

Hydrophobic Self-Cleaning Coating Based on Siloxane Modified Waterborne Polyester

Garima Verma¹, Sarojini Swain², A. S. Khanna³

^{1,3}Corrosion Science & Engineering, Indian Institute of Technology Bombay, Mumbai, Maharashtra, India,

²Crompton Greaves Ltd., Mumbai, Maharashtra, India, 400042

Abstract: Considerable efforts have been made over the last few decades for developing self-cleaning surfaces exhibiting high water contact angles. In this respect, a chemical method has been used to develop a hydrophobic self-cleaning coating for metal substrates which involves the use of hydroxyl terminated polydimethyl siloxane (PDMS) to achieve a rough surface with lower surface energy. The coating was prepared using lower molecular weight polyester as resin, dimethylethanolamine (DMEA) as neutralizing agent, hexamethylmethoxymelamine (HMMA) as cross-linker and *para*-toluene sulphonic acid (p-TSA) as catalyst. The influence of PDMS on the hydrophobicity and self-cleaning property was studied by static contact angle and dust repellency test respectively. It was observed that the contact angle got increased from 70° to 104° with no further change even after increasing the coating thickness. The hydrophobicity of the PDMS modified coating was sustained upto a temperature ranging from 25°C to 90°C and also upto 48 hrs of water exposure. The PDMS modified polyester coatings were characterized by surface roughness measurements (AFM), scanning electron microscopy (SEM), EDAX, Fourier transform infrared (FTIR) spectroscopy, self-cleaning test and water contact angle measurements.

Keywords: Waterborne, Hydrophobic, Self-cleaning, Siloxane

1. Introduction

Self-cleaning coatings have received a great deal of attention lately, both in research and in commercial applications. Concept of self-cleaning surface has come from nature, such as lotus plant leaves [1] and the exoskeleton of some insects [2]. This natural self-cleaning property depends upon surface hydrophobicity. In order to mimic the available super hydrophobic surfaces available in nature, different artificial super hydrophobic surfaces has been prepared by different means, including the generation of roughness and also the rough surfaces coated with low surface energy molecules [3-8]. It has also been reported that the contact angle or wettability is a function of surface roughness. However, the modification of the liquid droplets behavior and in particular of their wetting properties on these surfaces is still a challenging issue. Functional surfaces with controlled wetting

properties, which can respond to external stimuli, have attracted huge interest of the scientific community due to their wide range of potential applications, including microfluidic devices, controllable drug delivery and self cleaning surfaces. The water drop obtains a spherical shape on the hydrophobic surface. Therefore, the adhesion and contact area both reduces noticeably and water drop rolls off over such surface, picks up dirt particles with it and cleans the surface. Wenzel developed an equation that relates the roughness with the contact angles of a flat surface of a certain material and that of the rough surface of the same material and is given by:

$$\cos\theta = Rf\cos\theta_0 \quad (1)$$

Where θ = contact angle of a rough surface, θ_0 = contact angle of a flat surface, and Rf = roughness factor of the rough surface. The roughness factor is defined as the ratio of the total surface area of the rough surface and the projected area of the rough surface or the footprint of the total surface area.

This model predicts that for a surface to become more hydrophobic by introducing roughness, then θ_0 must be greater than 90° . If θ_0 is less than 90° then the contact angle for the rough surface will decrease with increasing R_f . [9] Contact angle or wettability is a deciding factor for self-cleaning property of a surface which is controlled by chemical composition and the morphology of the surface [10, 11]. A number of physical and chemical methods have been used to control the surface roughness and lower the surface energy to enhance the water contact angle. Static water contact angle is a criteria used for evaluation of the hydrophobicity for the estimation of self-cleaning property [12].

The water contact angles in the range of $95-115^\circ$ were reported on smooth surfaces using chemical method and further enhancement of contact angle occur due to an increase in surface roughness [13, 14]. Chemical method involves the use of different chemical like silanes, siloxanes, fluoro compounds and nano-particles to modify the surface properties to achieve hydrophobic surfaces. By far, the most common material is poly (dimethylsiloxane) (PDMS). Central to its widespread use for surface modification is the fact that it has a lower surface tension than other hydrocarbon-based polymers [15]. The main objective of the work is to produce a dust repellent surface for out door application where the hydrophobicity was taken into consideration. In the present work, chemical method has been used to achieve hydrophobic surface. Hydroxyl terminated polydimethyl siloxane has been used as surface modifier with waterborne polyester to reduce surface energy as well as to create rough surface [16].

