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Hydrophobic Hierarchical Structures – Anti Corrosive Coating

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Abstract—*Shipping industry extensively confronts the corrosion which takes place onboard ships, barges, oil rigs and other marine related equipment (Aprox. Rs. 6.21 Lakhs per layer for underwater coating of 105 m ship). In order to reduce these efforts, non toxic anti corrosive coatings are being developed which can sustain long in the corrosive environment and keep the operational availability of these platforms. Presently epoxy based paints are mainly used for ships and offshore structures, in particular for underwater areas, boot top zone, tide and splash zone, underdeck areas, decks, holds and in various tanks as epoxy has the characteristics of corrosion resistant, strong adhesion and resistance to chemicals. In this paper, we have demonstrated hydrophobic hierarchical surface of the epoxy by spin casting technique on glass substrate by reinforcing nano carbon particles obtained from controlled combustion of camphor in the polymer matrix. Hydrophilic pristine epoxy surface was converted to hydrophobic surface using easily available camphor soot. Water contact angles of the coating were measured using sessile drop technique. Contact angle was observed upto 85^o compared to 52° with pristine epoxy showing an increment of upto 70% at 0.5 weight percentage of additive. Thus wettability of the resultant coating is reduced enhancing the corrosion resistance. We have measured and compared the contact angle with varying percentage of the camphor soot from 0.5% to 5% in epoxy. The hydrophobicity of the composite surface is explained by the McCarthy hypothesis. Also addition of carbon soot as additive may improve anti fouling properties of the coating as carbon is known for antibacterial, anti-settlement and salt rejection properties.*

Keywords*: hydrophobicity, wettability, contact angle, hierarchical structure.*

1. INTRODUCTION

During its operational period, ship is always operated in saline environment. This environment causes various chemical influences on ship's material. This results in different corrosion damages to the ships material. The material damage caused by corrosion especially on the underwater area (structural material) can affect both the safety and overall life of the ship and its crew there by defeating its intended purpose to float. Corrosion protection is an important process in shipping industry which affects economically to not only its operational life and maintenance but also ship building. Hence in order to improve the operational availability and safety of the ship, various measures and technological procedures are being adopted to prevent corrosion damages. These procedures include use of protective coatings and corrosion resistant materials, cathodic protection, and the application of inhibitors.

Underwater hull area of the ship submerged in the sea water is highly vulnerable to the corrosion. Therefore total five to six coatings of anti corrosive and antifouling paints are generally applied on the underwater area. (Aprox. expenditure is Rs. 6.21 Lakhs per layer for underwater coating of 105 m ship). In order to reduce this cost and improve the life of these coatings, we have tried to develop hydrophobic coating with low cost polymer system and cheapest additive for the ship's underwater hull by simple fabrication technique. In this paper, we have used epoxy polymer with the soot of camphor.

Excellent adhesion property to a variety of surfaces is the main reason of wide usage of epoxy resin in surface coating field. Further because of its unique balance of properties like surface hardness, flexibility and toughness, these resins are widely used in coating of underwater hull. As compared with most of polymer matrices, epoxy resins are having good dimensional stability and chemical resistance. In addition to that, they exhibit better thermal, mechanical and electrical properties.

As the coal tar based paints are harmful to environment, ban on use of them is eminent. Hence presently research is going on to use other environment friendly materials as binders/ fillers. However limited information is available on alternate materials for coal tar in protective coating formulation. Jagtap et al studied an alternative to Coal tar epoxy (CTE) paint and found composition of epoxy-hydrocarbon resin (HR)-flexibilizer (FL)-polyamide-polyamine has similar corrosion protection and mechanical properties as of coal tar epoxy paints [1]. Dhanalaxmi et al have tried a variety of curing agent with two part epoxy resin for underwater paint application and reported better underwater adhesion strength and in situ curing with ketimine based curing agent [2].

