

Anticorrosive Polyurethane Clear Coat with Self-Cleaning Character

Nihit Madireddi, P. A. Mahanwar

Abstract—We have aimed to produce a self-cleaning transparent polymer coating with polyurethane (PU) matrix as the latter is highly solvent, chemical and weather resistant having good mechanical properties. Nano-silica modified by 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane was incorporated into the PU matrix for attaining self-cleaning ability through hydrophobicity. The modification was confirmed by particle size analysis and scanning electron microscopy (SEM). Thermo-gravimetric (TGA) studies were carried to ascertain the grafting of silane onto the silica. Several coating formulations were prepared by varying the silica loading content and compared to a commercial equivalent. The effect of dispersion and the morphology of the coated films were assessed by SEM analysis. All coating standardized tests like solvent resistance, adhesion, flexibility, acid, alkali, gloss etc. have been performed as per ASTM standards. Water contact angle studies were conducted to analyze the hydrophobic character of the coating. In addition, the coatings were also subjected to salt spray and accelerated weather testing to analyze the durability of the coating.

Keywords—FAS, nano-silica, PU clear coat, self-cleaning.

I. INTRODUCTION

SELF-CLEANING coatings in the recent times have received a high recognition considering the performance aspects that are required in the modern era fighting pollution and global warming related aspects saving time and money in various ways explained in literature [1], [2]. The concept evolved from the Lotus plant which tend to keep their leaves clean despite growing in dirty waters [3], [4] and many more plants and animals [5]-[7]. However, most of the self-cleaning progress has been carried out toward the limited substrate application like glasses and waterproofing textiles [8], [9]. Water resistant coatings for stones especially to preserve ancient archaeological architectures from harsh climates were in existence for long periods [10], but over the years, the approach has been diversified into other substrate applications to metal, textiles, and wood. Considering a much more general application of a self-cleaning mechanism to automotive will help to fight corrosion and maintain the aesthetics of vehicle, in the sense keep it dirt free all times achieved by the beading effect of the paint film. The self-cleaning can be achieved by two methods, hydrophilicity and hydrophobicity. However, application in consideration i.e. for automobile where corrosion is driven factor, a hydrophobic concept would ease

out the solution [10]. Numerous researches have been carried out extensively on the use of materials for decreasing surface energy and increasing the roughness of the surface to impart the self-cleaning characteristics [5], [11]-[13]. One of the key materials to do so will be the use of fluoro alkyl silanes (FAS) whose CF_2 links have the lowest possible surface energy thus making the surface hydrophobic [12]. In addition, fluoropolymers provide low T_g , low viscosity along with best thermal and UV stability making them ideal for use in outdoor applications.

Polyurethanes have gained high commercial importance due to excellent solvent, chemical and weather resistance along with excellent adhesion, flexibility, and hardness due to presence of soft and hard segments [14]. Their application is wide spread from original equipment manufacturer (OEM) coats, automotive refinish, industrial, and other sectors [15]. On the other hand it is learnt that organic-inorganic hybrids are redefining the industry due to their potential in redefining the applications. Most of the researches carried with these materials make use of nano scaled materials due to the well-known fact that properties of material at nano scale are very different from that of a micron scale. For example, a nano particle of gold displays rich red color whereas the micron particle emits gold yellow due to their difference in absorption spectrum. So in making of these hybrids, nano-silica was found to be one of the highly used inorganic material apart from TiO_2 . However, due to the high thermal and UV stability of nano-silica it can be considered as highly suitable material for outdoor application. Even though many works were reported using TiO_2 for outdoor applications considering its potential to generate radicals to destroy dirt and dust etc., there is high probability that the generated radicals degenerates the binder of the coating in the process of degrading dirt and dust thereby losing the sole purpose of protection. Different from additives there exist a class of materials called silanes which can effectively react with the inorganic materials and can control the interactions with water. They have been highly useful in either generating hydrophilic or hydrophobic materials.

In the current study, we created an organic-inorganic coating using nano-silica modified with fluoro based silane (a fluoropolymer) and incorporated into a polyurethane based system for outdoor application. Thus, the coating is a cluster of all the significant characteristics of individual class of materials as explained above. The coated films were then subjected to standard coating performance tests and self-cleaning properties were assessed.

Nihit Madireddi is with Department of Polymer and Surface Engineering, Institute of Chemical Technology (corresponding author, phone: +919867946106, e-mail: nihitchemical@gmail.com).

P. A. Mahanwar is Professor in Department of Polymer and Surface Engineering, Institute of Chemical Technology, Mumbai, India (e-mail: pa.mahanwar@ict.edu.in).

