Leather Surface Refinement with Application of the TiO$_2$-SiO$_2$-GLYMO Nanocomposite and Lacquer Coating

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Abstract

In the present study the effect of TiO[2]-SiO$_2$-GLYMO nanocomposite on surface properties of leather was investigated. The TiO$_2$-SiO$_2$-GLYMO composite was prepared through the sol-gel route from tetraethoxysilane (TEOS) and titanium n-butoxide (TBO). 3-glycidoxypropyltrimethoxysilane (GLYMO) was added as coupling agent to provide a stable bond between metal oxides and leather substrate. The prepared composite was applied by spraying on the top coat of leathers in finishing. The surface properties observed by scanning electron microscopy (SEM) showed an even and homogenous coating obtained on leather by application of the composite in the presence of lacquer. The chemical structure of composite films was examined via Fourier transform infrared (FTIR) and Si-O-Ti bond and opening of epoxy rings of GLYMO were revealed. The presence of Ti and Si in the composite treated leather samples was ascertained by inductively coupled plasma optic emission spectrometer (ICP-OES). The results of the physical and fastness tests indicated that the use of TiO$_2$-SiO$_2$-GLYMO nanocomposite improves some performance characteristics of leather such as finish adhesion, dry and wet rubbing fastness, colour fastness to light and UV light. The results are promising for the refinement of leather surface with the application of the nanocomposite in the finishing process.

INTRODUCTION

The fastness properties of leather determine greatly the character of the finish coating. The finish of leather can vary mainly depending on the final leather product. Leather for shoes proposed for wearing under heavy weather or for hiking/climbing requires a thick, water and scuff resistant coating. On the other hand, thin coatings are needed on shoes for wearing mainly in warm weather or in offices. Leather for car or furniture upholstery requires a special coating with UV radiation, scratch and stain resistances which can be provided by the pigments and polymers used.[1] Leather is subjected to finishing in order to improve its physical properties, such as light and rub fastness, resistance to water, solvents, abrasion, etc., to modify its surface properties or to improve its appearance.[2,3]

With the development of polymers and technology it is possible to change the leather surface in many ways by application of functional coatings. These surface coatings provide better protection against wet, soiling and different mechanical actions.[4] Therefore, development of new materials with advanced properties is necessary to meet the increasing demand for sustainable products with long lasting, high performance, safe and efficient properties. However, sometimes one material does not possess all those properties, thus two or three materials are mixed and necessary properties can be imparted by the addition of suitable substances.

The separate use of nano-TiO$_2$ and nano-SiO$_2$ for improving some performance characteristics of leather has already been investigated by several researchers.[5-8] Moreover, when a TiO$_2$-SiO$_2$ nanocomposite was applied as finish, adhesion, dry and wet rub fastness, colour fastness to UV-light and self-cleaning properties have been improved.[9,10] In this research 3-glycidoxypropyltrimethoxysilane (GLYMO) which is an organically modified alkoxide and contains organic and inorganic reactivity in the same molecule, has been used due to its unique properties and applications as anti-scratch coatings, multifunctional coatings and binder.[11] It can be cross-linked to form a poly(ethylene oxide) chain and acts, therefore, as network former. Furthermore, the use of GLYMO as a binder in leather finishing presents a better cross-linking reaction and improved the wet rub fastness property of leather.[12] In the previous study, the colloidal TiO$_2$-SiO$_2$-GLYMO nanocomposite was successfully synthesized through the sol-gel route at ambient temperature.[13] Thus, the main objective of the present study was to enhance the fastness properties of leather using TiO$_2$-SiO$_2$-GLYMO nanocomposite in the leather finishing process.

EXPERIMENTAL PROCEDURES

Materials

Tetraethyl orthosilicate (TEOS) and 3-glycidoxypropyl)-trimethoxysilane (GLYMO) were purchased from Sigma-Aldrich (USA). Titanium n-butoxide (TBO) was provided by Merck (Germany). All of these materials were used as received. Acetic acid (Merck, 100%) as catalyst and distilled water for hydrolysis of alkoxides were used. Ethyl alcohol

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(Merck), analytical grade, was the solvent in the preparation of the sol. Acetylacetone (Merck) was used to stabilise the colloidal solution. Garment crust leathers (goat, brown colour) were supplied from Menemen Leather Industrial Area in Izmir, Turkey. Nitrocellulose lacquer (EL 8081) which is made of nitrocellulose combined with other resins dissolved in water (in our case) was provided by Verpol (Turkey).

