The Effect of Nano Polysiloxanes on the Permanence of Feel Touch of Finished Leathers

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Abstract

Nano sized aminofunctional and micron sized dimethyl polysiloxane emulsions were applied to garment leathers as topcoats, to investigate the improvement on feel touch permanency of finished leathers. Fourier Transform Infrared Spectroscopy (FTIR) and particle size analysis of these two polysiloxane emulsions were carried out. The optimum application amount of emulsions was determined to be 15% based on the results of organoleptic evaluation and dynamic friction coefficients. After the application of nano and micron sized polysiloxane, three different accelerated ageing processes were applied to leathers under controlled temperature, humidity and UV light conditions. For determining the effect of the ageing processes on these polysiloxanes, dynamic friction coefficient measurements, ICP-OES and SEM analysis were carried out. The results revealed that nano sized polysiloxanes clearly improved the feel touch permanency of finished leathers in comparison to the leathers coated with micron sized polysiloxanes. Thereby, it was demonstrated that nano polysiloxanes can maintain the appearance and feel touch of leather product for a longer periods of time.

Resumen

Nano y microemulsiones aminofuncionales de dimetilpolisiloxano se aplicaron a los cueros de vestimenta como acabado final, para investigar la mejora en la permanencia del toque en el cuero terminado. Espectroscopía Infrarroja por Transformada de Fourier (FTIR) y análisis de tamaño de partícula de estas dos emulsiones de polisiloxano se llevaron a cabo. La cantidad óptima de aplicación de las emulsiones se determinó en 15% sobre la base de resultados de la evaluación organoléptica y los coeficientes de fricción dinámica. Después de la aplicación de polisiloxano de tamaño nano y micro, tres diferentes procesos de envejecimiento acelerado fueron aplicados a los cueros bajo condiciones controladas de temperatura, humedad y luz ultravioleta. Para determinar el efecto de los procesos de envejecimiento en estos polisiloxanos, mediciones del coeficiente de fricción dinámica, ICP-OES y análisis SEM fueron llevados a cabo. Los resultados revelaron que los polisiloxanos de tamaño nanométrico claramente mejoran la permanencia de la sensación de toque en los cueros terminados, en comparación con los cueros acabados con polisiloxanos de tamaño micrométrico. De esta manera, se demostró que los nano polisiloxanos puedne mantener la apariencia y la sensación del toque de productos de cuero por un período de tiempo más largo.

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INTRODUCTION

In recent years, specific products that provide better chemical bonding and improved physical properties have come into use in different industry fields, in order to increase the productivity of the materials used in processes. Within this scope, polymeric materials are playing an important role, since these materials allow the modification and improvement of material properties and reduction in feed stock costs.[1]

Polysiloxane is a polymer composed of macromolecules containing alternating oxygen and silicon atoms in the backbone. Polysiloxanes are often referred to as silicones and the most widely used basic, important silicone polymer is the linear polydimethylsiloxane (PDMS) that is composed of an inorganic siloxane backbone in which every silicon atom is bonded to two oxygen atoms and two organic methyl groups. The silicon at the end of the polymer chain is end-capped with three methyl groups.[2-4] Siloxane based polymers can be considered as hybrid materials that combine the properties of both organic and inorganic components such as good thermal stability, resistance to ozone and weather conditions, film-forming ability, low surface energy, high permeability to gases, good dielectric and hydrophobic behavior.[1,5-9] In addition, polysiloxanes are highly stable materials with good resistance to oxidative and thermal ageing and in particular, they retain their elasticity and mechanical properties over wide temperature ranges from -50°C to +75°C.[10] Therefore, these products are regarded as a valuable commercial polymer group. However, the main disadvantage of polysiloxanes is their poor mechanical properties due to their high elasticity.[1,11] But, the polysiloxane properties can be modified by introducing the organic functional groups onto the PDMS backbone instead of having methyl side groups.[2,3] Organofunctional PDMS polymers have the same Si-O-Si backbone as PDMS does, but some of the silicon atoms are substituted with functional organic groups, such as amino, carboxyl, epoxy and amide.[2] Aminofunctional polysiloxane is one of the most common organofunctional PDMS polymers and it provides a better binding advantage of the silicone on a substrate and thus enhanced durability and protection of the leather. In addition, aminofunctional silicones will also provide hydrophobicity effect due to the orientation of amino group itself to the leather surface, thus exposing the hydrophobic methyl groups.[2,3]

