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ORIGINAL PAPER

Surface modification of TiO_2 nanoparticles with 1,3,5-triazine based silane coupling agent and its cumulative effect on the properties of polyurethane composite coating

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Abstract The present work focuses on the development of functional polyurethane hybrids through the incorporation of surface modified TiO_2 nanoparticles. For improving the nanoparticle dispersion and increasing possible interactions between nano-particles and polyurethane matrix, the surface of the nano-particles was modified with 1,3,5-triazine core silane coupling agent. The surface modification of nanoparticles was confirmed by FESEM, FT-IR and Raman spectroscopic techniques. The functionalized nanoparticles were then inscribed in 0, 1 and 2 weight percentages into polyurethane matrix. The as prepared composite coatings were investigated for various anti-microbial, thermo-mechanical and anticorrosive properties. The tensile strength of polyurethane was improved by 300 % upon addition of 2 wt% of modified TiO_2 nanoparticles as compared to neat polyurethane. Fog test and electrochemical polarization studies suggest that the corrosion resistance increases with increase of the modified TiO_2 content in the coating formulation. The composite coatings also have good resistance towards various bacterial and fungal stains as compared to the pure polyurethanes. The coatings substantially gain hydrophilic nature symbiotically with TiO_2 content suggesting its potential application as self-cleanable material.

Keywords TiO_2 nanoparticle · Composite · Polyurethane hybrid coating · Hydrophilic materials

Introduction

In recent years, nanomaterials are being wieldy sought after as an effective additive in coating formulations so as to enhance the properties of coatings and also provide desirable functionality to the material [1–3]. Usually, inorganic nanoparticles are preferred as a potential filler owing to their superior mechanical strength, thermal stability, corrosion resistance and antimicrobial properties [4, 5]. Amongst many of the nanomaterials used in coating formulation, Titanium dioxide (TiO_2) nanoparticle has been widely commercialised for a variety of coating applications [6–8]. TiO_2 is a transition metal oxide which posses either of the four common polymorphs namely: anatase, rutile, brookite and monoclinic [9]. TiO_2 possess high refractive index and low density which could be exploited in the development of optical grade coatings [10, 11]. The strong ability of TiO_2 nanoparticles to absorb ultraviolet rays (UV rays) is highly useful in the design of potential UV-blocking additives for development of UV-resistant coatings and fabrics [12, 13]. Further, when TiO_2 nanoparticles are incorporated into polymer matrix, contact angle with water is found to be substantially reduce owing to their inherent hydrophilic nature. This could increase the wettability and cleanability of composite coatings which could be exploited for the development of self-cleaning coatings [14–17]. The self-cleaning coating consist of photo-catalytic TiO_2 that offers three unique properties when exposed to ultraviolet light: 1) strong oxidation power that removes odour causing bacteria; 2) the breakdown of long chain organic molecules into smaller ones; and 3) the surface becomes super-hydrophilic, which allows these small chained organic molecules and everyday dirt and stains to be easily washed away with water. Therefore, TiO_2 nanoparticle based composite could be a dependable choice for the development of self-cleaning coatings [18].

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The excellent antimicrobial nature of these nanoparticles useful in the development of anti-bacterial coating surfaces [19]. Due to their large surface to volume ratio, nano-particles tend to agglomerate easily, hence reducing the resultant mechanical properties of the nanocomposite materials [20]. Thus, in order to produce suitable nanocomposites it is necessary to disperse the nanoparticles without aggregation in organic binders. The most common method used attaches a suitable organic group on the surface atoms using silane coupling agents [21]. This type of surface modification stabilizes the nanoparticle against the agglomeration and also makes them compatible with the other phase [22]. The suitable surface modification of nanoparticles, not only leads to enhanced dispersion and compatibility in polymer matrix, but also undergoes chemical or physical interactions with the polymer matrix [23, 24]. The surface modification of TiO_2 nanoparticle reduces substantially the thermodynamic and kinetic barriers which hinder its optimal dispersion in polymer matrix [25].

In view of the recent developments in TiO_2 based coating materials, the present work seeks to develop a novel polyurethane-TiO_2 nano-hybrid with good thermal stability, improved mechanical properties, durability, antimicrobial and anticorrosive properties. In first stage, a three dimensional silane coupling agent i.e., 1,3,5-triazine core silane coupling agent (TSC) was synthesized and the structure was confirmed by different spectroscopic techniques. In the next stage, the surface of TiO_2 nanoparticles were modified with the above prepared TSC cross-linker. The presence of heavy siloxane end groups on TSC cross-linker helps in the effective modification TiO_2 nanoparticles and the highly polar 1,3,5-triazine improves the dispersibility of the modified nanoparticles in various organic solvents [26]. The surface modification was confirmed by thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy and field emission scanning electron microscopy (FESEM). These silane functionalised TiO_2 nanoparticles were finally incorporated in different weight percentages such as 0, 1 and 2 % into the polyurethane matrix. Additionaly, the presence of secondary amine groups on TiO_2 nanoparticles helps in the formation of chemical linkage with isocyanate groups during the polyurethane formation. The resulting nanocomposite coatings were characterized by FT-IR, TGA, FESEM techniques. These nanocomposites were tested for their corrosion resistance properties by using Tafel plots, tensile strength by universal testing machine, antibacterial nature and water contact angle.

