HYDROXYAPATITE NANOPARTICLES AND POLYETHYLENE GLYCOL TREATMENT OF HISTORICAL LEATHER: MECHANICAL PROPERTIES

by

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ABSTRACT

Historical leather objects are at risk of deterioration through mechanical stress such as viscoelastic and plastic deformation as well as natural aging erosion. So, it was expected that appropriate leather treatment should improve their mechanical properties. For this purpose, the mechanical behavior of goat historical leather treated with hydroxyapatite (HA) and polyethylene glycol 400 (PEG400) was studied and compared with the mechanical properties of untreated sample (control). The samples were subjected to a dynamic tensile stress by dynamic mechanical thermal analysis (DMTA) as well as static stress by tensile test. In addition, the treatment effects on the leather mechanical properties were investigated after accelerating aging test. It was shown that treated sample exhibited more softness, better mechanical properties and less structural changes than the untreated sample. The Scanning Electron Microscopy studies show uniform distribution of nanoparticles in the leather matrix as well as the nano hydroxyapatite particles, which are placed between collagen fibers.

INTRODUCTION

Leather products have been used by humans since ancient times and tannery has been taken into consideration as the first industry of mankind civilization.[1] Protecting and preserving many of these old objects is a challenging task for the museums, conservationists and restorers. Historical leather objects are very sensitive because of their fragile structure against the change of environmental conditions such as relative humidity (RH) fluctuation. These objects can face tensile stresses when the relative humidity changes, especially in parts that are under high pressure and tension. This stress can cause breakage of the collagen fibers and crushing of the historical leather structure and wrinkling of the leather ultimately.

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On the other hand, flexibility is a desirable quality of leather objects such as book cover against tension. It is necessary for the leather fibers to have enough flexibility, for slipping over each other which leads to good mechanical properties against tensile tension and long stability of leather objects.[2] Since the 19th century, various lubricants have been used for leather book covers to increase the flexibility, better appearance and conservation of its strength in libraries and archives.[3] During the leather softening process, a lubricant is applied to the surface. This treatment can cause softening of the collagen structural fibers for slipping over each other, and as a result, making the leather more flexible.[2] However, many of these treatments are challenging because lubricant usage for this kind of old objects is difficult to adapt by conservation principal. Furthermore, it has little or no preservative effect and sometimes can cause minor damage on the leather objects. On the other hand, these lubricants are not effective against further chemical deterioration problems, although they can be useful to some extent in case of physical damages. The study of Wallac et al show that chestnut tanned leather treated by Sulphonated cod liver oil wears faster than untreated leather.[4] The British Leather Manufacturers Research Association (BLMRA) has investigated the leather degradation for a long-period of time and their results indicate that using lubricant materials for leather objects cannot protect them from further structural deterioration process.[5] However, more archivists agree that this treatment helps preserve the treated objects from dryness by making them a little softer in the hinges and spine.[3] Although the lubricant's material can induce better softening properties in the treated leather objects, the effect of these materials on mechanical properties with correlation of morphological fibrous structure gains less attention in the literature.[6]

Various industrial lubricants are used in archives and libraries for leather objects without considering their effects on long time protection ability. Many of these industrial lubricants contain unknown ingredients. For this reason they cannot be reliable materials for lubrication of conserved leather objects.

Nowadays, the usage of nanoparticles in restoration science has replaced conventional methods that merely focus on treatment rather than preventive conservation method. At present, the conservation of historical objects is altering with new methods including nanotechnology, synthesis and application of nano particles.[7] The nano particles are effective in the cleaning, deacidification, consolidation and restoration of old objects. The treatment of artworks is discussed in details by Blee and Matisons in their paper entitled: "nano particles and the conservation of cultural heritage".[7] This paper points to the establishing work of Baglioni and Giorgi as the foundation for several innovative methods. In other research Bonini, Baglioni and Giorgi, introduced nonmagnetic sponges that associated with chemical gels for cleaning of art works.[8] The application of calcium and magnesium hydroxide nano particles for the deacidification of paper artifacts is studied by Dehghani and Abed Isfahani.[9]