A new approach to supplement the polymer matrices with nano sized particles such as carbon nano fibres (CNFs), nano clays, carbon nano tubes (CNTs), and metal oxide nano particles etc. is offering enhanced properties of the polymer matrices. The nano particles are being reinforced to take advantage of their unique properties such as nanometric size, high specific surface areas and the possibility of combining them with conventional reinforcements. This approach is presently gaining momentum in research field of nano composites [3]. Manoj Singla et al tried fly-ash reinforcements in epoxy polymer, and found rise in compressive strength of composite with the addition of fly-ash because of hollowness of its particles & strong interfacial energy [4]]. Sahoo et al investigated candle soot particles and suggested use of these water repellent soot particles as feelers with different polymer matrices for preparation of superhydrophobic surfaces [5]. Further they have synthesized a series of EPF (Expanded Polystyrene Foam) matrices with fillers such as graphite, candle soot and camphor soot and found the increase in surface hydrophobicity [6]. The nano broccoli like hierarchical microstructure was achieved for PVDF/DMF and camphor soot particle, which reveals the superhydrophobic surface [7]. Hence we selected the camphor soot as the feeler for the experimentation.

Camphor ($C_{10}H_{16}O$), a botanical hydrocarbon is a white crystalline solid that sublimates at room temperature and melting point at 180 deg C [8]. Camphor if burned atmospherically undergoes thermal decomposition process to form soot. Soot is the black solid primarily composed of carbon and consists of agglomerated particles with diameter of about 10-30 nm [9]. These nano sized particles exhibited diamond-like carbon nanostructure and with the presence of hydrophobic functional groups, it showed superhydrophobic characteristics [10].

The epoxy polymer matrices with nano-sized feeler particles such as camphor soot to improve the properties of the composite over epoxy resin. The epoxy composite is studied for wettability to test its usefulness as anti corrosive paint. The wetting phenomenon describes the interfacial interactions between a liquid and solid in the presence of a gas, usually air. The nature of wetting interaction is defined by the balance between the cohesive forces within the liquid and solid and its adhesion to the surrounding environment. The wettability can be measured using contact angle technique and the water contact angles (WCA) are classified as hydrophobic and hydrophilic i.e. if contact angle of the water with the surface is below 90^{O}, it is termed as hydrophilic and if it is more than 90^{O} then the surface is called as Hydrophobic. The superhydrophobic surfaces are those surfaces with contact angle more than 150^{O}.

2. EXPERIMENTAL DETAILS

2.1. Materials

Epoxy LY 1564 (DGEBA) and its hardener XB 3486 (Amine type) were purchased from Huntsman Chemicals and Acetone used as solvent was purchased from Sigma–Aldrich (India) and both these chemicals are used as received. Glass slides (30 x 35 x 3 mm) were received from Fisher Scientific (India). Camphor ($C_{10}H_{16}O$) in tablets form with a size of 8 x 5 mm were used without any further purification. Millipore Milli-Q system produced Deionized water (DI water) at ambient temperature was used as liquid for measurement of contact angle.

2.2. Surface treatment of glass slides and collection of camphor soot particles

Glass slides were prepared by ultrasonication in Sonicator (Model-EI-6LH-SP) at 20 kHz/ 20 W in ethanol for 15 min. Ethanol is replaced with DI water and glass slides were again ultrasonicated for 20 min. Post ultrasonication, these glass slides were used as substrates to coat. Camphor tablet was placed in a simple laboratory fume hood and was burnt in atmosphere. A glass slide was held at approximate distance of 50mm above the flame of the camphor tablet to collect soot emitted from it. The soot particles were collected from glass slides and stored in a glass bottle without any treatment for further use as feelers.

2.3. Preparation of epoxy composite matrix

Epoxy composites were prepared using two processes as enumerated below. In one process, Acetone is used as solvent and in another process composites were made without solvent i.e. direct reinforcing of campor soot in the epoxy matrix. In the solvent based method, first camphor soot was mixed with acetone in the ratio of (100 ml to 0.1 gm). The sample was ultrasonicated for 20 min for proper dissolving of soot powder in acetone. Post ultrasonication, epoxy polymer was added in the mixture in calculated amount as per weight percentage and kept 8 hours for mechanical stirring at 300 rpm to complete the removal of the solvent. After completion of stirring, the hardener was added in 100:34 weight ratio into the mixture for curing. Mixture was stirred manually to avoid any bubble formation. Samples were prepared for 0.5,1,3 and 5 weight % of epoxy.