Preparation and characterization of TiO2-SiO2-GLYMO composite

The TiO$_2$-SiO$_2$-GLYMO composite solution was produced in the following way as described in Ref.13. Two different concentrations of the materials in the prepared composite with molar ratios as 40/40/20 and 60/20/20 (Ti/Si/GLYMO molar ratio, %) were used in this study in order to find out the best one. In brief, the required amounts of ethanol, acetic acid, distilled water and TEOS were mixed in the round-bottomed flask with continuous stirring. A defined amount of TBO was then added into this solution dropwise and the mixture was stirred for 30 minutes to complete the hydrolysis process of SiO$_2$ and TiO$_2$. GLYMO was added into the TiO$_2$-SiO$_2$ dispersion and stirring of the mixed solution continued for 2 hours. The ultrasonic treatment was applied with 15 kW power. The transparent sol obtained was aged overnight. The composites were named as composite A (40/40/20) and composite B (60/20/20) according to the ratios of precursors used. The composite solutions (A and B) had pH values of 4.8 and 5.1, viscosities of 2-5 and 1-3 mPa.s, turbidity values of 9.9 and 8.4ntu, particle sizes of approximately 22.1 and 10.3nm, respectively.

Application of TiO$_2$-SiO$_2$-GLYMO composite on leather

The prepared composites (A and B) were applied on leather according to the three different variations of coating formulae given in Table I. The base coat was applied by a conventional method. The TiO$_2$-SiO$_2$-GLYMO nanocomposites obtained were applied by spraying on the top coat of the finished leather

Characterisation and determination of surface properties of leathers treated with TiO$_2$-SiO$_2$-GLYMO nanocomposite

FTIR analysis was conducted to investigate the chemical and structural changes of leather treated with nanocomposite and untreated leather. FTIR studies were carried out on a Spectrum 100 device with ATR equipment (Perkin Elmer, USA). The wavenumber was set between 4000cm^{-1} to 400cm^{-1} wave numbers, and consisted of 64 scans at 4cm^{-1} resolution. The results were evaluated with FTIR Spectrum Software.

The examination of the surface morphology was performed *via* scanning electron microscope (SEM, Philips XL-30S FEG). Elemental analysis of the nanocomposite on leather was conducted with the help of an inductively coupled plasma optic emission spectrometer (ICP-OES, Perkin Elmer, USA).

Leather samples to be tested were conditioned in laboratory conditions (23 ± 2°C, 50% RH) for 24 hours before any measurements were performed.[14] Colour fastness of leather to wet and dry rubbing evaluates both the damage of the finish layer and colour transfer to felt.[15] The evaluation of colour changes was done according to grey scale standard. The measurement of the adhesion of the finish to leather or the adhesion between two adjacent layers of the finish was also done.[16] Colour fastness to light and UV light, the resistance of the colour of leather to the action of a

		TABLE I Coating formulation	
	Top coat	
I	Composite (A or B)	2 coatings by gun spraying with intermediary hung up drying Press-ironing with 20kgf plate at 100°C/90 bar/3 sec
II	Composite (A or B)	2 coatings by gun spraying with intermediary hung up drying Press-ironing with 20kgf plate at 100°C/90 bar/3 sec
	Nitrocellulose lacquer	2 coatings by gun spraying with intermediary hung up drying Press-ironing with 20kgf plate at 100°C/90 bar/3 sec
III	Nitrocellulose lacquer	2 coatings by gun spraying with intermediary hung up drying Press-ironing with 20kgf plate at 100°C/90 bar/3 sec
	Composite (A or B)	2 coatings by gun spraying with intermediary hung up drying Press-ironing with 20kgf plate at 100°C/90 bar/3 sec
	Nitrocellulose lacquer	2 coatings by gun spraying with intermediary hung up drying Press-ironing with 20kgf plate at 100°C/90 bar/3 sec

Coding used for the leather samples:
Control - Control leather without treatment,
A (I) or B (I) - leather treated with composite A (40/40/20, %) or composite B (60/20/20, %),
A (II) or B (II) - leather treated with composite A or B and lacquer,
A (III) or B (III) - leather treated with lacquer + composite A or B + lacquer.

standard artificial light source (Xenon lamp) or UV light was evaluated according to blue scale standard.[17,18] Determination of resistance to grain cracking and grain crack index was carried out using a lastometer.[19]

RESULTS

Characterisation of the leather samples

Investigation of chemical and structural changes in the molecular level by detection of the appearance, disappearance or change of environment of chemical bonds is possible by FTIR analysis. Thus, FTIR spectra were taken to reveal the chemical changes taking place in the leather samples treated with the TiO_2-SiO_2-GLYMO nanocomposite solution in comparison with the untreated sample (Fig. 1). The corresponding assignments are displayed in Table II.