In this study, hydroxyapatite (HA) and poly ethylene glycol 400 (PEG400) nanocomposite is used for treatment of historical goat leather samples. The PEG400 is usually used in the leather objects for the following reasons: leather moisture conservation and better softening agent when compared with other traditional lubricants. In addition, there is not any report about demolition effects of this material in combination with other traditional lubricants, for example: decomposition and weakness of the collagen fibers.[2] On the other hand, hydroxyapatite (HA) acts as scaffolding in tissue and interacts with collagen filaments. These mineral particles consolidated the bio cells by connecting to the collagen.[10]

The development of specific analytical techniques such as dynamic mechanical thermal analysis (DMTA) is used for distinguishing between historical leather, parchment and a recently manufactured object, evaluation of environmental risks when on display as a result of natural aging, identification and development of suitable preservation treatments.[6] Therefore, DMTA can provide useful information about the changes of the sample structure. But, there are very limited published studies about these techniques in leather investigation.[11] DMTA was also found very useful for studying phase changes and softness of leather structure. This method can be applied to investigate the modulus as well as the transformations occurring in polymeric chain relaxations in the wide range of temperature and frequency.[11] Some researchers studied pure collagen, new and old parchments, and new and old vegetable tanned leathers by dynamic mechanical thermal analysis (DMTA).[12] Their investigations are useful for the distinguishing qualitatively the structural changes and assessing the deterioration.[12]

A quantitative criterion of flexibility or softness can also be measured by the tensile stress. The criterion may be obtained best by measuring the initial slope of the stress-strain curves in the elastic section. Tensile test evaluations included tensile strength, Young›s modulus, elongation at break and fracture strength. The main aim of applying oils in the leather making processes is to serve elasticity for collagen fiber in the leather. Liu et al. in their research found that the tensile strength of leather increases steadily as increasing PEG concentration until reach a plateau around 15% and further increasing PEG shows a decreasing in tensile strength, as the result of lubricating of the leather fibrous structure.[2]

Our research indicated that the nanocomposite of hydroxyapatite (HA) and poly ethylene glycol 400 (PEG400) has the synergic effect for leather conservation when compared with each of them alone.[13] For this reason, the effect of this nanocomposite on the historical leather consolidation in static and dynamic mode in low and high domain of strain is studied by tensile test and DMTA respectively. Then, correlations between tensile test and DMTA results are discussed. In addition, the structural and morphological changes of the treated samples are studied by SEM method. Furthermore, the thermal analysis of the treated leather by this composite will appear in a separate paper.[14]

EXPERIMENTAL

MATERIALS AND METHODS

A type of historical goat leather from the Qajar era (19thcentury) with vegetable characterization tanning and hand colored[1] was used throughout the experiments. Poly ethylene glycol with molecular weight of 400 and nano hydroxyapatite suspension in water were supplied from Merck and Sigma-Aldrich, respectively. Then, a solution of 15 volume percent of PEG in deionized water was firstly prepared and then 0.1 volume percent of HA was added to it. The resultant two-phase solution was vigorously stirred at a rate of 240 rpm for 30 min at ambient temperature by magnetic stirrer. Finally, the solution became semi-transparent and homogenous. For nanocomposite treatment, a rectangular form of historical leather sample is placed in this solution while magnetic stirring for 15 min at room temperature; then removed from the solution and the treated leather surface was softly dried by a soft cloth and stored in the desiccator at room temperature for about one week before mechanical testing. In addition, the samples were conditioned in the test room at 23ºC and 50% relative humidity (RH) for 24h before mechanical property testing. Our experiments were carried out on following samples:

- A piece from a 19th century book cover, coded “control”
- A piece of the control sample that was treated with hydroxyapatite and poly ethylene glycol 400, coded “optimum”
- An artificially aged control sample, coded “AC”
- An artificially aged optimum sample, coded “AS”

Aging Procedure

The samples (control & optimum) were artificially aged in a chamber for 1000 h. The samples were exposed to a cyclic test: at first 16 h at 40°C under 80% relative humidity, following 8h at 15°C under 5% relative humidity and UV radiation with using UVb lamp (model Hitachi, Japan), that had a radiation power of 8W.