2. Experimental

2.1 Materials

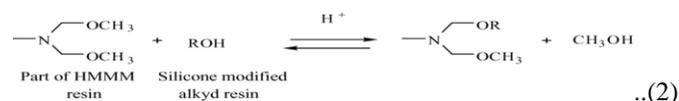
The waterborne polyester resin (Worlee Pol 191); and cross-linking agent hexa (methoxymethyl) melamine (HMMM) were purchased from Worlee-Chemie GmbH, Germany. Hydroxyl terminated polydimethylsiloxane (OH-PDMS) was procured

from BYK, Germany. Dimethylethanolamine (DMEA) was used as neutralizing medium. Some additives such as defoamer & wetting agent were also procured from BYK. Flash rust inhibitor, long-term corrosion inhibitor and blocked acid catalyst *paratoluene* sulphonic acid (*p*-TSA) were purchased from King Industry, Germany, and were used in as received condition. Aluminum panels were purchased from Popular Panels Mumbai.

2.2 Preparation of the waterborne coatings

A low molecular weight polyester resin was first neutralized by dimethylethanolamine (DMEA) neutralizing agent and then followed by the addition of de-ionized water with adequate agitation till a clear solution was obtained. The pH of resin solution was maintained between 8.0-8.5. Cross-linking agent, hexamethylmethoxy melamine (HMMM) and *para*-toluene sulphonic acid (*p*-TSA) catalyst were added after the completion of neutralization of resin. The mixing ratio of resin: crosslinker (70: 30) was fixed on the basis of literature available [17]. Different additives such as flash rust inhibitor, long term corrosion inhibitors, wetting agents and defoamer were added.

To modify with PDMS, siloxane (OH-PDMS) (6 wt%) was added before the neutralization and the ratio of siloxane and resin was adjusted in such a way that the amount of resin with siloxane was 70% of the formulation. The coating was applied on the metal panels using brush application. The panels were cured in oven at 160°C for 20 min and were allowed to attain room temperature.



2.3 Preparation of the Coated Panels

The mild steel panels of size ($10 \times 6 \text{ cm}^2$) are de-greased and cleaned with acetone and then roughened mechanically with

emery paper (grade no. 600) prior to coating. Both polyester and PDMS modified polyester coating formulations were applied using brush onto the aluminum substrate to achieve uniformly coated panels with good finish. The coated panels were allowed to oven cure for 20 min at 160°C.

2.4 Characterization & testing

2.4.1 Microscopy & Spectroscopy

The structural properties were studied using controlled scanning electron microscope (SEM), (Hitachi S-3400N) and the same was also used for the EDAX analysis with a tungsten source, working distance of 10 mm and beam intensity of 15kV.

The surface roughness was measured using a Digital Instrument nanoscope IV Multimode Scanning Probe Microscopic controller, veeco metrology group, operated in contact mode with etched silicon probe which has a nominal radius of 20 nm. The AFM used has a Z-range of about 7 µm and calculated surface roughness average (Ra) values from AFM image analysis.

The FT-IR was done using Nicolet Magma 550 FT-IR spectrometer to understand the extent and effectiveness of cross-linking by observing the appearance of the new peaks related to siloxane modification.

2.4.2 Contact Angle Measurement

The hydrophobic properties of the coated panels were assessed from contact angle measurement using Phoenix instrument. The measurements were made using deionized water droplets at room temperature in ambient atmosphere. For each measurement, a 0.5 µL droplet was dispensed onto the sample under investigation. Superhydrophobicity was identified in cases where the water droplet did not adhere to the surface (i.e., it rolled off). Therefore, the contact angle values were measured by increasing the droplet volume to 5 µL and further

touching a water droplet toward the underlying surface until the water droplet can be pulled down to the sample surface.

2.4.3 Hardness Measurement

The hardness properties of the coatings were evaluated using Nanoindenter instrument named TI-900, Hysitron Inc, USA with a Berkovich diamond indenter tip to calculate surface hardness and scratch resistance. The nanoindentation experiments were performed under the displacement control mode. The rates of loading and unloading were both 100 nm/s and a 10 s holding was applied at the maximum indentation depth of 1 µm.

2.4.4 Dust repellency Test

These tests were carried out to check the self-cleaning property of coating according to ASTM 3450 & 4828. This test method covers the determination of the relative ease of removal of common soil, stains and soilant discolorations from the dried film of an interior coating with or without washing. This includes a way to evaluate the film for washability properties and changes in appearance.

