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Research Article

Preparation of an anti-corrosive coating from waste pet bottles to inhibit the corrosive effects of water

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Abstract

It has been determined that among all types of corrosions, water corrosion is responsible for a large fraction of the total expenditure incurred in several industries. Therefore it is imperative that we minimize the ill-effects of the aforementioned corrosion. Since Polyethylene Terephthalate (PET) absorbs very little water and shows good resistance towards it, it can be used to form a coating that will help protect several key equipment in industries such as boilers, pipes etc. Furthermore PET can easily be obtained from the discarded soft-drink bottles, alcoholic beverages etc. In addition to finding an effective means to combat water corrosion, the present study will also help to facilitate the overall reduction of PET waste using landfills and other waste disposal techniques. Basically the PET obtained from waste bottles is converted to Bis-2 Hydroxyethyl Terephthalate (BHET) by transesterification, followed by the synthesis of poly ethylene terephthalate-co-isophthalate .The poly ethylene terephthalate-co-isophthalate is then converted into nano form through sonication technique . Mild steel has been chosen as the substrate for this study, due to its low cost and high preference in the salt industry. Polyethylene terephthalate-co-isophthalate nanoparticles are coated onto the substrates surface and is then tested for its efficiency against 5% salt water solution using a salt spray chamber.

Keywords: Polyethylene; Terephthalate-co-Isophthalate; Anticorrosive coating; Nanoparticles; Salt spray analysis.

Introduction

Recent studies on effects of corrosion have estimated that close to 276 billion dollars is being spent to protect mega structures, equipment's and machines from the harmful effects of corrosion. Corrosion is the deterioration of a material as a result of chemical reactions between the material and its surroundings. They tend to degrade the useful properties of the material including strength, appearance and their permeability to liquids and gases. It generally occurs due to the natural tendency of these materials to return to their original state. Since nearly all industries utilize metals in some way or another the problem of metallic corrosion occupies center stage in nearly all research on corrosion.

Furthermore as methods to combat environmental pollution are becoming part of the mainstream rhetoric, it is becoming incumbent on industries and ordinary citizens alike to reduce the quantity of waste generated. Industries are facing the brunt of these challenges as they now have the twin objectives of scaling up their production processes while minimizing the negative externality they pose on the environment.

It is against such a backdrop that studies are being undertaken to find ways by which we can recycle or re-utilize some of the waste generated. A significant portion of these studies are focused on the re-utilization of polymers by making them undergo various chemical changes. One such polymer frequently experimented on is Polyethylene Terephthalate bottles or commercially known as PET bottles. This is due to the large solid waste generation after their use as a packaging medium in water bottles, among other items. Furthermore low cost of PET bottles makes it an attractive material to research on.

PET is a thermoplastic polymer obtained from terephthalic acid and ethylene glycol, and possesses various properties which include good hydrophobicity , exceptional dimensional

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stability, excellent electrical properties and resistance to chemical attack .It possesses high environmental stress crack resistance in particular, in comparison to polycarbonates, due to the semi-crystalline nature of polyesters, very good heat and ageing resistance and also low creep, even at elevated temperatures. In addition to the aforementioned properties it also has very good color stability and excellent wear properties. PET exhibits very good chemical resistance to dilute acids, oils and greases, aliphatic hydrocarbons, alcohols and an appreciable resistance to alkalis, –aromatic hydrocarbons, and halogenated hydrocarbons [2]

These properties make PET non-biodegradable but, it also strengthens its use as a protective anti-corrosive coating for metals. Keeping the aforementioned points in mind the objectives of nearly all research on this polymer are to, reduce the quantity of PET bottles present in the environment and Use the properties of PET to form an anticorrosive coating. Despite the various advantageous properties of PET, PET alone cannot be used to create an efficacious coating. For this reason there arises a need to modify the structure of PET. Hence the process of copolymerization is done to produce the copolymer poly (ethylene terephthalate-co-isophthalate) by reacting bis-2-hydroxyethyl terephthalate and Ethylene isophthalate cyclic dimer (EI c-2mer) acid under specific conditions [12]. Poly (ethylene terephthalate-co-isophthalate) was found to have a number of properties that supported its use as an anticorrosive coating [9] [10].