Polysiloxane based polymers are used in different industries such as textile, leather, cosmetics, drug delivery, fabric care, coating, paints and inks, rubbers, sealants, pressure sensitive adhesives, construction industry, structural glazing, airbags, electronics and so on for different purposes.[3,9] In leather industry, polysiloxane emulsions, mostly traditional PDMS and aminofunctional polysiloxanes, are widely used in topcoat finishes of footwear, upholstery, garment and other leather goods applications as a surface modifier for improving the feel touch, handle, appearance and protection properties like rubbing fastness of finished leathers. The studies on silicone containing polymers are still being carried out for product development and quality improvement of finished products. Yiding et al. 2007 reported that cationic organosilicone/polyurethane micro-emulsion was successfully applied to leather finishing and found to be a good finishing agent with improved mechanical properties and the leather finished with this emulsion was bright, soft, full, and had a smooth surface which improved the quality of leather.[11] Ollé et al. 2010, used polysilane as a cross-linking agent in leather finishing and the results showed that polysilane had a better cross-linking reaction than polyaziridine, polyisocyanate, epoxy resin and polycarbodiimide, leading to improved mechanical properties.[12] Beside their usage in leather finishing, different kind of silicone containing polymers can also be used in fatliquoring and dyeing processes for enhancing the mechanical and physical properties of leathers.[5,13] Amino siloxane modified by acetic anhydride was used as fatliquoring agent and improved results of tensile strength and tearing strength were obtained.[13] The amino-functionalized siloxanes were used to increase the dye fastness of leather by increasing the number of active sites in leather, especially for suede leathers by improving dye fixation and best results were obtained by the use of reactive dyes on siloxane pre-treated leathers.[5]

Recently, organic/inorganic nanocomposites and hybrids have become one of the popular nano research fields and consequently, similar nanotechnological researches have gained an interest for the researchers in leather industry.[14] The studies including the usage of nanomaterials in leather production have been mostly focused on tanning/retanning processes for achieving better qualified leathers.[15-25] There are also a limited number of studies related to usage of nanocomposites in leather finishing, where mostly nanolayered silicates and nano SiO_2 were used as inorganic fillers for binders which resulted in improved physical, mechanical and rheological properties of the materials and/or finished leathers.[14,26,27,28] However there is no information about nano polysiloxane applications used as a feel modifier in leather finishing.

This paper reports the application of nano aminofunctional polysiloxane as a feel modifier in leather finishing, which is a well-known silane compound and commonly used in sectors other than the leather industry. A comparative analysis on the feel touch permanency of leathers coated with nano and micron sized polysiloxane feel modifiers was also performed and the results were discussed.

EXPERIMENTAL

Materials

In the study, twenty-four untopcoated full grain garment leathers, coated with conventional cationic-anionic finishing formulation, were used. All leathers had the same origin and were randomly collected from the same batch.

Siligen SIS nano, which has a solid matter of 35% (BASF Group, Germany) for textile finishing, was used in finishing process of garment leathers as nano sized aminofunctional polysiloxane feel modifier. It offers soft and smooth handle, good washing fastness, shear stability; and it improves sewability, abrasion resistance and resilience. YM-7600 (Verbo Companies Group, Turkey) was used as micron sized feel modifier agent to improve the wet and dry rubbing fastness of leathers as an aqueous silicon dispersion of polydimethylsiloxane with a solid content of 27.5%.

For topcoating of leathers, EL–8181 (Verbo Companies Group, Turkey) water based, clear, glossy emulsion lacquer with a solid content of ~12% was used. Tetramethylamonium hydroxide-TMAH (25%, Merck Chemicals, Germany) was used for the sample preparation of Inductively Coupled Plasma-Optical Emission Spectrometer (ICP- OES).

Methods

Finishing Application

Twenty-four pieces of garment leather were randomly divided into 2 groups. Micron sized feel modifier was applied to the first half of leathers and the other half was coated with nano feel modifier. The topcoat application of leathers was carried out with hand spray gun according to the formulation given in Table I. The amount of the nano and micron sized polysiloxane feel modifiers were chosen as 15, 20, 25% and 5, 10, 15% respectively, based on the hydrolacquer weight used for topcoating. Subsequent to the application, the leathers were dried through a drying cabinet at 80°C for 3 minutes and hot plated at 100°C and 100bar.