II. EXPERIMENTAL

A. Materials

Acrylic polyol used for the study was Setalux D A 365 BA/X from Nuplex Industries Limited, a free sample supplied by Aroma Agencies, Mumbai. Hexa methylene di-isocyanate (HMDI) was obtained from Bayer India under the trade name of Desomudur N3390. Hydrophilic nano-silica AEROSIL 200 was supplied by Degussa, Germany. 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane (POTS) procured from Alfa Aesar, UK. Tinuvin 900 and 292 were procured from BASF India. Di butyl tin di laureate (DBTDL) from Sigma Aldrich and surface slip additive used was Byk 333 of BYK additives supplied by Aroma Agencies, Mumbai. The solvents Methoxy propyl acetate (DOWANOL PMA) was obtained from Dow India Limited and Toluene, Ethyl acetate (EA) and Butyl acetate (BA) was supplied by SD fine Chem Limited. All the chemicals were used as received.

B. Functionalization of Nano-silica

5g of silica was taken in 150ml excess of toluene and ultrasonicated for an hour and kept under mechanical stirring at 700 rpm thereafter. The mixture was heated to 50°C and maintained. Calculated amount of fluoroalkylsilane was added to the mixture and allowed it to stir for 12h under continuous mechanical stirring. The mixture was then centrifuged at 4500 rpm to collect the suspended particles. These particles were later washed with toluene four times to remove any leftover FAS content and then with water. The particles were then dried at 60°C for three days.

C. Preparation of Nano-composite Coating

The composition of the prepared paint was shown in Tables I and II. Varying on the addition of nano-silica content from 0%, 2%, 4%, 6%, 8% and 10% weight basis on solid content of resin, various batches have been prepared B1 to B5 using non modified silica and M1 to M5 using functionalized silica. A standard batch S without nano-particles was considered to be standard or a commercial equivalent throughout the study. The steps involved are initial dispersion of nano-silica into the solvents using ultra sonication. Then UV absorber tinuvin 900 and hindered amine light stabilizer tinuvin 292 were added under mechanical stirring followed by the resin. Later the slip additives and catalyst DBTDL was added and then mixed with HMDI.

TABLE I
COMPOSITION OF VARIOUS NANO-COMPOSITE BASED PAINTS USING NON MODIFIED SILICA

Material	S wt%	B1 wt%	B2 wt%	B3 wt%	B4 wt%	B5 wt%
Acrylic Polyol	61	60.29	59.58	58.86	58.15	57.43
Nano-silica	0	0.79	1.59	2.39	3.19	3.99
HMDI	9.15	9.04	8.94	8.83	8.72	8.61
Tinuvin292	0.5	0.49	0.48	0.48	0.47	0.47
Tinuvin 900	0.79	0.78	0.77	0.77	0.76	0.75
Byk 333	0.3	0.3	0.3	0.3	0.3	0.3
DBTDL(5%)	0.08	0.08	0.08	0.08	0.08	0.08
PMA	6.38	6.38	6.39	6.40	6.41	6.42
BA	19.55	19.58	19.60	19.63	19.66	19.68
EA	2.25	2.25	2.26	2.26	2.26	2.27
Total	100	100	100	100	100	100

TABLE II
COMPOSITION OF VARIOUS NANO-COMPOSITE BASED PAINTS USING MODIFIED SILICA

Material	M1 wt%	M2 wt%	M3 wt%	M4 wt%	M5 wt%
Acrylic Polyol	60.29	59.58	58.86	58.15	57.43
Func. Nano-silica	0.79	1.59	2.39	3.19	3.99
HMDI	9.04	8.94	8.83	8.72	8.61
Tinuvin292	0.49	0.48	0.48	0.47	0.47
Tinuvin 900	0.78	0.77	0.77	0.76	0.75
Byk 333	0.3	0.3	0.3	0.3	0.3
DBTDL(5%)	0.08	0.08	0.08	0.08	0.08
PMA	6.38	6.39	6.40	6.41	6.42
BA	19.58	19.60	19.63	19.66	19.68
EA	2.25	2.26	2.26	2.26	2.27
Total	100	100	100	100	100

D. Application

The mild steel panels were used in the study. The panels are surface treated by wiping with toluene and dried for use. The treated surface was then casted with synthesized paint and dried at 80°C for 1 hour to enable curing of the coating.

