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Silicone functionalized pigment to enhance coating performance

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ABSTRACT

The present study reports chemical treatment of pigment titanium dioxide (TiO_2) with silicone to give surface functionalized TiO_2. The surface functionalization was confirmed by Fourier Transform Infra Red Spectroscopy, Scanning Electron Microscopy, Transition Electron Microscopy and Dynamic Light Scattering analysis. Coatings were formulated by incorporation of these functionalized TiO_2 into the epoxy polymer matrix and compared for coating properties with untreated TiO_2. The effect of the functionalized TiO_2 on various coating properties with respect to physico-mechanical properties, anticorrosion efficiencies, UV resistance and chemical resistance was studied in detail. The results revealed remarkable enhancement of coating properties with functionalized TiO_2 when compared with the coatings formulated with untreated TiO_2.

1. Introduction

Pigments and extenders in paint and coating formulations significantly contribute to their mechanical, chemical and performance properties [1,2]. These are majorly inorganic materials and inorganic particles have tendency to agglomerate. However, these inorganic materials are homogeneously dispersed into the paint vehicles with the help of various dispersing additives and mechanical stirring to obtain the best performance properties of paints and coatings [3–5]. Pigment manufacturers also provide fine size and surface modified pigment particles to facilitate better dispersion and reduce paint defects. Besides the dispersibility of these pigments and extenders, their interaction with polymeric binders largely decides the performance properties of paints and coatings. The pigments and extenders having strong interactions (covalent or Vanderwaal) with the binders (matrix polymer) provide better performance properties over simple physically dispersed system.

Silicones are recommended as surface treating agent in several literatures for surface functionalization of pigments to achieve proper dispersion of inorganic materials in polymer matrix and to yield better compatibility between the particles and host polymeric materials [6–8]. As most pigments and extenders are inorganic oxides and silicates having hydroxyl groups on their surfaces, when treated with silicones, these surface hydroxyl groups react with alkoxy groups of silicones forming a covalent bond between the two. The appropriate surface modification on pigment, not only leads to better dispersion and compatibility of them in polymer matrix, but also by formation of chemical and physical interactions with polymer matrix, could guarantee a durable chemical junction between two incompatible phases.

Bauer et al. [9] found that oligomeric siloxane structures treated nanoparticles lead to covalent bond formation between the surface-modified nanoparticles and the epoxy resin improving the thermal stability of the system. Zhang et al. [10] reported that 3-glycidoxypropyltrimethoxy silane-modified nanosize silicon dioxide could effectively improve the toughness and thermal stability of cycloaliphatic epoxy resin. Zunjarrao and Singh [11] compared the effect of nanometer- and micrometer-sized aluminum particles on the fracture toughness and found that proper silane treatment and improved particle dispersion resulted in the improved physical and chemical properties [12–14].

In this work, we have selected rutile grade titanium dioxide (TiO_2), a most commonly used pigment in the paint formulations

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and functionalized the same by silicone treatment. This functionalized TiO_2 was then used to formulate epoxy paint and evaluated its effect on the coating performance. It was observed that epoxy coatings formulated using silicone functionalized TiO_2 exhibited phenomenal improvement in properties when compared with that using untreated TiO_2.

2. Experimental

2.1. Materials

The epoxy resin (GY250) supplied by Huntsman was used as matrix resin and cycloaliphatic amine (EPIKURE F-205) from KIANRESIN was used as hardener. Ti-pure R902, rutile TiO_2 powder from DuPont was used as pigment. Polymethylphenyl methoxy siloxane from Dow Corning was used as surface treating agent. ANTI-TERRA U from BYK Chemie and thickener Bentone 38 from Elementis were additives used for paint preparation. Solvents like xylene butanol and tetrahydrofuran (THF) were of commercial grade. All the chemicals were used as such without any further purification.

2.2. Surface functionalization of TiO_2 particles (F-TiO_2)

Surface functionalization of TiO_2 surface was carried out as per the method provided in the literature [15]. In this method polymethylphenyl methoxy siloxane was hydrolyzed for about 24 h in double distilled water whose pH had been adjusted to a value of 3 by adding acetic acid. TiO_2 powder was added to the solution of the siloxane agent and the suspension was vigorously stirred for about 1 h at room temperature. The TiO_2 particles were removed from solution in a buchner 1 h filter and subsequently washed with THF to remove the loosely bonded physisorbed compounds attached to the particles. The surface functionalization of TiO_2 was completed after drying the slurry in a vacuum oven at 105 °C for 12 h.