Experimental details

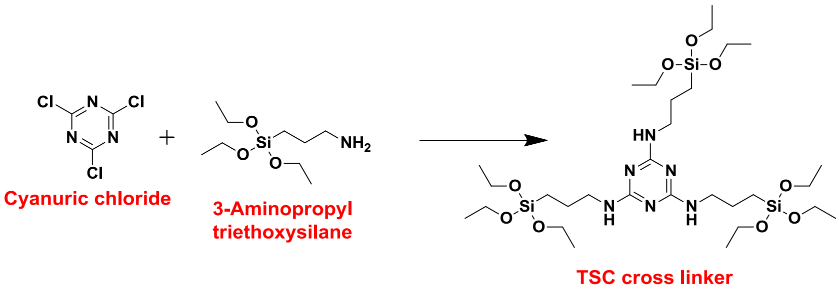
Materials

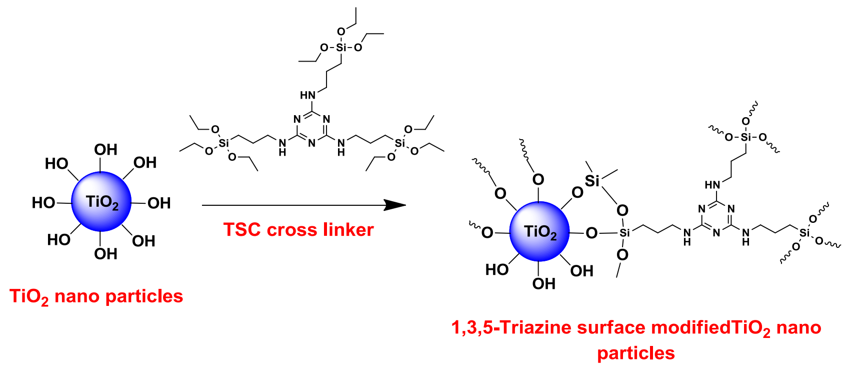
Cyanuric chloride, 3-amino propyl trimethoxysilane (APTES), ethylenediamine, titanium dioxide nanoparticles (anatase and particle size 80–100 nm), triethyl amine, poly tetramethylene glycol with an average molecular weight of 1000 (PTMG-1000) were purchased from Aldrich Chemicals (Milwaukee, WI, U.S.). Desmodur VL (an aromatic polyisocyanate based on diphenylmethane diisocyanate with NCO equivalent weight ~133) obtained from Bayer material science, Germany. Toluene, ethanol, N,N-dimethyl formamide were purchased from Finar Reagents (Mumbai, India).

Characterization methods

FT-IR spectra of synthesized samples were recorded by Thermo Nicolet Nexus 670 spectrometer. The ^1H and ^{13}C NMR analyses were done in VARIENE-200 and BRUKER-300 MHz spectroscopy by taking tetra methyl silane (TMS) as standard at room temperature and dissolving in DMSO-d_6 solvent. The molecular weight of TSC cross-linker was recorded on a LC-MSD-Trap-SL mass spectrometer. Raman spectra was recorded using Horiba JobinYvon Raman spectrometer with a laser excitation wavelength of 632.81 nm. The changes in morphology of nanoparticles and polyurethane composites were observed under FESEM using S4300 SEIN HITACHI Japan at 10 kV. The samples were coated with a thin gold layer of ~5 nm of thickness by sputtering process to make them conducting for SEM analysis. The thermo gravimetric analysis (TGA) experiments were conducted on TGA Q500 Universal TA instrument (UK) at temperature ramp rate of 10 °C min^{-1} from 25 to 600 °C with a continuous N_2 flow at the rate of 30 ml min^{-1}. The universal testing machine (UTM) analysis of free film of coatings was done with AGS-0kNG, SHIMADZU (Japan),

Scheme 1 Synthesis of TSC cross-linker





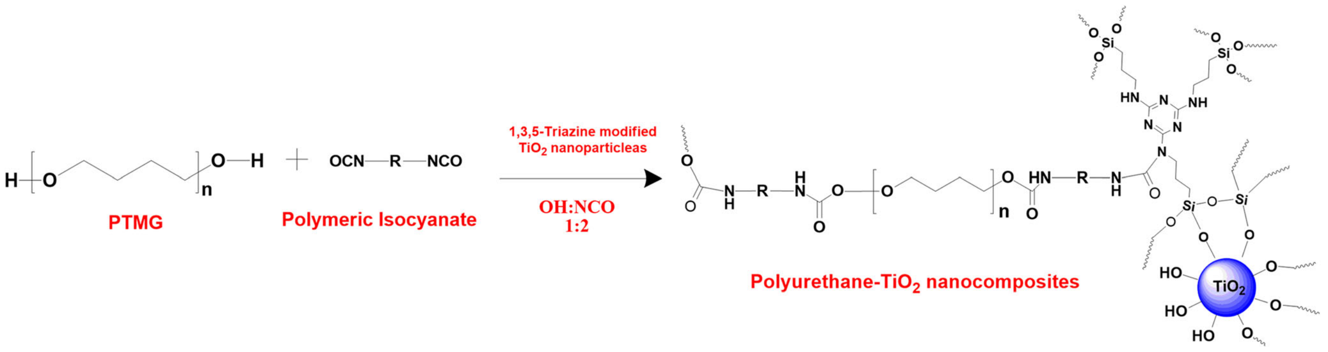
Scheme 2 Representative reaction involved in surface modification of TiO_2

connected with AUTOGRAPH controller/measurement unit using dumbbell shape specimen having 5 cm length. Water contact angle of different polyurethane-TiO_2 nano composite coatings were recorded on Goniometer KRUSS, GmbH Germany (G10MK2 model) by placing a water drop on coating surface using micro syringe. The electrochemical polarization study of the coatings on mild steel panel was done in three electrode method by IM6ex (ZAHNER Elektrik, Germany) Instrument. The electrolyte used is 3.5 % NaCl solution. The salt spray tests were carried out in a salt mist chamber following ASTM B 177–94 standard. A 3.5 wt % NaCl solution was atomized by compressed air in the chamber containing the specimen.

