

Poly-siloxane modified poly-urethane based long life, high gloss and colour retaining coatings for marine applications

Abstract

Life at sea is difficult, and to maintain marine vessels and structures in good shape is a daunting task. It is every mariner's constant endeavour to keep the catwalks, bridge face, bulwarks, decks and ship's sides corrosion free and shiny. The environments in which these ships operate are unforgiving to the very steel that they are made up of. The above water structure, which is exposed to high humidity, oxygen and UV radiations, are able to damage the best known coatings.

Polysiloxane technology, introduced in the mid 90's, has evolved over the period and expanded to several new applications such as aviation, aerospace, defence, bridge coatings, etc. Siloxane resin is the main backbone of a Polysiloxane, which can be blended/ grafted (co-polymerized) with an organic resin and is responsible for the superior UV durability, which is the main advantage of this system. The main strength of siloxane resin is UV resistance which is due to the Si-O bond, i.e. more energy is required to break the Si-O bond as compared to the C-C bond, which is mostly found in organic coatings. When the energy required is more, the coating will resist degradation by UV for longer duration.

In this work, the aim is to modify poly-urethane coatings with poly-siloxane to achieve better flexibility; surface hardness; adhesion and barrier effect, with enhanced mechanical properties as well as resistance to UV radiations, hence ensuring augmented life of the coating. It is aimed to create a system which can last up to a service life of 7-10 years in the marine environment, without notable loss in gloss, colour difference or mechanical damage.

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Introduction

A ship or a marine structure operates in extremely harsh corrosive environment. Marine environment is more aggressive than most inland environments. Several areas of sea going vessel, typically consist of, the superstructure, boot-top area under splash zone, fully immersed areas such as ship-hull. It is well known now that the rate of corrosion of is generally, the highest for splash zone where it is exposed to dry and wet cycles alternately. That is why excessive corrosion takes place on boot top areas of the ship.

Application of protective coatings is, perhaps, the most common method of protection of ship from corrosion. Coatings are based on either metallic or non-metallic materials. Several paint formulation are available with highly cross-linked coatings, modified with several inorganic ingredients. Besides providing corrosion protection, coatings also fulfil, many a times, certain specific functional requirements. As an example, the coating system in the interior of ships must possess fire retardant characteristics to slow down the flame propagation in case of fire. Or a coating applied on the external above water hull must be resistant to heat, UV radiations and should be flexible enough to withstand high mechanical and thermal loads.

There are two basic purposes of paint scheme on above water hull structure (Figure 1). Firstly, Hull protection - the basic and most important function of a coating remains to be its ability to protect the base metal from corrosion damage and second, the Ship Camouflage - Naval ships function in a basic role of Man of War. This requires the vessel to be discrete and hence avoid detection by the enemy. The common paint systems being used are limited by their life and mechanical properties. This results in the ship's crew to use non-conformal paints to undertake urgent repairs and meet immediate

camouflage and aesthetic requirements. This practice severely affects the properties of the existing paint system and further degrades the colour, reflectance and gloss in a very short interval.



Figure 1 External above water Hull.

Hence, it is necessary to improve the life and properties of the existing system of paint coating being used for above water hull areas. This can be done by modifying the top coat, which is generally by polyurethane system to improve the durability and colour fastness and gloss. Grafting with siloxane backbone can further enhance these properties.¹⁻³ Figure 2 shows the main strength of siloxane resin, i.e. more energy is required to break the Si-O bond as compared to the C-C bond. A single layer of polysiloxane (Figure 3) modified resin can replace two layers of base coat and finish coat (PU) to achieve

similar or in most cases, better mechanical and weathering properties for a structure required to be protected from external environment. In addition to the augmented properties, this system will reduce time required for coating the structure and will also facilitates ease of repairs, as and when required. The augmentation of life and properties should be comparable to the increased cost that would be required for the siloxane modifications.⁴