All of the functional groups of the chromium crust leathers (aniline) were determined in the FTIR spectra of all leather samples.[9] The comparison of FTIR spectra of the leather samples showed that the bands emerging in relation to stretching vibration of the (0) C-O, (1) C-O-C, (2) OR-C-C, (3) C-N, (4) COO-CH_3 (asymmetric), (5) N-O, (6) C=C, (7) C=O, (8) -CH_2 and (9) -CH_3 groups on the structural chain of the control leather samples and those treated with nanocomposite were found to be at wavenumbers of (0) 1020, 1082 (1) 1063, (2) 1140, 1174, (3) 1275-1281, 1376-1378, (4) 1452-1457, (5) 1552-1556, (6) 1633-1647, (7) 1723, 1727, (8) 2854-2857 and (9) 2924-2926 cm^{-1} respectively (Table II). Peaks of 1275-1281cm^{-1} and 1376-1378cm^{-1} were interpreted as amide band I, and peaks of 1552-1556cm^{-1} as amide band II.[20] As shown in Table I, the peak of 745-746cm^{-1} was from the Ti-O-Ti stretching mode.[21,22] It was determined that the clearest peaks were observed for the SiO- group bond at a wavenumber of 999cm^{-1}, and at 1530-1582cm^{-1} for the Si-O-R bond.[23] Peaks at 934-946cm^{-1} were determined in all the treated samples and were assigned to Si-O-Ti stretching vibration, which overlap with residual Si-OH stretching and non-bridging oxygen Si-O.[24,11] A broad band or peaks of between 3316-3671cm^{-1} observed in leather samples were attributed to the O-H stretching mode.[25] It was proposed that the peak at 3337-3338cm^{-1} indicated opening of the epoxy rings as it was reported in the literature.[11]

It was reported that a silane coupling agent will act at an interface between an inorganic substrate and an organic material to bond or couple the two dissimilar materials. The adhesion mechanism is due to two groups in the silane structure. The $Si(OR)_3$ portion reacts with the inorganic reinforcement, while the organofunctional (vinyl-, amino-, epoxy- *etc.*) group reacts with the organic material.[11] Based on FTIR results it can be concluded that chemical binding of the TiO_2-SiO_2-GLYMO nanocomposite to the surface of the treated leathers takes place with the additional help of the epoxy-groups. It was presumed that the epoxy-group opens and reacts with carboxylic groups of collagen.[12]
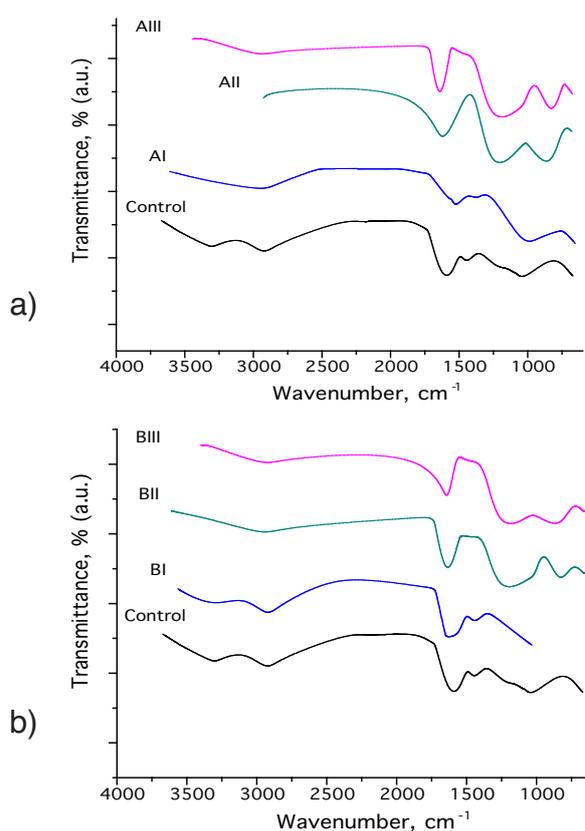

Figure 1. FTIR spectra of the leather samples treated with nanocomposite A (**a**) and B (**b**).