3. Results & Discussion

3.1 Microscopy & Spectroscopy

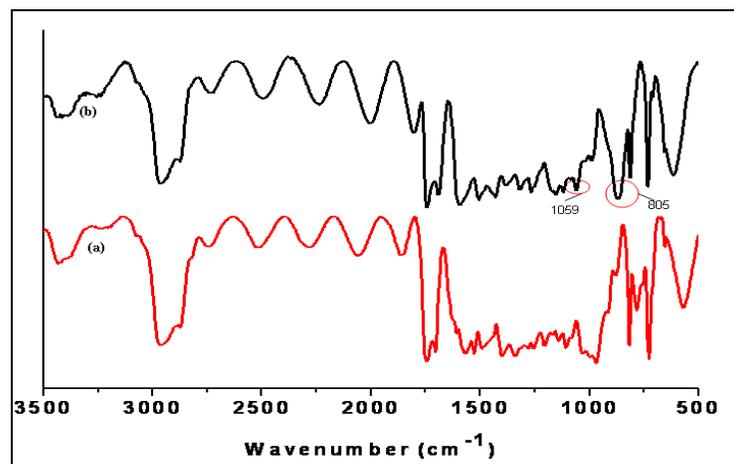


Fig.1 FTIR spectra of (a) neat polyester, (b) PDMS modified polyester after curing

The study of change in the chemical structure of the polyester coating before and after modification with PDMS was performed by FTIR analysis. The FTIR spectrum of unmodified and modified polyester is shown in Figure 1. The crosslinking reaction between polyester and HMMM was already given in equation 2. The same reaction occurred between siloxane modified polyester and HMMM.

Figure 1 clearly indicates that the spectra of siloxane modified polyester coating was very similar to that of neat polyester coating; however a major difference being the intensification of peak at 1058 cm^{-1} which was due to the formation of Si-O-Si bonds and at 805 cm^{-1} assigned to symmetric Si-O stretching mode in the siloxane modified polyester resin. The peak intensity at about 3500 cm^{-1} , corresponding to O-H stretching of the secondary hydroxyl in polyester resin, decreased after the siloxane modification, indicating that the hydroxyl groups were consumed by the modification reaction, leading to a decrease in intensity of the absorption peak.

Fig. 2 shows the SEM surface micrographs of neat polyester and PDMS modified polyester coatings. Fig. 2(a), represent SEM surface micrograph of polyester coating depicted as neat sample. The presence of small crater or void like structure on the surface can be clearly seen. The EDAX results at three different points confirm that the crater like structure is a feature of neat polyester and elemental composition is same every where. The presence of voids was confirmed by AFM results shown in Fig. 3(a). The section analysis was also done at three different voids and it was found that the depth of these voids is less than 100 nm with small diameter as shown in Fig. 3(a). The surface roughness of neat polyester is $\sim 14\text{ nm}$ due to the presence of voids or crater like feature.

Fig.2 (b), shows SEM micrograph of PDMS modified polyester coating and it was observed that the size (diameter

as well as depth) of the voids or crater increases after modification with PDMS and it becomes broader and deeper. The EDAX results at three different points confirm the presence of the siloxane modification since the percentage of Si element become significantly very high at point 1 and 2 (crater or void like structure). Increase in the size of voids was confirmed by AFM microstructure analysis Fig. 3(b). The depth of the craters or voids was calculated approximately 500 nm using section analysis in AFM which confirms significant increase in the surface roughness (Fig. 3(b)).