A similar procedure was followed for untreated TiO_2 without the use of polymethylphenyl methoxy siloxane whereby TiO_2 was added to double distilled water whose pH had been adjusted to a value of 3 by adding acetic acid. The suspension was vigorously stirred for about 1 h at room temperature. The TiO_2 particles were removed from solution in a buchner 1 h filter and the slurry was completely dried in a vacuum oven at 105 °C for 12 h. This untreated TiO_2 was used for comparison with F-TiO_2 in epoxy paint formulation.

2.3. Preparation of epoxy paint

The epoxy paint was prepared using a high speed disperser. TiO_2 or F-TiO_2 powder was directly added to vessel charged with epoxy resin and solvent mixture (butanol/xylene) followed by addition of additives. The pigment was dispersed by stirring at 400 rotations per minute (RPM) for 30 min and then increasing the stirrer speed to 2000 RPM. The vessel was externally cooled using cold water to avoid rise in temperature during processing. The dispersion was continued for 45–60 min to give a uniform white paint. The epoxy paint formulation is given in Table 1.

2.4. Curing of epoxy paint

For curing, epoxy paint and cycloaliphatic amine were mixed in a weight ratio 100:27 of epoxy to amine. Solvents mixture of xylene and butanol was used for dilution as per the convenience of spray coating application.

Table 1
Epoxy paint formulation.

Ingredient	%Wt composition
GY250	47
Untreated TiO_2 or F-TiO_2	30
Xylene	17.20
Butanol	5
Bentone 38	0.5
Anti Terra U	0.30
Total	100

2.5. Panels and free films preparation

Coatings films were prepared on carbon steel panels as substrates having dimensions 120 mm × 50 mm × 0.5 mm for testing the paint properties. The substrates were polished with Emery paper 800 and then degreased with cleaner solution for 5 min. The coating films were applied by spray coating and were allowed to cure at room temperature for 7 days. The average thickness of the dried coated films was about 80–90 μm. The free-standing films with average dry film thickness of 150 μm were prepared by application of epoxy based paint on the silicone sheets. The films were left for about 2 weeks at room temperature for complete curing.

2.6. Methods and measurements

Physicochemical properties such as oil absorption value and bulk density of TiO_2 before and after modification are determined as per ASTM D281-07 and ASTM B329-06 respectively. The surface modification of pigment and type of reaction between a silicone coupling agent and TiO_2 were evaluated using FTIR (Nicolet 6700) spectroscopy. FTIR analyses of the untreated TiO_2 and F-TiO_2 were conducted in the spectra range of 400–4000 cm^{-1} using attenuated total reflectance (ATR) method with a resolution of 4 cm^{-1} with KBr pellets for solid specimens.

The transition electron microscopy (TEM) was examined using a one-step replica method in TEM 1200 EX II electron microscope. Elemental analyses were performed using Energy dispersive X-ray spectroscopy (EDXS) JEOL JED-2300T EDS system with high energy resolution and high sensitivity. Studies of the morphology and microstructure of the untreated TiO_2 and F-TiO_2 particles were conducted using scanning electron microscopy (SEM) of ZEISS make at an accelerated voltage of 15 kV and 2.8 A probe current with a working distance of 10 mm.

The size distribution of the untreated TiO_2 and F-TiO_2 particle agglomerates and aggregates was estimated using Dynamic light