The imaging of the finishing layer on the surface of the leather was carried out *via* a scanning electron microscope (SEM). The SEM surface images of the control leather samples and those treated with the TiO_2-SiO_2-GLYMO nanocomposite solutions at a magnification of x1000 are presented in Figure 2. It was seen from the SEM images that the surface of the control leather sample had a natural appearance with clear scratches and pores (Fig. 2a); but in the films formed on the surface of the leather sample treated with composite A (AI and AII) cracks and bubbles occured (Fig. 2b,c), while the films on the sample treated with a double coat of lacquer and composite A (AIII) were more homogeneous, smooth and without cracks (Fig. 2d).

Better films were obtained on the leather surface treated with composite B. When composite B was applied the natural appearance of the leather was not affected (BI) (Fig. 2e). However, the best results were obtained when composite B was applied with lacquer in both variations (BII and BIII) (Fig. 2f,g).

Table III shows the Ti and Si contents in leather samples obtained by ICP-OES analysis. Si was found in the small amount of 7.2ppm in the control leather. The element Si is not used directly in the stages of leather processing, but it is thought that it may be included in the leather structure from impurities in chemicals used in the production process.[9] Thus, it was proposed that Si had arisen from the operations before finishing. Ti was not detected in the control leather sample. When the amounts of Si and Ti in the TiO_2-

Functional groups	Control	AI	AII	AIII	BI	BII	BIII
			TABLE II				
			FTIR spectra of leather samples				
C-O	1035	1040	1022	1023	1034	1028	1023
C-O-C			1063	1063		1064	1064
C-O	1082	1082			1082		
=C-H	810		832	833		835	834
OR-CC	1140						
OR-CC	1174						
C-N	1275	1281	1275	1275	1276	1277	1276
C-N	1378	1376	1377	1377	1377	1377	1376
COOCH3	1454	1453	1457	1456	1452	1456	1456
N-O	1552	1552	1556	1555	1552	1554	1554
C=C	1642	1645	1643	1642	1647	1643	1643
C=O	1723		1723	1727		1723	1727
- CH2	2854	2856	2857	2857	2854	2855	2856
- CH3	2924	2926	2926	2925	2924	2924	2925
-OH	3316						
-OH		3337	3337	3338	3337	3337	3338
-OH				3446			3446
-OH	3543				3524		
-OH	3589				3589	3589	
-OH	3671	3610				3610	
TiOTi			746	746		745	745
SiOTi		934	934	946	934	934	946
SiO			999			999	
SiOR			1535	1530		1535	1530
SiOR		1575		1563			1582
SiOTi				3387			3387
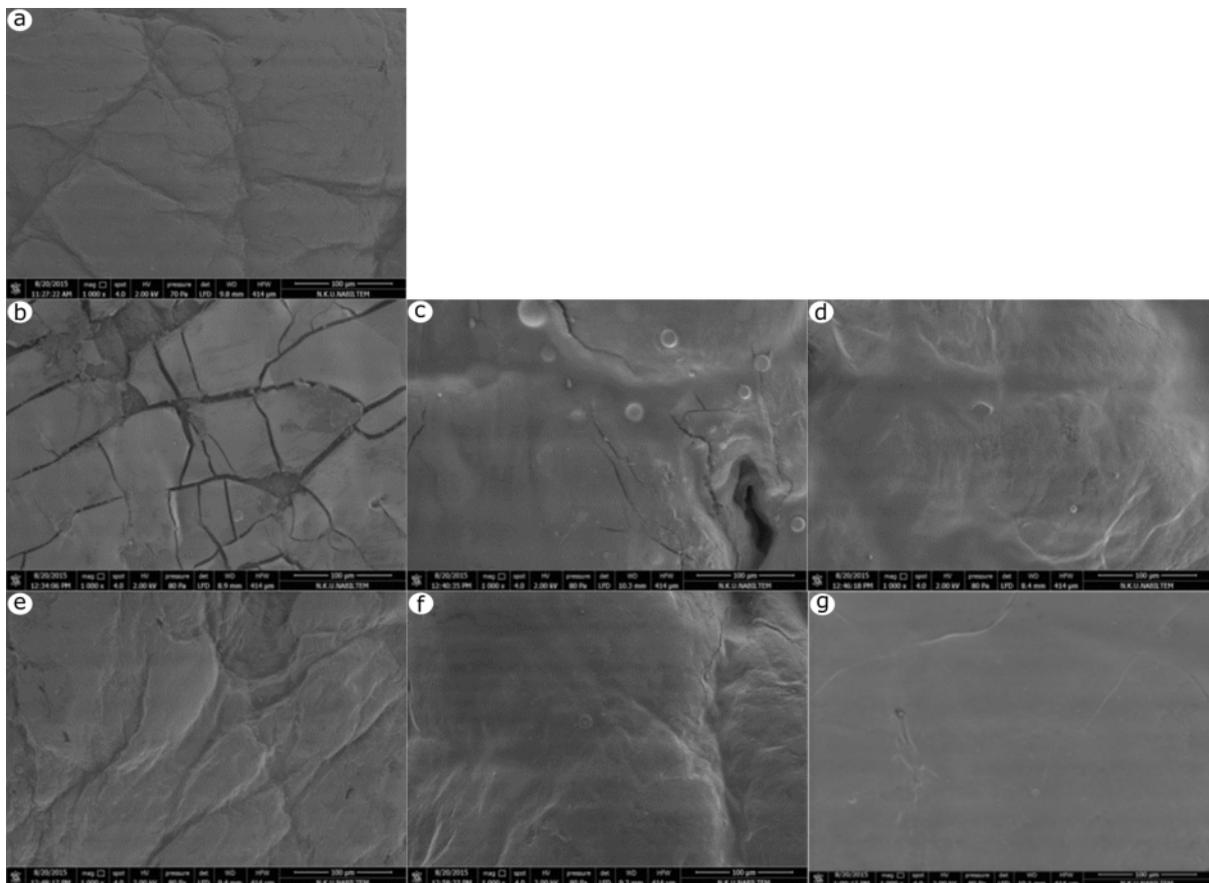
Figure 2. SEM images of the leather samples (with x1000 magnification); Control leather sample – without treatment (a); Composite A: b) AI c) AII d) AIII; Composite B: e) BI f) BII g) BIII.