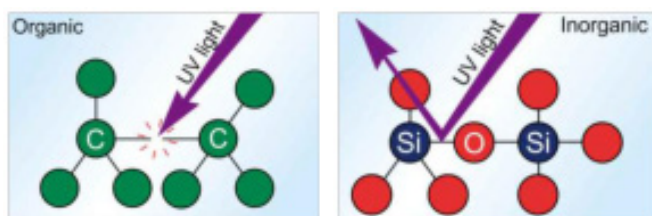


Figure 2 Effect of UV on C-C vs Si-O bonds.¹

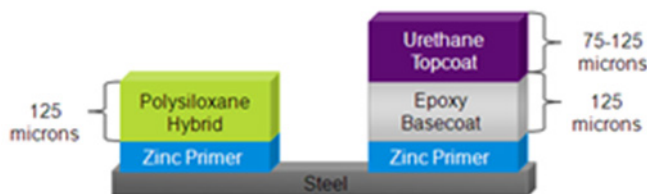


Figure 3 Polysiloxane hybrid as replacement to Epoxy + PU.¹

Experimental

Materials and methods

The experimental work involved modification of commercially available polyurethanes with siloxanes. Clear coat Polyurethane - polyol with aliphatic poly-isocyanate hardener, procured from Esdee Paints Limited, and 3-Aminopropyl-trimethoxysilane (APTMS), received from Sigma Aldrich group, Lab synthesized nano-ZnO and nano-TiO₂. Mild steel was used as substrate, post surface preparation (Abrasive blasting to SA2.5)

Coating formulation and optimization

Siloxane resin makes it very unique. This resin can be blended/ grafted (co-polymerized) with an organic resin. Use of Nano-ZnO and nano-TiO₂ was also made to improve the UV weathering properties of the coatings along with providing improved mechanical properties. Based on the above hypothesis, the project work is categorized into following sections:

- Modification of polyol component of PU by grafting with APTMS (3-Aminopropyl) tri-methoxy silane to improve its UV resistance, mechanical properties and corrosion performance.⁵ Varying concentrations (1-6 wt%) of APTMS were added to the base formulation (neat PU) to obtain the optimum concentration. The samples were then coated on steel and after curing they were tested for the UV resistance. Colour change was measured. The concentration of APTMS was optimized based on the results of above mentioned tests.
- Addition of Nano-ZnO and Nano-TiO₂ particle dispersion and study their effect on corrosion and mechanical properties^{6,7} Dispersion of surface-treated Nano ZnO and Nano-TiO₂ was used to improve weatherability for siloxane modified polyurethane. Varying concentration of Nano-ZnO (0.5-2 wt%) and Nano-TiO₂ (0.1-1 wt%) dispersion was added to the optimized formulation, Polyurethane modified by siloxane - APTMS (1-1.5 wt%). The samples were coated, cured and then tested for

Weatherability, physical and corrosion resistance properties. The concentration of Nano-ZnO and Nano-TiO₂ was optimized based on the results of these tests.

Characterization of the formulation

Once the optimum concentration of APTMS, nano-ZnO and nano-TiO₂ was obtained, the final formulation was subjected to characterization to ascertain the morphology and chemistry of the formulation and to correlate the physical improvements to the same. Morphological studies (SEM), FT-IR, Pull off adhesion, Nano Indentation and Atomic force microscopy techniques were used to evaluate the properties of the coatings.

Mechanical properties

The change in the mechanical properties of the coatings after modifying with various additives and their comparison with neat PU coating was done. Pencil Hardness, Cross hatch adhesion, Scratch hardness, flexibility, shored D hardness, permeability and taber abrasion tests were carried on the optimized formulation.

Results and discussion

Figure 4 compares the results of FTIR spectrum of the neat PU and that grafted with Siloxane. There is a significant broad peak observed at 2950-2850 cm⁻¹ showing N-H stretching. There is also a presence of stretching vibrations of C-H (Methyl) group in the control polyurethanes at 2515.1 cm⁻¹. In addition C-N (isocyanides) stretching and C=O (carboxylic derivatives and aldehydes) stretches have also been observed in the control polyurethanes at 2139.69 cm⁻¹ and 1748.39 cm⁻¹ respectively. Post modification of the control polyurethane by APTMS, the FT-IR spectrum were analyzed and it was observed that there is a significant reduction in the intensity at the 2950-2850 cm⁻¹ N-H stretch and the C-H (Methyl) stretch at 2515.1 cm⁻¹. This confirms that the grafting of APTMS on control polyurethane is occurring in the formulation. The results and comparison of FT-IR spectrum is shown in Figure 4.

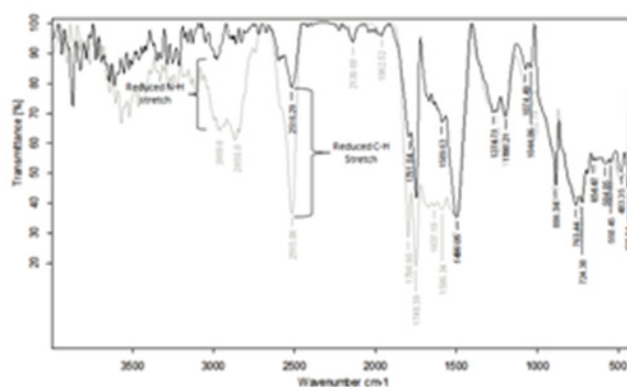


Figure 4 FT-IR plot for-Siloxane (APTMS) modified Polyurethane and comparison with control PU.