2.4. Fabrication of surface coating and film characterization

Spin coater (Holmarc make) was used to coat the epoxy polymer/camphor soot particles solution on the glass slide prepared. Approximately 2ml of composite solution was poured on the glass slide and spin coated at 2000 rpm for 30 sec. This step is repeated twice to form a dense layer on the surface of the substrate. Uniform coating thickness was maintained on all coated glass slides for comparative study of wettability property. Morphology of the epoxy composite coated samples and its Energy Dispersive X-ray (EDX) analysis were studied using FE-SEM (Carle Zeiss make, Germany). The water contact angles (WCA) of the samples were measured by the sessile drop technique using Krüss DSA25 (Germany) contact angle goniometer. During this measurement, sessile drop was formed on the of the glass substrate by delivering 8μL of DI water from the syringe. Five measurements were taken and average of them is used for the analysis.

3. RESULTS AND DISCUSSION

Combustion of camphor in atmosphere is a thermal decomposition process, which emits carbon soot particles without using any catalyst precursor. Several particles are seen to form aggregates on the glass slides.

3.1. Microstructure of camphor soot

SEM images of combustion products of camphor at 25000x and 100000x magnification in figure 1 show the non uniform surface morphology of carbon deposits and numerous grains of nano material. These extremely small carbon soot particles are having size varying from 20-80 nm. These carbon particles are not present as discrete entities, but rather as a gathering of spherically shaped bodies agglomerated to form various clusters. This conglomeration might be the result of higher reaction times as well as a consequence of the cooling from synthesis to room temperature. Reactive dangling bonds on the surface of these nanospheres provide them with a high surface reactivity which results in the agglomeration of nano particles. Carbon nanospheres are characterized by high surface area and porosity, relatively high thermal and chemical stability and low density [11].

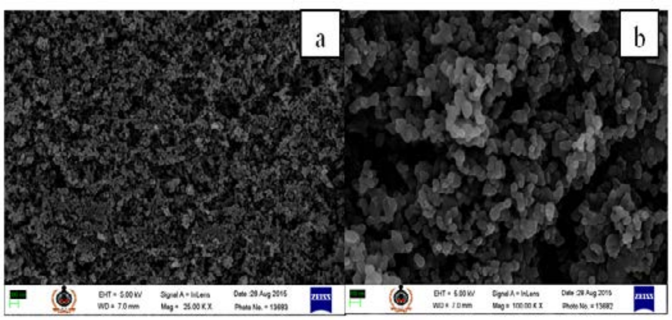

Fig. 1: SEM images of camphor soot at 25000x (a) and 100000x (b)

EDX analysis of camphor soot particles shows the significant amount of carbon in the soot particles, as shown in figure 2. The thermal decomposition of camphor in atmosphere produces soot which is primarily composed of carbon (86.93%) and the remaining is Oxygen (12.46%) which might be present due to incomplete combustion. Presence of very small amount of gold (0.61%) is due to sputter coating requirement of the sample prior loading in FESEM machine and can be safely neglected. Hence camphor soot is not required to be purified further for use as feeler in epoxy polymer matrix since no impurity is present in it as revealed by the EDX analysis. This shows combustion of the camphor in atmosphere is the easiest and cheap technique of synthesizing carbon nanoparticles without use of any catalyst precursor and with no further purification required.

Element	Weight%	Atomic%
C	86.93	90.25
O	12.46	9.71
Au	0.61	0.04

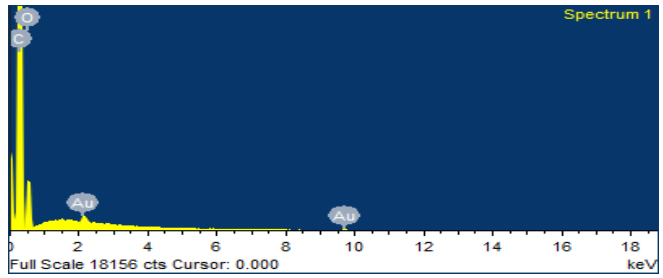

Fig. 2: EDS analysis of camphor soot

3.2. Microstructure of epoxy composite

As observed in the morphology of the pristine epoxy and its composite in fig.2, the composite prepared using solvent method (e & f) shows better dispersion of soot particles than non solvent method (c & d). In the non solvent method, the agglomerated soot is clearly visible in the images showing less dispersion of soot particles in epoxy polymer matrix. This indicates requirement of solvent method for filler addition with epoxy matrix to achieve uniform mixing.