This copolymer is then converted into nanoparticles with the help of a sonicator [3]. Along with the copolymer, certain other additives are also added so as to obtain the required composition and properties in the paint emulsion to form the anti-corrosive coating [15]. Once the mild steel piece is coated, a number of tests will be performed on the test piece to determine the performance of the coating in several corrosive media [1].

An anticorrosive coating consists of multiple layers of different coatings with different purposes. The various coatings can be organic, inorganic or metallic. The first coat is called the primer followed by the intermediate coat and finally there is the topcoat. The functions of the various coats are the primer, intermediate and top coat. The primer protects the substrate from corrosion and should be adhesive with the substrate, the intermediate coat provides an increase in the thickness of the coat and prevents the penetration of undesirable species onto the substrate surface, and the top coat provides good resistance to a range of external environments [16]. For testing the efficiency of the coating, the coating must be subjected to accelerated laboratory tests with a specific substrate and coating. This project uses mild steel as the substrate medium.

Mild steel is the most commonly used steel in all forms of industrial applications and industrial manufacturing. It is basically made up of 0.25-0.29% carbon, 0.2% copper, 98% iron and 1.03 % manganese. Salt industries generally tend to use mild steel for construction of pipelines, tanks due to their low cost. But the problem with using mild steel is that it is in constant contact with the sea water reducing its lifespan [1,6,14].Therefore to prolong the life of the metal it's important to utilize an effective anti-corrosive coating. This paper studies the manufacturing and effectiveness of polyethylene terephthalate-co-isophthalate anticorrosive coating on mild steel.

Materials and methods

Chemicals and reagents

The A.R grade of Ethylene glycol, zinc acetate, dimethyl isophthalate and ethylene glycol diacetate were purchased from Sigma Aldrich Private Limited and was used for the preparation of the co-polymer, polyethylene terephthalate-co-isophthalate. Reagent grade hydrochloric acid, n-hexane, chloroform, sodium chloride, distilled water and acetone were mainly used for characterization and for washing purposes. The mild steel sample used for this study helps to identify the efficiency of the coating.

Instrumentation

An important aspect of the project involves the utilization of a number of equipment for preparation, characterization as well as for analytical purposes. During the preparation process Vibra-Cell ultrasonic processor, R-8C laboratory Centrifuge and Hot Air Oven/ Sterilizer were used .For characterization of the prepared sample , V - 630 UV spectrophotometer ,Spectrum 2- FTIR spectrometer, X-Ray diffractometer with high temperature attachment, and 500 MHz FT NMR spectrometer were used. Finally the neutral salt spray analysis of the PET-co-Isophthalate coated mild steel sample was done using a TZ4STearee salt spray chamber.

Sample Preparation

Formation of bis-2-hydroxyethyl terephthalate

10 g of PET in scales and 0.015 g of $ZnAc_2$ were refluxed with 20 g of EG at atmospheric pressure for 2 hours. The solution at the end of the time period was hot filtered and then allowed to cool to room temperature. Once cooled, the mixture, in the form of a paste was filtered. The residue obtained from the second filtering phase, consists mainly BHET, EG and oligomers. 50 ml of hot water was added to this product, and filtered at 70^o C obtaining a solid filtrate predominantly consisting of oligomers. The filtered solution was cooled to 15^o C and then filtered again. A residue containing BHET with small amounts of water and EG were obtained [14].

Production of ethylene isophthalate cyclic dimer

5 g of dimethyl isophthalate and 20 ml of ethylene glycol diacetate were measured out. 50 ml of n - hexane was measured and poured into a beaker. The beaker was heated to 50^oC and to it dimethyl isophthalate and ethylene glycol diacetate were added. The contents of the beaker were continuously stirred whilst heating it till only a small amount of the solution remained. The solution was cooled, distilled water was added and poured onto a petri dish so as to allow precipitation of the dimer. The precipitate was dried in a hot air oven to evaporate any moisture present.

Production of polyethylene terephthalate-co-isophthalate

50/50 mole ratio of ethylene isophthalate cyclic dimer (EI c-2mer) and bis-2-hydroxyethyl terephthalate (BHET) were finely ground by a pestle and mortar before use. The 2 were then taken in a small crucible and heated to 80 ^{o}C for 20 min. Once done, the product was cooled to room temperature yielding a solid product. The solid product was then broken to yield smaller portions of the product [12].