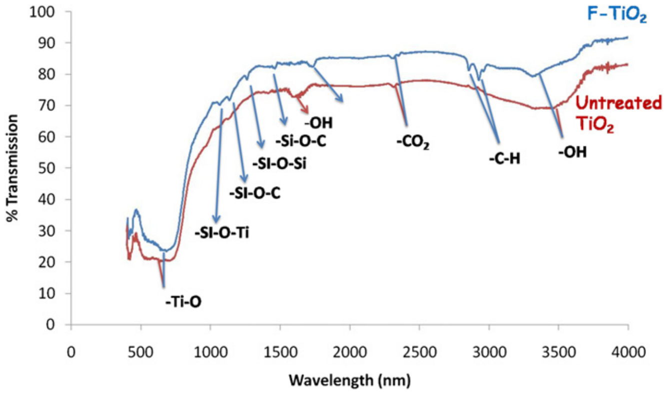
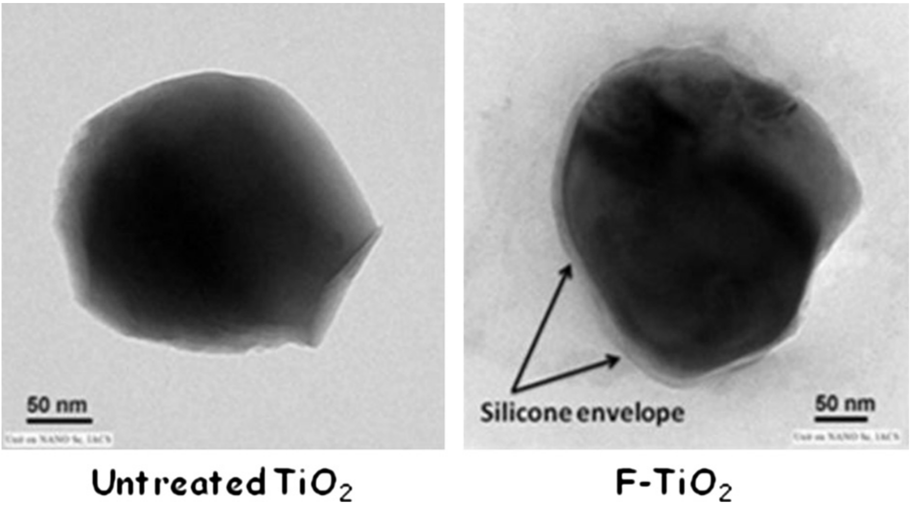


Fig. 1. FTIR spectra of untreated and F-TiO_2.



Untreated TiO_2 F-TiO_2

Fig. 2. TEM micrographs of untreated and F-TiO_2.

Table 2
EDXS analysis of untreated and F-TiO_2.

System	C K	O K	Al K	Si K	Ti K	Cu K	Al K	Zn K
Untreated TiO_2	12.57	38.72	1.20		34.67	2.02	1.23	9.59
F-TiO_2	17.23	45.44	1.01	0.17	24.78	1.20	1.05	9.14

scattering (DLS) technique Malvern Inst, U.K. Nano ZS by a quasi-static light scattering detector at 173° using laser wavelength of 630 nm. The samples were prepared by diluting the 0.007 g sample in 50 ml of ethanol and then introduced into the detector using a syringe pump. Data Physics Inc. OCA15 was used to measure the contact angle of a drop of water placed on untreated TiO_2 and F-TiO_2 in accordance with ASTM D5725. Water was taken in a dropper and drops were allowed to fall on the substrate and contact angle were measured immediately.

Water vapor transmission of free films containing untreated TiO_2 and F-TiO_2 powder was measured as per ASTM E96-94. Scratch hardness was measured on hardness tester according to ASTM D 171. The adhesion test was carried out using pull off adhesion tester as per ASTM D 4541. Flexibility of the coatings from substrate was measured by conical mandrel and impact tester as per ASTM D 522 and ASTM D 2794. Abrasion resistance of the coated sample was measured using Taber abrasion tester as per ASTM D 4060.

All polarization studies were carried out at room temperature in 3.5% NaCl solution. Test system consisted of a three-electrode cell, in which a saturated calomel electrode (SCE), a carbon steel electrode and a coated coupon were used as reference, counter, and working electrodes, respectively. The exposed area of the coupons to the NaCl solution was 12.56 cm^2. Salt spray exposure was performed according to ASTM B117. The coated panels were exposed to a 5% NaCl solution at 35 ± 2 °C for 1000 h. In this experiment, the carbon steel substrates were coated with TiO_2 incorporated epoxy resin. The panels were evaluated under scratched (using X shape) condition.

Accelerated weathering test was conducted in the QUV chamber (Model QUV/Spray, Q-Panel Co.) as per ASTM G 154. Coated panels were then placed in the QUV chamber for 120 h. According to test procedure, the specimens were alternately exposed to UVB radiation (313 nm, 0.71 W m^{-2}) at 60 °C for 4 h and followed by 4 h of water condensation at 50 °C cyclically. The surface degradation of epoxy paint containing untreated TiO_2 and F-TiO_2 was characterized by color change, defined as the color measurement, after being exposed to accelerated weathering conditions. The tests were performed accordance with ASTM D 65 using a colourimeter apparatus (Gretag Macbath, USA) illuminant D65, in angle 45°.

