Preparation, Characterization and Application of Silica Metal Oxide Nanoparticles for Leather Coating

by

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Abstract

Synthesis of silica sol-gel nanoparticles was carried out by the Stober's process and the resulting products were used in leather finishing mixtures as a coating ingredient. The physical and chemical properties of the synthesized sol-gel nanoparticles were characterized by TEM, FE-SEM, EDAX, FT-IR, TGA and XRD. The surface morphology of the nanoparticle coated leathers were evaluated by AFM. The silica sol-gel nanoparticles-coated leather exhibited improved water spotting resistance, water vapor permeability, and increased adhesion values. Therefore, a conventional system of leather finishing has been upgraded by using silica sol-gel nanoparticles, especially in the base coat application.

Resumen

Síntesis de nanopartículas de sílice sol-gel se llevaron a cabo por el proceso de Stöber y los productos resultantes se utilizan en las mezclas de acabado del cuero como un ingrediente de cobertura. Las propiedades físicas y químicas de las síntesis de nanopartículas sol-gel se caracterizaron por TEM, FE-SEM, EDAX, FT-IR, TGA y XRD. La morfología de la superficie de los cueros acabados con nanopartículas fueron evaluados por AFM. Los cueros acabados con las nanopartículas de sílice sol-gel exhibieron mejoras en la resistencia al manchado de agua, en la permeabilidad al vapor de agua, y mayores valores de adherencia. Por lo tanto, un sistema convencional de acabado del cuero ha sido mejorado mediante el uso de nanopartículas de sílice sol-gel, especialmente en su aplicación en la capa base del acabado.

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INTRODUCTION

Owing to the quick development of nanosciences and nanotechnology, nano composites are of growing interest in polymer industry because they display enhanced or even novel mechanical and thermal properties, which are attributed to the nano effect and strong chemical coalescence between the nanoparticles and the polymer. They have been widely used for coating, adhesion, plastic and fiber applications.[22-27] Correspondingly, the engineering of porosity in common materials as sol-gel silica nanoparticles has been emerging as a new area of great technological and scientific interest.[2-22] The thin films of SiO_2 were utilized as antireflection coating on monocrystalline silicon wafer for photovoltaic application.[1] Dense silica sol-gel nanoparticles have received considerable attention since monodispersed sol-gel colloidal silica spheres, obtained from ammoniacal TEOS-Tetra Ethyl Ortho Silicate, [Si $(OC_2H_5)_4$] solution, were reported in the late 1960's by Stober et al.[2] The particles prepared by acid or base hydrolysis-condensation of TEOS, [2-10] have a non-porous core and a relatively low surface area directly related to the size of the particles.

Porous silica sol-gel nanoparticles have both a narrow mono-dispersity and a well-defined pore size and connectivity, for a wide range of applications: catalysis, separation, chromatography, controlled release, dielectric materials of low relative permittivity fillers, customs-designed pigments, optical hosts,[23-26] electrical insulators, thermal insulators, humidity sensors and coating for scratch and abrasion resistance.[33, 34] Leather is made from a natural hide or skin and becomes a dry, stable material after tanning, retanning, dyeing, fatliquoring and finishing.[25] Leather is an aesthetic bio material; it has its innate values of softness, fullness, roundness, tightness, pliability, flexibility, visco-elastic behaviors, stretch, adaptability, etc. Conventional finishing systems are primarily composed of pigments, dye solutions, resin binders (polyacrylic / acrylate), polyurethane binders, waxes, fillers and nitro cellulose lacquers for leather finishing.[31] We use different sol-gel nanoparticles to enhance the performance of leather coating. Our special interest here is sol-gel nanoparticles of silica. In our work we have used the prepared silica sol-gel nanoparticles in shoe upper leather finishing formulation to increase the mechanical properties of coating. Materials at nano sizes show special properties due to the large surface to volume i.e., aspect ratio. When size reduces from bulk to nano scale, the electron density is more, so the reactivity in nano size materials will be better and it will be faster than bulk materials.