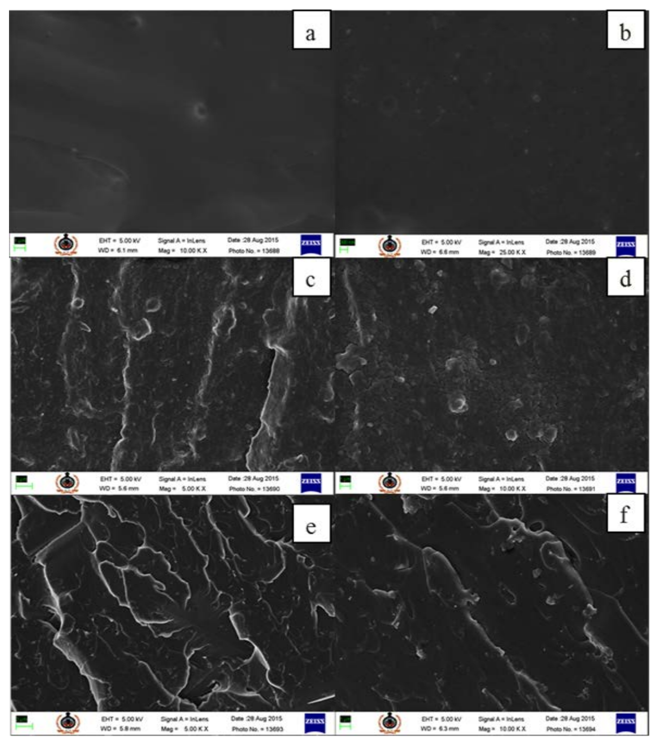

Fig. 3: SEM images of epoxy composite: Pristine epoxy (a & b), fractured epoxy composite with 0.5% carbon non solvent method (c & d), solvent method (e & f)

3.3. Wettability

The wettability property was analyzed by measurement of water contact angle. The water contact angle measurement on any surface is carried out to understand its hydrophilic/ hydrophobic nature of the surface. This depends on the interfacial forces between the water molecules and the surface materials. After addition of the soot particles as filler in epoxy matrix, Epoxy composite coated glass substrate demonstrated the following contact angles as shown in figure 4.

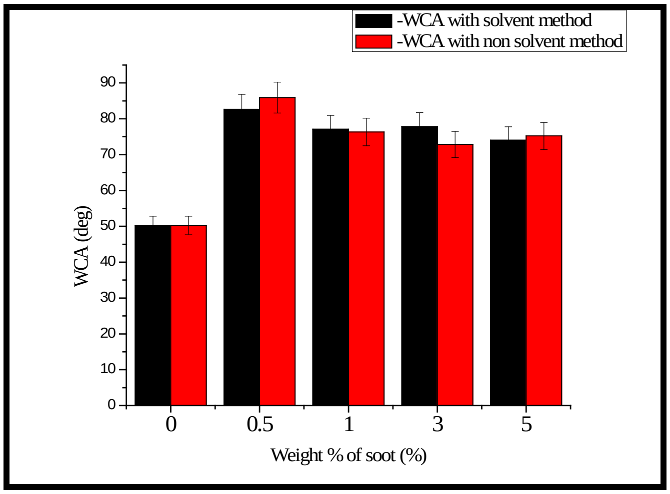

Fig. 4: Weight % of camphor soot in epoxy matrix v/s water contact angle

The contact angles of solvent based and non solvent based composite surfaces are similar though the surface morphology differs in the dispersion of soot particles as observed in SEM images. As shown in figure 4, it is clearly evident that enhancement in water contact angle values of epoxy composite were observed on addition of feeler material camphor soot in the epoxy polymer matrix. This increase in contact angle values is highest at 0.5 weight % in the selected percentages for experiments. About 70% of rise in the value of contact angle has been noted at this weight percentage. On increasing the weight percentage of the water repellent soot from 0.5%, slight decrease in contact angle values observed and the contact angle values were found to be stable at ($75^O \pm 2.5^O$) with any further addition of camphor soot percentage. Saturation can be one of the causes of the stability in value of contact angle. The rise in contact angle is attributed to the addition of the filler material camphor soot which is having strong water repellant property. Hence due to its strong water repellent property, while curing of the epoxy composite; hierarchical structures were created on the surface which provided the increase in contact angle. However further increase in percentage of camphor soot have not improved the contact angle showing saturation. The epoxy coating surface which showed the contact angle of 50^O (hydrophilic surface) has been converted to approach the hydrophobic surface (contact angle $>90^O$) by addition of 0.5% camphor soot. The theory of contact angle is discussed in paragraphs below.