III. CHARACTERIZATION

The particle size and distribution was determined using Nanoplus make Particulate systems analyzer. The structure of particles was elucidated by scanning electron microscopy. FTIR spectra were recorded from Bruker make Fourier transform infrared spectroscopy (FTIR) instrument. Thermo gravimetric analysis was performed using Pyris of Perkin Elmer make. Energy dispersive spectra were recorded by EDAX instrument. The self-cleaning properties like contact angle and surface energy were assessed by using contact angle goniometer of Rame-hart make. Gloss evaluated using Glossmeter of Gardener instrument make at 60° inclination. Corrosion tests were carried using salt spray chamber as per ASTM B117. The accelerated weather testing was carried out by using QUV of Q-panel lab instruments as per ASTM D4587. Adhesion was ascertained with cross cut adhesion test ASTM D2197 using 3M adhesion tapes, scratch hardness of the films were determined with 3M hardness pencils ASTM D3363 and also using mechanical load bearing hardness tester. In addition to this, some general tests like impact resistance ASTM D2794, solvent resistance ASTM D5402, hot water resistance ASTM D870, alkali and acid resistance ASTM D1308 and flexibility analysis using conical mandrel ASTM D522 were investigated. The dry film thickness was measured by nondestructive test methods ASTM D1186 using elcometer make nondestructive DFT meter.

IV. RESULTS AND DISCUSSION

A. Studies on Size and Morphology of Functionalized Nanoparticles

Ascertained from the lotus leaf morphology it is necessary to create roughness on the surface to attain hydrophobic characteristic [16]. In order to do so the particle size plays an important role. In this study, we have aimed to use nano dimensioned particles to create the roughness on the surface

and it becomes mandatory to quantify the size after modification. The sample preparation involved mixing both silica's into water and ultra-sonicated for 15min. The analysis indicated that the functionalized silica had particle size varying between 70nm and 300nm while the unmodified silica is less than 50 nanometers. The increase in particle size after modification clearly indicates the attachment of long fluoro organic chains to silica particles as shown in Fig. 1. The nano-silica particles were subjected to scanning electron microscope to reconfirm the dimensions and the nature of particles. SEM images of modified particles as shown in Figs. 2 (a) and (b) confirmed the presence of various particle sizes from 70nm to 170nm with particle being spherical in shape and bulkier compared to unmodified particles. Thus, this study confirms that the modified particles have retained their size in nanometers as desired and the modification of nanoparticles is not 100%.

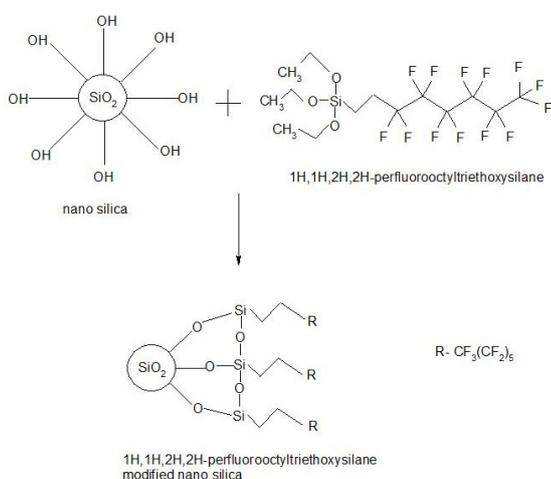


Fig. 1 Schematic representation of modification carried on nano-silica particles

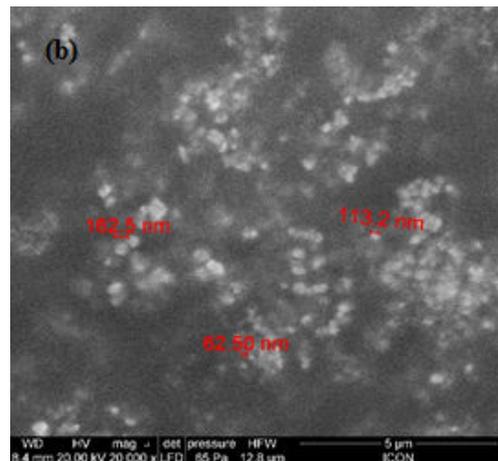
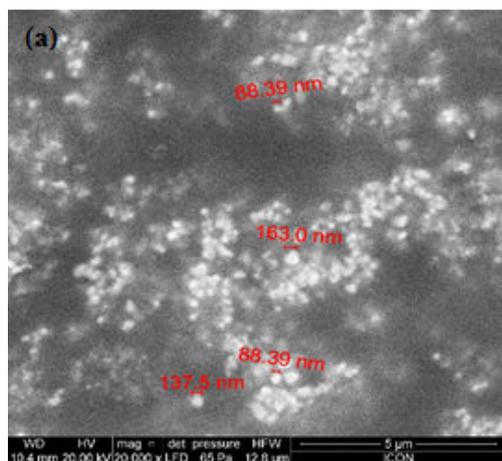