The aim of the work is to combine the fields of leather technology and nanotechnology for improved performance of leather. The focus is on the area of leather finishing by employing different nanoparticles. This paper reports the synthesis of silica sol-gel nanoparticles by Stober's Process and these were used in the coating formulation mixtures in the finishing of cow shoe upper leather, especially in base coat applications.

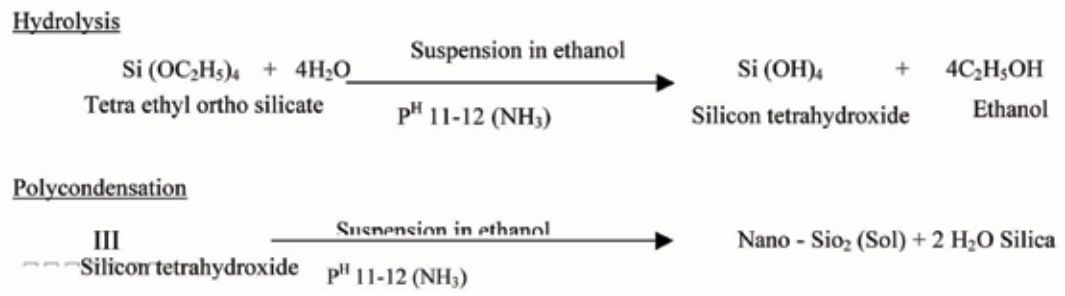
EXPERIMENTAL

Materials

Ethanol; Tetraethylorthosilacate (Sigma Aldrich); Ammonium Solution (S.D. Fine chem. Limited); Deionized distilled water.

Synthesis of Silica Sol-Gel Nano Particles

Silica nano particles were synthesized by sol-gel method, from tetra ethyl ortho silicate (TEOS), ethanol and de-ionized water in presence of ammonia as catalyst at room temperature. A simple one step base hydrolysis and condensation process which involves the condensation of TEOS in ethanol and water mixture at alkaline condition at room temperature.[28] Generally adopting the sol gel technique of base hydrolysis will result in nano silica having large pore diameter. The introduction of water into the system initiates hydrolysis in basic solution. It is a nucleophilic substitution (S_N2) reaction, and is characterized by the penta coordinate transition state of Si. The controlled hydrolysis process produces the singly-hydrolyzed monomer [(OR) Si(OH)]. These intermediate reaction products participate in the condensation reactions and finally silica sol-gel nanoparticles are formed. An experiment was carried out by taking 20 ml of ethanol in a 50 ml beaker, followed by 2 ml of TEOS and 4 ml of concentrated ammonia solution. The mixture was stirred for 8 hours, at the end of which a milky white curdy solution was obtained and this was centrifuged. This resulted in a fine white powder, which was characterized by TEM, FE-SEM, EDAX, FT-IR, TGA, XRD and confirmed as nano silica. Given below is the scheme for the preparation of silica sol-gel nanoparticles.



Preparation of Conventional Base Coat Finish Formulation, Incorporating Silica Sol-Gel Nanoparticles, for Shoe Upper Leather

The synthesized silica sol-gel nanoparticles were applied separately in conventional shoe upper leather finishing formulation with various concentrations as per following Table I. After finishing the performance properties of leather were evaluated. Nanoparticle, dispersing agent and water were pre-mixed and sonicated for 30 minutes and it was added to the coating mixture formulation i.e., with water, acrylic binder, polyurethane resin binder, casein, wax and pigment.[33] Further the final mixture was sonicated for 30 minutes. Cow shoe upper crust leather from Indian origin with substance 1.1/1.2 mm was taken for evaluation. The sonicated finish formulation mixture was sprayed on the cow shoe upper leather by HVLP gun at 30 psi. The base coat deposition was 8 g/sft by two cross coat spray, with inter mediate drying. The dried leather was pressed at 80°C/80 kg/cm^2 then again two cross coat coating mixture was sprayed on the leather. After drying the leather was sprayed one cross coat of polyurethane top and the deposition was 4 g/sft.