CHARACTERIZATION

Tensile Test

The tensile test measurements were recorded using a tensile machine (SANTAM-STM20) at a crosshead speed of 2 mm min^{-1} at room temperature, with load cell 60KN. Tensile samples were prepared as dumbbell-shaped specimens having 35mm x 7 mm x 0.5mm dimensions.

Dynamic Mechanical Thermal Analysis (DMTA)

The DMTA measurements were performed using DMTA equipment (Traition, 85 Tritec 2000 DMA) on the rectangular samples which were (5mm x 5.5mm x 0.5mm) mounted in the tensile mode between 0 to 250°C at $3Kmin^{-1}$ under a controlled strain (0.2%) and 0.3 N static force, at 1 Hz frequency, in static air environment.

Scanning Electron Microscopy (SEM-EDX) Study

The morphology of the grain surface and fracture surface of the control and optimum were observed by scanning electron microscopy (TSCAN-VEGA, Cambridge, Checkoslavaki) at an accelerating voltage of 1500 (KV). The fracture surface was provided by the temperature of liquid Nitrogen and the samples were coated with a thin layer of gold, thickness 15 (nm), density 19.32 (g/cm^3). The distributions of Ca and P atoms as well as the elements EDX spectra on the nanocomposite treated and untreated leather substrates were obtained by SEM EDX mapping (LEO 440).

Transition Electron Microscopy (TEM) Study

The morphology and dimension of the nano particles were observed by Transition electron microscopy (CM120, PHILIPS, Holland).

RESULTS AND DISCUSSION

Tensile Strength Test

Adequate pliability is a very important quality requirement for certain leather products. It provides comfort and a good “handle” for use. The quantitative assessment of pliability, or its reverse term “stiffness”, can be based on measurements of the resistance to a small deformation by tensile stress. The resistance may be quantitatively represented best by the initial slope of the load-displacement curves or the stress-strain curves in the elastic deformation region. The main objective of using lubricants (fat liquors) in the leather making process is to provide flexibility and compliance for collagen fibers in leather.[2]

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[1] This sample kindly provided by the library, museum and documentation center of Islamic consultative assembly (ICAL).

TABLE I
The tensile properties of leather samples.

Young's modulus (N/mm²)	Strain at Break (%)	Ultimate Strength (N/mm²)	Strain at yield point (%)	Yield strength (N/mm²)	Samples
1.88	25	6.08	21	6.43	Control
0.93	39	9.25	35	9.85	Optimum
1.73	21	3.96	19	4.46	AC
1.66	36	5.19	34	5.64	AS

Tensile property measurements including: yield strength, ultimate strength, and Young's modulus, both of the control and treated leather (i.e. optimum) samples, and the tensile results of the same samples after accelerated aging test were obtained from their stress – strain curves and presented in Table 1.

By comparison of control and optimum samples in Table 1, both yield and ultimate strengths as well as the strain at yield and strain at break increased while the Young's modulus decreased in optimum sample. This means that the mechanical properties and the surface area under tensile- elongation curve was improved in the treated sample. On the other hand, the artificial aged optimum samples (i.e. AS) had better tensile properties in comparison with the control aged (i.e. AC) sample. However, a general reduction in the tensile properties is observed after artificial aging process.