Fig. 2 SEM images of the Modified Silica Nanoparticles

B. FTIR Studies

Fig. 3 shows the FTIR spectra for the unmodified and modified silica. The aerosil graph (a) indicates the characteristic peaks at 470cm^{-1} , 807cm^{-1} and 1100cm^{-1} attributed to rocking, bending, and asymmetric stretching of Si-O-Si bonds [17]. The peaks at 3400cm^{-1} and 1630cm^{-1} are due to the OH groups from nano-silica [18]. In addition to the above peaks the (b) indicates the presence of C-O-Si asymmetric stretching modes due to the strong bands present between $1200\text{-}1000\text{cm}^{-1}$ and bands between $1000\text{-}600\text{cm}^{-1}$ likely due to C-C stretching modes, Si-H deformation and C-O-Si symmetric stretching. The presence of C-F group is detected on the intense absorptions around 1046cm^{-1} . The adsorption bands for C-F₂ and C-F₃ were found at 1192cm^{-1} and 1098cm^{-1} [19].

C. Thermogravimetric Analysis

This test was performed to confirm the grafting of 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane onto silica particles. The samples were subjected to continual heat up to 800°C at $30^\circ\text{C}/\text{min}$. Fig. 4 shows the TGA graph for unmodified and modified silica. As seen in Fig. 4, the observed weight loss up to $100\text{-}110^\circ\text{C}$ in both cases is due to evaporation of water or any leftover traces of toluene. The continual loss in weight of the unmodified silica is due to dehydroxylation of the silanol groups. Even though same phenomenon was expected in modified one but the weight loss increased over 500°C attributed to the degradation of long chain fluoro organic present on silica. The weight loss was found to be 34% higher than non-modified silica at 600°C as shown in Table III.

D. Contact Angle Studies

The static contact angle of the casted paint panels are shown in Fig. 5. The standard panel (S) indicated a contact angle of 70° . The contact angles made by panels loaded with non-modified silica into the urethane matrix system had no significant change and the values varied between $70\text{-}80^\circ$ only, even though the loading increased from 2wt% to 10wt% indicating that roughness is not the only parameter sufficient enough to generate hydrophobic nature [5], [11]. It should be

noted that there was decrease in surface energy and the surface energy was measured using sessile drop method which uses young's Laplace equation to determine the surface energy where ΔP is differential pressure between liquids at interface and R_1 and R_2 are radii of curvature of drop

$$\Delta P = \gamma(1/R_1 + 1/R_2) \quad (1)$$

However, in the case of modified silica the contact angle increased from 71° to reach a maximum of 119° on an average.

Fig. 6 shows the highest recorded contact angle was 125° on a panel with 8% loading. However loading of 8% modified silica into the urethane matrix was found optimum as further increase led to the decrease in measured contact angles. A sharp decrease in surface energy levels with increase in modified silica loadings noted might be due to the migration of low surface energy fluorine materials towards the top surface of the film indicating that both roughness and surface energy modifier required to attain better water repellent nature as shown in Fig. 7.

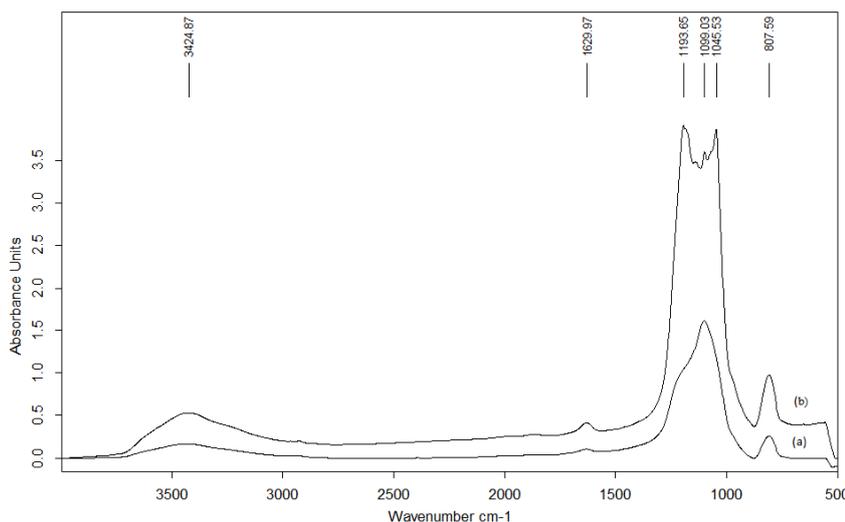


Fig. 3 FTIR spectrum of (a) aerosil (unmodified silica) and (b) fluoroalkylsilane modified silica