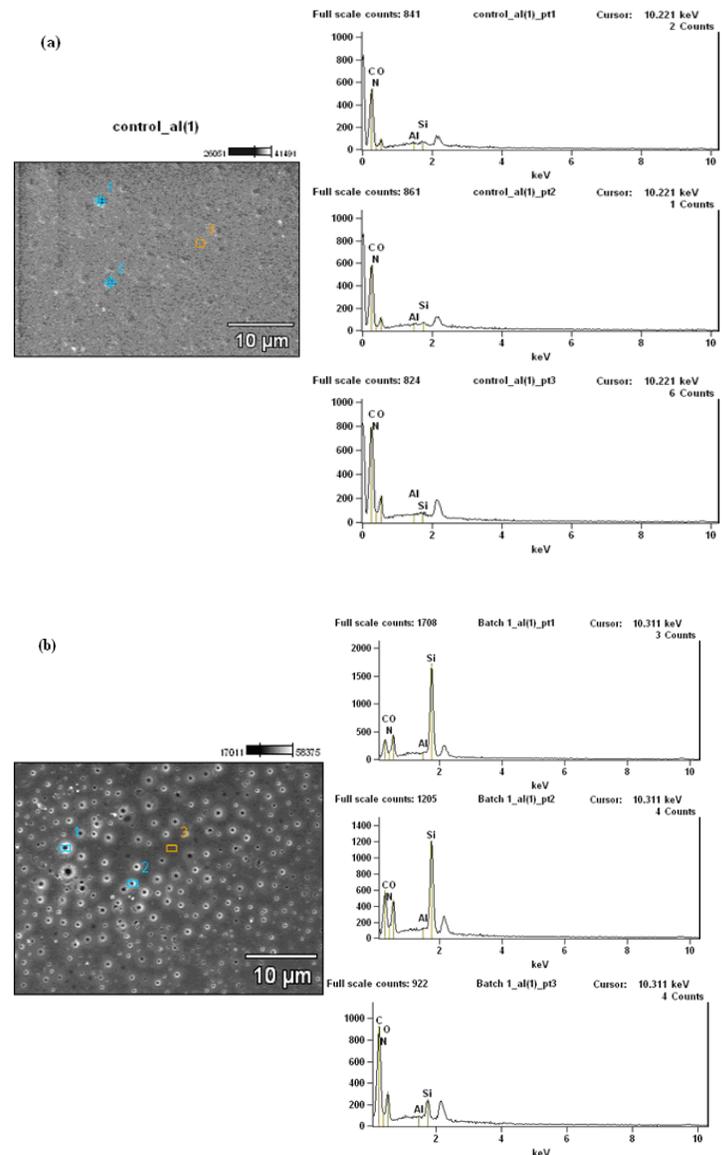


Fig. 2 SEM & EDAX images of the (a) Neat Polyester (b) PDMS modified Polyester

As the polyester resin used here is water based therefore it has the tendency to dry faster. Once the surface dry is achieved the below layer tends to release the water and which creates a channel like structure to release water and the water vapor creates the void on the surface of the film where the PDMS Leaching site is created and as shown in the EDAX, at that point only the Si is higher and other part of the film the concentration of Si is lower.

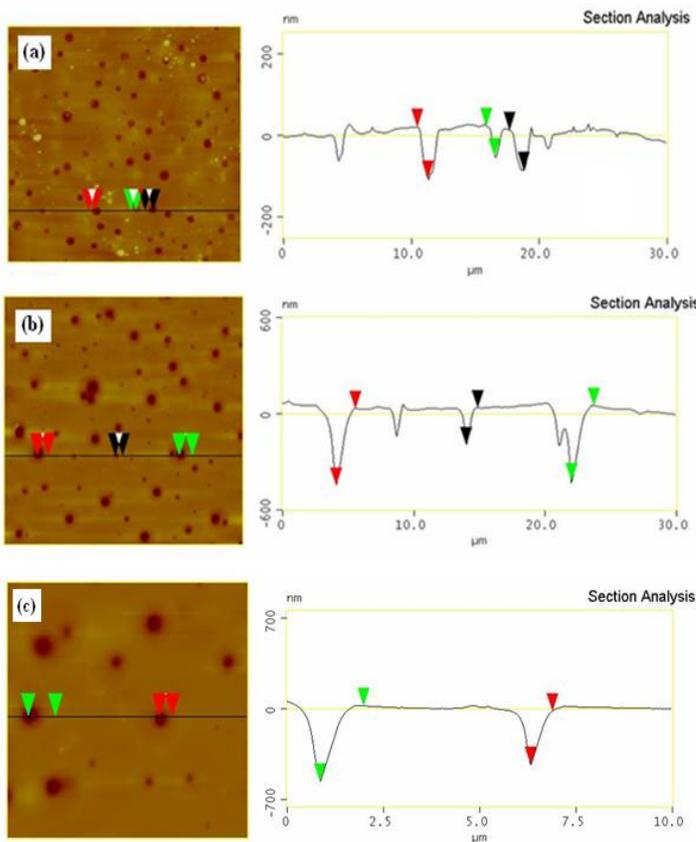


Fig. 3 AFM section analysis images of the coated surface at 30 μ m x 30 μ m (a) Neat Polyester (b) PDMS modified Polyester (a & b) both single coated, (C) Double coated (80 \pm 5 μ) PDMS modified polyester

Table 1 Values obtained from AFM for neat polyester & PDMS modified polyester resin

S. No.	Sample details	Mean Roughness (Ra) in nm	Max Height (Rmax) in nm
1.	Neat Polyester resin (coated surface at 30 μ m x 30 μ m)	15.07	99
2.	PDMS modified Polyester resin (coated surface at 30 μ m x 30 μ m)-SINGLE COAT	50.05	532.72
3.	PDMS modified Polyester resin – DOUBLE COAT	49.85	459.49

Table 1 shows the surface roughness (Ra) and crater or void height (Rmax) recorded by AFM technique. The mean roughness value for polyester resin is recorded to be 15.07 nm and Crater or voids height (Rmax) is 99 nm. Where as for PDMS modified polyester resin at the same coating thickness, the Ra was 50.05 nm and Rmax was 532.72 nm. Since water contact angle depends on surface roughness, therefore contact angle increases from 70⁰ to 104⁰ after modification of waterborne polyester with PDMS due to increase in surface roughness. Fig. 2(C) and Table 1 shows that there is no change in the surface roughness with the increase in the coating thickness as the Ra value remains almost same around 50 nm.