TABLE I
Conventional Base Coat Formulation Incorporating Silica Sol-Gel Nanoparticles for Shoe Upper Leather

INGREDIENTS	Trial I	Trial II	Trial III	Trial IV	Control
Water	459.9	459.5	459	455	460
Primal 863 Acrylic resin	150	150	150	150	150
RU 3901 PU binder	150	150	150	150	150
Lustral UT Casein binder	50	50	50	50	50
SFT6004Wax emulsion	50	50	50	50	50
Pigment	125	125	125	125	125
Silica sol-gel Nanoparticles*	0.1	0.5	1.0	5	0
Dispersing agent*	5	5	5	5	5
Water*	10	10	10	10	10

(*Nano particles, dispersing agent, water are pre-mixed and sonicated. All the quantities given in the above table are in grams)

Top Coat Formulation for Silica Sol-Gel Nanoparticles Applied Leather

Sarugan 919 PU Top (Sarkem) – 500 parts

Water – 500 parts

Akualene AKU Crosslinker (Clariant) – 5 parts (Crosslinker was pre-mixed with 5 parts of water)

The above formulation was sprayed one cross coat on leather by HVLP gun at 30 psi. Top coat deposition was 4 g/sft. Then the leather was dried and pressed at 80°C/80 kg/cm^2.

RESULTS AND DISCUSSIONS

Structural and Morphological Characterization of Silica Sol-Gel Nanoparticles.

Field Emission Scanning Electron Microscope Imaging and Energy Dispersive Analysis

The formed silica sol-gel particles morphology was obtained from FE-SEM (HITACHI S–6600) which confirmed that it was in spherical shape. Figure 1 showed the FE-SEM image of SiO_2 nanoparticles which formed a string of beads structure.[29]

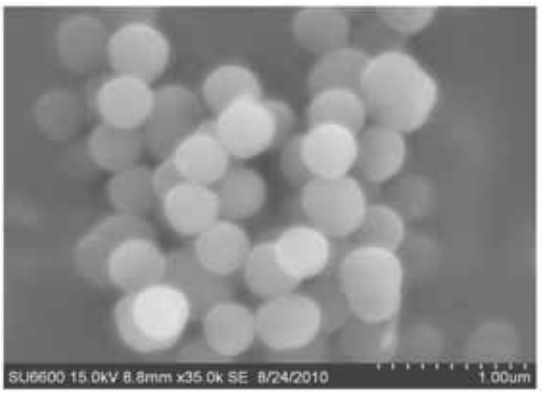


Figure 1. FE-SEM images of SiO_2 nanoparticles.

Edax Peaks of Nano Sio_2 Powders

Figure 2 showed the EDAX results, which confirmed the presence of Si and Oxygen elements, and the formation of SiO_2 nanoparticles.[30]

Elemental Composition Analysis

Table II conferred the elemental composition analysis of silica sol-gel nanoparticles. Atomic % of silica was 29.91%.

Determination of Applied Physical Properties for Silica Sol-Gel Nanoparticles Coated Leather

The following performance tests were carried out on the silica sol-gel nanoparticles coated leathers.

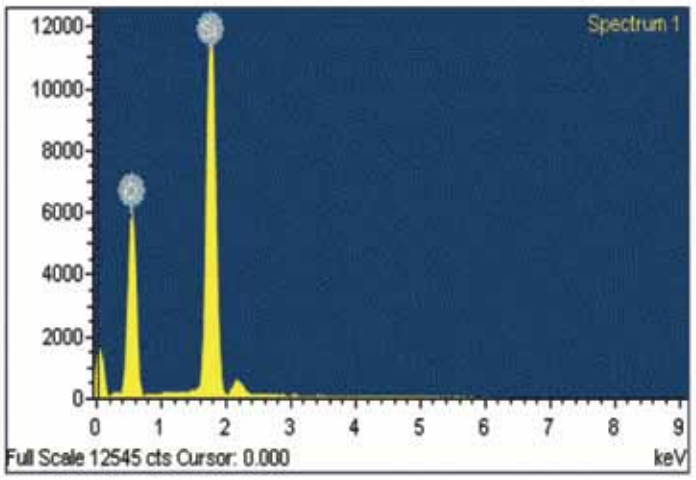


Figure 2. EDAX peaks of SiO_2 nanoparticles.