3. Result and discussion

F-TiO_2 was characterized using FTIR spectroscopy to investigate the surface modification. The FTIR of spectra of F-TiO_2 (Fig. 1) against untreated one clearly indicate chemical reaction between the silicone alkoxy groups and TiO_2 surface hydroxyl groups resulting into covalent bond formation between the two. The peaks were assigned based on the data reported by Chiang et al. [16]. The bands observed at 2958, 2928 and 2870 cm^{-1} are assigned to C–H

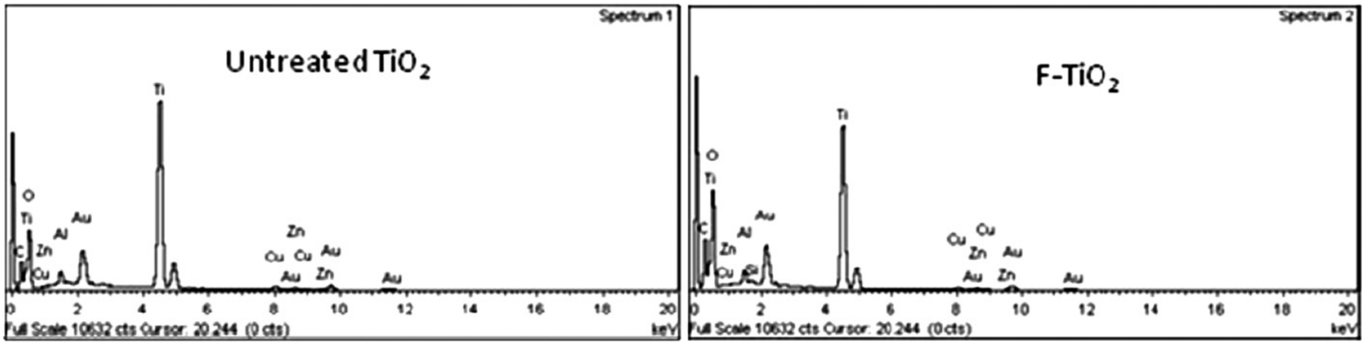


Fig. 3. EDXS analysis of untreated and F-TiO_2.

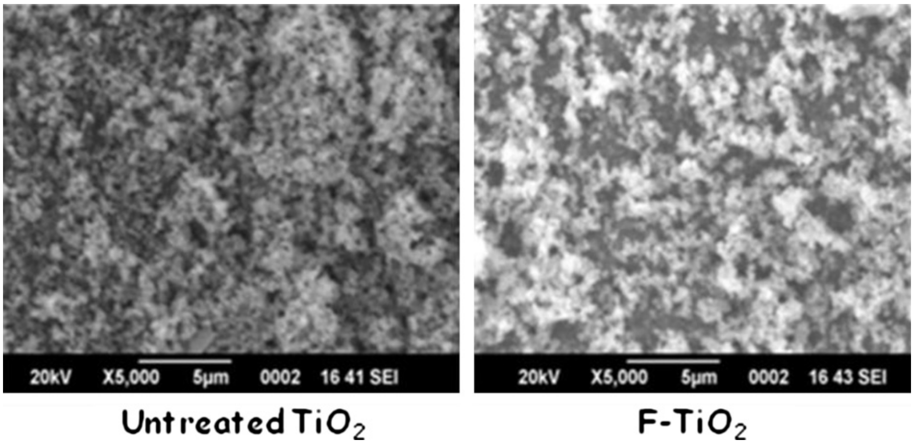


Fig. 4. SEM micrographs of untreated and F-TiO_2.

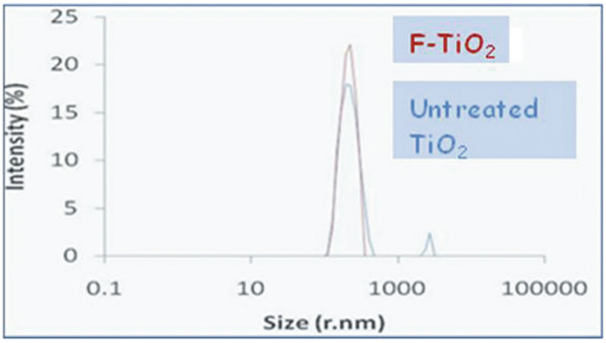


Fig. 5. Dynamic light scattering (DLS) results for particle size of untreated and F-TiO_2.

asymmetrical stretching vibration (methyl group), C–H asymmetrical stretching vibration (methylene group) and C–H symmetrical stretching vibration (methylene group) respectively from polymethylphenyl methoxy siloxane treating agent. Furthermore, the peak at around 1020 cm^{-1} in the spectra assigned to the stretch vibration band of Ti–O–Si [17,18] indicates the successful condensation reaction between silicone alkoxy groups and surface hydroxyl group on TiO_2. In addition, the broad band at around 1250 cm^{-1} corresponded to Si–O–Si, indicates the self condensation of silanol groups itself [18] (Fig. 1).