3.2 Contact Angle Measurement

Surface wetting ability of the hybrid films was investigated by contact angle measurement. Table 2 represents the contact angle of water droplet on coated aluminum panels. From Table 2 it can be seen, that the angle made on neat polyester coated panel shows a contact angle of 70⁰ at room temperature, indicating a hydrophilic nature of polyester coating. However, after modification with PDMS it was found that there was an increase in contact angle up to 104⁰ \pm 2,

resulting into hydrophobicity. It is noted that hydrophobicity depended on both surface roughness and the chemical composition that can lower surface energy sufficiently [16]. In present work, PDMS typically has been used as the hydrophobic constituent due to its low surface energy of 16-21 mN·m⁻¹ [18] which makes it a good candidate for hydrophobic coating. Water contact angle depends on surface roughness and surface energy. There are different factors such as temperature, coating thickness and exposure to water, which can affect surface roughness and surface energy and consequently it can reduce the water contact angle. To study the effect of temperature on water contact angle, thermal stability test of the coated panels of Al substrate were conducted at different temperatures. No change was observed in the water contact angle even after heating the coated panels at different temperature ranging from 25^oC to 90^oC as shown in Fig. 4 which indicate the thermal stability of Si-C bond of the coating.

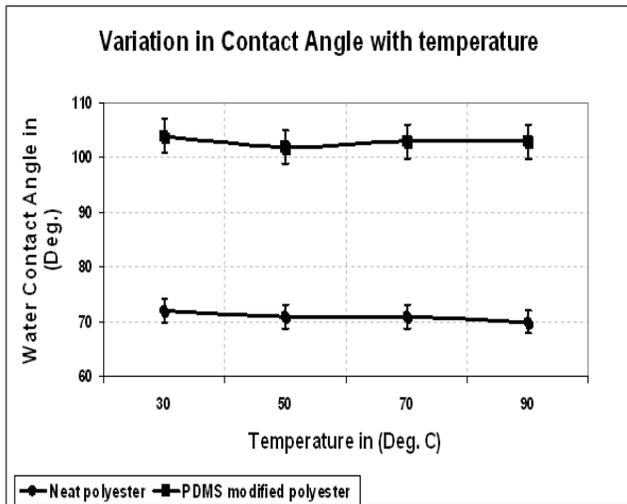


Fig. 4 Variation of water contact angle at different temperatures

To study the sustainability of hydrophobicity of coating, it was exposed to water from 24 to 48 hr and it was observed that contact angel of neat polyester reduces significantly after 24 hr but it increased after 48 hr whereas no significant change in contact angle was observed in case of siloxane modified polyester coating even after 48 hr (Table 2). It could be

attributed to the sensitivity of polyester coating towards water which has been improved after modification with siloxane.

3.3 Hardness Measurement

The hardness of the film was measured using nano indentation technique where it was found that the hardness of the neat polyester film was 0.085 GPa and for PDMS modified polyester resin it was 0.317 GPa which is around 273 % rise in the hardness value as shown in Fig. 6. Similarly the Hmax (Depth of penetration) is determined in nm. It was observed that the depth of penetration in case of neat polyester resin is much higher i.e. 823 nm in comparison to PDMS modified polyester resin (429 nm), which shows that the film with neat polyester resin is soft in comparison to that of PDMS modified polyester resin and allows easy penetration in to the film so the depth of scratch will be higher in neat polyester than PDMS modified polyester resin as shown in Fig. 5(a). On the other hand, the profile of the scratch was not straight and uniform for PDMS modified coating (Fig. 5b), suggesting the resistance towards scratch damage after modification. It can be attributed that the crosslinking between PDMS modified polyester coating and HMMM resulted into complex structure with higher crosslinking density, where the presence of inorganic content from PDMS (Si-O-Si) resists the coating from scratch damage resulting into non uniform scratch track as compared to the neat polyester coating where the appearance of scratch track is comparatively smooth [19].

