Superhydrophobic Leathers through Sustainable Nanocomposites Coating Technology

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Superhydrophobic Leathers through Sustainable Nanocomposites

CSIR-Central Leather Research Institute, Chennai-600020, India

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Coating Technology

D R Sangeetha, N Nishad Fathima*

Abstract:

Superhydrophobic surfaces found in nature, such as the lotus leaf, have inspired the development of materials with exceptional water repellency and selfcleaning properties. Leather, by contrast, is intrinsically hydrophilic and therefore requires surface modification to attain such characteristics. In this study, a sustainable and fluorine - free superhydrophobic coating was developed using SiO, nanoparticles functionalized with hexamethyldisilazane (HMDS), with 3-aminopropyltriethoxysilane (APTES) employed as a coupling agent to enhance nanoparticle–polymer interaction. The prepared material was characterized by FT-IR, TGA, particle size analyser, FE-SEM and the covalent network of HMDS, -APS with SiO2 was confirmed. The modified silica nanoparticles were incorporated into acrylic resin (AR) and polyurethane (PU) binders to form hybrid nanocomposite coatings, which were deposited on leather substrates through a spray-coating application as base and top layers. The optimized formulation achieved a static water contact angle above 150°, confirming excellent water repellency along with a pronounced self-cleaning effect. Fastness tests demonstrated strong adhesion, abrasion resistance, and mechanical durability under practical usage conditions. This environmentally friendly approach eliminates the use of fluorinated compounds and provides a viable route for producing robust, self-cleaning, and waterrepellent leather surfaces suited for footwear, garment, and automotive upholstery applications.

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Corresponding author email : nishad@clri.res.in

1. Introduction:

Leather is widely in daily life and it is composed of collagen. It is well known that the leather is highly hydrophilic in nature due to abundance presence of hydrophilic groups such as amino group (-NH2), carboxyl group (-COOH) and hydroxyl group (-OH). Due to this, leather products are highly susceptible to damage from water and microbial attack1. Imparting superhydrophobicity to leather can effectively mitigate these issues. The concept of superhydrophobicity, also known as the lotus effect, was first discovered through observations of lotus leaves in nature Superhydrophobic coatings are characterised by high water contact angle (CA>1500) and low sliding angle (SA< 100) which is explained by Cassie-Baxter model. Superhydrophobic surfaces are designed by inducing the Cassie-Baxter state, in which microscopic air pockets trapped beneath a water droplet minimize its contact with the surface, resulting in high water repellence and self-cleaning property. To achieve this effect, two major attributes are there one is nano/micro scale roughness and the other one is low surface energy. When surface roughness is present water droplets rest partly on the air and partly on the solid forms the Cassie-Baxter state which leads to higher contact angle and lower sliding angle at the same time low surface energy material on the surface reduces adhesive forces between water droplets and the surface which enhances the self-cleaning property of the surface. Superhydrophobic surfaces have attracted significant area of research interest due to their extraordinary properties such as self-cleaning2, anti-corrosion,3 anti-fouling4, oilwater separation5, water resistant, anti-freezing6 and so on. Based on the above principle, numerous methods have

been developed to design and fabricate superhydrophobic surfaces, such as sol–gel process 7,8, chemical etching9,10, chemical or electric deposition11, polymerization and the combination of them12 . Although these techniques are capable of producing effective superhydrophobic most of them are expensive, which requires high equipment and reduces the chances for large scale production and also not suitable for leather applications. . Haung et al. developed a technique two step spraying method, one layer sprayed with

commercial adhesive and the other layer with 1H,1H,2H,2H-perfluorooctyltrichlorosilane(FOTS) on the CNC framework and the contact angle obtained was 158Ú and 156Ú. 13 Junfei Xu et al. prepared F-SiO2 suspension by modification of SiO2 by Heptadecafluoro1,1,2,2-tetrahydrodecyl dimethylchlorosilane (HFTD) coated it on nanochitin membranes and obtained contact angle about 1500.14 However, these approaches used fluoro based coupling agents or used fluoro based modifiers to obtain superhydrophobicity. In this study simple, facile and cost-effective spray coating method which is bottomup approach was used to develop fluorine-free coating for producing superhydrophobic surfaces on leather. SiO2 nanoparticles are ideal material for surface modification because due to their excellent chemical stability and the presence of abundant hydroxyl group(-OH), which readily reacts with organosilicon compounds like HMDS to achieve functional surface modifications. On modification of SiO2 with HMDS the surface hydroxyl groups(-OH) of SiO2 replaces by (-Si(CH3)3) groups while releasing ammonia as a by-product. This surface functionalisation results in the formation of an inorganic-organic hybrid structure, where the inorganic SiO2 core provides rigidity and thermal stability while the functional groups (- Si(CH3)3) from HMDS produce hydrophobicity which helps in reduce the surface energy of the material. The modified SiO2 (Sh) gives a base material of the coating, binders are used to fix the hydrophobic SiO2 on to the leather surface and APTES is used as a coupling agents between the binder and inorganic-organic hybrid which forms the micro/nano composite for coating. The prepared micro/nano composites with various binders were spray coated on leather surface.