Weather ability and colour retention

The weathering test was carried out for varying concentration of APTMS, viz 1%, 1.5%, 2% and 2.5%, and the change in colour (ΔE) was compared and the optimum concentration was determined based on these results. Based on the above results (Figure 5), the optimum amount of APTMS required for modification of Polyurethane was set at 1.5 wt%. Further tests and modifications were carried out on 1.5 wt% siloxane modified polyurethane. Post optimization of APTMS wt% in the control Polyurethane, the second stage of modification

was carried out by using nano additives. In this stage, nano-additives were added to the formulation with an aim to further improve the performance and properties to achieve the best possible combination to be used in a marine environment. These formulations were further analysed for morphology in the following sections and further subjected to mechanical testing in the later part.

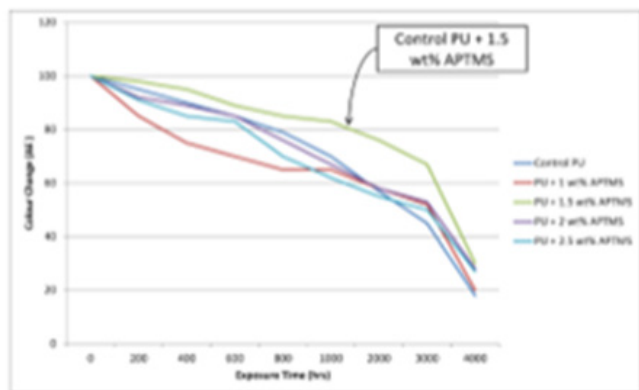


Figure 5 ΔE values with UV exposure for varying APTMS concentrations.

It is intended to use nano-Zinc Oxide as an additive to further improve the properties of the formulation. It is a known fact that nano-ZnO improves the UV resistance, hence the weatherability properties of the coating and the corrosion resistance to a great extent. This can be attributed to the 'Torturous path' effect of the nano-ZnO particles and the UV absorption property of the nano Zinc Oxide particles dispersed in the coating. The color change measurements of control polyurethane coating, the siloxane modified PU coated panels (1.5 wt% APTMS) and modified PU added with nano-ZnO (varying wt%) were compared. This test was primarily considered to optimize the amount of nano-ZnO required for the modification, to obtain best results. The values obtained for the test samples are shown in Figure 6. The weathering test was carried out for varying concentration of ZnO, viz 0.5%, 1%, 1.5% and 2%, the change in colour (ΔE) was compared and the optimum concentration was determined based on these results. Based on the above results (Figure 6) the optimum amount of ZnO required to be added in APTMS modified Polyurethane was set at 1 wt%, to get optimum results.

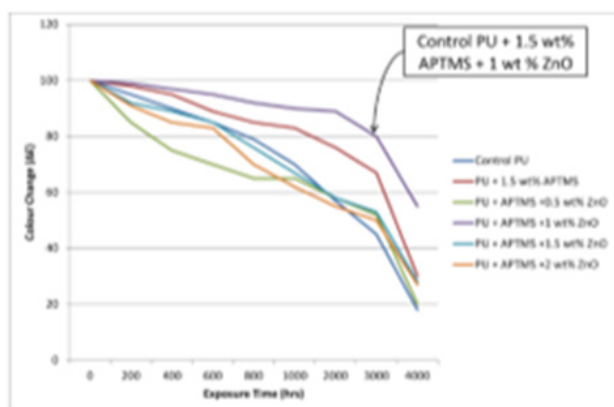


Figure 6 ΔE values with UV exposure for varying nano-ZnO concentrations.

Further, it is opined that the nano-Titanium dioxide could impart augmentation to the mechanical properties of the base formulation. In addition it is known that nano-TiO₂ can absorb the UV-B spectrum, which would improve the weatherability of the coating. As an added effect the 'torturous path' effect could improve the corrosion

resistance property of the modified polyurethane coating. In this stage of modification, nano-TiO₂ was added to the already optimized formulation. To optimize the amount of nano-TiO₂, these formulations were subjected to accelerated weathering tests and further subjected to mechanical testing in the later part. The values obtained for the test samples are shown in Figure 7. Based on the above results (Figure 7) the optimum amount of TiO₂ required to be added in APTMS modified Polyurethane was set at 0.5 wt%, to get optimum results.