Conversion of polyethylene terephthalate-co-isophthalate to nano-particles

Polyethylene terephthalate-co-isophthalate particles are added to a solvent (distilled water) such that it remained in a suspended state. The solution was placed in a sonicator for 40 min at 30^oC temperature and amplitude of 20%.It was then centrifuged and dried in a hot air oven to obtain the nano particles in its powdered form.

Coating of polyethylene terephthalate-co-isophthalate onto the substrate

The nanoparticles were dissolved in a solution of acetone and then sprayed onto the substrate. This was done so as to provide a uniform coat on the substrate. The coated substrate was then allowed to dry so as to evaporate the acetone solution and to allow the nanoparticle to bond with the surface as well as amongst each other. The drying process was done in a cool and open environment allowing the coating to set and also removing the excess acetone on the surface [8,15].

Testing for applications

The nanoparticles formed were tested for various applications with the help of instruments such as NMR spectroscopy, IR spectroscopy, UV spectroscopy, and X-Ray diffraction measurement. These tests help to determine the longevity of the coating under the given conditions. The following are the test to be performed.

Neutral Salt Spray Analysis

The salt spray (or salt fog) test is a standardized and popular corrosion test method, used to check corrosion resistance of materials and surface coatings .Usually, the materials to be tested are metallic (although stone, ceramics, and polymers may also be tested) and finished with a surface coating which is intended to provide a degree of corrosion protection to the underlying metal.

Salt spray testing is an accelerated corrosion test that produces a corrosive attack to coated samples in order to evaluate (mostly comparatively) the suitability of the coating for use as a protective finish. The appearance of corrosion products (rust) is evaluated after a predetermined period of time. Test duration depends on the corrosion resistance of the coating; generally, the more corrosion resistant the coating is, the longer the period of testing before the appearance of corrosion/ rust. .The test was conducted in a specific salt spray chamber within which 5% sodium chloride solution is atomized to form a fog or mist like environment [4].

Acid corrosion test

The resistance of the coating in an acidic medium is an important parameter as it will be exposed to chloride based ions at sea and may form hydrochloric acid. This may lead to corrosion of the coating protecting the pipe. Thus a study of the coatings stability in a solution of hydrochloric acid is required. This is achieved using UV spectroscopy. The sample was kept in a solution containing 0.5N hydrochloric acid for 7 days. The beaker containing the solution was kept in a dark place at room temperature. After 7 days the sample was separated from the HCl solution, washed in distilled water and dissolved in n-hexane. The original sample was also dissolved in n-hexane. UV analysis of the sample was then conducted [6].

Result and discussions

X-Ray Diffraction of polyethylene terephthalate-co-isophthalate

This analysis was used to determine the size of the particles produces using the sonicator. It was also used to determine the phase of the copolymer produced. Figure 1 is the XRD graph of the sample polyethylene terephthalate-co-isophthalate. The sharp peaks observed in the graph indicate that the copolymer is crystalline in nature. The materials provide values ranging from 10^{o} to 47.72^{o}. Determination of the particle size is based on the peaks produced.

The Scherer equation, in X-ray diffraction and crystallography, is a formula that relates the size of sub-micrometer particles, or crystallites, in a solid to the broadening of a peak in a diffraction pattern. The formula is,

$\tau = K\lambda/\beta cos\theta$

Where, τ is the mean size of the particle, K is the dimensional shape factor, λ is the x- ray wavelength, β is the line broadening at half the maximum intensity and θ is the Bragg's angle. The peak width was found to be 0.09^{o} and the peak position was 19.96^{o}. The X-ray wavelength was taken as 0.154056 nm and K value was assumed to be 0.9 [16]. Thus substituting the values for the formula, τ = 93.65 nm.