The increase of the strain quality in AS in comparison with the control and AC can be attributed to the nanocomposite treatment effect. The nano hydroxyapatite particles can be considered as spherical balls, which are placed between collagen chains and induce easy slipping of them over each other. This treatment promotes the movement of collagen fibers and decreases the frictional resistance of fibers when leather is subjected to a tensile force. The reduction of friction leads to a more uniform stress distribution in stretched leather and consequently leads to an increase in tensile strength.[2]

Dynamic Mechanical Thermal Analysis (DMTA)
Viscoelastic properties of historical leather can be studied by Dynamic Mechanical Thermal Analysis (DMTA) at fixed frequency over a specific temperature range under a sinusoidal mechanical deformations (or forces).[1] The measured DMTA parameters are the storage modulus E´, the loss modulus E˝, and the loss factor Tan δ, which represents the mechanical damping. The changes in displacement under a static load can also be measured by DMTA which is a sensitive technique in detecting thermal transitions corresponding to molecular movements in polymeric chain. In addition, hydrothermal structural stability of leather can be characterized by its shrinkage when it is heated in water. The temperature at which fully hydrated material shrinks under definite conditions is called the shrinkage temperature (Ts).[15] The Ts value depends on the raw material, the methods of tanning, and the deterioration degree which the leather has undergone during its lifetime.[16] Recently, DMTA technique is used for determination of Ts from historic or cultural artifacts.[1] Smaller samples are required for this test in comparison with other analysis methods which is an advantage of this technique. Cohen et al. have studied the shrinkage behavior in tensile mode of leather and parchment by measuring the changes in sample displacement as a function of time and temperature.[17,18] Their results showed the unaged leather sample had a longer shrinkage and drying time than the aged sample and a smaller initial displacement. Figure 1 indicates the values of displacement recorded as a function of temperature for untreated and treated historical goat leathers. It was possible to calculate values for the shrinkage temperature (Ts) as well as the amount of shrinkage from values of displacement versus temperature curves. The untreated sample showed a higher shrinkage temperature (Ts) than the treated sample while the initial displacements are about the same for both of them.

Figures 2 and 3 show the storage modulus (E´) and loss factor (Tan δ) curves of the control and optimum samples as well as their aged samples (i.e. AC and AS) as a function of temperature in 1 Hz.

Jeyapalina et al. have found that the changes in modulus are related to the moisture content of the samples and not to the drying temperature.[19,20] A typical DMTA behavior of a vegetable tanned leather within the temperature range of -100 to 300°C shows three major viscoelastic transitions, whereby the α and β peaks are suggested to be the shrinking-related transition and the glass transition, respectively.[20] The study of Cucos et al. on viscoelastic behavior of new and historical leathers in tensile mode exhibited a major melting process above 200°C.[11,12] By comparison of the storage modulus (E') and loss factor (tan δ) of the leather samples versus temperature at progressive heating, the following information can be obtained: (1) An initial decrease of E' followed by a slight

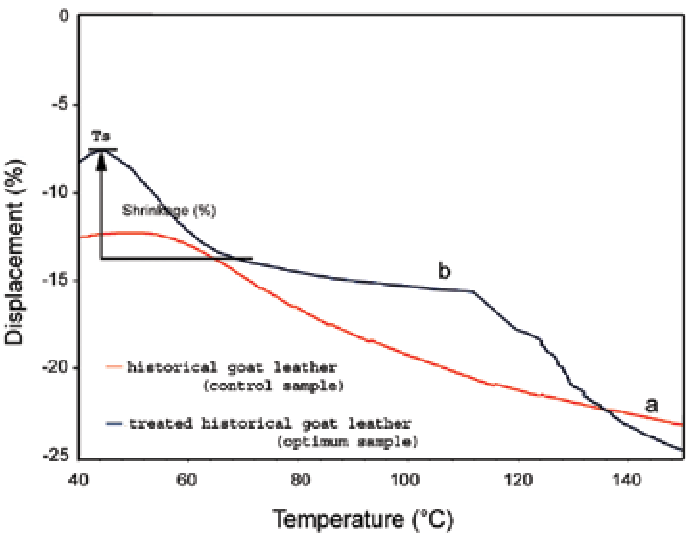

Figure 1. Displacement (%) versus temperature for untreated (a) and treated (b) historical goat leathers.

