DEVELOPMENT OF SUSTAINABLE SUPERHYDROPHOBIC LEATHERS

Sangeetha Dhanapathy Renukadevi [1,2], Nishad Fathima Nishter [1,2,3]

1. Inorganic and Physical Chemistry Laboratory, Council of Scientific and Industrial Research-Central Leather Research Institute (CSIR-CLRI), Adyar, Chennai-600020, India.

2. Academy of Scientific and Innovative Research (AcSIR), Ghaziabad-201002, India.

3. Department of Leather Technology, AC Tech Campus, Anna University, Chennai-600025, India.

Abstract

Superhydrophobic surfaces have their significant applications due to their water repellency nature and self-cleaning properties. Generally, to create a superhydrophobic surface, fluoro-based compounds are used. In this work, we have developed a sustainable superhydrophobic leather coating using HMDS (Hexamethyldisilazane) modified SiO_2 (Sh) nanoparticles with 3-aminopropyltriethoxysilane (CA) as a coupling agent to coat acrylic resin (AR) and commercial PU binders onto the leather surface. We tried different combinations of this nanocomposite coatings to achieve superhydrophobic leather surface. Nanocomposite was tried for both base coat and top coat application as well.

Contact angle of about 150˚ has been achieved and the leathers exhibited self-cleaning behaviour as well. The fastness properties of the treated leather were tested according to the standard tests and the results showed that the coated material has good adhesion onto the leather surface. Thus, a sustainable superhydrophobic coating has been achieved successfully, which will have several applications including footwear, garment and upholstery applications.

Keywords: Superhydrophobicity, Self-cleaning leathers, Finishing, Nanocomposite.

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 attack[1]. 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>150˚) and low sliding angle (SA< 10˚) 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-cleaning[2], anti-corrosion,[3] anti-fouling[4], oil-water separation[5], water resistant, anti-freezing[6] 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 etching[9,10], chemical or electric deposition[11], polymerization and the combination of them[12] . 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 158˚ and 156˚. [13] Junfei Xu et al. prepared F-SiO_2 suspension by modification of SiO_2 by Heptadecafluoro-1,1,2,2-tetrahydrodecyl dimethylchlorosilane (HFTD) coated it on nanochitin membranes and obtained contact angle about 150˚.[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 bottom-up approach was used to develop fluorine-free coating for producing superhydrophobic surfaces on leather. SiO_2 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 SiO_2 with HMDS the surface hydroxyl groups(-OH) of SiO_2 replaces by (-$Si(CH_3)_3$) groups while releasing ammonia as a by-product. This surface functionalisation results in the formation of an inorganic-organic hybrid structure, where the inorganic SiO_2 core provides rigidity and thermal stability while the functional groups (-$Si(CH_3)_3$) from HMDS produce hydrophobicity which helps in reduce the surface energy of the material. The modified SiO_2 (Sh) gives a base material of the coating, binders are used to fix the hydrophobic SiO_2 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 report

Method:

The obtained silica nanoparticles were dispersed in hexane. For the modification of SiO_2 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 SiO_2 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 175˚. 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 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 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.

Sample Name	Leather used	Type of coat	Material used for coating formulation
AR	Crust	Base coat	Sh+ AR +CA
CAR	Crust	Base coat	Sh+ CAR +CA
PU1	Base coat finished	Top coat	Sh+ B1 +CA
PU2	Base coat finished	Top coat	Sh+ B2 +CA
PU3	Base coat finished	Top coat	Sh+ B3 +CA

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 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.