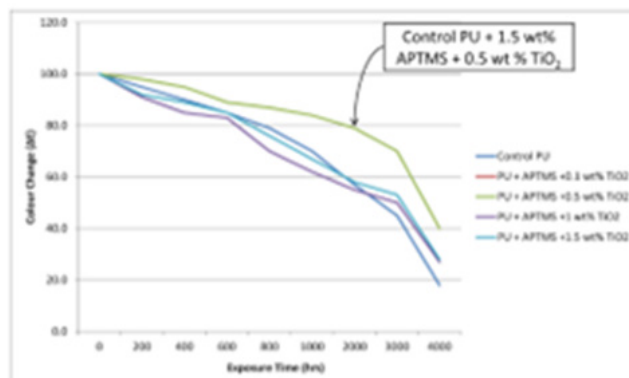


Figure 7 ΔE values with UV exposure for varying nano-TiO₂ concentrations.

Surface morphology of coated substrate

FT-IR studies of coated substrates suggested the possibility of covalent bonding between APTMS and PU resins. Presence of chemical linkage decides the phase homogeneity of coating. SEM image of the modified coating reveals the homogeneity of coating matrix as shown in Figure 8. There was no phase separation of silicones or PU which are attributed to chemical and physical interaction between Si-OH groups, and hydroxyl groups of PU. **Figure 8** SEM images of (a) PU+1.5% APTMS+0.5% nano TiO₂, (b) PU+1.5% APTMS+1% nano ZnO.

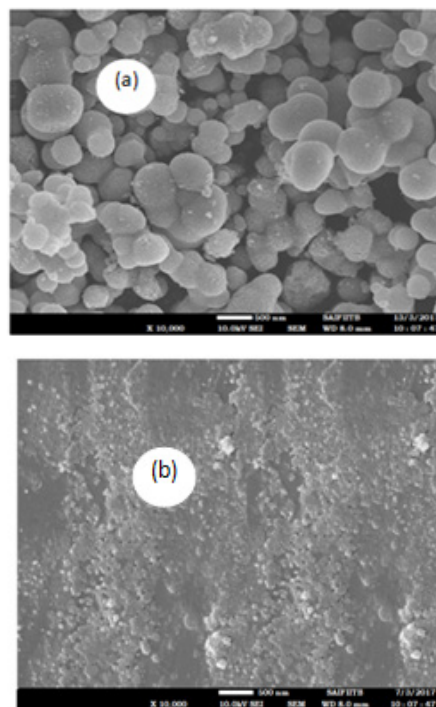


Figure 8 SEM images of (a) PU+1.5% APTMS+0.5% nano TiO₂, (b) PU+1.5% APTMS+1% nano ZnO.

Corrosion resistance and mechanical properties

Preliminary mechanical tests were carried out on the control coating as well as the modified coatings and the results were compared and correlated with the morphological property changes. These are listed in the order of modifications done to the basic formulation with various additives.

Pull off adhesion test: The pull off (dolly) test was conducted on the coated samples of control polyurethane and on the siloxane (APTMS) modified Polyurethane. The values on individual dollies and the average stress are given below:

The test results show that there is a marked improvement in the adhesion properties of the control polyurethane, post modification with APTMS. This is in conjunction with the accelerated weathering test results and coagulates the fact that, there is augmentation of mechanical properties of the coating along with the UV resistance. The formulation was further modified by addition of nano-ZnO and nano-TiO₂, and the samples were subjected to pull off testing. The

results indicate only marginal variation in the coating adhesion. Hence it is deduced that there are no adverse effects on the coating adhesion properties due to addition of nano particles.

Impact test: Impact test results for the four optimized formulations (as per previous sections) are given in the table below. It is to be noted that the impact resistance has increased considerably with the siloxane modification (approximately 20% increase in the impact test values). This can be considered as a remarkable improvement in the physical property of the control coating. It is however evident that there is negligible change in the impact test values post addition of nano particles, which is understandable (Table 1).

Pencil hardness: The pencil hardness test shows a slight increase in the surface hardness of the modified coatings. There is a 16% increase in hardness of control PU on modification with APTMS and subsequent addition of ZnO. It is also seen that there is a total 33% increase in the hardness on modification with APTMS and addition of nano-TiO₂. The results of pencil hardness test are given in the Table 2.