Particle Size Analysis

The average particle sizes of micron and nano polysiloxanes were determined by Malvern Mastersizer 2000 particle size analyzer to verify the average particle diameter of the samples before the application of polysiloxanes to garment leathers.

Fourier Transform Infrared Spectroscopy (FTIR) Analysis

Perkin Elmer Spectrum-100 FTIR-ATR device was used to investigate the chemical structures of the feel modifiers. The spectra of the samples were recorded by co-adding 4 scans at a resolution of 4 cm^{-1} over the region 4000–650 cm^{-1}. The structural differences of the nano and micron sized polysiloxanes were evaluated according to the IR spectrum library.

Organoleptic Evaluations and Dynamic Friction Coefficient Measurements of Feel Touch of Finished Leathers

The evaluation of feel touch and handle of leathers coated with two kinds of feel modifier was performed by organoleptically and by measuring the dynamic friction coefficient of leather surfaces. For organoleptic evaluation, leathers were examined by five different leather specialists. They evaluated each leather sample by scoring 1 to 5 point which 5 represents the best score depending on the slippery feel of samples. The points were summed up for the final evaluation. Dynamic friction coefficient measurements were performed using Testometric Universal Strength Tester. A 0.02 gram weighing plate (63.43mm x 62.68mm x 6.27mm), which was covered with a white cotton cloth in accordance with ISO 105-F09 standard[29], and leather samples that were cut into 16x24cm specimens were used for this measurement. Leather specimens were fixed to the tester platform, and then the plate was slided with a speed of 850 mm/min over the leather samples. Leather surface shows resistance towards the plate and the dynamic friction coefficient was calculated by dividing the resistance value to plate weight.[30]

Accelerated Ageing Process

Leather samples coated with micron and nano polysiloxanes were conditioned and prepared in accordance with the official standards of TS EN ISO 2419 and TS EN ISO 2418

TABLE I
Formulation used for topcoat application

Water	100
Hydro lacquer	100
Feel Modifier	M*/N**
Spray X2 Plate 100°C/100 Bar	

M*: 5-10-15% micron sized feel modifier consist of 1.38, 2.75 and 4.13g solid matter respectively
N**: 15-20-25% nano sized feel modifier consist of 5.25, 7 and 8.75g solid matter respectively

TABLE II
Accelerated ageing process conditions

Ageing Process in accordance with TS EN ISO 17228[39]	24h at 55ºC and 90% humidity
	48h at 55ºC and 90% humidity
Ageing Process with UV light in accordance with IS 6191 (LF:4)[40]	20h at 63.5ºC and 30% humidity

TABLE III
Particle size analysis results of micron and nano sized feel modifier

Parameters	Micron sized feel modifier	Nano sized feel modifier
D[3,2]:Average of surface weight *(μm)*	4.155	0.177
D[4,3]: Average of volumetric weight *(μm)*	22.250	0.187
D(90) *(μm)*	64.455	0.254
D(50) *(μm)*	4.065	0.180
D(10) *(μm)*	2.475	0.133
Specific surface area *(m²/g)*	1.45	34.0

respectively, prior to accelerated ageing process.[31,32] Subsequently, three different accelerated ageing processes, which were given in Table II, were performed. For ageing the leathers Challenge 340 climate and Atlas Suntest XLS+ UV light chambers were used.[33,34]

Rub Fastness of Aged Leathers

The artificial corrosion of finishing films was performed with Bally Finish Tester 9029 to determine the loss of Si content of the feel modifiers after the ageing process. For this analysis, dry felt pad was rubbed back and forth for 50 times on the leather samples that have been stretched at the rate of 10%. Thus, partially removal of the silicone that is used as a modifier in topcoat was performed artificially.