The antibacterial activity of the different coating films were performed on both gram positive and gram negative bacterial strains. The test was conducted according to the procedure of our previous report [27]. In the present work, the *Staphylococcus* spp., *Bacillus* spp., and *Pseudomonas* spp. were used as gram positive bacterial strain and *Escherichia coli* as gram negative. The 24 h aged active bacterial cultures were poured in the Luria Agar medium and allowed to solidify. After solidification of the medium, polymer samples films with 2×2 cm^2 (approx) embedded in the medium and incubated at 37 °C for 24 h. The polymer samples were washed and dried with double distilled water before experiment.

Synthesis of 1, 3, 5-triazine core silane coupling agent (TSC)

Calculated amount of cyanuric chloride (2 gm, 0.010845 moles) was dissolved in 20 g of dry toluene and stirred for 1 h at 50 °C. Then 3-aminopropyltrimethoxysilane (16.8 gm, 0.0759 moles) was added drop wise to the reaction mixture. The reaction mixture was then refluxed for 6 h at 110 °C under nitrogen atmosphere. To neutralize the formed HCl by-product, moisture free ethylenediamine (3.8 gm, 0.06322 moles) was added drop wise. The obtained mixture separated in two layers. The upper layer was carefully removed, from which the solvent and unreacted materials were distilled under vacuum. Finally, a pale-yellow transparent liquid of TSC was obtained as a product (Scheme 1). The structure of the formed product was confirmed by using ^{1}H-NMR, ^{13}C-NMR, FT-IR and ESI-MS spectroscopic techniques.



