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Synthesis and characterization of titanium oxide nanotubes and its performance in epoxy nanocomposite coating

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ABSTRACT

Titanium oxide nanotubes (TiO_2 nanotube, TNT) were prepared from hydrothermal treatment of TiO_2 particles in NaOH at 140 °C, followed by neutralization with HCl. The structure of the nanotubes was characterized by transmission electron microscopy (TEM) and X-ray diffraction (XRD). TNT synthesized under the optimal conditions with approximately 10–20 nm wide, and several (100–200) of nanometers long. TNT is used as white pigment for two component epoxy-based coating. Ultrasonication followed by mechanical stirring has been applied for dispersion of TNT powder in an epoxy matrix. The resulting perfect dispersion of TNT particles in epoxy coating revealed by scanning electron microscopy (SEM) ensured white particles embedded in the epoxy matrix. The effects of TNT particle concentrations on thermal, mechanical and corrosion resistance of epoxy coatings composite were studied and compared to that of submicron particles. It was found that the TNT significantly enhances the heat resistance, the thermal stability and the glass transition temperature of epoxy resin. Epoxy/TNT nanocomposite with 5.0 wt.% TNT shows the highest thermal stability, the temperature of 50% weight loss increased from 365 to 378 °C, the amount of char yields or residues at 600 °C increased from 7.13 to 13.50 wt.%, respectively to 1.0 and 5.0 wt.% TNT. The glass transition temperature (Tg) increased from 182 to 220 °C too. The mechanical properties and corrosion resistance of epoxy resin greatly improved by using reinforcing TNT and this improvement increases with increase TNT wt.%.

1. Introduction

After the discovery of carbon nanotube (CNT) [1], large attention has been paid to this unique low-dimensional nanostructured material because of its attractive various physical and chemical functions which arise from the synergy of low-dimensional nanostructure and anisotropy of carbon network, thus known as graphite structure. Besides CNTs, various inorganic nanotubular materials have been reported in nonoxide compounds, boron nitride (BN) [2] and molybdenum disulfide (MoS_2) [3]; in oxides such as vanadium oxide (V_2O_5), aluminum oxide (Al_2O_3) [4,5], silicon dioxide (SiO_2) [6], titanium oxide (TiO_2) [7–9]; and also in natural minerals like imogolite [10]. Except natural mineral materials, fabrication of nanotubes is roughly classified into two methods; one is the template or replica method, in which some template materials are used to form a tubular structure. The other one is based on the self-structuralization or self-organization of matter during chemical or physical synthesis/fabrication processes. TiO_2 has been widely studied by many researchers from 1950s to utilize it as a photocatalyst [11], an electrode of dye-sensitized solar cell [12], a gas sensor [13], and so on. Kasuga et al. [14,15] have succeeded in the synthesis of nanotubular TiO_2, which has an open-end structure with typically 8–10 and 5–7 nm in outer and inner diameters, respectively, using a simple and low temperature solution chemical processing. Various methods such as anodizing of metal substrates [16], replica [7], and template methods [9] have been investigated to prepare tubular TiO_2. However, the synthesis method developed by Kasuga et al. is based on a self-organizing and templates route that is achieved by a low temperature process to form nanometer-sized tubular morphology. Using this so-called Kasuga method, many related investigations have been extensively carried out on structural analysis, process optimization, property evaluation, and so on [17,18]. Recently Tsuyoshi Kijima has provided an excellent summary on the synthesis and applications of titanium nanotubes [19]. Titanium dioxide (TiO_2) is the most important of all white pigments. It has almost completely displaced the other white pigments from the coating sector [20,21]. Titanium oxide nanotube (TiO_2 nanotube, TNT) is one of the promising

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nanostructured oxides with tubular structure. It is inexpensive, chemically stable, and harmless and has no absorption in the visible light region [22]. Many attempts have been made by researchers to improve TiO_2 performance in epoxy composites. The most common method for improving the effect of TiO_2 particles on mechanical properties is reducing its size to the nanoscale [23–25]. Several authors reported that, the presences of TNT particles in epoxy resins can improve mechanical [26,27] and thermal properties [28] and corrosion resistance [29,30] than submicron particles. On the basis of all of this evidence, our aim is to enhance thermal, mechanical and corrosion resistance of epoxy resin using TNT pigment.

2. Experimental

2.1. Materials

All the chemicals used during the research project were sourced internationally, or from local companies, and were of pure grade quality. TiO_2 pigment manufactured by Fisher Scientific, England, was selected for this study. TiO_2 had a 20 μm crystal diameter. Commercial two component, epoxy resin was used as the polymer matrix. The typical characteristics of the epoxy resin are as follows: epoxy equivalent weight (184–190 g/eq), viscosity at 25 °C (12.0–14.0 Pa. s), density at 25 °C (1.16 kg/l) and mixing ratio by volume (base to hardener 4:1).