Determination of Silicone Content of Leather Samples by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES)

Silicone content of leather samples were measured by Perkin Elmer Optima 2100DV ICP-OES device using the standard of TS EN ISO 11885.[35] Tetra methyl ammonium hydroxide (TMAH) was used for the dissolution of leather samples in order to take advantage of nonuse of any masking agent, prevention of SiF_4 loss and requirement of much less chemicals.[36,37] Also for improving the effectiveness of the dissolution and reducing the process time, leather samples were prepared with a microwave assisted high-pressure autoclave.[38]

Scanning Electron Microscopy (SEM) Micrographs of Leather Samples

The surfaces of the leather samples before and after the ageing processes were investigated with JEOL Scanning electron microscopy device[39,40] in order to observe and compare the leather surface properties.

Statistical Analysis

The data were analysed by using SPSS 15.0 statistical package for Windows. The GLM method was used to compare mean values among the applications. Descriptive statistical test and analysis of variance were performed on each attribute.

RESULTS AND DISCUSSION

Particle Size Analysis

The average particle size diameters of micron and nano polysiloxanes were found to be 4.145μm and 177nm, respectively. According to these results, the particle sizes were found acceptable for the purpose of the study (Table III).

Fourier Transform Infrared Spectrophotometer (FTIR) Analysis

The FTIR spectra of micron and nano sized polysiloxanes, in the region of 4000-650cm^{-1} are shown in Figure 1. The IR bands related to silicon atoms are usually found within the range of 1300-600cm^{-1}. These are characteristic bands of organosilicone polymers and related materials. Similarly, the characteristic bands of modifiers were observed at around 1089, 1257-1008 and 773-796 cm^{-1}, which can be attributed to the stretching vibrations of cyclic tetramer Si-O-Si band, symmetric deformation vibrations and rocking vibration of the band belonging to Si-N bonds, respectively. These findings are similar to IR spectra obtained from the other studies.[41,42,43,44] The bands around 2950 and 2900 cm^{-1} are characteristics of alkyl chains (2957.40,2872.49 and 2963.14, 2908 cm^{-1}) and within the band 1455 and 1450 cm^{-1}, amino groups can be easily seen. The findings are supported by a study that demonstrated the aminofunctional groups in aminopolysiloxanes.[45]

Organoleptic Evaluations and Dynamic Friction Coefficient Measurements

The results of organoleptic evaluations and dynamic friction coefficients were shown in Figure 3, which was performed for the determination of the optimum quantity of micron and nano