TABLE II
Elemental Composition Analysis

Element	Weight%	Atomic%
O K	58.01	70.81
Si K	41.99	29.19
Totals	100.00	100.00

Wet and Dry Rub Analysis

Measurement of Wet and dry rub fastness test [32] was carried out according to Veslic IUF 450, and the results were given in Table III.

Measurement of Lastometer

According to grain crack SATRA TM 24 and the values were given in Table III.

Water Spotting Resistance

Measurement of Water spotting resistance test was carried out according to SATRA TM 185 and the results were given in Table III.

Measurement of Water Vapour Permeability

Measurement of Water Vapour Permeability was carried out by ISO 14268; 2002, and the values were given in Table III.

Measurement of Finish Adhesion

Measurement of Finish Adhesion was carried out by ISO 11644:2009 method and type of machine used was CRE. The values were given in Table III.

These Performance test result for the silica sol-gel nanoparticles coated leather are shown in Table III.

Subjective Evaluation Result for Silica Sol-Gel Nanoparticles Coated Leather

All the finished leathers were assessed for following physical and visual assessment parameters like gloss, covering, levelness, filling, touch / feel, tackiness, fish-eye and plate release. The values were given in Table IV.

CONCLUSIONS

The results showed that silica sol-gel nanoparticles improved the water vapor permeability, water spotting resistance and finish film adhesion (dry in N/10mm). The gloss level gets reduced by increasing the concentration of silica sol-gel nanoparticles in the finish formulation. An improved filling and covering properties are obtained when compared to control.

In fastness (IUF 450) test [32] results there was a 20% improvement in wet rub noticed on 50 wet rubs in material. The rating of sample was 2 to 3 and control was 2.[33] It was noticed that there was 25% improvement on 50 rubs of wet, in felt. Fastness rating of sample was 2 and control was 1 to 2. [34] All the samples passed 150 rubs of dry rub fastness, which meets the conventional shoe upper leather requirements and the rating value was 4 or 5. [34] It has already been reported that silica sol-gel nanoparticles improve the scratch and abrasion resistance. [33] The improvement noticed in fastness properties is due to the nano effect and strong chemical coalescence between the nanoparticle and acrylic, polymeric binders that are used in the coating mixture[35].

The optimum value of finish film adhesion (dry) was found when the silica sol-gel nanoparticle was used in the range of 0.1g/L to 1g/L. [34] All the leather samples treated with silica sol-gel nanoparticles in finishing conferred finish film adhesion 3 N/mm and no finish film peel off was noticed. This fully meets the conventional shoe upper leather requirement. [34]

All the leather samples treated with silica sol-gel nanoparticle showed an improvement in water spotting resistance over control. J. Ma et al (2007) reported that water resistance increased by 14.02% on using silica sol-gel nanoparticle in leather coating. [34] The subjective evaluation results were given in Table IV. The leather samples treated with silica sol-gel nanoparticle conferred dull gloss when compared to control, so by using a minimum quantity of silica sol-gel nanoparticles gloss modification could be done. The value for control leather was 4 or 5 and for Trial IV it was 2 (5 g/L silica sol-gel nanoparticle used).