Table 3
Physicochemical parameters of untreated and F-TiO_2.

Properties	Untreated	F-TiO_2
Oil absorption (cm^3/100 g)	22	9
Bulk density (g/dm^3)	90.6	97.8

The success of surface treatment was further confirmed by TEM analysis. Fig. 2 depicts the TEM micrographs of the untreated TiO_2 and F-TiO_2. A thin envelope of about 10 nm silicone layer can be noted at the edge of the F-TiO_2. In order to confirm that the observed contour could be attributed to the silicone attached to the surface, EDXS analysis of the F-TiO_2 was performed on selected sites, as shown in Table 2 and in Fig. 3. Examination of the EDXS results revealed silicon and carbon signals together with other signals attributed to the TiO_2. The existence of all signals is clearly consistent with the presence of the TiO_2 modified with silicone, agreeing to the FTIR data.

Fig. 4 shows the SEM micrographs of untreated TiO_2 and F-TiO_2. The surface morphology of the two indicates the advantageous effect of silicone functionalization on surface structure and an increased tendency for the presence of numerous primary particles of small diameter in F-TiO_2. It is interesting to note that modification with silicone practically restricted the tendency for particle agglomeration too.

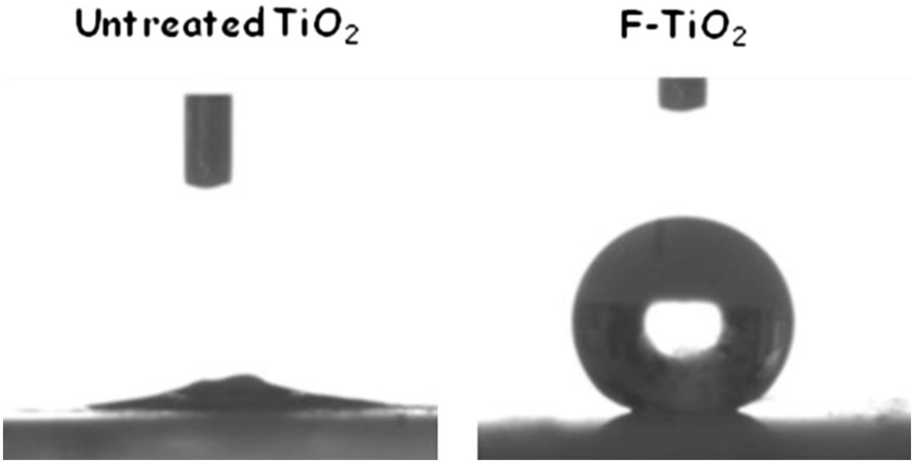


Fig. 6. Contact angle of untreated and F-TiO_2 powders.

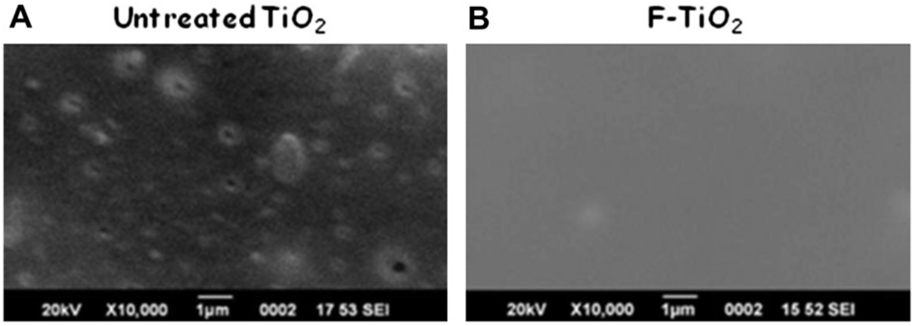


Fig. 7. SEM image of epoxy paint using untreated and F-TiO_2.