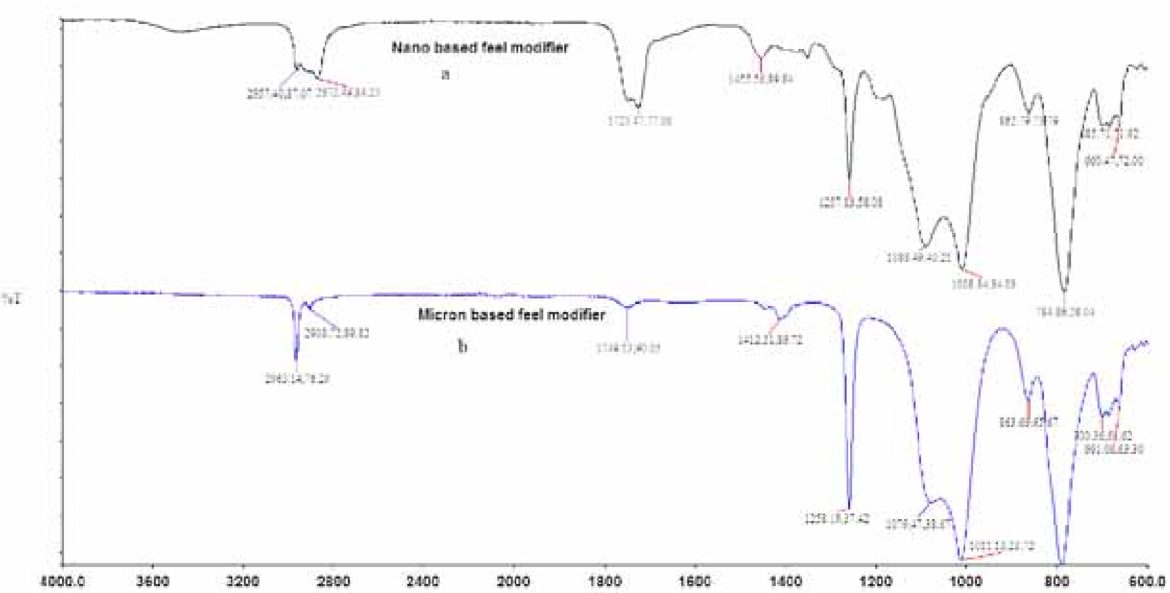

Figure 1. Overlapped FTIR spectra of nano (a) and micron (b) sized polysiloxane

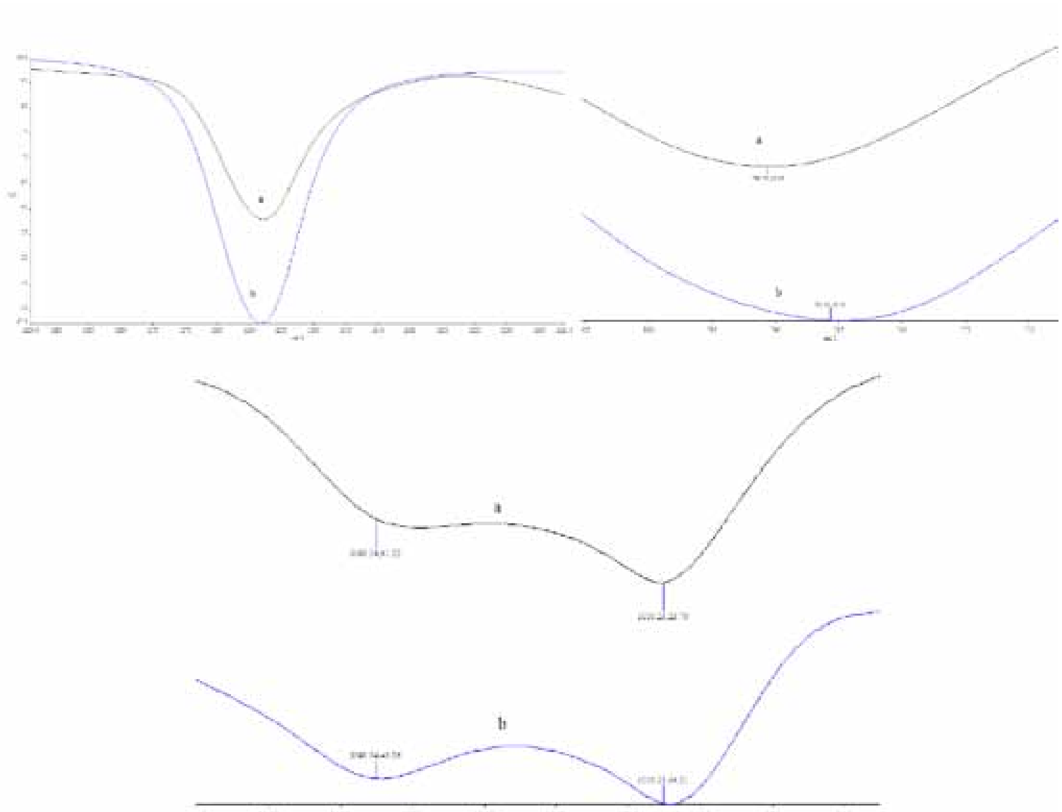

Figure 2. Overlapped FTIR spectra of fingerprint region of Si bonds (785-790nm, 1257-1258nm and 1090nm and 1100 nm) bands belonging to nano (a) and micron (b) sized polysiloxane