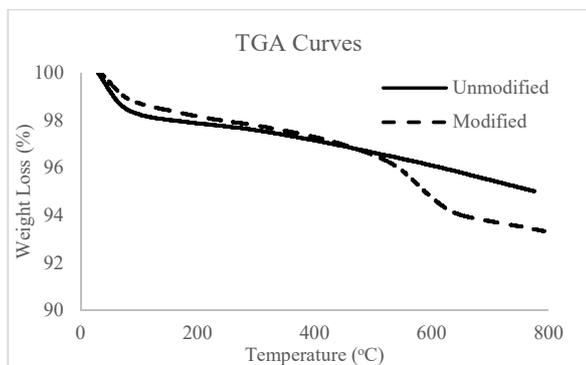


Fig. 4 Thermogravimetric curves for unmodified and modified silica

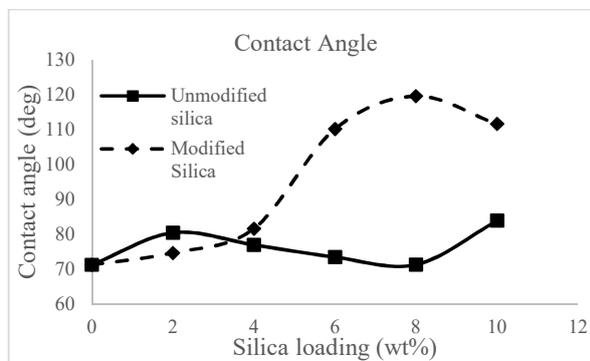


Fig. 5 Contact angle for unmodified and modified silica systems

TABLE III
TGA DATA FOR THE UNMODIFIED AND MODIFIED SILICA

Temperature (°C)	100	500	600	700	800
Silica weight loss (%)	1.74	3.36	3.90	4.51	4.99
Modified silica weight loss (%)	1.28	3.46	5.25	6.25	6.67

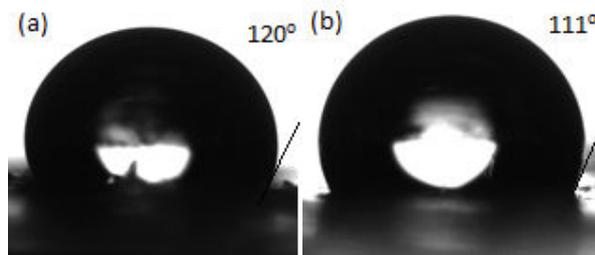


Fig. 6 Contact angles made by films with 8wt% and 10wt% modified silica as shown in (a) and (b) respectively

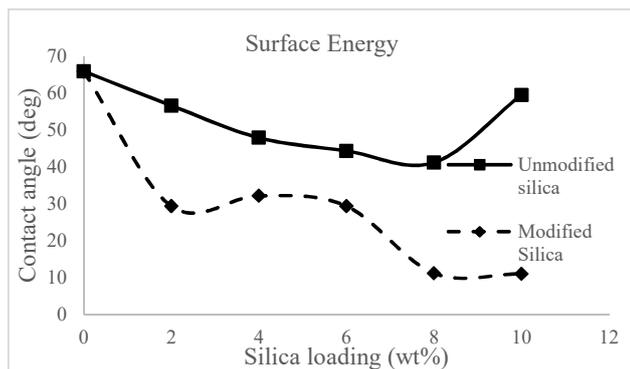


Fig. 7 Surface energy of unmodified and modified silica systems

E. SEM and EDS Analysis

From the contact angle study, it was found that films with 8% loading of functionalized silica had given best performance. To ascertain the factors that were responsible to this we have carried out topological and elemental analysis. The SEM image of the film as shown in Fig. 8 indicates the presence of the silica particles in the polyurethane matrix. It was clear from the images that there are minimal silica void areas in the film and thereby dispersion was effective. However, the presence of agglomerates is keenly visible on the image and can be avoided by using high shear mixers. Fig. 9 shows the elemental analysis of the film obtained by energy dispersive X-ray spectroscopy. The results clearly indicate the presence of silica and fluorine ascertaining that during the curing process the modified silica particles with low surface energy 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane migrated towards the top layer and justifies the increase in contact angle and decrease in surface energy primarily attributed to presence of C-F_x linkages.