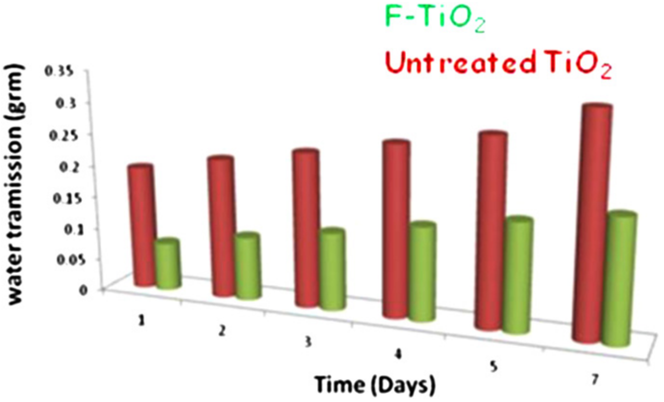


Fig. 8. Water vapor transmission test of epoxy paint using untreated and F-TiO_2.

Dynamic light scattering (DLS) results for particle size distributions and the tendency to form aggregates and agglomerates of untreated TiO_2 as well as F-TiO_2 are shown in Fig. 5. In the case of untreated TiO_2, the presence of primary structures (particle aggregates) was noted. The size distribution of aggregates was 100–400 nm. The tendency to form secondary agglomerate structures of low intensities was also observed in case untreated TiO_2, which is in the range of agglomerate sizes of 2471.1–2761.9 nm.

Whereas the silicone treatment resulted in the TiO_2 particles being markedly more uniform, lowering the range of the aggregate sizes ranged in size between 100 and 300 nm and the mean diameter was 150.7 nm with no tendency to form agglomerate structures. Thus, the studies of the particle size distribution of TiO_2 confirmed that the treatment completely eliminated particle agglomerates (so called secondary structures).

Further silicone treatments are known to make the surfaces hydrophobic and contact angle measurement is the most important parameter for quantitative characterization of hydrophobicity [19,20]. Same phenomenon is also observed in this case, when untreated TiO_2 particles absorb water and exhibited a contact angle of nearly 0°, the water contact angle had a value of 148° on the F-TiO_2 particles, as shown in a Fig. 6. The higher value of the contact angles indicates a pronounced hydrophobic character of the surface after silicone functionalization of TiO_2.

Table 4
Mechanical characterization of epoxy paint using untreated and F-TiO_2.

Properties	Standard	Untreated TiO_2	F-TiO_2
Scratch hardness (g)	ASTM G 171	3400	4400
Pull of adhesion (mPa)	ASTM D 4541	153	310
Impact resistance (J)	ASTM D 2794	22.78	63.29
Abrasion resistance (mg/1000 cycles)	ASTM D 4060	73.2	64.6
Flexibility (mm)	ASTM D522	25	20

The physicochemical parameters were evaluated for F-TiO_2 and tabulated in Table 3. F-TiO_2 exhibits low oil absorbing capacity and increased bulk density with respect to the untreated TiO_2. Lowering of oil absorption value improves the compatibility of functionalized pigments with the organic polymer. The alterations in physicochemical parameters also corroborate the role of treatment in facilitating pigment dispersion in organic media.

As mentioned earlier, dispersion of inorganic material in organic polymer matrix plays a crucial role not only to make a defect free paint but also its long term performance. The F-TiO_2 was further evaluated for coating properties in epoxy paint. Two epoxy paints were separately prepared using F-TiO_2 and untreated TiO_2 and both were cured with polyamide curing agents as discussed in Sections 2.3 and 2.4. The dispersion of both functionalized and untreated TiO_2 in the epoxy polymer matrix was studied with the help of SEM. The SEM images of coatings using untreated and F-TiO_2 are shown in Fig. 7A and B respectively. Microstructure of paint containing untreated TiO_2 suggested that coating is non-uniform and having pores which may be attributed to an inappropriate dispersion of the particles whereas F-TiO_2 particle are more uniformly distributed in the paint system forming a smooth continuous film.

The epoxy coatings were then subjected to water vapor transmission test and the results are compared in Fig. 8. The coating formulated with F-TiO_2 showed lower water vapor transmission compared to the coated sample containing untreated TiO_2. This

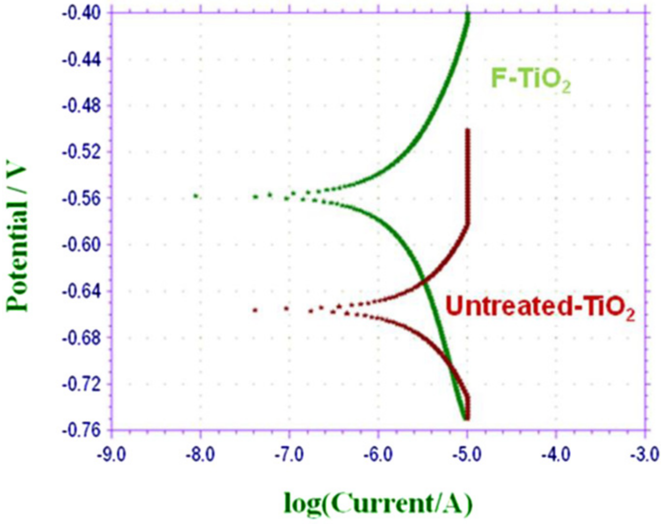


Fig. 9. Potentiodynamic polarization curve of epoxy paint using untreated and F-TiO_2.