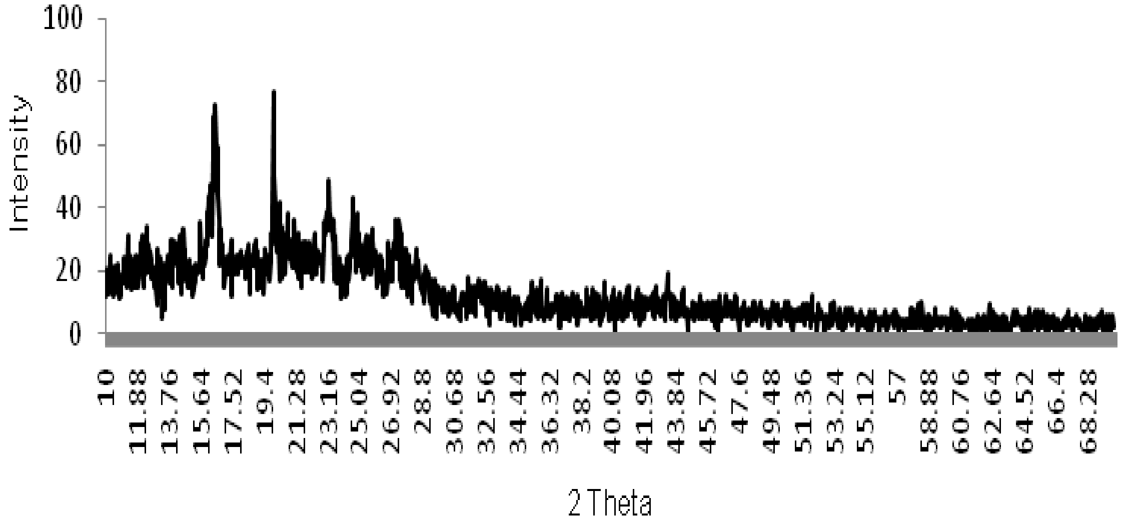

Figure 1. X-Ray Diffraction of polyethylene terephthalate-co-isophthalate

Fourier Transform InfraRed spectroscopy of polyethylene terephthalate-co-isophthalate

The characterization study was done so as to determine the various functional groups present in the sample so as to identify it as polyethylene terephthalate-co- isophthalate. Each functional group has a specific wave number and based on that we can determine whether the sample consists of the particular functional group or not. Figure 2 is the FTIR graph of the sample polyethylene terephthalate-co-isophthalate. Presence of C=C and C-H bonds in aromatics with medium intensities between 1400 to 1600 cm^{-1} and medium - weak intensities with multiple bands at 3000 to 3100 cm^{-1}, -C-H bonds in alkanes with varying intensities between 1350 to 1480 cm^{-1} and acyclic ketone with high intensity between 1705 to 1725 cm^{-1}. The functional groups present above are mainly found in the structure as they repeat themselves in the copolymer, thus providing proof that the sample is polyethylene terephthalate-co-isophthalate.