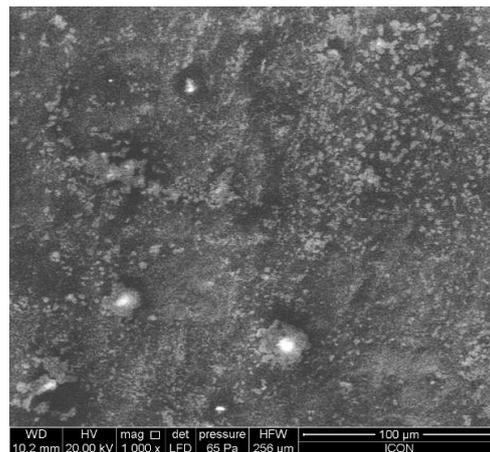


Fig. 8 Scanning electron micrograph of the silica containing film

F. Mechanical Properties of Coating

The films were subjected to various general performance tests and the results are displayed under Table IV. The films were found to pass all the tests without abnormality. Few points to note from the table are that of gloss and hardness. Gloss is an important parameter which is evidential for aesthetics. A comparative study of gloss has been made as shown in Fig. 10. It can be learnt from the graph that with an increasing content of silica the gloss decreased. A huge drop in gloss value observed for film loaded with 6% or more but the films with modified silica attained a stable value probably due to the crosslink network of modified silica particles. However, in comparison to the standard the overall gloss of the films reduced. Another key property is the hardness of the coating. The hardness of the coating is attributed to chain mobility. Modified silica films had better hardness due to more networking and less chain mobility of the silica particles in the matrix compared to unmodified silica which was evident when loading increased over 8% as shown in Fig. 11. However, in comparison to a standard or non-silica film the hardness increased from a minimum of 55% at 4% loading to maximum of 125% at 10% loading while the 8% loading yielded an 80% increase.

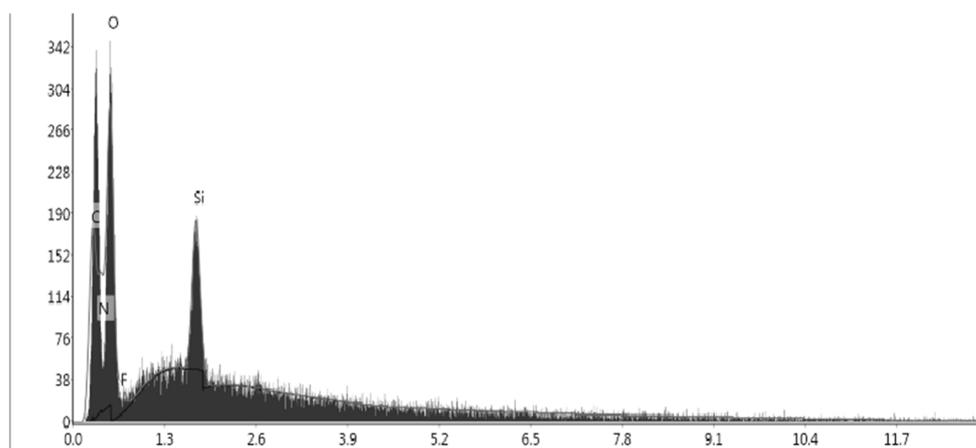


Fig. 9 Energy dispersive spectra of the silica containing film

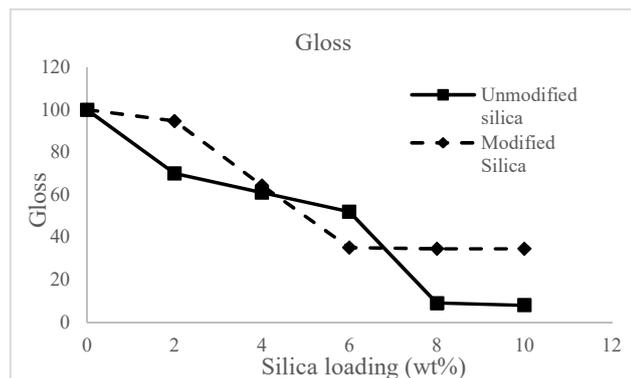


Fig. 10 Gloss readings of the coated films with unmodified and modified silica

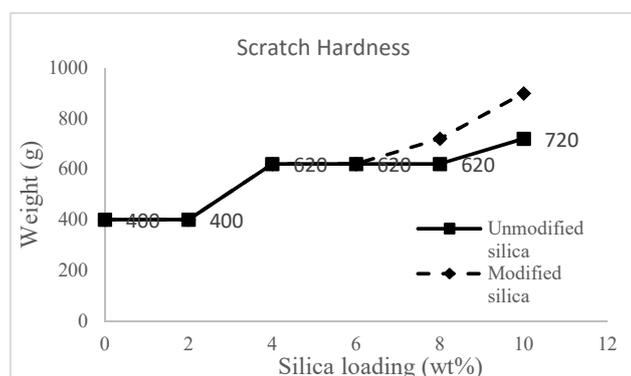


Fig. 11 Scratch hardness results of modified and unmodified films

G. Corrosion Studies

The test results of the panels subjected to salt spray as per ASTM standard are shown in Fig. 12. The standard panel has

passed the corrosion test of having less than 3mm creep and no adhesion failure along with panels loaded with 2% and 4% silica. However, the increasing content of silica made the matrix porous for the chemical to penetrate through, resulting in failure of the corrosion test and the physical condition is shown in Figs. 12 (c)-(f). In contrast and as per expectation the panels with modified silica loadings were much stable at the end of 120h as shown in Figs. 12 (g)-(k). This is due to the presence of highly chemical resistant fluorine on the surface and the silica modification with long chains helped forming networks there by reducing the porous nature of the film. Thus, we can say these films are highly corrosion resistant.