Table 5
Corrosion rate of epoxy paint using untreated and F-TiO_2.

Coating system	Corrosion rate (mil/year)
Untreated TiO_2	6.931
F-TiO_2	0.942

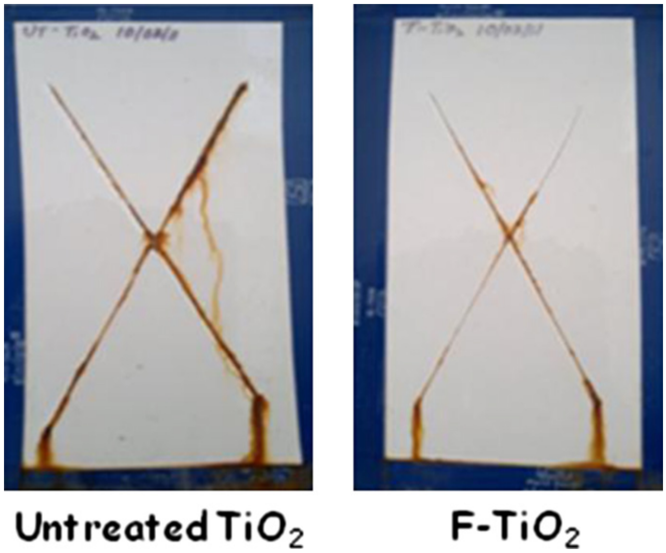


Fig. 10. Salt spray test of epoxy paint using untreated and F-TiO_2 after 1000 h.

may be due to hydrophobic nature of silicone groups on the surface as well as compact microstructure formed with F-TiO_2 particle as already seen in the SEM image (Fig. 7). The compact and pore free microstructure helps in a resisting the water vapor penetration whereas for paint containing untreated TiO_2, inappropriate dispersion of the particles and in turn the presence of aggregates, air pockets as well as discontinuity of the film results in increase in water vapor transmission.

The role of F-TiO_2 in the performance parameters of epoxy coating was evaluated in detail. The results of mechanical characterization of cured epoxy coating containing untreated TiO_2 and F-TiO_2 are compared in Table 4. The results clearly show that the F-TiO_2 based epoxy coatings have higher values of scratch hardness, pull-off adhesion and impact resistance, the loss after 1000 cycles of abrasion was less and more flexible than its untreated counterpart. These may be attributed to the increase in mechanical reinforcement of epoxy coating due to the synergistic interaction between pigment and polymer matrix through chemical bonding for F-TiO_2 based epoxy coatings.

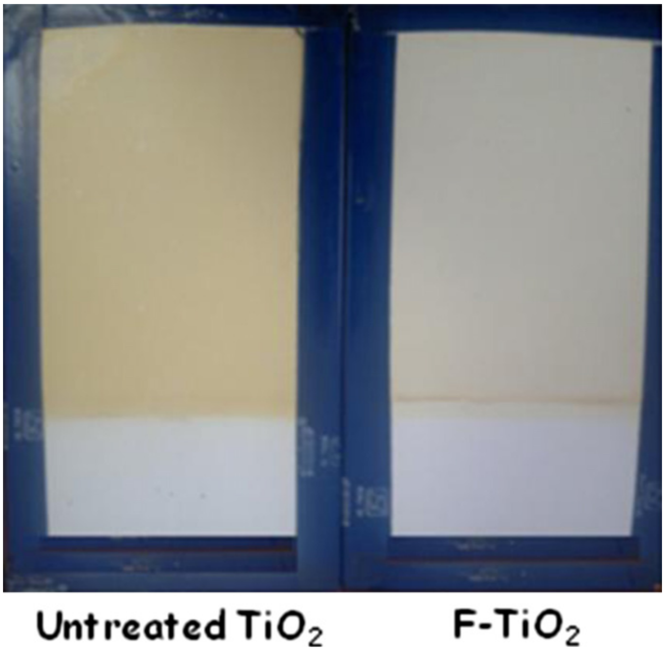


Fig. 11. Weatherability test of epoxy paint using untreated and F-TiO_2 after 1000 h.