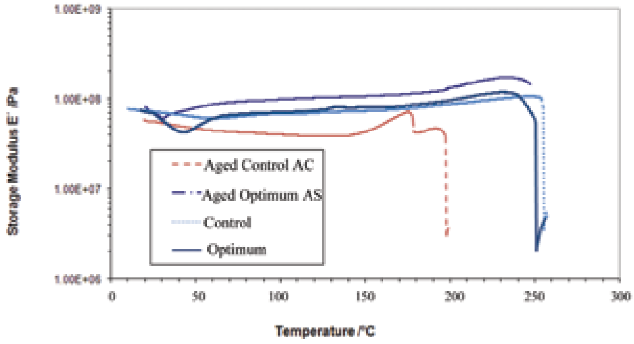

Figure 2. Storage modulus curves of historical goat bookbinding leathers at 1 Hz (a) untreated "control," (b) treated "optimum," (c) untreated after artificial weathering aging "aged control, coded 'AC' " and (d) treated after artificial weathering aging, "aged optimum, coded 'AS.' "

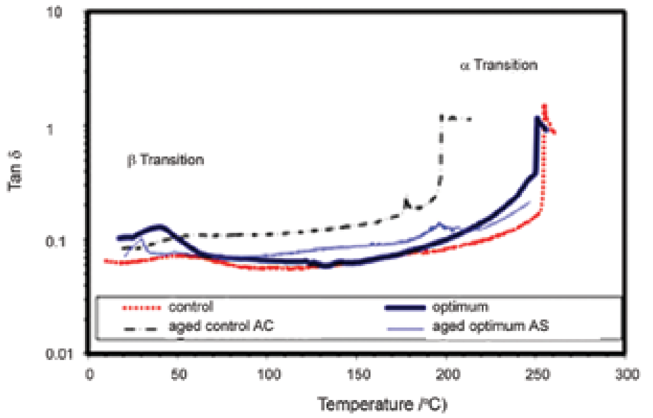

Figure 3. Tanδ curves of historical goat bookbinding leathers at 1 Hz (a) untreated "control," (b) treated "optimum," (c) untreated after artificial weathering aging "aged control, coded 'AC' " and (d) treated after artificial weathering aging, "aged optimum, coded 'AS.' "

increase and a large plateau; (2) a continuous increase of storage modulus at around 230-250°C (except for artificial aged untreated historical leather, i.e. AC which exhibited two shoulder at about 177 and 196°C) and (3) a drop of two decades in the storage modulus E'. The first part of the curves is due to moisture loss. Similar features of E' vs. T curves were previously observed by Nguyen et al. for reconstituted collagen and by Odlyha et al for a new parchment.[21,22] The abrupt decrease of modulus at temperatures above 200°C, also observed by Nguyen et al. and Odlyha et al. is attributed to melting of the crystalline fraction of collagen. The inflexion point of this decrease of storage modulus, (indicated as Ts), was used to estimate the melting temperature of the samples. In this study T Storage was found to be 253°C for historical leather, i.e. control, 241°C for treated leather i.e. optimum, 247°C for artificial aged treated historical leather, i.e. AS and 197°C for artificial aged untreated historical leather, i.e. AC. The tan δ curve dependence on temperature for the leather samples indicated the following trends: a broad and weak peak at about 30–70°C, a continuous increase to about 200°C, and a very sharp peak at about 250°C (except for artificial aged untreated historical leather, i.e. AC which exhibited a sharp maximum peak at about 200°C).