H. Accelerated Weather Testing

The samples are subjected to 500 hours of UV exposure as per ASTM D4587 subjecting the coated panels for 8h UV irradiation and 4 hours condensation cycle repeatedly. The effect on gloss, delta E values as shown in Figs. 13 and 14. It is evident that the coating are stable in terms of gloss and delta E as minimum decrement was observed both with modified and unmodified versions of silica. Contact angle studies are made to analyze the effect of UV on the hydrophobic nature of the sample as shown in Fig. 15. The films with unmodified silica were found to exhibit better gloss and color retention compared to the films containing modified silica after UV treatment. The films were found to lose the hydrophobic character drastically when modified silica content was greater than 6 wt%. The increase in hydrophilic character might be due to the increase in surface silanol groups on the leftover unmodified silica during the condensation part of the testing phase.

TABLE IV
PERFORMANCE PROPERTIES OF COATED PANELS

Test	B0	B1	B2	B3	B4	B5	M1	M2	M3	M4	M5
DFT	65	70	60	60	70	62	66	70	63	70	67
Gloss	100	70	64.3	52	9	8	94.7	64	35	34	34
Hot water resistance	P	P	P	P	P	P	P	P	P	P	P
Adhesion	P	P	P	P	P	P	P	P	P	P	P
Pencil Hardness	4H	4H	5H	5H	6H	6H	4H	5H	5H	6H	6H
Scratch Hardness (in g)	400	400	620	620	620	720	400	620	620	720	900
Impact resistance	P	P	P	P	P	P	P	P	P	P	P
Flexibility	P	P	P	P	P	P	P	P	P	P	P
Acid resistance	P	P	P	P	P	P	P	P	P	P	P
Alkali resistance	P	P	P	P	P	P	P	P	P	P	P

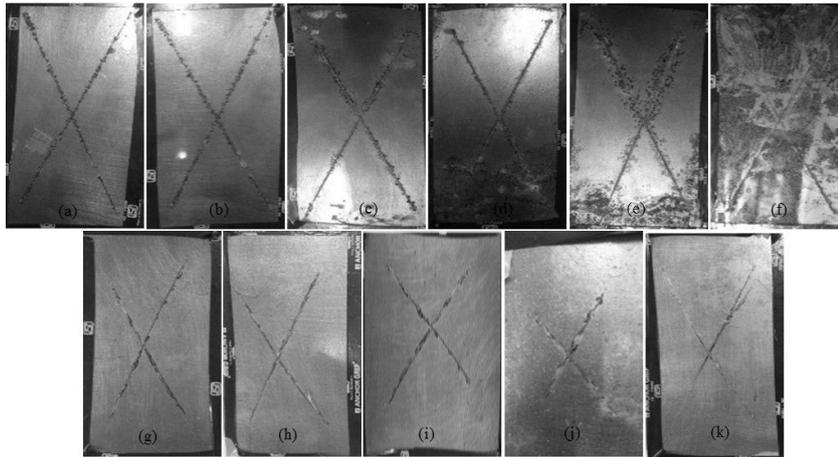


Fig. 12 Panels subjected to salt spray for 120h (a) standard (b-f) with unmodified silica loading in increasing order from 2 wt% to 10 wt% left to right and (g-k) with modified silica from 2 wt% to 10wt% left to right

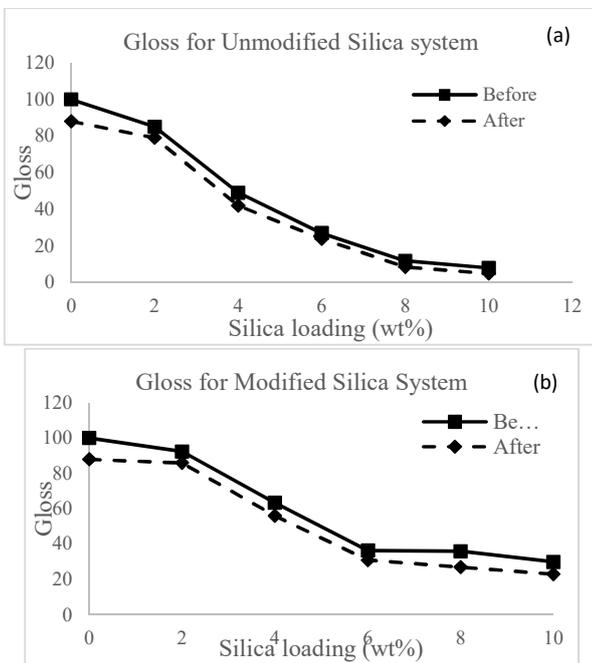


Fig. 13 Gloss readings after QUV test for (a) films with unmodified silica and (b) films with modified silica