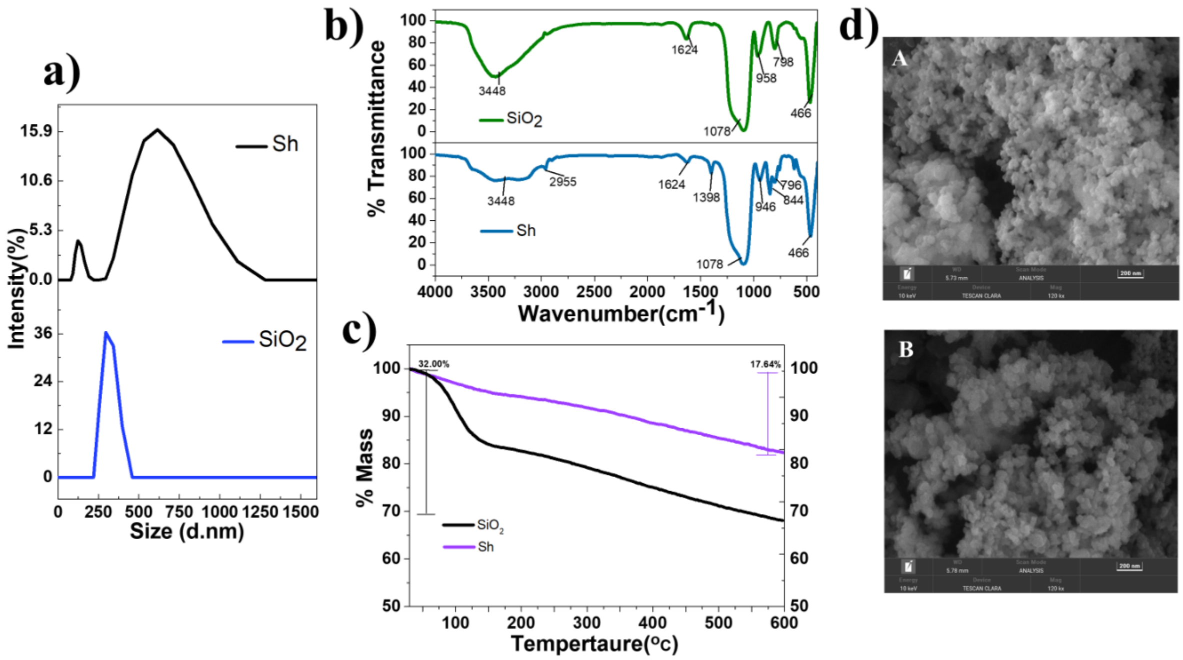

Figure 1. a) Particle size of SiO_2 and Sh. b) FT-IR spectra of SiO_2 and Sh. c) TGA of SiO_2 and Sh. d) SEM micrographs of SiO_2 and Sh.