The comparison of the obtained results shows the following: (1) the treated historical leather, i.e. optimum exhibits a viscoelastic behavior similar to historical leather while it has less stiffness and higher viscoelastic behavior from room temperature up to 70°C; (2) However, historical leather, i.e. control, has a higher melting temperature than treated leather, i.e. optimum; this could be due to either cross linking occurring by natural aging. (3) The treated leather after artificial aging process, i.e. AS, shows the same E'-T feature as optimum and control samples with a shift of E' to higher amount and a displacement of β relaxation peak to less temperature and amplitude. In addition, artificial aging increased its melting temperature from 241°C to 247°C (4). The explanation of the viscoelastic behavior of untreated leather after artificial aging process, i.e. AC, is difficult, due to the complexity of the degradation processes, the heterogeneity of the samples and unknown previous preservation treatment. The shapes of E' vs. T curve of AC represent a viscoelastic behavior similar to historical leather while it has a shift of E' to smaller amount and two lower melting temperatures than historical leather, i.e. control. These shifts can be related to various levels of the deterioration, which are related to the artificial aging process or heterogeneity of the samples. Artificial aging of the leathers can affect collagen and the non-collagen components of the leathers (tannins, oils, etc.) due to their oxidative and hydrolytic degradation, as shown, for example, by the decrease of tannin extracts for old leathers in comparison with the new samples.[15] These results are confirmed when fibrils and bundles come closer, resulting in more compact and rigid network.[12]

On the whole, the nanocomposite treatment of the historical leather can induce storage modulus curves of control and optimum to show similar features at higher temperature and less stiffness and viscoelastic behavior up to 70°C, which means the treated leather is softer than control even in progressive increasing temperature. The decrease in the storage modulus of the optimum sample and increase in tan δ amplitude and shifting to less temperature may be attributed to the formation of hydrated collagen fibers and (HA) nano particles which act like spacers between the collagen chains in the leather matrices, which in turn reduces the interchain interactions. It suggests that the lubricating of leather with HA and PEG can improve the mechanical properties; however, other properties of the treated historical leather after this treatment need to be approved. For this reason, the investigations on these materials must be correlated with other criteria, as those mentioned in our future paper.[14]

SEM

SEM technique was employed to observe the fracture surface of the historical leather as well as the nanocomposite treated leather. Figures 4a and 4b present the SEM micrographs of the collagen fibers belonging to the control and optimum samples.

In these figures, the collagen filaments, cell attachment and distribution of the nano hydroxyapatite crystals on collagen fibers are seen. The presence of HA nano particles on the collagen fibers indicates good penetration of these particles into the leather structure. Also, the attachment between the HA particles and the fibers can be due to electrostatic interactions of the mineral phase, Ca^{+2} from hydroxyapatite, on the organic phase (carboxyl groups of collagen at the sample).[23]

By comparison of SEM images of the treated collagen filaments of the optimum sample and of the collagen fibers of control sample in same magnification, an increase in fiber thickness is observed for the treated sample. This can be attributed to absorption of humidity that accompanied by the penetration of the PEG. Also PEG in the leather can act as plasticizer and lubricating agent. On the other hand, the hydroxyapatite nanoparticles rest between collagen filaments as globules and decrease the interaction of them in slip and tensile state.

EDX

The elemental spectra and distribution of Ca and P atoms at fracture surface of the nanocomposite leather sample (i.e. optimum) and untreated leather (i.e. control) was characterized by SEM EDX mapping. Figures 5 and 6 present the calcium and phosphorous maps in which Ca and P atoms are denoted by white points in control and optimum leather samples. As seen from these images, these calcium particles (white pointes) have uniform distribution and they are more condensed in the treated nanocomposite leather (i.e. optimum) than the historical untreated leather (i.e. control). Untreated sample (control) does not indicate any existence of phosphorous atoms in the fracture surface while it was uniformly distributed in the treated sample (optimum). Therefore, it can be concluded the HA nano particles is uniformly distributed in the optimum sample.