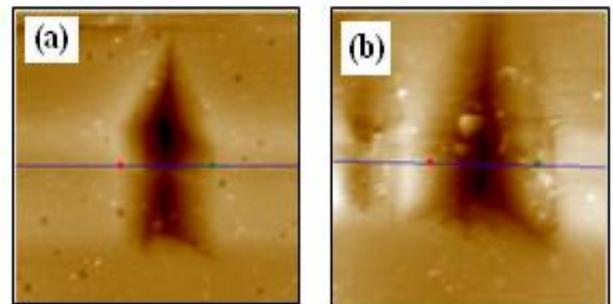


Fig. 5 Scan of scratch of (a) Neat polyester & (b) PDMS modified polyester

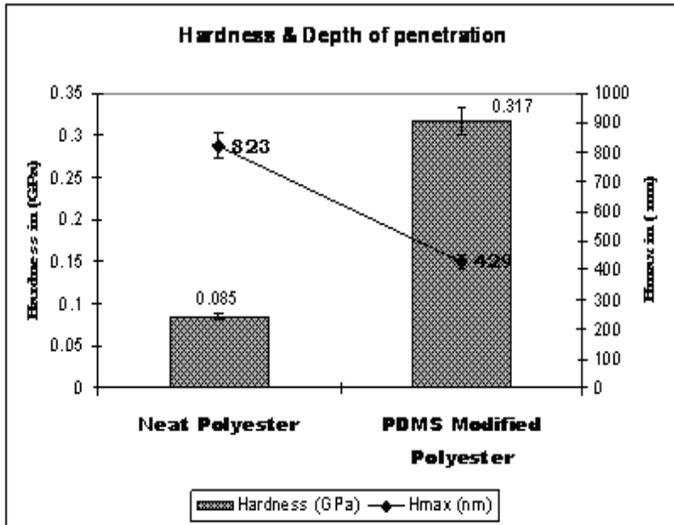


Fig. 6 Hardness & Depth of penetration for (a) Neat Polyester and (b) PDMS modified polyester

Table: 2 Variation of contact angle at different conditions

S. No	Sample details	Water Contact Angle in Degree (Average value) with Standard Deviation
1.	Neat Polyester At 30 ⁰ C	72 ⁰ ± 0.8 ⁰
2.	PDMS modified Polyester resin At 30 ⁰ C	104 ⁰ ± 0.9 ⁰
3.	Neat Polyester At 50 ⁰ C	71 ⁰ ± 0.7 ⁰
4.	PDMS modified Polyester resin At 50 ⁰ C	102 ⁰ ± 0.8 ⁰
5.	Neat Polyester At 70 ⁰ C	71 ⁰ ± 0.9 ⁰
6.	PDMS modified Polyester resin At 70 ⁰ C	103 ⁰ ± 1 ⁰
7.	Neat Polyester At 90 ⁰ C	70 ⁰ ± 0.8 ⁰
8.	PDMS modified Polyester resin At 90 ⁰ C	103 ⁰ ± 0.9 ⁰
9.	Neat Polyester after 24 hrs Water Immersion	62 ⁰ ± 0.6 ⁰
10.	PDMS modified Polyester resin after 24 hrs Water Immersion	100 ⁰ ± 0.9 ⁰
11.	Neat Polyester after 48 hrs Water Immersion	69 ⁰ ± 1 ⁰
12.	PDMS modified Polyester resin after 48 hrs Water Immersion	99 ⁰ ± 0.8 ⁰

It is clear from the results that the hardness of the coating increases after modification with PDMS due to the incorporation of Si-O-Si linkage, hard inorganic content. Also, it can be seen from the depth of the indent made in neat and the PDMS modified polyester coating, the depth of indent for the neat polyester coating is more, whereas the depth of indent for PDMS modified coating is very less almost half of the neat polyester coating. It indicates that PDMS modified coating does not allow the probe to go deeper as it goes in case of neat polyester coating due to increased hardness as observed in depth of penetration in Fig. 6.

3.4 Dust repellency Test

Fig. 7 shows photographs of panels stained with different type of dust (carbon black & methyl red powder). There tests were conducted at room temperature as well as 100⁰C on Al substrates for neat polyester and PDMS modified polyester. Fixed amount of the dust is placed on the coated panel for 15 min and then dust is removed by holding the panel vertically and tapping three times on the table. From the visual appearance in Fig. 7 it is clear that PDMS modified polyester coating shows good dust repellency at both the temperatures in case of carbon black which is attributed to the low surface energy of coating due to siloxane modification while methyl red left a stain at 100⁰C. It could be attributed to chemical reactivity of methyl red at 100⁰C since color of methyl also changed at 100⁰C.