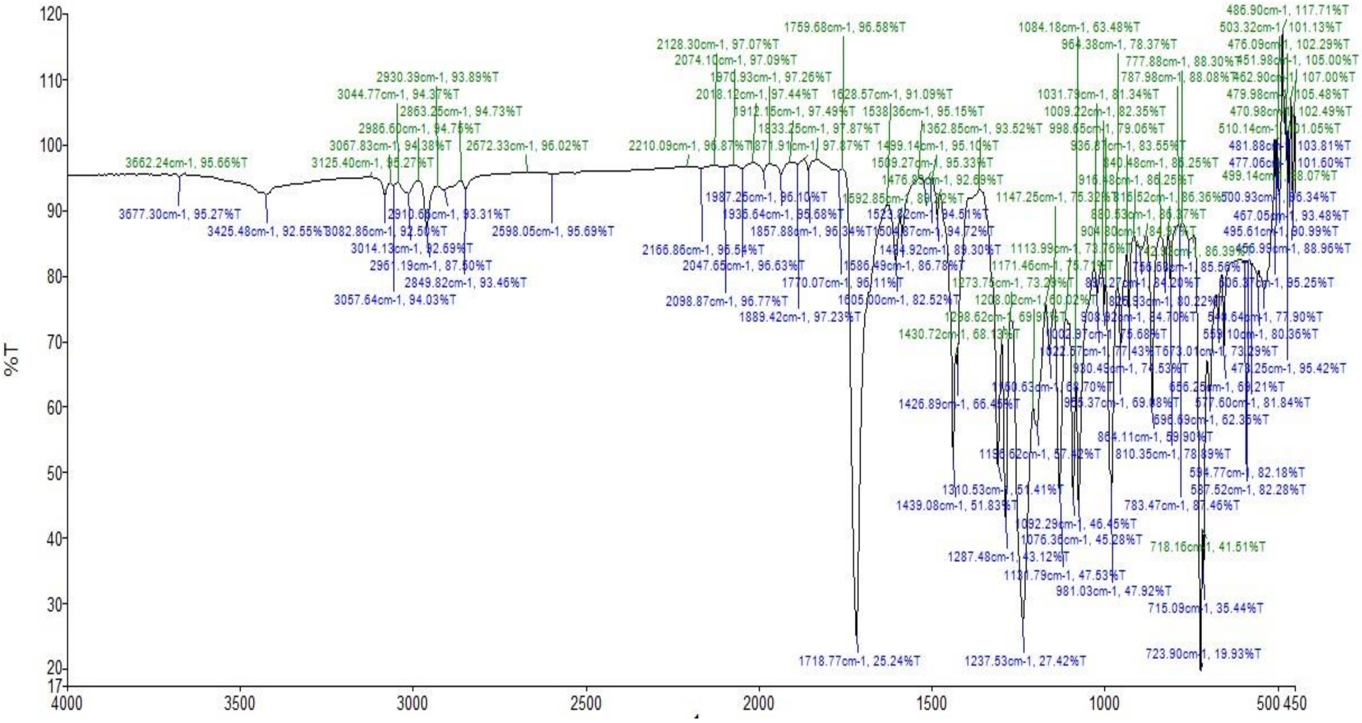

Figure 2. FTIR spectroscopy of polyethylene terephthalate-co-isophthalate

Nuclear Magnetic resonance spectroscopy of polyethylene terephthalate-co-isophthalate

The H-NMR or proton NMR Spectroscopy was done so as to determine the structure of the product using the hydrogen atoms present in the sample. Figure 3 shows the proton NMR spectra of the sample polyethylene terephthalate-co-isophthalate. The H-NMR spectra shows that the structure of the sample is that of polyethylene terephthalate-co- isophthalate. The aI, aT, dI, dT, e and f can be observed in figure 3 where I stands for Isophthalate Protons and T stands for Terephthalate protons. The presence of some amount of the reactants can be observed due to the spikes at 3.9,4 and 4.4 ppm. Therefore the spectra provides strong evidence that the copolymer is polyethylene terephthalate-co-isophthalate [17].

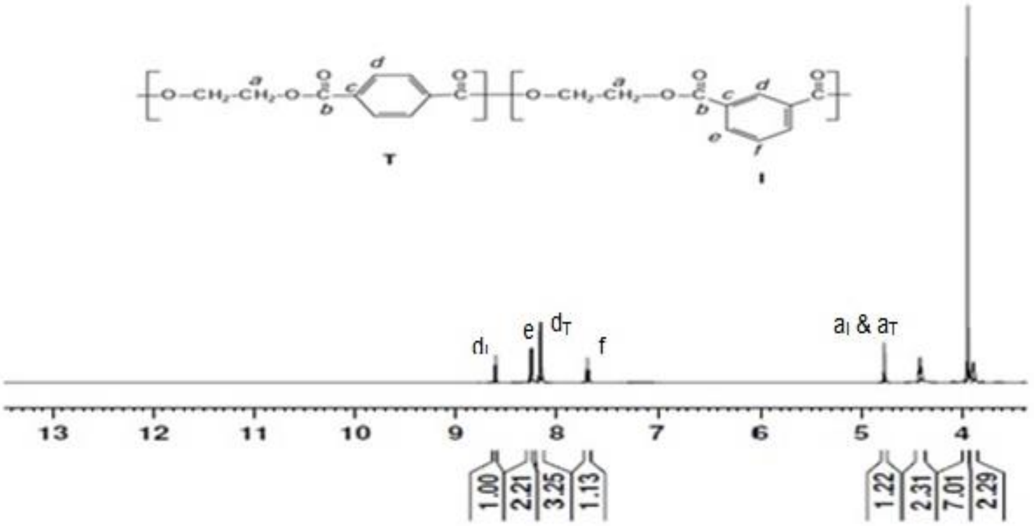

Figure 3. NMR spectroscopy of polyethylene terephthalate-co-isophthalate

Acid test

This study is done so as to test the stability of the sample in dilute acid solutions. The results are obtained using a UV spectrophotometer. Figure 4 and 5 are the UV graphs for the original sample and the sample placed in a 0.5 N HCl solution [18]. The two UV spectrums are similar in nature and therefore prove that there hasn't been any change in the sample after its presence in the hydrochloric acid solution. This shows that the sample is stable in the presence of 0.5 N hydrochloric acid solution.