Scheme 3 Representative reaction involved in the synthesis of PTNs

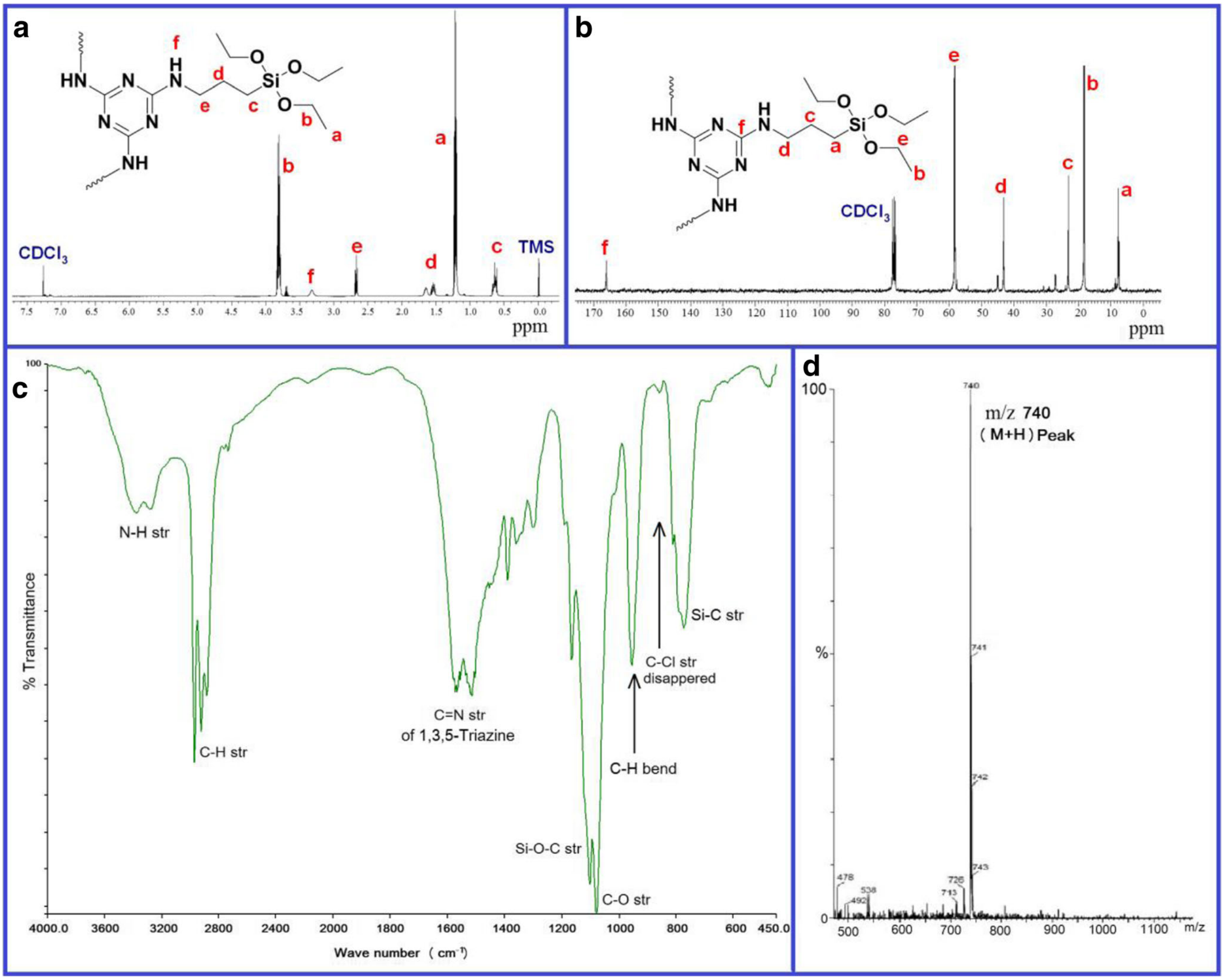


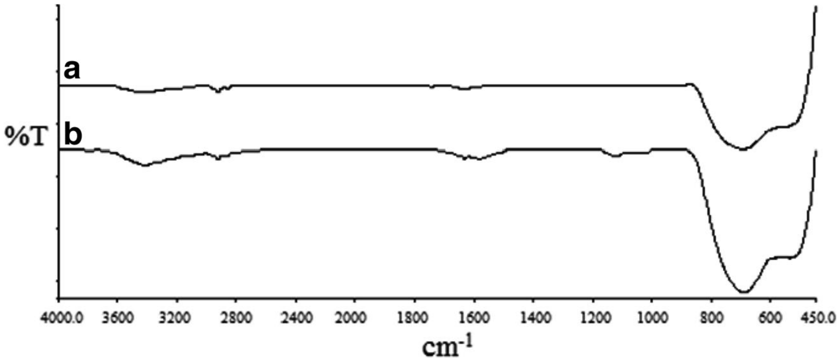
Fig. 1 (**a**) ^{1}H NMR, (**b**) ^{13}C NMR, (**c**) FT-IR and (**d**) ESI-MS analysis of TSC cross-linker

^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.63 (t, 6H, −C$\underline{H}_2$-Si), δ 1.21 (m, 27H, C$\underline{H}_3$-CH_2-O-Si), δ 1.49–1.69 (quintet, 6H,-CH_2-C$\underline{H}_2$-CH_2-), δ 2.66 (t, 6H, −C$\underline{H}_2$-NH-), δ 3.32 (s,3H, −N$\underline{H}$-CH_2-), δ 3.80 (m,18H, CH_3-C$\underline{H}_2$-O-Si).

^{13}C NMR ($CDCl_3$, 300 MHz): δ 7.46 (−$\underline{C}H_2$-Si), δ 18.19 ($\underline{C}H_3$-CH_2-O-Si), δ 22.85 (−CH_2-$\underline{C}H_2$-CH_2-), δ 43.06 (−NH-$\underline{C}H_2$-CH_2-), δ 58.13 (Si-O-$\underline{C}H_2$-CH_3), δ 166.16 (−N=$\underline{C}$-NH-).

FT-IR: 3350.29(N-H str), 2974.77(C-H asym.str), 2927.49(C-H str), 2886.99(C-H sym.str), 1573.92 (−NH_2

Fig. 2 FT-IR analysis of (*a*) pristine TiO_2 and (*b*) 80 % TiO_2



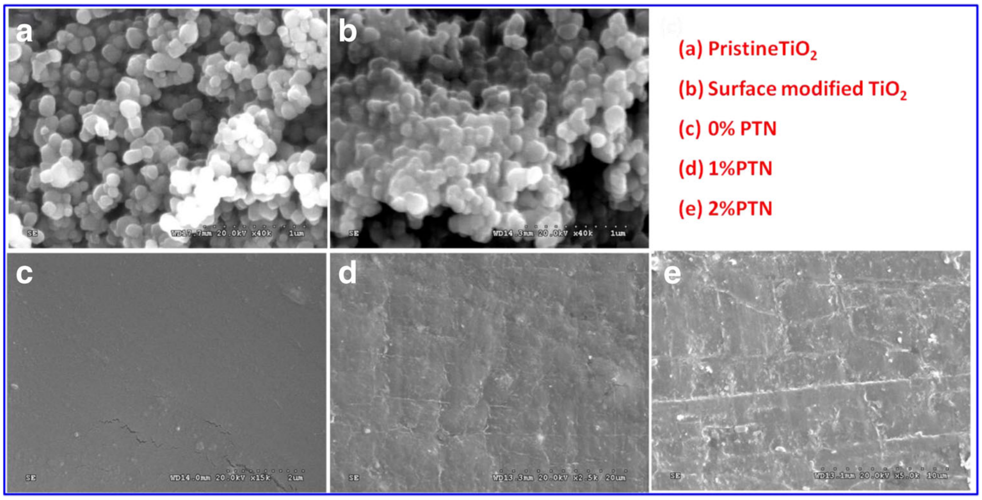


Fig. 3 FESEM results of TiO_2 nanoparticles and corresponding polyurethanes

scissoring), 1517.60 (C=N str), 1103.73(Si-O-C str), 1080.02(C-O str), 480.19 (Si-O str).

ESI-MS: m/z 740 (M+H) peak

Surface modification of TiO_2 nanoparticles

TiO_2 nano particles were dried in a vacuum oven at 100 °C for 24 h to ensure complete drying. These nanoparticles were dispersed in dry toluene using ultrasonic bath for 30 min. Then the nano particles were stirred at room temperature for 1 h at 300 rpm. To this, 80 weight percentage (with respect to TiO_2 nanopowder) of synthesized 1,3,5-triazine core silane coupling agent (TSC) was added. To this, 1.5 ml of Triethyl amine was added as a catalyst. The reaction mixture was then refluxed at 110 °C with stirring under nitrogen atmosphere for 24 h (Scheme 2). The modified nano particles were collected by centrifugation of the reaction mixture at 1500 rpm and washed with toluene and ethanol for 3 times. The modified nanoparticles were dried under vacuum for 24 h.

Synthesis of polyurethane-TiO_2 nano composites (PTNs)

The nanocomposite films were synthesized by in situ polymerization method, i.e., the polymeric diol (PTMG) and polymeric isocyanate are polymerized in presence of surface modified TiO_2 nanoparticles at OH: NCO ratio of 1:2. The secondary –NH groups on the surface of TiO_2 nanoparticles undergo urea formation by reacting with –NCO of the polymeric isocyanate. After reaction the left over –NCO groups react with atmosphereic moisture to form urea segments. Two polyurethane-urea nanocomposites with different TiO_2 particle loading of 1 wt% and 2 wt% were fabricated (Scheme 3). In the case of neat polyurethane (0 % PTN) the excess –NCO present improves the number of hard segments and caters the film formation. All the polymer coatings were casted on a tin foil supported on a glass plate. All the PTNs were cured under atmospheric moisture (25–30 % humidity) at room temperature (30–35 °C) for 1 week The supported films were extracted after amalgamation and cleaning. The free films were characterized by using TGA, UTM, Fog test, electrochemical test, Anti-microbial Test and Contact angle techniques.