3.4. Theory of contact angle

Young's equation relates the contact angle of a solid surface with the three interfacial surface energies involved in the formation of liquid droplet on the surface namely solid - liquid (γ_{sl}), solid-vapour (γ_{sv}), liquid-vapour (γ_{lv}). The equation is given as

$$\cos\theta = (\gamma_{sv} - \gamma_{sl}) / \gamma_{lv} \tag{1}$$

However, Wenzel has pointed out that the real surface of any solid material is always greater than its geometric surface due to its surface irregularities i.e. roughness. This roughness factor (r) is quantified by the ratio of actual surface area to the geometric surface area. Thus this roughness directly affects the wetting properties of that solid substance. He has developed the equation for determining the water contact angle using roughness factor (r) and is given by

$$\cos\theta_{rough} = r.\cos\theta_{smooth} \tag{2}$$

Further, he stated that the wetting properties of the solid are magnified by the effect of a roughened surface. As the surface becomes rougher, solid substance having positive wetting tendency will wet the surface more readily and if it is having water-repelling tendency, it will repel the water more strongly [12].

Cassie further modified the above equation for the composite surfaces. He stated the following equation:

$$\cos\theta_c = f_1 \cos\theta_1 + f_2 \cos\theta_2 \tag{3}$$

$$f_1 + f_2 = 1$$

Where, (θ_c) is contact angle of a binary composite surface which contains two components with contact angles of θ_1 and θ_2 and area fractions of f_1 and f_2 [13].

All the above equations are focused on the wetting area, however Mccarthy experimentally proved that, the contact angle behavior (advancing, receding, and hysteresis) is determined by interactions of the liquid and the solid at the three-phase contact line alone and that the interfacial area within the contact perimeter is irrelevant. Wenzel's and Cassie's equations are valid only to the extent that the structure of the contact area reflects the ground-state energies of contact lines and the transition states between them [14].

3.5. Surface roughness analysis

The SPIP software is used to plot the 3D image of the pristine epoxy and its polymer composite for surface analysis. As shown in figure 5, on comparison of the surface area roughness values (Sa values) of the two images, it clearly shows the roughness values of pristine epoxy surface is less rougher than with camphor soot doped epoxy composite. Thus surface has became rougher on addition of feeler and hierarchical structures are formed which improved the water contact angle of the composite

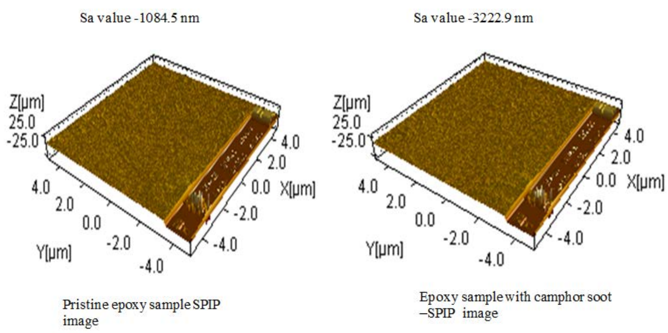

Fig. 5: SPIP image of the clear epoxy and epoxy composite with Sa value

Further the use of various carbon materials such as graphite, CNTs, diamond-like-carbon (DLC), fullerene, carbon blacks etc. as feelers in antifouling coatings is extensively studied because of their known antibacterial, anti-settlement and salt rejection properties [15]. Hence using camphor soot as an additive for underwater paint in epoxy polymer matrix may also improve its anti-fouling property.

4. CONCLUSION

Carbonaceous soot produced from camphor without use of catalyst precursor show the presence of significant amount of carbon nanomaterials as revealed by EDS analysis. This proved the camphor as a good precursor. The camphor soot having excellent water resistance properties used as a feeler material in the epoxy polymer matrix with excellent adhesion property. On addition of filler camphor soot in the epoxy polymer matrix, we have observed enhancement in the water resistance property of the epoxy. An increase of about 70% in the value of water contact angle has been observed on addition of 0.5% weight of feeler material in epoxy hence reducing the surface wettability. This resulted in improvement in the corrosion resistance. Thus a composite with excellent adhesion and good water resistance property has been formed and it can be used in preparation of paint for application on underwater hull area of the ship. The addition of filler in epoxy matrix should be done using solvent based methods only to achieve uniform dispersion. The above composition can also provide an environment friendly alternative to Coal tar epoxy paint in future.

5. ACKNOWLEDGEMENTS

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