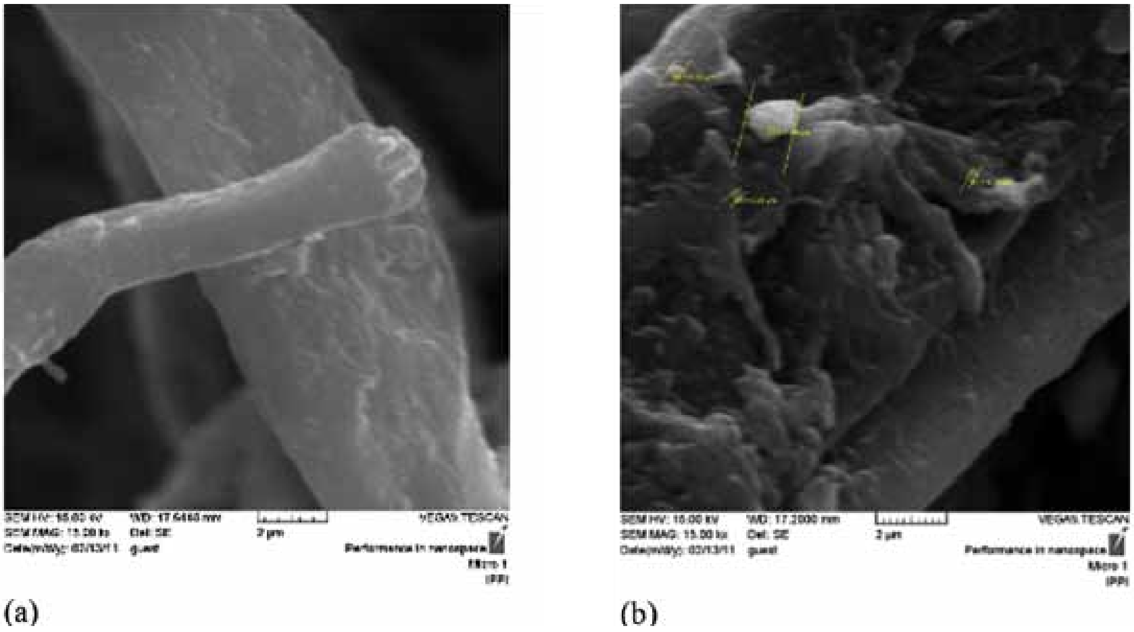

Figure 4. Collagen fiber of the control sample (a) and the optimum sample (b) at 15.00kx magnification.

TEM

To acquire more information on Hydroxyapatite particle's size, a sample was prepared for TEM analysis. Figure 7 shows the TEM image of Hydroxyapatite particles. It is observed that hydroxyapatite particles dimension remains at nano-scale (50-120 nm) after curing.

The TEM results show that the size of majority of the particles is about 50 nm. Therefore, it can be concluded that no agglomeration of particles has occurred in the solution before the coating. Other samples have similar distributions.

CONCLUSION

The results obtained by these tensile tests have confirmed that the treatment with the PEG and HA nanoparticles promoted the movement of collagen fibers and decreased the frictional resistance of the fibers. This reduction in friction led to more softness and an increase in tensile strength. The results obtained by DMTA analyses show the treated samples were softer than untreated sample even in increasing temperature. The SEM-EDX of the samples showed the penetration of nano particles in the leather substrate and their attachment on the collagen fibers. Moreover the collagen filaments of the treated sample were thicker than those belonging to untreated samples. This means that the nanocomposite induced plasticizer quality and decreased the interaction of the filaments in slip and tensile state. Also the calcium and phosphorus mappings in treated sample show the uniform distribution of these elements in the leather substrate.

Our results indicate that the DMTA technique was shown to be a very useful method for determination of suitable lubricating treatment as well as characterizing treated leathers after artificial aging. These data could be correlated with