Dust repellency was also checked by putting a drop of carbon black mixed in vegetable oil on coated panels and then panels were tilted at a small angle as shown in Fig. 8. It was observed that drop of oil spread on the surface of neat polyester coating whereas it slides immediately without leaving trail or dust particle on the surface in case of PDMS modified coating. It can be seen clearly that contact angle of oil is not very high but it slides easily due to the lower surface energy of the surface.

Fig. 9 (left) shows photographs of panels having methyl red dust particles and water drops on the surface. It is clearly seen that water drop slides and remove dust particles with itself on the PDMS modified polyester coated panel whereas it did not slide on neat polyester coated panel. It could be attributed to the higher contact angle due to higher surface roughness. Consequently, water drop slides on the surface after modification with siloxane. Fig. 9 (right) shows the effect of permanent marker on neat polyester and PDMS modified polyester coated panels. It is clear that permanent marker is not visible on PDMS modified polyester coating in comparison of neat polyester coating because of lower surface energy after modification.

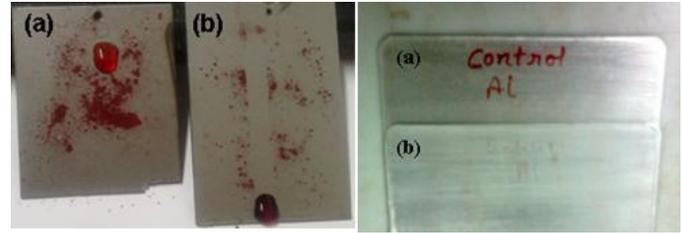


Fig. 9 Photographs showing self-cleaning property of (a) neat polyester, (b) PDMS modified polyester coating with methyl red dust and sliding water drop on the surface (LEFT). Effect of permanent marker (a) neat polyester, (b) PDMS modified polyester coating (RIGHT)

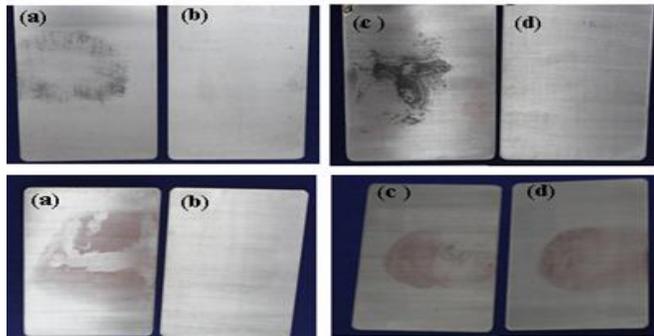


Fig. 7- Dust (carbon black, Methyl Red) adherence test on Al substrate (a) & (c) neat polyester (b) & (d) PDMS modified polyester substrate (a & b at 25 °C and c & d at 100 °C)



Fig. 8 Carbon black mixed with vegetable oil on Al substrate
(a) Neat polyester & (b) PDMS modified polyester

4. Conclusion

In the present work, chemical method has been adopted to achieve hydrophobic surface. Hydroxyl terminated polydimethyl siloxane (PDMS) has been used as surface modifier with waterborne polyester to reduce surface energy as well as to create rough surface. Crater like features of relatively big size and depth around 459 to 532 nm are obtained after modification of polyester resin with OH-terminated polydimethyl siloxane. This modification resulted in increase of surface roughness from 14 nm for neat polyester resin to 50 nm for PDMS modified polyester resin. As a result of the change in roughness the water contact angle got increased from 72° to 104° which is though not very high, but exhibited good self-cleaning properties as the surface profile does not allow the dust particles to adhere or stick on the surface. It was found that the water contact angle (104°) remains unchanged with rise in temperature from 30°C to 90°C indicating the thermal stability of the coating. Even it was observed that the hardness of the coating increased around 273 % with PDMS modification in comparison to that of neat polyester resin. The dust repellency and stain proofing nature of the coating was found to be good enough to be used in industrial application like surface of the fan blades for dust repellency and other outdoor applications where dust repellency is a must.

Acknowledgement

The authors sincerely thank Global Research and development centre Crompton Greaves Ltd for financial support.