As epoxy coatings are well known for their chemical resistance, the study would be incomplete without investigating their anticorrosive properties using F-TiO_2. The epoxy coatings based on untreated and F-TiO_2 were subjected to accelerated corrosion test using Tafel analysis and salt spray test. In Fig. 9, the potentiodynamic polarization of F-TiO_2 epoxy coating was compared with that of untreated TiO_2. In Table 5, the corrosion rate of F-TiO_2 epoxy coating was compared with that of untreated TiO_2 to find out the extent of reduction in corrosion. It can be seen that corrosion rate of F-TiO_2 epoxy coating is 0.942 mil/year while that of untreated TiO_2 epoxy coating is found to be 6.931 mil/year indicating excellent resistance against corrosion using treated F-TiO_2. The F-TiO_2 being uniformly dispersed throughout the film apparently serves to increase the hydrophobicity of the coating, repelling water and corrosion initiators and improving corrosion protection properties [21,22]. In case of untreated TiO_2, inappropriate dispersion forming aggregates, air pockets as well as discontinuity of the film resulted in decrease in corrosion resistance.

The aspects of epoxy coatings containing untreated and F-TiO_2 after exposure in salt fog for 1000 h are shown in Fig. 10. The corrosion resistance was determined by the rusts and blistering along the "X" marks on the substrates. After salt spray for 1000 h,

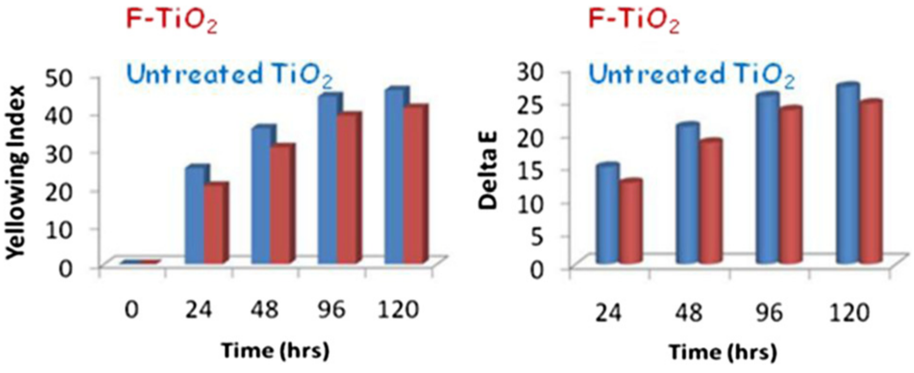


Fig. 12. Yellowness index and ΔE values of epoxy paint using untreated and F-TiO_2.

serious blistering appeared along the "X" marked for epoxy paint containing untreated TiO_2, with diameter of blisters more than 5 mm. However, no apparent blistering along the marks was observed in case of F-TiO_2 coating. The corrosion results complemented the Tafel analysis results, implying that the use of F-TiO_2 can effectively reinforce the epoxy coating against blistering and delamination.

The weatherability of epoxy paint based on F-TiO_2 was tested against the control (epoxy paint with untreated TiO_2) by exposing to accelerated weathering cycle in QUV weathering tester. The scanned images of untreated and F-TiO_2 epoxy paint panels after exposure for 1000 h are shown in Fig. 11 where remarkable difference in their yellowing tendency is observed. The coated panels evaluated for yellowness index and ΔE values before and after exposure are highlighted in Fig. 12. It can be observed that F-TiO_2 based coating showed less ΔE values and yellowing tendency with more than 15% improvement in weathering. The higher photocatalytic activity of untreated TiO_2 causes strong reaction induced by the illumination of UV light decomposing epoxy polymer. The surface modification of TiO_2 reduces its photocatalytic activity thereby improving the weatherability.

4. Conclusion

Pigment TiO_2 has been functionalized by chemical treatment with silicone. The functionalized TiO_2 shows remarkable enhancement of coating performance when tested against untreated TiO_2 in epoxy paint with respect to physico-mechanical properties, anticorrosion efficiencies, UV resistance and chemical resistivity of the paint film. The improvements can be summarized by concluding that silicone functionalization of TiO_2 leads to

- Restricted pigment particle agglomeration.
- Improved pigment dispersibility.
- Enhanced hydrophobicity.
- Improved mechanical properties.
- Improved corrosion resistance and weatherability.

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