Table 1 Variation of Pull off test values for control Polyurethane with change in wt% of siloxane (APTMS)

Test Samples	PU (MPa)	Modified PU (MPa)	Modified + TiO ₂ (MPa)	Modified + ZnO (MPa)
S 1	D 1	5.2	7.2	7.3
	D 2	5.5	7	7.1
	D 3	6	7.1	7
S 2	D 1	5.6	7	6.9
	D 2	6.1	7	6.5
	D 3	5	6.9	6.2

Table 2 Comparison of impact test and pencil hardness values for control Polyurethane and modified formulations

Sample	Avg Energy Joules	Pencil Hardness H	Shore D MPa	Load (Passed) kg	Taber Wt Loss (mg)
Control PU	24	5H	83.2	8	346.5
PU + 1.5 wt% APTMS	29	6H	84.5	10	229
PU + 1.5 wt% APTMS + ZnO	30	6H	84.8	10	237
PU + 1.5 wt% APTMS + TiO ₂	29	7H	85.2	11	204.5

Scratch hardness: Scratch hardness test results are given in the Table 2. It was observed that control Polyurethane failed at 8 kg load whereas the APTMS modified coatings could resist up to the 10 kg load, which was same for the modified coating with ZnO additive. However, it was seen that there is a further increase in the load to 11 kg in the TiO₂ added formulation. This shows that the modified coatings have better scratch resistant values as compared to the control coating; this is in accordance with the previous test results.

Cross hatch adhesion: In the cross hatch adhesion tests, it was observed that the modified coatings and the formulations with the additives have experienced no peeling while the control coating has experienced peeling which is less than 5%. Hence under ASTM standards modified coatings and coatings with additives have been assigned 5B and the control PU is assigned 4B. This shows there is an improvement in the film adhesion property due to the APTMS and nano-particle based modifications to the control coating.

Shore D hardness: Shore D hardness test was conducted by taking three readings at staggered locations on the test panel using durometers and calculating the average value. The results showed that modification by APTMS has increased the hardness of the control polyurethane coating. It was further observed that there is minor improvement in the hardness values on addition of nano additives. The average test results are tabulated in Table 2.

Taber abrasion: During this test, it was observed that the formulation with modified PU along with TiO₂ particles has experienced the

lowest weight loss when compared to the other formulations. This shows that the siloxane modified coating has better abrasion resistance (about 34% improvement) and the addition of nano-TiO₂ has further improved (41% approx.) the property of the coating. This test result is also in agreement with the superior scratch and abrasion properties of siloxane modified PU added with nano-TiO₂. The weight loss values of samples subjected to taber abrasion test are given in Table 2.

Salt spray test: Coated panels with APTMS modified Polyurethane was put in salt spray conditions as per ASTM B117 specifications i.e. the coated substrates were exposed to a salt fog chamber having 3.5 wt% aqueous NaCl solutions at temperature of 35±1.7 °C for 1000 hrs. Results for the Salt spray test are presented in the figure below. After 1000 hrs of salt spray exposure no blisters, colour change or adhesion loss was observed in the modified coating. It was observed that the control PU was undergoing heavy corrosion damage in less than 1000 hours, however the modified coatings were still intact and did not exhibit any colour change. Only after 1300 hrs, the onset of corrosion began at the inscribed cut on the APTMS modified PU coating, however the nano-additive induced coatings held on till 1500 hrs.

Conclusion

A modified PU with grafted siloxane [APTMS] was made successfully which was further modified with nano-ZnO and nano TiO₂. The introduction of (3-Aminopropyl) trimethoxy silane

[APTMS] into the polyurethane polymer chains improved the colour fastness by 75% in 2000 hrs (approx. 5 years equivalent) and 67% up to 3000 hours (close to 7.5 years equivalent), which is a considerable improvement compared to the control polyurethane sample. The improvement in the mechanical properties, for example, Pull off adhesion was 7.03 MPa (25% improvement over control sample), 6H pencil hardness, impact test value of 29 joules, and 5B cross hatch test value. The surface hardness (shore D) was found to be 70 (34% improvement). These improvements make the modified coating a more viable and suitable option for marine applications.

Dispersion of Nano-Zinc Oxide particles with average size of 30 nm and Nano-Titanium dioxide with an average size of 300 nm added to the modified PU (1.5 wt% APTMS) showed a clear increase in the UV weatherability. This could be attributed to the better UV absorption properties of nano-ZnO dispersion. The nano-ZnO induced formulation was seen to retain about 80% of the original colour up to 3000 hrs (7.5 years equivalent). The improvement in the mechanical properties, viz a Pull off test value of 6.8 MPa, 6H pencil hardness, impact test value of 29 joules, 5B cross hatch test value (equal or lesser than the PU + APTMS formulation). The conventional PU coatings are known to survive for a maximum life of 2-3 years. Improvements by siloxane grafting and addition of nano ZnO and TiO₂ resulting in improved UV weatherability and increment of overall coating performance and life. This will extend the life of the coating to about 7.5 years, as compared to the present systems. These improvements make the modified coating more suitable for marine applications.

Acknowledgments

None.

Conflicts of Interest

None.

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