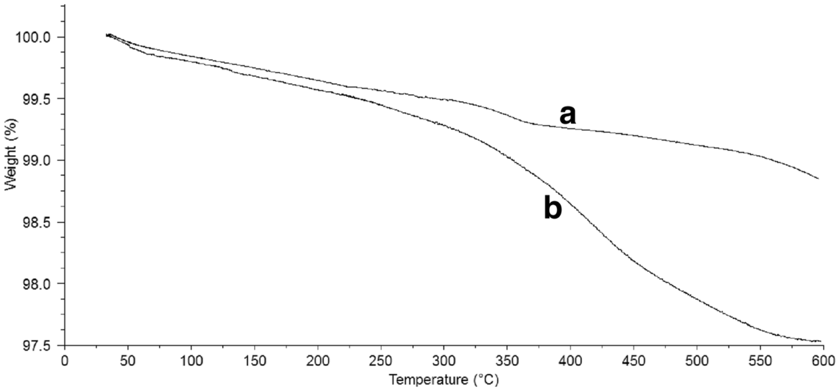


Fig. 4 TGA profile of (*a*) pristine TiO_2 and (*b*) 80 % surface modified TiO_2 nanoparticles

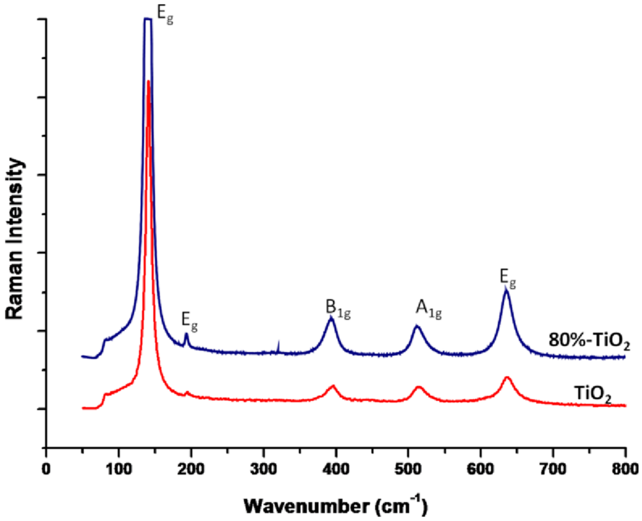


Fig. 5 Raman analysis of pristine TiO_2 and 80 % TiO_2

Results and discussions

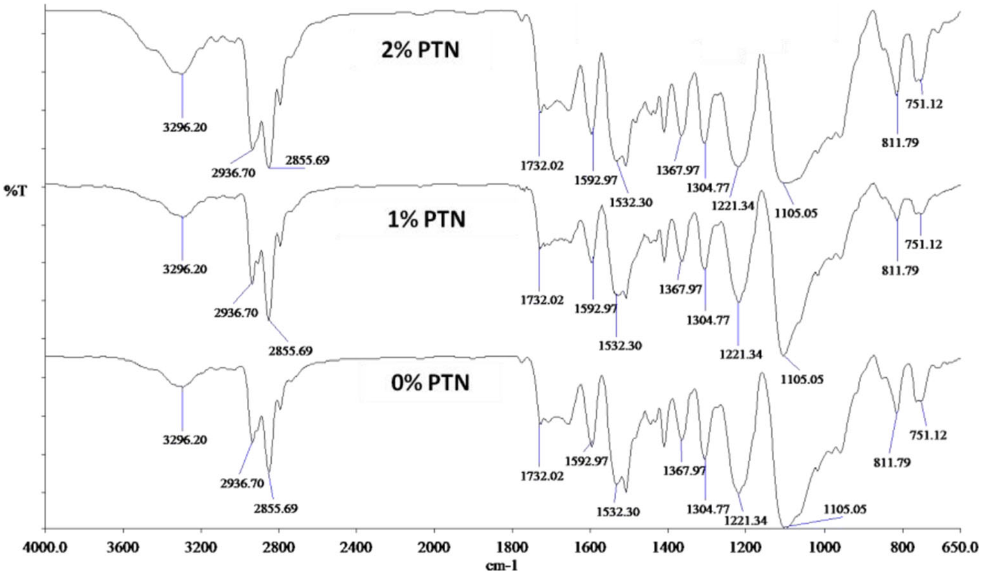
Surface modified TiO_2 nanoparticles

The surface of the TiO_2 nanoparticles was initially terminated with a TSC cross-linker. The structure of TSC cross-linker was confirmed by various spectroscopic techniques. From the FT-IR, the peak at 1517 cm^{-1} correspond to C=N str of 1,3,5-triazine unit; the peak at 1103 cm^{-1} corresponds to Si-O-C str and the peak at 1080 cm^{-1} corresponds to C-O str of TSC cross linker. Moreover, the disappearance of stretching frequency around 850 cm^{-1} corresponding to C-Cl str (cyanuric chloride) assures the formation of TSC cross-linker. The detailed data of ^{1}H-NMR and ^{13}C-NMR of TSC cross-linker are discussed in the experimental section. It could be seen that from ESI-MS spectrum that the formation of (M+H) peak at m/z 740 confirms the formation of TSC cross-linker. All the spectral analysis about TSC cross-linker is shown in Fig. 1.