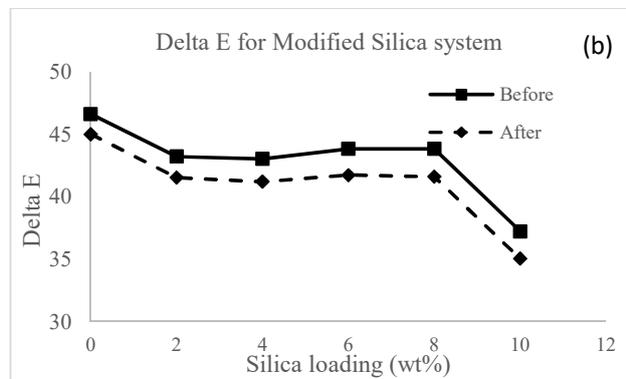
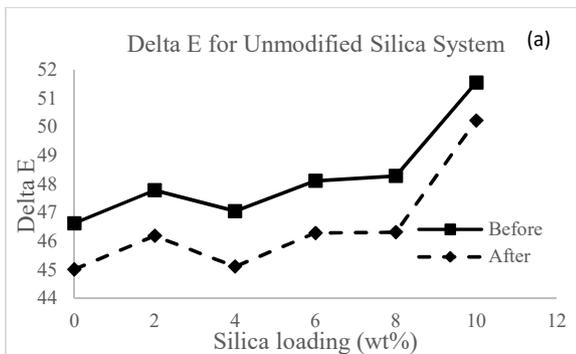
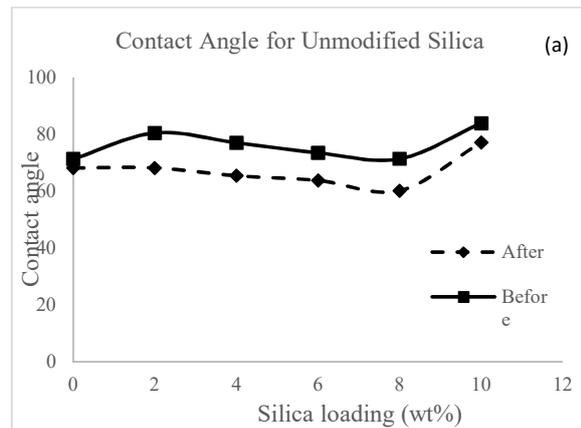


Fig. 14 Delta E readings after QUV test for (a) films with unmodified silica and (b) films with modified silica



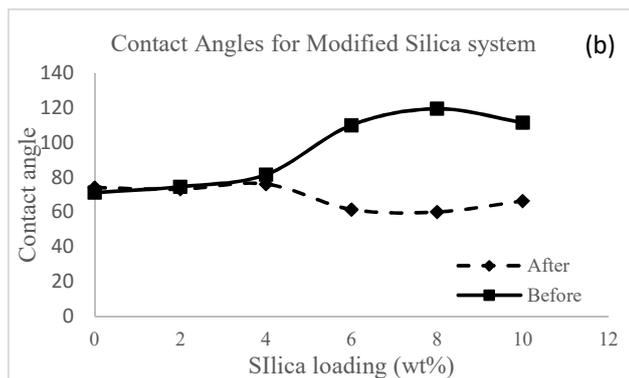


Fig. 15 Contact angle readings after QUV test for (a) films with unmodified silica and (b) films with modified silica

V. CONCLUSION

In this work, a polyurethane based hydrophobic clear coat has been designed to aim at self-cleaning outdoor application like that of an automobile using nano-silica modified by fluoroalkyl silanes for surface energy modification. The modified particles were in nanometers ascertained by SEM and particle size analysis which are required to create the desired roughness. The dispersion of silica into matrix was also found to be good. The resultant coating showed a prospective increase in contact angle compared to the commercial standard along with improvement in several general coating performance parameters except for gloss which may be enhanced by using additives to deliver glossy surface or by improving the orientation of silica. The coating was found to be highly anticorrosive based on salt spray test for 120hours of single coat on bare substrate without primer protection. The decrease in self-cleaning capability of the coating post UV exposure can be overcome by complete functionalization of nano-silica with the silane.

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