SiO$_2$-GLYMO nanocomposite (A and B) treated leather samples were compared, it was observed that the contents of both metals in leather samples had increased depending to the variations applied. It was seen that when only the composite A was applied (AI) the contents (ppm) of Si and Ti were 52.9 and 54.8, respectively. The results for the composite B (BI) were 31.7 and 30.3 of Si and Ti, respectively. Although the proportion of Ti/Si/GLYMO in the composite A was 40/40/20, there was a higher amount of Ti in the AIII sample (252.2) than Si (161.1), but not in the AII sample (Si-116.5; Ti-109.1). However, when the proportion of Ti/Si/GLYMO in the composite B was 60/20/20 the content of Ti was higher than that of Si in BII and BIII leather samples (Si-74.7 and 96.3; Ti-140.7 and 160.0, respectively) but not in BI sample. Besides, the highest amount of each element was found in the third variation of the finishing treatment. It was assumed that a higher amount of both elements in AIII and BIII samples were found due to the better adhesion of the composite in the presence of a double lacquer coating as it was also seen in SEM images as well. In spite of the proportions, non- uniform distribution of elements in the leather samples was probably due to application of the nanocomposite by spraying and high affinity of TiO$_2$ toward hydroxyl and carboxylic groups of collagen.[9,26]

TABLE III				
ICP-OES results of Si and Ti contents in leathers				
Sample	Si, ppm	SD	Ti, ppm	SD
Control	7.1	0.4	0.0	0.0
AI	52.9	0.3	54.8	0.2
AII	116.5	0.2	109.1	0.4
AIII	161.1	0.6	252.2	0.4
BI	31.7	0.3	30.3	0.6
BII	74.7	0.1	140.7	0.2
BIII	96.3	0.1	160.0	0.0