References

1. Barthlott, W. and C. Neinhuis, Purity of the sacred lotus, or escape from contamination in biological surfaces. *Planta*, 1997. **202**(1): p. 1-8.
2. Parker, A.R.L., Chris R., Water capture by a desert beetle. *Nature*, 2001. **414**(6859): p. 33-34.
3. L. Feng, S.L., H. Li, J. Zhai, Y. Song, L. Jiang, D. Zhu, Super-hydrophobic surface of aligned polyacrylonitrile nanofibers. *Angew. Chem. Int. Ed.*, 2002. **41**: p. 1221.
4. L. Feng, Y.S., J. Zhai, B. Liu, J. Xu, L. Jiang, D. Zhu, Creation of a Superhydrophobic Surface from an Amphiphilic Polymer. *Angew. Chem. Int. Ed.*, 2003. **42**: p. 800.
5. M. Cao, X.S., J. Zhai, J. Wang, Y. Wang, Fabrication of highly antireflective silicon surfaces with superhydrophobicity. *J. Phys. Chem B*, 2006. **110**: p. 13072.
1. Barthlott, W. and C. Neinhuis, Purity of the sacred lotus, or escape from contamination in biological surfaces. *Planta*, 1997. **202**(1): p. 1-8.
2. Parker, A.R.L., Chris R., Water capture by a desert beetle. *Nature*, 2001. **414**(6859): p. 33-34.
3. L. Feng, S.L., H. Li, J. Zhai, Y. Song, L. Jiang, D. Zhu, Super-hydrophobic surface of aligned polyacrylonitrile nanofibers. *Angew. Chem. Int. Ed.*, 2002. **41**: p. 1221.
4. L. Feng, Y.S., J. Zhai, B. Liu, J. Xu, L. Jiang, D. Zhu, Creation of a Superhydrophobic Surface from an Amphiphilic Polymer. *Angew. Chem. Int. Ed.*, 2003. **42**: p. 800.
5. M. Cao, X.S., J. Zhai, J. Wang, Y. Wang, Fabrication of highly antireflective silicon surfaces with superhydrophobicity. *J. Phys. Chem B*, 2006. **110**: p. 13072.
6. Uhm, Y.C.H.H.S., Superhydrophobicity of a material made from multiwalled carbon nanotubes. *Appl. Phys. Lett.*, 2006. **88**(24): p. 244101.
7. K. Tadanaga, N.K., and T. Minami, *J. Am. Ceram. Soc.*, 1997. **80**: p. 1040.
8. E. Balaur, J.M.M., H. Tsuchiya, P. Schmuki, *J. Mater. Chem.*, 2005. **15**: p. 4488.
9. Yuranova, T., et al., Photocatalytic discoloration of organic compounds on outdoor building cement panels modified by photoactive coatings. *Journal of Photochemistry and Photobiology A: Chemistry*, 2007. **188**(2-3): p. 334-341.
10. Wenzel, R.W., Resistance of solid surfaces to wetting by water. *Journal of Industrial and Engineering Chemistry*, 1936. **28**(8): p. 988 - 994.
11. Hazlett, R.D., Hydrocolloids, in *Journal of Colloid Interface Science*, K. Nishinari, Editor 1990, Elsevier. p. 527.
12. Nosonovsky, M. and B. Bhushan, Superhydrophobic surfaces and emerging applications: Non-adhesion, energy, green engineering. *Current Opinion in Colloid & Interface Science*, 2009. **14**(4): p. 270-280.
13. Y.L. Wu., Z.C., X.T. Zeng, Nanoscale morphology for high hydrophobicity of a hard sol-gel thin film. *Applied Surface Science*, 2008. **254**: p. 6952-6958.
14. Xue-Mei Li, D.R.a.M.C.-C., What do we need for a super hydrophobic surface? A review on the recent progress in the preparation of super hydrophobic surfaces. *Chem. Soc. Rev.*, 2007. **36**: p. 1350 - 1368.
15. Kobayashi, H. and M.J. Owen, Surface tension of poly[(3,3,4,4,5,5,6,6,6-nonafluorohexyl)methylsiloxane]. *Macromolecules*, 1990. **23**(23): p. 4929-4933.
16. Zou, M., et al, Preparation and characterization of polysiloxane-polyacrylates composite lattices by two seeded emulsion polymerization and their film properties. *Journal of Applied Polymer Science*, 2007. **103**(3): p. 1406-1411.
17. Dhoke, S.K., R. Bhandari, and A.S. Khanna, Effect of nano-ZnO addition on the silicone-modified alkyd-based waterborne coatings on its mechanical and heat-resistance properties. *Progress in Organic Coatings*, 2009. **64**(1): p. 39-46.
18. Phani, A.R.a.H.H., Effect of annealing temperature on antireflection property and water contact angle of fluorine-based hydrophobic films by a sol-gel technique. *Materials Letters*, 2004. **58** (27-28): p. 3555-3558.
19. Gilmer, T.C., et al, Synthesis, characterization, and mechanical properties of PMMA/poly(aromatic/aliphatic siloxane) semi-interpenetrating polymer networks. *Journal of Polymer Science Part A: Polymer Chemistry*, 1996. **36**(6): p. 1025-37.