2. Materials and Method:

Materials:

The purchased chemicals were AnalaR grade and it was used as received without any further purification. Silicon dioxide nanopowder(5-20 nm particle size (TEM), 99.5% trace metals basis), hexamethyldisilazane(HMDS,>99%), (3-aminopropyl) triethoxysilane(>99%), were purchased from Sigma Aldrich. Isopropyl alcohol, hexane was purchased from Rankem chemicals. Crust leathers for coating were given by tannery, CSIR-CLRI, Chennai, India. Commercial binders used was commercial grade procured from Karthik Eco Technologies Pvt.Ltd, India. Acrylic resin was prepared according to our previous report5

Method:

The obtained silica nanoparticles were dispersed in hexane. For the modification of SiO2 surface quantitative amount of HMDS were added and the reaction kept for 8 hrs at room temperature. The obtained mixture was centrifuged, washed with hexane and dried to obtain superhydrophobic SiO2 nanoparticles.

Characterisation Techniques:

The morphology of the sample and coated leather was analysed using a field-emission scanning electron microscopy was performed with Tescan-Clara FE-SEM at an accelerating voltage of 10kV. The size of the modified silica and coating formulation were studied using Dynamic light scattering and zeta potential from Malvern Zeta-sizer nano ZS using a 4mW He/Ne laser (632.8 nm wavelength) with a scattering angle of 1750. The presence of functional groups in coating formulation was confirmed by Fourier transform infrared spectrum was measured using JASCO-FT/IR 4200 spectrometer with 4 cm-1

resolution in the region of 4000 to 400 cm-1 over a KBr pellet with an average of 32 scans, and ATR spectrum was measured in JASCO-FT/IR-4200 spectrometer using a PRO470-S ATR module recorded over a diamond prism with 4 cm-1 resolution in the region from 4000 to 400 cm-1

with an average of 32 scans. The thermal stability of the

Sample Name Leather used Type of coat Material used for coating formulation

AR Crust Base coat Sh+ AR +CA

coated samples was tested using Thermalgravimetric Analysis (TGA) by Q50 TA Instruments from 30 to 600oC in an air flow with a ramp of 10oC per minute. The contact angle of the leather samples before and after coating were measured in the Holmark Opto mechatronics Contact

CAR Crust Base coat Sh+ CAR +CA

PU1 Base coat

Top coat Sh+ B1 +CA

finished

PU2 Base coat

Top coat Sh+ B2 +CA

finished

PU3 Base coat

Top coat Sh+ B3 +CA

finished

For Control in coating formulation Sh and CA was not used

Table 1. Type of material coated, type of coat and leather used for leather coating and the sample names

3. Results and Discussion:

FT-IR spectra of SiO_2 and HMDS modified SiO_2 (Sh) are shown in (Figure 1b). The peaks at 466 cm^{-1}, 798 cm^{-1} and 1078 cm^{-1} shows bending, symmetric stretching and asymmetric stretching of Si-O-Si bond, the peak at 3448 cm^{-1} and 958 cm^{-1} are associated with stretching and bending vibration of -OH groups in SiO_2. In Sh peaks at 2955 cm^{-1} and 1398 cm^{-1} confirms the stretching and bending vibrations of C-H bond from $-CH_3$ groups after successful modification of SiO_2 by HMDS. The peak at 844 cm^{-1} shows the stretching vibration of Si-C which confirms the modification from Si-OH to $Si-CH_3$ and also

Angle Instrument. The fastness property of leather was

tested by circular rubbing technique using SATRA UK model

7350 machines. The abrasion for the leather was done using

Martindale abrasion tester GT-7012-M, Go tech.

there is decrease in intensity of 3448 cm^{-1} which shows

decrease in -OH terminal and successful modification of

SiO_2 by methyl groups from HMDS. From (Figure 1a),

it can be seen that there is increase in size from SiO_2 to Sh after successful modification of SiO_2 by HMDS.

Thermal Gravimetric Analysis of the sample are shown

in (Figure 1c). it can be seen that total weight loss of

SiO_2 is 32% whereas Sh is 17.64% which shows that

there is increase in thermal stability after the

modification of SiO_2. The SEM micrographs were

shown in (Figure 1d) which confirms the morphology

remains same after the modification.