Physical and fastness properties of leathers

The results of fastness tests such as wet and dry rub fastness, colour fastness to light and UV light and physical testing and finish adhesion are given in Table IV. It is seen from Table IV that the wet rub and the dry rub fastness of the control leather sample had values of 3/4 and 4, respectively. It was observed that treatment with TiO$_2$-SiO$_2$-GLYMO nanocomposite only

variation I did not have a great effect on wet and dry rubbing fastness. When composites A and B only were applied the dry rub fastness of the AI and BI leather samples (3) were close to that of the control leather sample while the wet rub fastness of the AI leather sample was lower than that of control (2) and this value for BI was higher (3/4). The AII, AIII and BII leather samples showed high dry rub fastness (4/5) and the BIII sample the highest (5). The highest wet rub fastness was obtained for AIII and BIII leather samples (4/5), while the wet rubbing fastness of AII was lower (2/3) than that of BII sample (3/4). The results show that the resistance to mechanical fastnesses of the finished leather surfaces in the IIIrd variation was increased. Moreover, it was observed that the dry rub fastness of TiO$_2$-SiO$_2$-GLYMO nanocomposite treated leathers was better than their wet rub fastness property.

The finish adhesion values of the control leather samples and the TiO$_2$-SiO$_2$-GLYMO nanocomposite treated samples are also presented in Table IV. For the control sample, this value was 6.8N. The finish adhesion value of the leather samples treated with nanocomposite A and B only (AI and BI) were close to each other at 7.8 and 7.3 N, which were lower than that of the lacquer and composite treated leathers (AII and BII) at 9.7 and 10.1, respectively. The value for the AIII sample, 10.3N, was close to that of BII. It was determined that the BIII sample had the highest finishing adhesion value (11.7N). The best adhesion result was obtained for the leather treated with the 3rd variation of the composite B (60/20/20, %).

The colour fastness to light and UV light values of the control and TiO$_2$-SiO$_2$-GLYMO nanocomposite treated samples are given in Table IV. Both values of the control leather sample were the same at 2/3. The highest value of fastness to light was obtained for BII and BIII leather samples (4). As for fastness to UV light, an increase was seen in all TiO$_2$-SiO$_2$-GLYMO nanocomposite-treated leather samples compared with the control leather sample. The highest value of fastness to UV light was obtained for BIII leather sample (4/5). It is concluded that due to the photocatalytic effect of TiO$_2$ the increases in the fastness values of the leathers treated with the TiO$_2$-SiO$_2$-GLYMO nanocomposite to UV light was obtained.

The leather cracking strength, crack elongation, grain burst strength and grain burst elongation values obtained in this study are exhibited in Table V. The

TABLE IV							
Physical and fastness properties of leathers							
Specimen	Finish adhesion	Dry rub fastness		Wet rub fastness		Colour fastness	
	(N)	Leather	Felt	Leather	Felt	UV light	Light
Control	6.8	3/4	4	4	4	2/3	2/3
AI	7.8	3	4/5	2	3	3/4	2/3
AII	9.7	4/5	5	2/3	3/4	4	3
AIII	10.3	4/5	5	4/5	4/5	4	3
BI	7.3	3	4/5	3/4	4	3/4	3
BII	10.1	4/5	5	3/4	4	4	4
BIII	11.7	5	5	4/5	5	4/5	4

	TABLE V			
Grain cracking and grain bursting strength values				
Specimens	Crack strength, N	Crack elongation, mm	Burst strength, N	Burst elongation, mm
Control	149.0 ± 0.4	12.3 ± 0.1	220.2 ± 0.6	14.9 ± 0.1
AI	150.0 ± 0.0	11.3 ± 0.5	235.9 ± 0.1	13.9 ± 0.1
AII	166.5 ± 0.1	11.5 ± 0.1	258.5 ± 0.3	14.7 ± 0.3
AIII	243.4 ± 0.3	13.4 ± 0.2	332.6 ± 0.2	15.8 ± 0.4
BI	80.6 ± 0.4	10.6 ± 0.3	105.5 ± 0.4	12.9 ± 0.6
BII	123.7 ± 0.2	11.3 ± 0.4	146.5 ± 0.2	12.7 ± 0.4
BIII	141.7 ± 0.1	11.2 ± 0.2	154.1 ± 0.1	13.3 ± 0.1

cracking and bursting strengths for the control sample were 149.0 and 220.2N, respectively. While for all B nanocomposite treated samples values were lower than those of the control samples, the values for the nanocomposite A treated samples were higher. In this group, the highest values of crack strength and burst strength were found in the AIII sample (243.4N and 332.6N). It was noticed that the best results were obtained from the nanocomposite A (40/40/20,%) treated leather group. These findings were in parallel to the findings regarding Ti and Si content detected with ICP-OES.