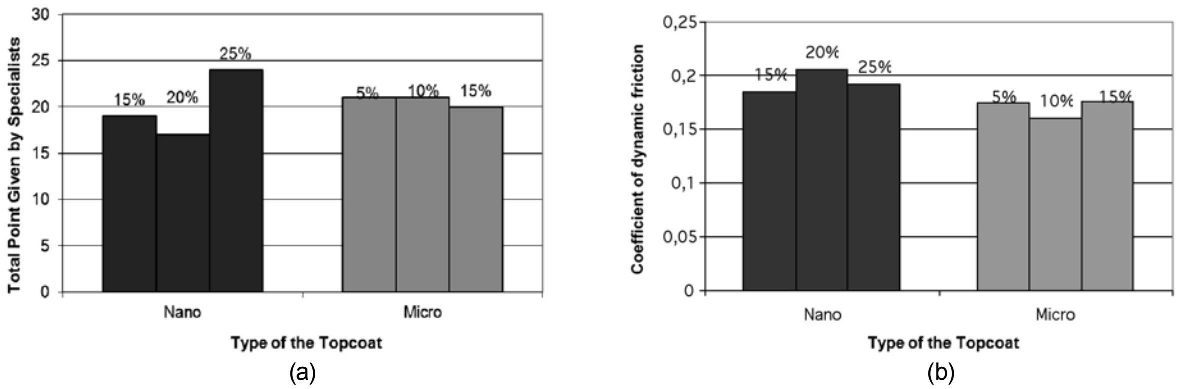

Figure 3. Results of Organoleptic Evaluations (a) and Dynamic Friction Coefficients (b)

polysiloxanes applied as topcoat. According to the organoleptic results, the closest points 19 and 20 were obtained for the 15% application quantity from micron and nano feel modifiers respectively. The dynamic friction coefficient results were obtained as 0.176 and 0.185 values for micron and nano feel modifiers respectively. Consequently, 15% was found reasonable for the optimum application quantity of polysiloxanes depending on the organoleptic evaluation and dynamic friction coefficient results.

Blau 2001 described that friction during smooth sliding tends like feel modifiers to be lower unless there is a significant amount of adhesion.[46] The increase in dynamic friction coefficient values of samples treated with micron sized feel modifiers, were found higher than the nano sized feel modifiers (Table IV and V) and the difference between the dynamic friction coefficient results of the samples are found statistically significant ($p<0.05$). Additionally, it was found that the leathers, which have nano sized topcoats, maintained their characteristics better than the micron sized topcoats.

The maximum increase in dynamic friction coefficient values were determined with the effect of UV light ageing for each type of feel modifier and it was followed by the results of 48h and 24h ageing processes under the conditions of temperature and humidity (Table IV and V). However, although increased dynamic friction coefficient values were determined in direct proportion to the ageing process intensity, there are no statistical differences between the ageing processes of 24h, 48h and UV-light condition depending on the feel modifier structure.

Determination of Silicone Contents of Leathers by ICP OES

ICP OES results revealed that the silicone content of the leathers treated with nano modifier were apparently higher than the leathers treated with micron sized modifier after

TABLE IV

Dynamic friction coefficient results of the leathers treated with micron sized feel modifiers

Ageing Process	n	Before Mean±S.D	After Mean±S.D	Increment (%)
24h	3	0.176±0.002	0.200±0.014	13.64
48h	3	0.171±0.007	0.198±0.018	15.79
UV	3	0.175±0.003	0.204±0.022	16.57

TABLE V

Dynamic friction coefficient results of the leathers treated with nano sized feel modifiers

Ageing Process	n	Before Mean±S.D	After Mean±S.D	Increment (%)
24h	3	0.195±0.010	0.208±0.016	6.67
48h	3	0.193±0.016	0.205±0.016	6.22
UV	3	0.193±0.011	0.212±0.016	9.85

TABLE VI
Silicone contents of leathers treated with micron sized modifiers before and after ageing and rubbing treatment

Ageing Process	n	Before Mean±S.D	After Mean±S.D	Loss of Silicone (%)
24h	3	4.137±1.157	0.530±0.484	87.19
48h	3	4.144±1.130	0.541±0.482	86.95
UV	3	4.158±1.146	0.537±0.486	86.85

TABLE VII
Silicone contents of leathers treated with nano sized modifiers before and after ageing and rubbing treatment

Ageing Process	n	Before Mean±S.D	After Mean±S.D	Loss of Silicone (%)
24h	3	1.101±0.577	0.441±0.206	59.95
48h	3	1.173±0.634	0.460±0.212	60.78
UV	3	1.161±0.601	0.456±0.224	60.72

ageing and corrosion of finishing films (Table VI and VII) and this difference was found statistically significant ($p<0.05$). It's obvious that the nano sized modifier retains on the leather surface 2 times higher than micron modifier from the results given in Table VI and VII. For instance after UV-ageing process, it was observed that almost all micron-modifier was removed from the leather surface whereas, more than one quarter of nano-modifier still remained on the surface. But, there is no statistically significant difference between ageing processes for silicone loss of nano and micron sized feel modifiers treated leathers.