Once the formation of TSC cross-linker was confirmed then the surface of TiO_2 nanoparticles were modified. The surface modification was confirmed through FT-IR, Raman, FESEM and TGA measurements. The characteristic peak at 1588 cm^{-1} in the FT-IR analysis correspond to C=N str of 1,3,5-triazine; the peak at 1122 cm^{-1}corresponds to Si-O-C stretching and peaks at 685, 539 cm^{-1} corresponds to Ti-O stretching vibrations (Fig. 2). Since pristine TiO_2 nanoparticles of 100 nm particle size were used, it is well observed (from FESEM analysis (Fig. 3a and b)) that following the surface modification the particle size considerable improved to about 250 nm. This could be due to the formation of hierarchial siloxane linkages and 1,3,5-triazine groups at the surface of TiO_2. To further ensure the functionalization of these nanomaterials TGA of the samples were performed. It is obvious from the Fig. 4 that the thermal stability of the surface modified nanoparticles is lesser than the untreated TiO_2 nanoparticles. For instance, the weight loss at temperatures 400 and 500 °C for pristine and surface modified nanoparticles are 0.71 and 1.38; 0.90 and 2.14 respectively. This decrease in the thermal stability was attributed to an oxidative thermal decomposition of organic groups such as 1,3,5-triazines and other organic chains present on the surface.

To further ensure the functionalization Raman analysis was performed. Raman spectroscopy is of keen interest in the characterization of TiO_2 nanoparticles owing to unusual narrowing and shifts with surface modifications.

Fig. 6 FT-IR analysis of polyurethane-TiO_2nanohybrids



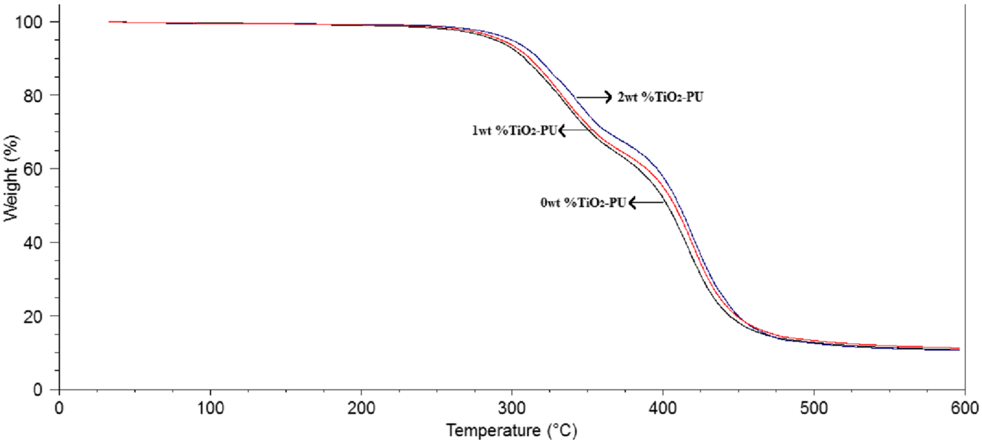


Fig. 7 TGA profile for Polyurethane-TiO_2nano hybrid coatings

Table 1 TGA profile of polyurethane –TiO_2nano hybrid films (PTNs)

Sample code	Onset decomposition temp. [T_{ON}] °C	10 % wt loss (°C)	30 % wt loss (°C)	50 % wt loss (°C)	Wt remaining at 450 °C (%)
0 % PTN	259.43	308.26	350.91	402.65	18.16
1 % PTN	262.68	311.67	353.75	407.29	19.56
2 % PTN	282.29	317.36	362.85	410.61	19.85

Xu et al. [28] explained this reason using phonon confinement model on the basis of Heisenberg uncertainty principle, where a decrease in particle size increases the phonon confinement within the particle and therefore increasing the phonon momentum distribution. This increase in phonon momentum leads to broadened scattering of phonons in accordance with the law of conservation of momentum. This phonon distribution leads to an asymmetric scattering leading to shift in Raman bands. Factor group analysis states that anatase TiO_2 possess six Raman active modes (A_{1g} +2B_{1g} +3E_g). The Raman spectra of TiO_2 contain six allowed modes appear at 144 cm^{-1} (E_g), 197 cm^{-1} (E_g), 399 cm^{-1} (B_{1g}), 513 cm^{-1}(A_{1g}), 519 cm^{-1} (B_{1g}), and 639 cm^{-1} (E_g). In the present study we analyze the Raman spectra of TiO_2 nanoparticles in comparison with that of surface functionalized TiO_2 nanoparticles. Comparing their respective Raman spectra, it is clear that the Raman bands shift towards higher wave number and their intensities relatively decrease in case of pristine TiO_2 nanoparticles, which show that there is an increase in size with surface modification (Fig. 5).

TiO_2 – polyurethane hybrid film

The surface modified TiO_2 nanoparticles were incorporated into the polyurethane nanocomposite in different weight percentages such as 0, 1 and 2 %. The resulting polyurethane-TiO_2 nanocomposite (PTNs) formation was confirmed from their characteristic peaks in the FT-IR spectra. From Fig. 6, the N-H str of urethane linkage observed at 3314 cm^{-1} peak around 2800–3000 cm^{-1} corresponds to C-H stretching vibrations. The peaks in the range 1720 to 1700 cm^{-1} correspond to the C=O str of urethane linkage and the peaks around 1532 cm^{-1} corresponds to C-N str and N-H bending of urethane linkage [29, 30]. The peak around 1100 cm^{-1} corresponds to the Si-O-Si linkage of modified nano particles. Moreover, it is also observed that the disappearance of NCO stretching frequency around 2200 cm^{-1}, which confirms the complete curing of the polyurethanes. The nanoparticle incorporation was also confirmed from FESEM results. With increase in the loading of surface modified nanoparticles into polyurethane matrix, the surface roughness increases due to the formation of pleats on the film surface (Fig. 3c–e). All the above

