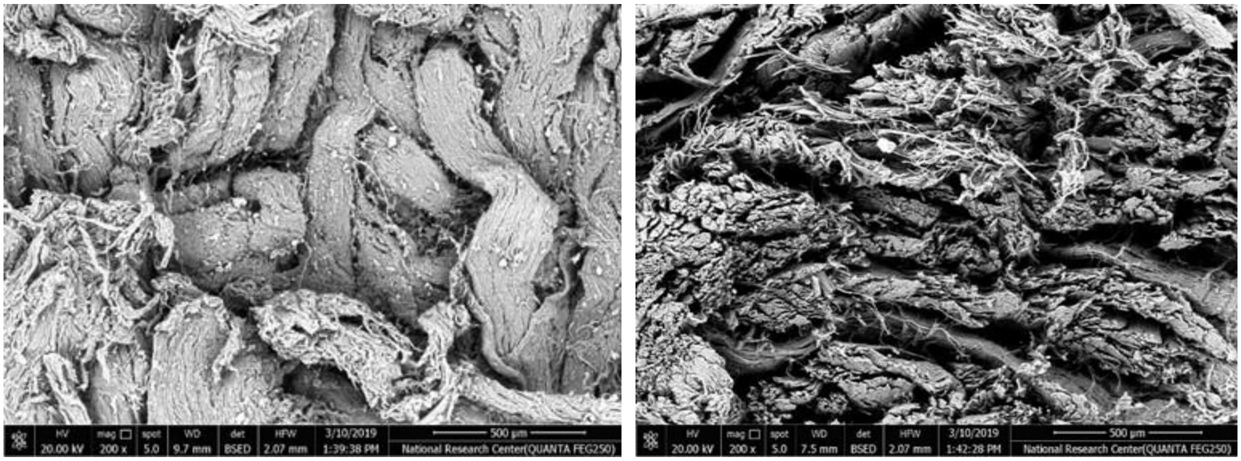


Figure 7 TGA of tanned leather with 3% chrome followed by 4%of different types of Polymers



(a) (b)

Figure 8 SEM of grain surface (a) and cross section (b) of leather tanned with 3% chromium sulphate followed by 4% Polymer B



(a) **(b)**

Figure 9 SEM of grain surface (a) and cross section (b) of leather tanned with 3% chromium sulphate followed by 4% Polymer F

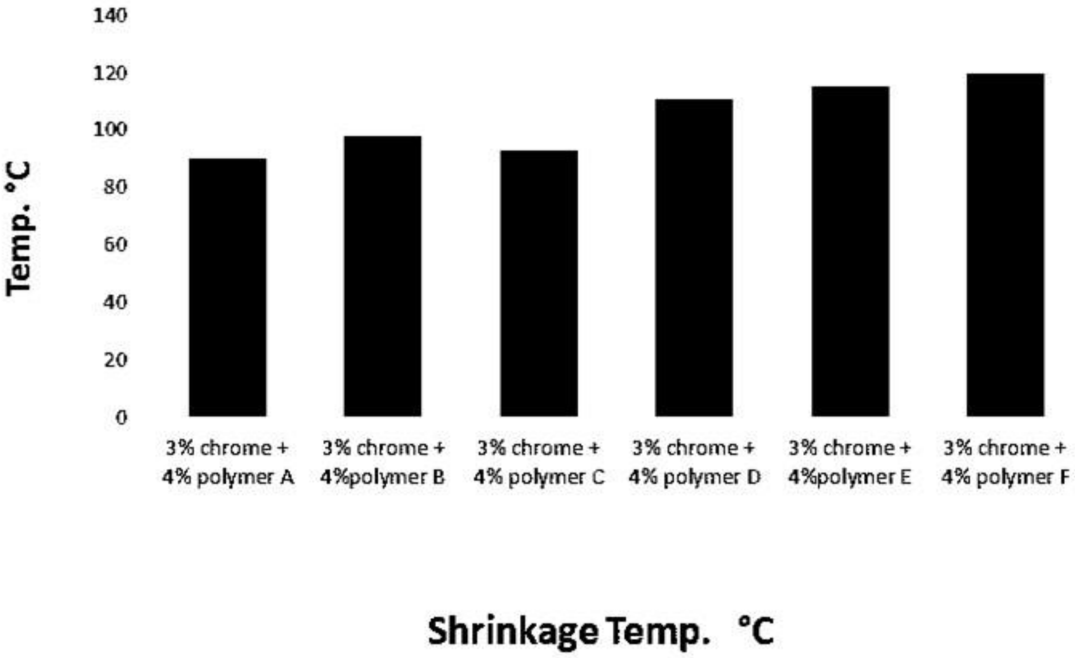


Figure 10 Shrinkage temperatures for the tanned leather