DISCUSSION

Thin films or coatings from the TiO_2-SiO_2-GLYMO nanocomposite previously investigated as composite material for optical waveguides have mostly been obtained on silicone substrates or slide glasses.[24, 25] This composite was also utilised on textile material, particularly on lyocell fibres, and it was indicated that a protection against the high oxidizing power of TiO_2 under exposure to daylight irradiation was provided by SiO_2 and GLYMO.[11]

In this study, the TiO_2-SiO_2-GLYMO nanocomposite was successfully synthesized through the sol-gel route at ambient temperature. Leather cannot withstand high temperature treatments, so that obtaining a TiO_2-SiO_2-GLYMO coating at low temperature is significant. The TiO_2-SiO_2-GLYMO nanocomposite solutions (A and B) were applied to leather and the coatings prepared with composite B (with 60/20/20 Ti/Si/GLYMO ratio) showed smooth surface morphology without cracking, while those with composite A (except IIIrd variation) exhibited cracking. According to the results obtained, it was observed that application of TiO_2-SiO_2-GLYMO nanocomposite with lacquer in the 3rd variation (AIII and BIII) increased not only the wet and dry rub fastness of the leather but also the finish adhesion and colour fastness to UV light.

When the best results previously obtained from the application of TiO_2-SiO_2 nanocomposite on leather were compared with the best results for the TiO_2-SiO_2-GLYMO nanocomposite from this study (AIII) it was noticed that there was an increase of 5% in finish adhesion, 8% in crack strength and 14% in burst strength values. Furthermore, there was an upgrade in colour fastness to light (4) and UV light (4/5), high

values of dry and wet rub fastness were also obtained (5 and 4/5, respectively).

It was interpreted that the TiO_2 formed a stronger bond with the leather fibres by penetrating easily through the leather pores because of its nano size, and that it increased the intermolecular linkages between the finish coating and the leather surface.[5] Further, the improvement may also be obtained also due to the particle size which enhances the reactivity of SiO_2 nanoparticles with finishing auxiliaries[8] in our case, with lacquer. Therefore, there is a chemical coalescence on the surface of the treated leathers between the TiO_2-SiO_2-GLYMO nanocomposite and lacquer as was observed in SEM images.

In addition, it was concluded that the fastness properties of leather using TiO_2-SiO_2-GLYMO nanocomposite were improved thanks to the addition of GLYMO molecules which are able to form strong bonds to inorganic particles and also to the surrounding polymer substrates, linking the different materials together via epoxy-groups.[27,11] Thus, the high surface properties are achieved by the crosslinking of the top coating to the leather which was demonstrated and verified by FTIR patterns and by the high amounts of Si and Ti determined in ICP-OES analysis of leather samples (AIII and BIII).

It is noteworthy to mention the increased colour fastness values of the leather to light and UV light which is thought to be related to not only the photocatalytic activity of TiO_2 in the composite,[9] but also to silica which promotes oxygen vacancies in the titania structure with an effect on enhancement of photocatalytic properties.[28] This fact was a background for obtaining leather with self-cleaning properties[10] and could be beneficial in obtaining leather with improved colour fastness to UV light. To sum up, it was revealed that leather finishing coating with the nanocomposite refined the physical and fastness characteristics of the treated leather samples.

CONCLUSION

In present study, evenly distributed and homogeneous films of TiO_2-SiO_2-GLYMO nanocomposite on leather, especially in the third variation, were obtained for AIII and BIII leather samples. By using the TiO_2-SiO_2-GLYMO nanocomposite the surface characteristics of leather

such as wet and dry rub fastness, fastness to light and UV, finish adhesion, grain crack and burst resistance values were upgraded and improved. Thus, our results indicate that these desirable functional properties can be imparted to other types of leather in finishing whether it is for automotive or furniture upholstery, shoe uppers, garments, bags or leather goods. Furthermore, due to such properties as transparency and homogeneity, the prepared composite could be applied on the leathers with different colours and would not affect their colours. The last and not least advantageous property of the composite is that it can be applied on leather surfacse without addition of binder or solvent solutions being needed to disperse or to form a coating. Further studies are focused on the introduction of the TiO_2-SiO_2-GLYMO nanocomposite in the base coat of a finishing formulation to modify surface characteristics and to focus on its applicability with pigments, binders or other finishing auxiliaries.

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