Table 2 Tensile strength of Hybrid films

S.No	Sample code	% of elongation	Tensile strength (MPa)
1.	0 % PTN	14.84	0.86
2.	1 % PTN	34.62	1.79
3.	2 % PTN	50.11	3.94

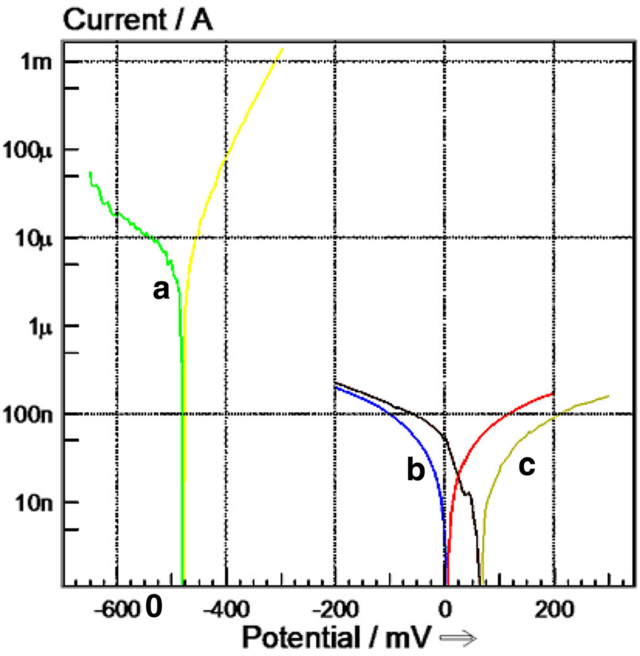


Fig. 8 The polarization curves of (*a*) bare metal (*b*) 1 % PTN (*c*) 2%PTN evaluated by the Tafel method in a 3.5 % NaCl solution

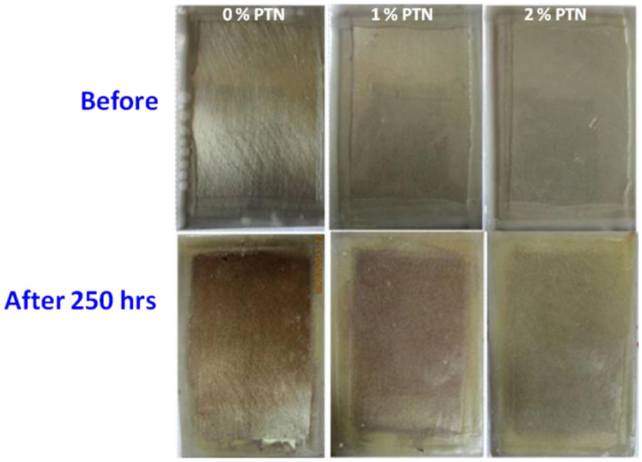


Fig. 9 200 h salt spray results of different hybrid coatings in 5 % NaCl solution (*Top row*-Before testing; *Bottom row*-After 250 h)

characterization clearly suggest the formation of polyurethane hybrids. Once the formation of PTNs was confirmed it was tested for their thermal stability. From TGA analysis, the onset decomposition temperature, 30 % weight loss temperature, 50 % weight loss temperature, weight remaining at 450 °C are given in the Fig. 7 and Table 1. With increase in nanoparticle content thermal stability of the polyurethane hybrids also increases due to the formation of highly cross-linked network structures. Since, the modified nanoparticles have a secondary N-H group and which can react with isocyanate groups to form urea linkages. These urea linkages can form highly cross-linked structures with polyurethane-urea network through hydrogen bondings. This type of cross-linked structures act as a thermal insulator and mass transport barrier to the volatile products generated during decomposition and hence increase the thermal stability of the polyurethane hybrid coatings. The addition of nanoparticles also shows an enhanced mechanical stability. From Table 2 the results for the mechanical tests are summarized. As it is evident, in comparision with neat polyurethane, the addition of TiO_2 nanoparticles increase tensile strength and elongation at break. In fact, TiO_2 particles are rigid and have a higher modulus than the neat polyurethane coating and therefore, both modulus and elongation at break of the polyurethane coating are greatly affected by their inclusion. For example, the % of elongation and tensile strength for the neat polyurethane, 1 % PTN and 2 % PTN are 14.84 and 0.86 MPa; 34.62 and 1.79 MPa; 50.11 and 3.96 MPa respectively. This improvement in the mechanical properties is mainly due to the uniform distribution of modified nanoparticles in the polyurethane matrix. The corrosion resistance of the polyurethane coating also increases with loading of modified TiO_2 content in the formulation. For instance, from electrochemical polarization studies, the corrosion resistance potential (E_{corr}) and corrosion current (I_{corr}) values of the bare metal, 1 % PTN and 2 % PTN are −476.6 mV and 3.86 µA; 3.74 mV and 24.7 nA; 81.07 mV and 40.4 nA respectively (Fig. 8 and Table 3). The above result implies that the TiO_2 modified hybrid coatings are more inert towards the electrochemical corrosion. Similar results were also observed from the fog test (salt spray analysis) and the results were shown in Fig. 9. It is observed that with increase in the nanoparticle content, the corrosion resistance of coating on the metal panels improved. This is again credited to the formation of more cross-linked structures with increasing TiO_2 content. The inorganic domain along