2.2. Methods and techniques

Fabrication of nanotubular TiO_2 is classified into two methods: template/replica route and direct synthesis (i.e., templateless) route. In the present work, Titanium oxide nanotube (TiO_2 nanotube, TNT) was prepared by direct synthesis route.

2.2.1. Synthesis of titanium oxide nanotubes (TiO_2 nanotube, TNT)

Typical TNT is synthesized by direct synthesis route via low temperature solution chemical processing. A commercial-grade titanium oxide powder consisting of 60% anatase and 40% rutile used as the source materials of TNT. The preparation was initiated by treating 3 g of the TiO_2 powder with 100 ml of 10 N NaOH, followed by hydrothermal treatment at 140 °C in a Teflon-lined autoclave for 24 h. The process was analogous to those reported [6,7], except that the present treatment was conducted hydrothermally, rather than under atmospheric pressure. The resultant product is washed many times by distilled water in order to remove sodium hydroxide. Then 0.1 M HCl aqueous solution is added to neutralize the solution under sonication. The product of TNT is then separated by filtration with subsequent drying at 100 °C for 5 h. The structure of the obtained material was studied using transmission electron microscope (TEM), X-ray diffraction (XRD) and scanning electron microscope (SEM).

2.3. Characterization study of titanium oxide nanotubes (TiO_2 nanotube, TNT)

2.3.1. Transmission electron microscope (TEM) analysis

Transmission electron microscopy (TEM) of TNT was conducted at an accelerated voltage of 200 kV electron microscopes (JEM2100 LaB6, Japan). In the TEM the solid sample was dispersed in ethanol solution using an Ultrasonicator and then dropped on a copper grid coated with carbon film prior to inserting the samples in the TEM column, the grid was vacuum dried for 15 min.

2.3.2. X-ray diffraction (XRD) analysis

X-ray diffraction (XRD) patterns of TNT was measured by using a Panlytical X'pent PRO (Netherlands) with monochromated CuKα radiation with scattering reflections recorded for 2θ angle between 4 and 70 corresponding to d-spacing between 1.47 and 3.26 A°. To confirm the resolution of the diffraction peaks with standard reproducibility in 2-theta (±0. 005), the sample measurement was recorded by using monochromator and detector which were used to generate focusing beam geometry and parallel primary beam. The standard diffraction data were identified according to the International Center for Diffraction Data (ICDD) software with PDF-4 release 2011 database.

2.4. Preparation of epoxy/(micro and nano TiO_2) composite coatings

To fully understand the TNT performance, it was physically incorporated into a commercial two component epoxy resin at the levels from 1.0 to 5.0 wt.%. The first step was dispersion samples containing 1–5 wt.% of TNT by ultrasonication for 25 min. The second step was mixing the dispersed TNT with an epoxy base for 30 min by means of mechanical stirring followed by degasification. Then the prepared samples were mixed with the correct ratio of epoxy hardener. The micro sized titanium oxide was added at the same level to epoxy resin to compare between epoxy nanocomposite and epoxy microcomposite coating performance. The samples of different molar ratio were then applied to both glass and steel panels by means of a conventional spraying. All efforts were made to maintain a uniform film thickness of 100 ± 5 μm for evaluating the thermal, mechanical and corrosion properties.

2.5. Scanning electron microscope (SEM)

The cross-sectional morphologies nancomposites coated film was measured by a field-emission scanning electron microscopy (JEOL JSM530). Before insertion into the chamber, the disk-like monolith substrates were fixed on SEM stage using carbon tapes. The Gold (Au) films were deposited on the substrates at room temperature by using an ion-sputter (EDWARDS S150). The power supply (100 W), and the deposition rate was kept constant throughout these investigations. Moreover, to better record the SEM images of disk-like monoliths, the SEM micrographs were operated at 20 keV.

2.6. Heat resistant property of films

This test method provides an accelerated means of determining the heat resistance performance of these coating systems designed for interior and exterior service. Coated panels are subjected to temperatures that increase in steps from 205 to 425 °C (400–800 °F). Increase the temperature in 55 °C (100 °F) increments, alternating the time periods as per ASTM D 2485-91(2000).

2.7. Thermal resistant property of films

Thermal degradation of the cured polymeric nanocomposites was conducted from 30 to 600 °C with a heating rate of 10 °C/min, under dynamic flow of nitrogen using differential scanning calorimeter (DSC) (Simultaneous DSC-TGA, Q, 600 STD, USA). The thermal properties of the films were done by means of thermo gravimetric analysis (TGA). The thermal behavior of the films was recorded in the charts.

2.8. Mechanical resistance property of films

A range of physical and mechanical evaluations of the painted films was undertaken according to appropriate ASTM standard test methods. The prepared steel panels (ASTM D 609-00) were used for measuring (i) the film coating thickness (ASTM D 1005-07);

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