Figure 1. (a) Particle size of SiO_2 and Sh. (b) FT-IR spectra of SiO_2 and Sh. (c) TGA of SiO_2 and Sh.

(d) SEM micrographs of SiO_2 and Sh.

Figure 2. Comparison of Contact angle of AR1, AR2, PU1, PU2, PU3 and contact angle images of their

respective experiment.

1 AR1-AR1 AR1 AR1 107˚ 149˚ 105˚ 140˚

2 AR1-PU3 AR1 PU3 103˚ 121˚ 89˚ 116˚

3 AR1-PU2 AR1 PU2 128˚ 132˚ 110˚ 129˚

4 PU1-AR1 PU1 AR1 126˚ 139˚ 122˚ 136˚

S.No Type Base coat* Top coat**

Control Experiment Control Experiment

5 PU2-AR1 PU2 AR1 106˚ 149˚ 103˚ 143˚

*(Binder+ Sh), **(Binder+Sh+CA), Sh-HMDS modified SiO_2, Crust leather was used for coating

Table 2. Different combination of base coat and top coat formulation using AR, CAR, B1, B2 and B3

Sample

Base

Top coat

Type of coating

Name

coat

(in IPA)

AC IPA AR1 Control 110˚ 105˚

AE Sh+IPA Sh+ AR1+

Experime

CA

FC IPA B2 Control 130˚ 122˚

FE Sh+IPA Sh+ B2+

Experime

CA

Table 3. Contact angle of coated leather AC, AE, FC and FE.

Coating of hybrid nanocomposites on the leather surface

The prepared hybrid nanocomposite using AR1 and various commercial binders like AR2, B1, B2, and B3 as shown in Table 1 were spray coated on leather surface as a base coat and top coat. Contact angle of the coated leather was taken for control and experiment. The obtained results suggest that the contact angle of the experiment is higher than the control leather as shown in Figure 2, maximum

Contact angle before

Contact angle after

plating

plating

Contact angle

Without

With plating

plating

nt 156˚ 143˚

nt 154˚ 140˚

contact angle of 1440 was achieved. After plating the contact angle of the coated sample decreased to almost 200. To overcome this issue and also to increase hydrophobicity another approach was taken for coating. The curst leathers were taken for this approach and various combination (shown inTable2) of base and top coat was done on the leather surface by spray coating method and their respective contact angle before and after plating are also tabulated. The contact angle of all the samples showed very good hydrophobicity even after plating. The

contact angle of the samples AR1-AR1 and PU2-AR showed almost 1490 which is close to superhydrophobicity and also those samples show sliding angle of 200 which was not enough to achieve superhydrophobic effect on leather. Therefore, AR and filler PU binders were further used to enhance superhydrophobicity. Another approach of spraying different formulation at the base coat and top coat were done. In that, base coat is primarily consists of Sh nanoparticles dispersed in IPA and the top coat consist of Sh nanoparticles, binder (AR and B2) and coupling

Figure 3. Contact angle images of coated leather samples for AR-AR, AR-NCS, AR-FPU, SPU-AR, FPU-AR.

Dry 512 rubs Wet 256 rubs

Sample Name

Material Felt Material Felt

AC 4/5 4/5 4/5 4/5

AE 4/5 4/5 4/5 4/5

FC 4/5 4/5 4/5 4/5

FE 2 2/3 4/5 4/5

Table 4. Rubfastness of coated leather AC, AE, FC and FE

agent (CA). Top coat helps to fix the Sh nanoparticles on to the leather surface and it also helps to further increase the hydrophobicity. The samples AC, AE, FC, and FE are acrylic based control, acrylic based experiment, filler PU based control and filler PU based experiment, detailed information are tabulated in Table 3. It also shows that contact angel of AE and FE are 1560 and 1540. The fastness property of these coated leathers is shown in Table 4. The reports suggest that the material has good adhesion on to the leather surface.

FE FC

AE AC

Figure 4 Images of water droplets beading up on the leather surface.

4. Conclusion:

Superhydrophobic SiO2 nanoparticles were taken on the leather surface by various synthesised acrylic resin and various commercial binders using spray coating method. The contact angle of the leather shows in range 13001490 with various micro/nano composites without losing the leather properties and higher coating stability. The micro/nano composites with synthesised acrylic resin and filler PU show higher contact angle of 1560 and 1540 with sliding angle of 80 and 100. The samples of leather AE and FE developed from synthesised acrylic resin and filler PU showed overall good performance in contact angle, sliding angle, fastness property and abrasion cycle. Therefore, superhydrophobic leather was developed by facile spray coating method and further development from this material is needed for the improvement of contact angle even after abrasion.

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