Scanning Electron Microscopy Micrographs of Leather Samples

The Scanning Electron Microscope images of each leather sample taken before the ageing process showed that the pores of nano film were smaller than the pores of micron feel modifier film. Therefore, the surface of nano modifier applied leathers was more homogeneous and smooth compared to the surface of micron modifier applied leathers (Figure 4).

After ageing process carried out at 55±2°C temperature and 90±5% humidity for 24h, fractures and cracks were observed in patches, on both micron and nano feel modifier coated finishing films (Figure 5). However, the deformation of finishing films of the leathers coated with micron feel modifiers was clearly observed in comparison with the leathers coated with nano feel modifier.

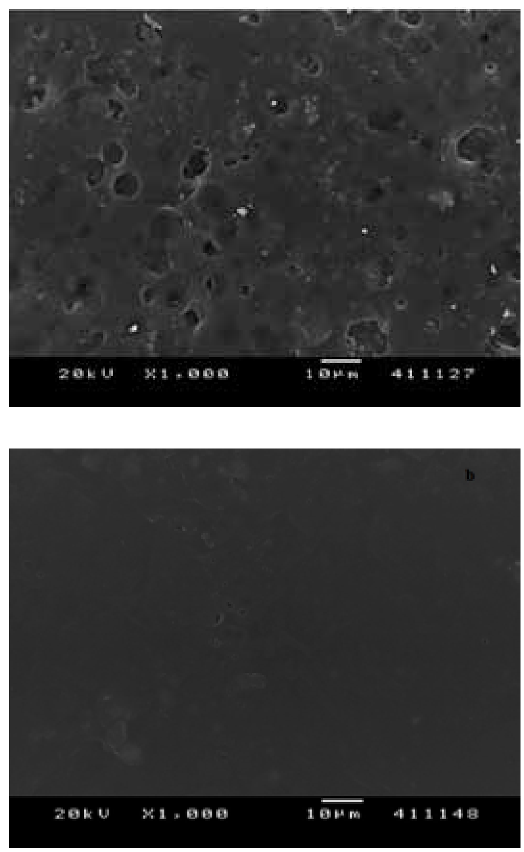

Figure 4 The images of micron (a) and nano (b) modifier treated leathers before ageing treatment (x1000)

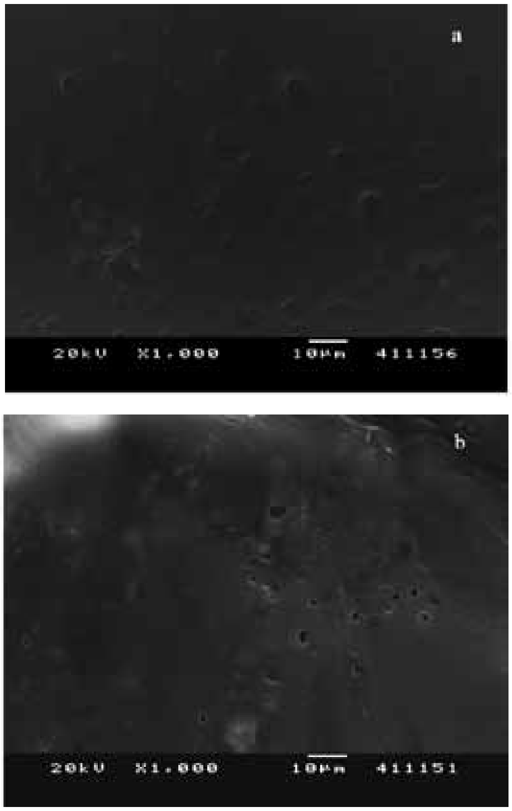

Figure 5 The images of micron (a) and nano (b) modifier treated leathers after 24h ageing treatment (x1000)

Fractures and cracks were observed more obviously on both micron and nano feel modifier applied finishing films after 48h ageing process when compared with the ageing results of 24h (Figure 6).

There has been more significant deterioration on UV light aged leather finishing films in comparison to 48 hours of ageing. As a result of this ageing process, the deterioration of finishing films that treated with both micro and nano feel modifiers was observed in the form of fractures and cracks, and finishing film was peeled off from the leather surface. The finishing film had split-up in the form of small cracks from the leather surfaces that were coated with nano-modifiers, but rough cracks were observed on leather surfaces coated with micron modifiers and these parts splitted like layers from the leather surface (Figure 7).