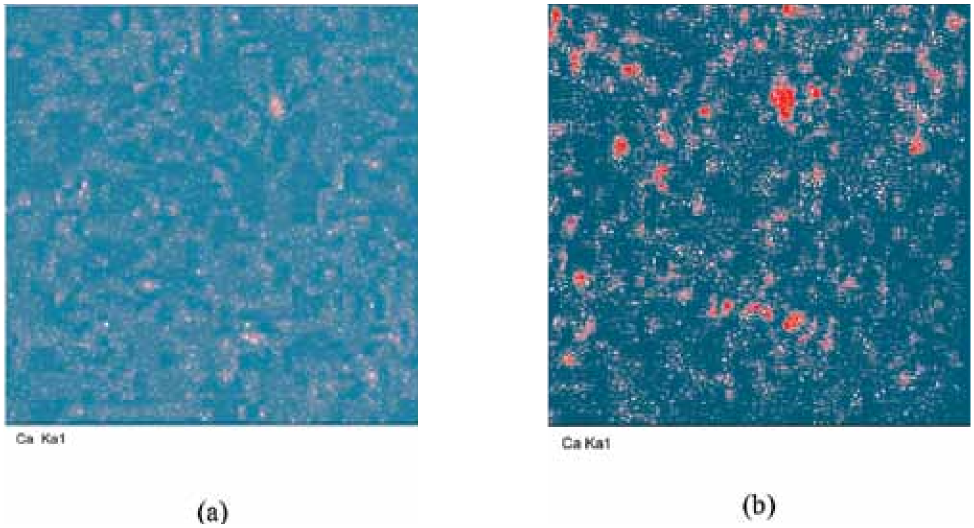

Figure 5. The distribution of Ca in the control (a) and optimum (b) samples.

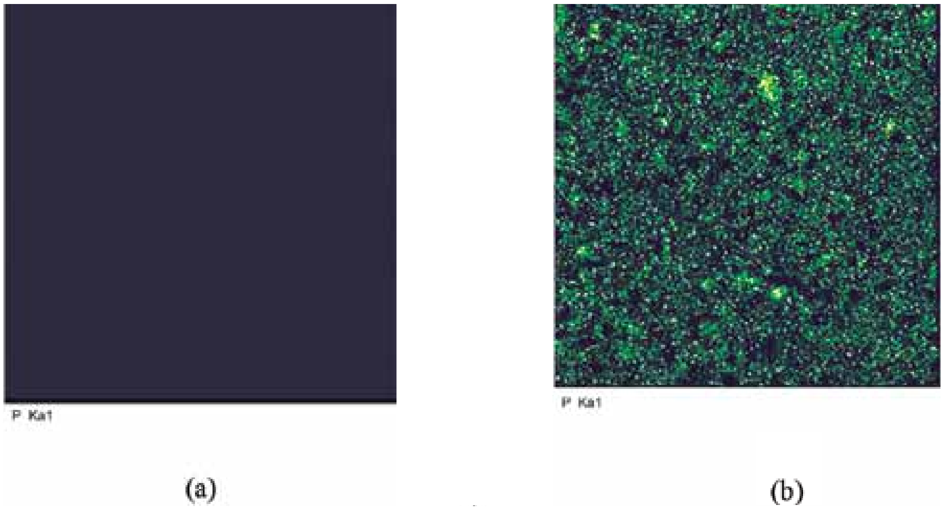

Figure 6. The distribution of P in the control (a) and optimum (b) samples.

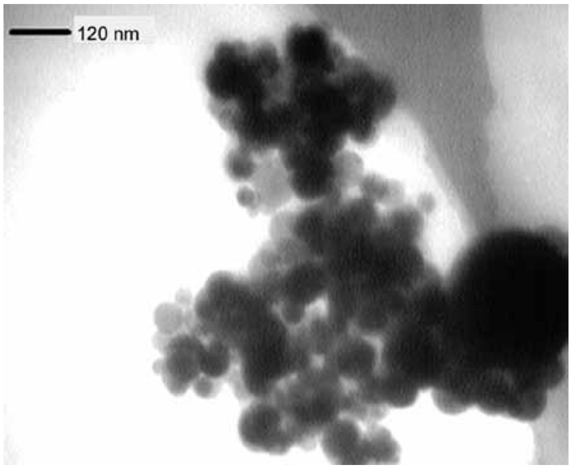

Figure 7. The nano HA particles.

other criteria, as well as tensile test, morphological and thermal analysis results which will be reported in future publications to improve the understanding of degradation processes of leathers and their procedures of conservation and restoration.

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