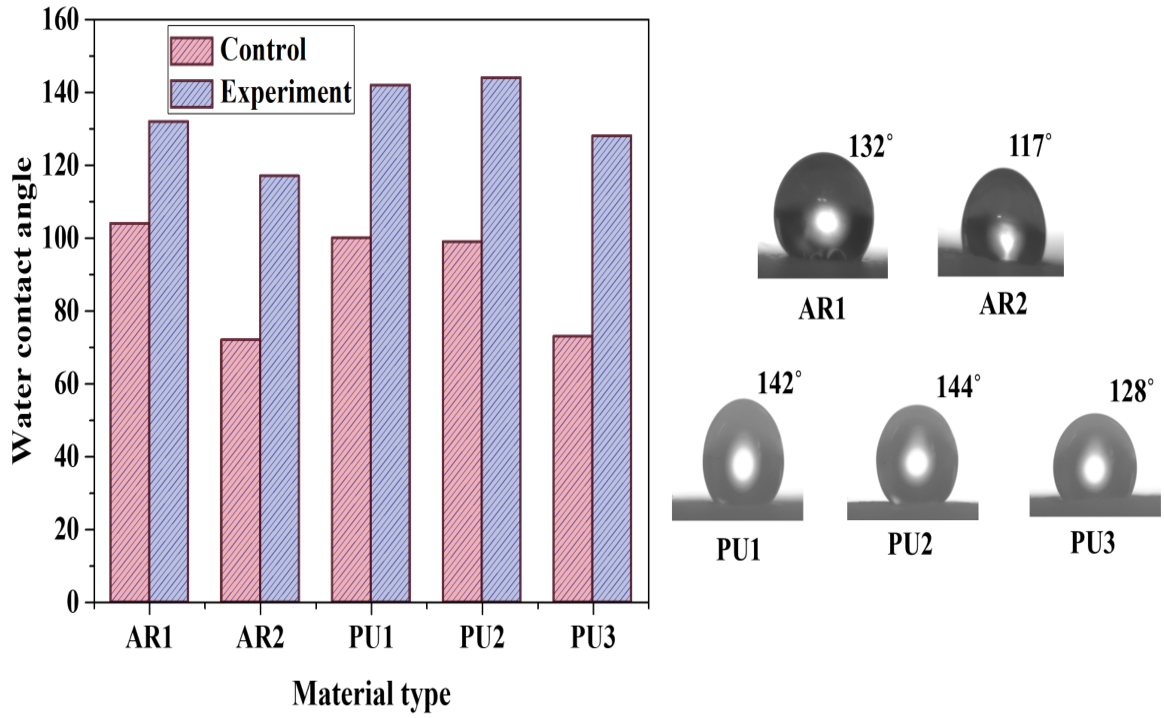

Figure 2. Comparison of Contact angle of AR1, AR2, PU1, PU2, PU3 and contact angle images of their respective experiment.

S.No	Type	Base coat*	Top coat**	Contact angle before plating		Contact angle after plating	
				Control	Experiment	Control	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˚
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

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 of 144˚ was achieved. After plating the contact angle of the coated sample decreased to almost 20˚. 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 149˚ which is close to superhydrophobicity and also those samples show sliding angle of 20˚ 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 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 156˚ and 154˚. 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.

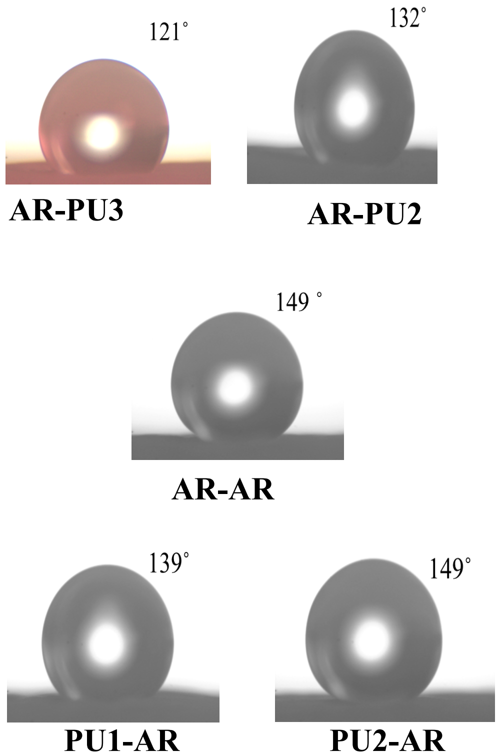

Figure 3. Contact angle images of coated leather samples for AR-AR,

Sample Name	Base coat	Top coat (in IPA)	Type of coating	Contact angle	
				Without plating	With plating
AC	IPA	AR1	Control	110°	105°
AE	Sh+IPA	Sh+ AR1+ CA	Experiment	156°	143°
FC	IPA	B2	Control	130°	122°
FE	Sh+IPA	Sh+ B2+ CA	Experiment	154°	140°

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

Sample Name	Dry 512 rubs		Wet 256 rubs	
	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

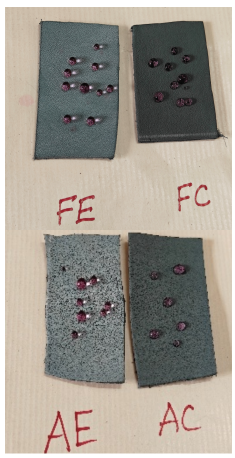

Figure 4 Images of water droplets beading up on the leather surface.

4. Conclusion:

Superhydrophobic SiO_2 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 130°-149° 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 156° and 154° with sliding angle of 8° and 10°. 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.

5. Acknowledgement:

The authors gratefully acknowledge Speciality Chemicals Mission project (MMP035201) for the financial support. The authors would like to DLT and ILTA(SR) for the travel grant.

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