Table 3 Electro chemical data of various polyurethane urea

Sample code	E_{corr} (mV)	I_{corr}	b_C (mV/dec)	b_a (mV/dec)	R_p kΩcm^2	Corrosion Rate(C_R) (Miles per year)
Bare metal	−476.6	3.86 µA	−140	50.4	8.85×10^3	–
PU- 1 % TiO_2	3.747	40.4 nA	−166	176	51.360×10^6	9.16×10^{-4}
PU- 2 % TiO_2	81.07	24.7 nA	−357	330	46.897×10^6	1.4986×10^{-3}

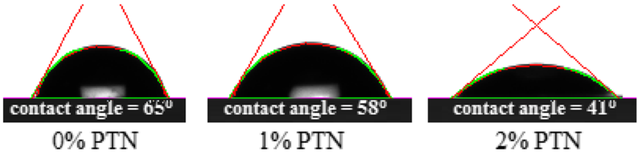


Fig. 10 Water contact angle results

Table 4 Contact angle data of various PTNs

S.No	Sample Code	Water Contact angle
1	0 % PTN	65°
2	1 % PTN	58°
3	2 % PTN	41°

with urethane and urea linkage combines to form a compact dense and well adherent coating at the metal surface. This impedes the migration of the corrosive ions there by providing protection to the metal substrate. This is due to the presence of the inorganic segments TiO_2 and the siloxane linkages in the coating formulation, which provide superior barrier protection over corrosive species. From the water contact angle study, the contact angle of the water drop was reduced with increasing the weight percentage of surface modified TiO_2 in the polyurethane composite coating. For instance, the water contact angles for 0, 1 and 2 % PTNs are 65°, 58°, 41° respectively (Fig. 10 and Table 4). The decrement in the contact angle is due to the inherent hydrophilic nature of the incorporated TiO_2 nanoparticles in the coating formulation. This type of behaviour leads to increase in the wettability of the polyurethane film and this helps in the development of self-cleanable coatings. Finally, the antibacterial active test result shows excellent antibacterial activity of the coating films against the bacterial stains except for *Candida Albicans*. The nano composite polyurethane coating films are showing good antibacterial properties compared to the pure polyurethane and which is again credited to the presence of inorganic groups in the coating formulation [31, 32]. These results were shown in Fig. 11 and tabulated in Table 5.

Conclusion

The present work is an attempt to exploit TiO_2 nanoparticles for the development of functional polyurethane hybrid. The surface modification of nanoparticles were established using 1,3,5-triazine containing silane coupling agent (TSC). The modified nanoparticle were decorated with secondary amine groups which covalently bond with the polyurethane matrix to generate potential functional hybrids. The engineered hybrids were anti-corrosive, microbial resistant and hydrophilic in

Fig. 11 Anti bacterial activity of 0, 1 and 2 % PTNs

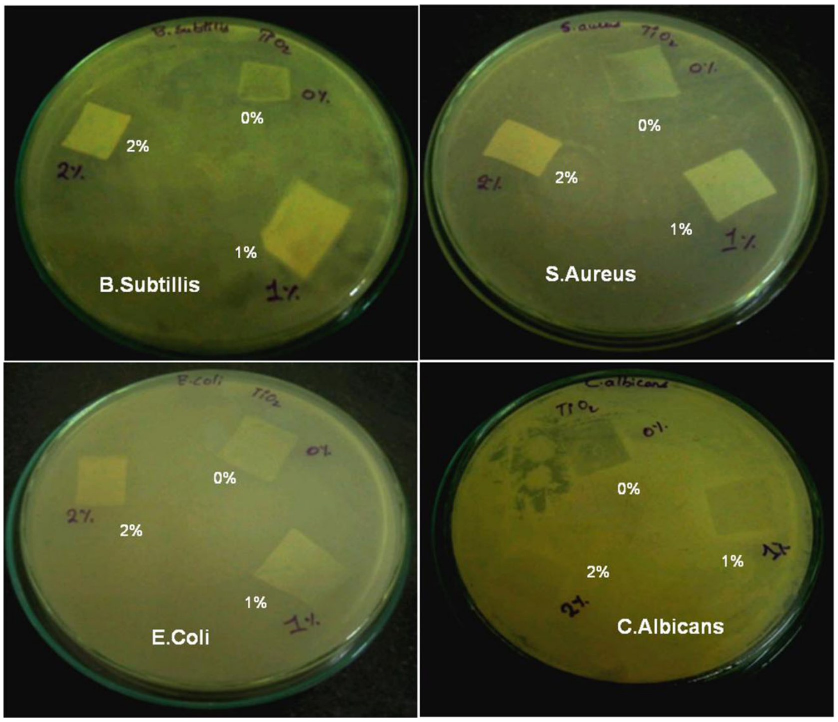


Table 5 Anti-microbial results of various PTNs on different bacterial and fungal solutions

Sample code	Bacillus subtilis	Escherichia coli	Staphylococcus aureus	Candida Albicans
PU- 0 % TiO_2	+	+	−	−
PU- 1 % TiO_2	++	+	+	−
PU- 2 % TiO_2	++	++	++	−

Here, "+" indicates showing of antimicrobial activity of the coating film. "-"indicates the negative test result of the coating film

nature. The filler material, TiO_2 nanoparticles is economic and easily available, it is fiscal to develop such coatings. The developed hybrid coatings were inherently hydrophilic which could be useful in the development of self-cleanable coatings on glass, tiles, ceramics, textiles etc. Since the coatings are thermo-mechanically stable, corrosion resistant and anti bacterial in nature, they could be used in marine and moist environment. In view of the promising potential applications TiO_2 based hybrid coatings, there are many interesting questions to be answered which could open up new avenues of research in functional coating technologies.

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