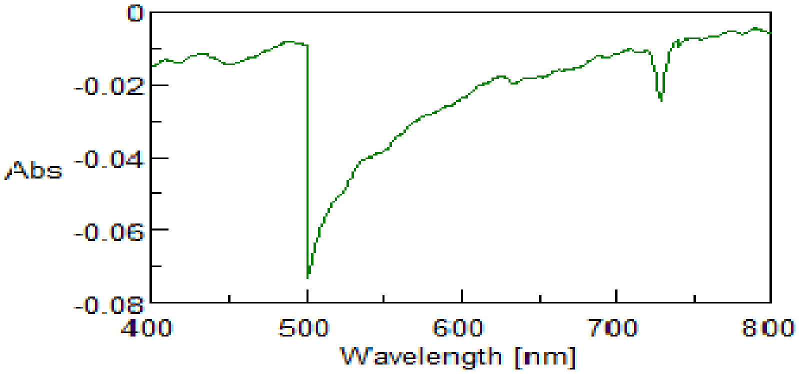

Figure 4. UV spectrumh of PET-Co-Isophthalate before placing it in a 0.5 normal HCl solution

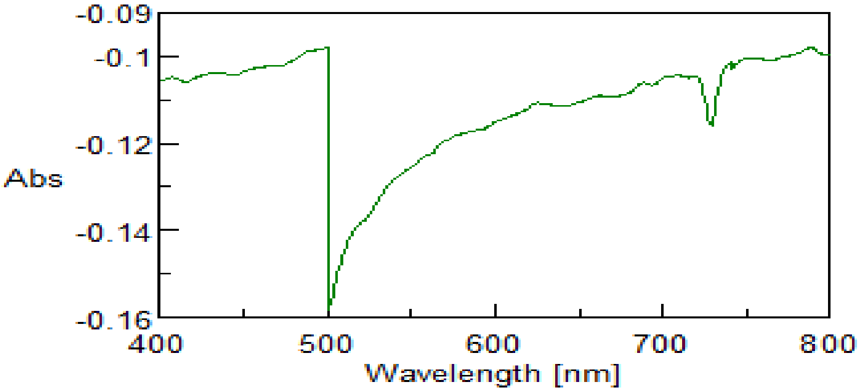

Figure 5. UV spectrum of PET-Co-Isophthalate after placing it in a 0.5 normal HCl solution

Neutral salt spray analysis

This analysis method is done to test the effectiveness of the coating in marine environments. Due to the accelerated nature of the experiment, samples placed within the chamber for 24 hours generally equate to about two and a half years in the actual environment. Therefore it’s mandatory for coatings to undergo this test in case the coating may come in contact with marine environments. The mild steel sample was coated with the sample, polyethylene terephthalate-co-isophthalate and was placed within the chamber for 24 hrs. The following were the parameters that were maintained within the salt spray chamber. 1.2 - 1.3 ml of 5% salt solution was collected every hour and parameters such as pH, temperature, concentration and air pressure were recorded. The solution had a pH in the range of 6.94 - 6.97, a temperature in the range of 34.6 - 35.6^{o}C, air pressure range of 12- 17 psi and salt concentration in the range of 5.1 - 5.2%. The mild steel coated with the polymer was subjected to test in a salt spray chamber for a period of 24 hours. After the stipulated time, the sample was removed and was studied for signs of corrosion. The studies showed no signs of corrosion [10].

Conclusions

Polyethylene terephthalate-co-isophthalate anticorrosive coating was successfully prepared using waste plastic, thereby serving the twin purpose of reducing the concentration of used PET bottles found in the environment and at the same time re-utilizing them. This goal seems to have been achieved fairly successfully, with the anticorrosive coating being able to withstand a variety of highly corrosive environments as evidenced by its performance in a battery of tests and its direct comparison with another coating. X-Ray diffraction, FTIR, NMR and UV spectroscopy were conducted to ascertain the structure and composition of the generated compound. Once characterization of the compound is completed its use as an anticorrosive coating has to be determined using salt spray analysis utilizing 5% sodium chloride solution. The coated sample showed no signs of corrosion. Hence, it was concluded that polyethylene terephthalate-co-isophthalate nanoparticles showed good resistance to corrosion in sea water. This study can be further expanded upon to modify the coating, thereby creating an even stronger and useful anti corrosive coating.

Conflict of interest

Authors declare there are no conflicts of interest.

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