CONCLUSION

In this study, which based on the improvement of feel touch permanency with nano technological application, it was demonstrated that nano sized aminofunctional polysiloxane was successfully applied to leathers in the topcoat of finishing process and its feel touch effect was found to be more permanent than the micron sized traditional polysiloxane.

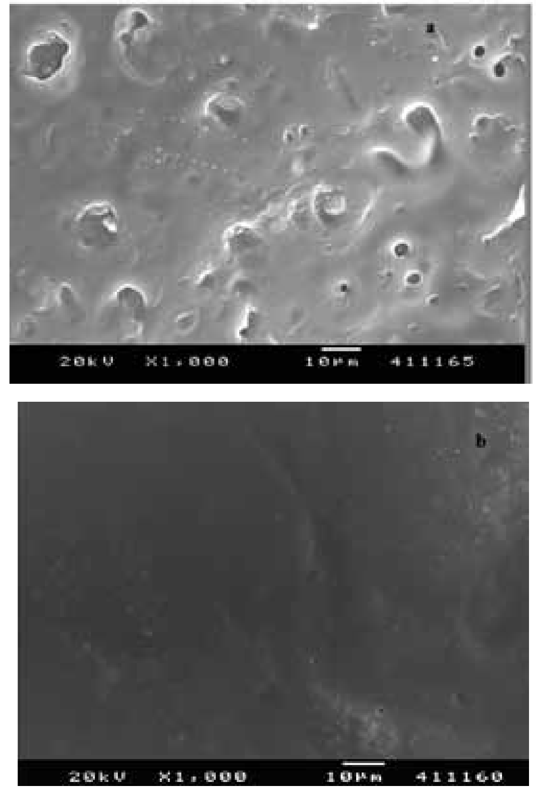

Figure 6. The images of micron (a) and nano (b) modifier treated leathers after 48h ageing treatment (x1000)

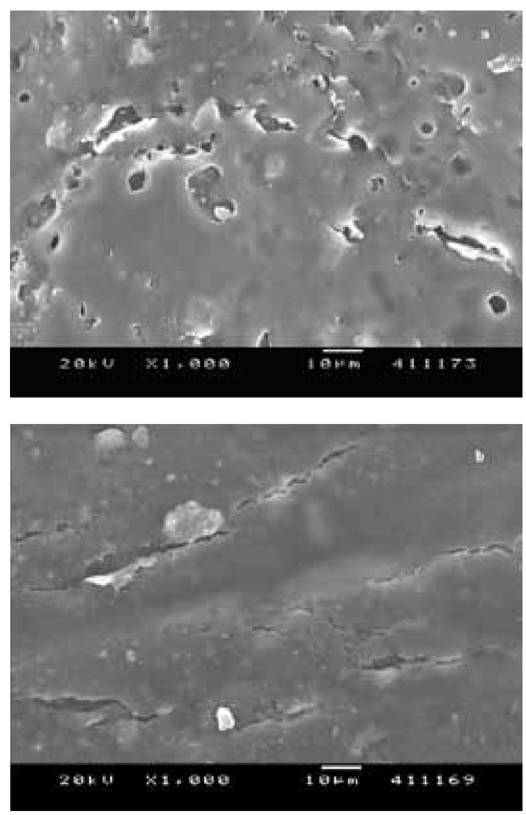

Figure 7. The images of micron (a) and nano (b) modifier treated leathers after UV treatment (x1000)

Moreover, it is determined that leathers coated with nano polysiloxane enables protecting the appearance and feel touch of any kind of leather product for a longer time. This improved performance could be ascribable to the difference in molecular structure of feel modifiers and its nano structure. As a result of this improvement on feel touch permanency, the quality of leather products was also improved; therefore it is expected to positively affect the quality of all types of leather products such as garment, footwear, upholstery and accessories.

It is also estimated that the application of nano polysiloxane will introduce a technological innovation into leather industry that will result in nano technological applications of other finishing chemicals like dyestuff, binder, wax and auxiliary chemicals commonly used in leather finishing process, on all types of leathers. Lastly, it is believed that these kinds of applications will get the attention of the consumers and it will make an economical contribution to leather industry by the increased marketing opportunity.

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