TABLE III
Performance Test Result for the Silica Sol-Gel Nanoparticles Coated Leather

Performance Properties	Trial-I	Trial-II	Trial-III	Trial-IV	Control
Wet & dry rub fastness- IUF 450 Dry 150 rubs (Material)	4 or 5	4 or 5	4 or 5	4 or 5	4 or 5
Wet & dry rub fastness- IUF 450 Dry 150 rubs (Felt)	4 or 5	4 or 5	4 or 5	4 or 5	4 or 5
Wet & dry rub fastness- IUF50 Wet 50 rubs (Material)	2 or 3	2 or 3	2 or 3	2 or 3	2
Wet & dry rub fastness- IUF 450 Wet 50 rubs (Felt)	1 or 2	2	1 or 2	2	1 or 2
Lastometer TM 24:1992 Load at grain crack, kg Mean	23.33	31.33	34	31.33	32.67
Lastometer TM 24:1992 Distension at grain crack, mm Mean	8.42	10.42	10.41	9.62	10.223
Water spotting SATRA PM185:1995 After 30 Minutes	No Mark	No Mark	No Mark	No Mark	Permanent Mark
Water spotting SATRA PM 185:1995 After 16 Hours	No Mark	No Mark	No Mark	No Mark	Permanent Mark
Water Vapor Permeability	3.4	3.5	3.3	5.3	3.3
Finish Adhesion Dry N/10mm	6.55	6.5	6.7	5.2	5.65
Finish Adhesion Wet N/10mm	1.7	2	2	2	2.05

TABLE IV
Subjective Evaluation Result for Silica Sol-Gel Nanoparticles Coated Leather

Performance Properties for Silica Sol-gel	Trial-I	Trial-II	Trial-III	Trial-IV	Control
Gloss	4	3 or 4	3	2	4 or 5
Covering	4	4	4	4 or 5	3 or 4
Levelness	5	5	5	5	5
Filling	3 or 4	3 or 4	3 or 4	4	3
Touch / Feel	Moderately waxy & smooth, 3	Highly waxy & smooth, 4	Highly waxy & smooth, 4	Highly waxy & smooth, 4	Moderately waxy & smooth, 3
Tackiness	5, Fully tack free	5, Fully tack free	5, Fully tack free	5, Fully tack free	5, Fully tack free
Fisheye	5, No fish eye	5, No fish eye	5, No fish eye	5, No fish eye	5, No fish eye
Plate Release	5, very easy plate release	5, very easy plate release	5, very easy plate release	5, very easy plate release	5, very easy plate release

Rating description: 5-Excellent, 4- Good, 3-Medium, 2-Poor, 1- Very poor.

The leather samples treated with sol-gel nanoparticles conferred better filling, levelness and settled appearance than the control. Low grade leathers could be up-graded by using minimum quantity of silica sol-gel nanoparticles.

Water vapor permeability of leather is a combination of two process viz., movement of water through stomas and transfer of water by hydrophilic groups of collagen under a certain vapor pressure. [35, 36] Generally, water vapor permeability of leather will decline after leather finishing. All the leather samples treated with silica sol-gel nanoparticles showed an improvement in water vapor permeability over control and this clearly indicates the porous nature of the coatings. [35, 36] Jianzhong Ma et al. (2006) reported that water vapor permeability increased by 11.5% on using silica sol-gel nanoparticle in leather coating and J. Ma et al (2007) reported that water vapor permeability increased by 9.15% on using silica sol-gel nanoparticles in leather coating[35] .In this experiment the water vapor permeability increased by 37.73% at a concentration of 5 g/L, when compared to control. The silica sol-gel nanoparticles have more intermediate pore space which may lead to better permeability characteristics in the finish film. The existence of SiO_2 nanoparticles increases the space of leather coating film and helps to improve water vapor permeability of finished leather. Nano SiO_2 increases the hydrophilic groups, which quickens the transmission of H_2O molecules[35] and the network formed by SiO_2 nano particles with the other acrylic and polymeric binders in the coating mixture during the film forming period improves water-vapor permeability of finished leather. [35] Finish formulations incorporating silica sol-gel nanoparticles enhance the physical, aesthetic and chemical properties of leather. An improved covering, filling and other finish performance properties were obtained because of the particle size, more surfaces to volume ratios (aspect ratio), which enhances the reactivity of SiO_2 nanoparticles with binders and other finishing auxiliaries.

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