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Effects of nano-silica contents on the properties of epoxy nanocomposites and Ti-epoxy assembles

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ABSTRACT

In order to get a strong Ti-epoxy bond, nano-silica was added to epoxy as the reinforcement, and the effects of the presence of nano-silica on the properties of epoxy nanocomposites and Ti-epoxy assembles were investigated. The results showed that, although glass transition temperature of nanocomposites decreased with the increase in silica addition, mechanical properties of the nanocomposites such as flexural strength, fracture toughness, and hardness rose to the highest values when silica content was 15 wt%. However, the shear strength of the Ti-epoxy assemble was 45.38 MPa when the silica content was 2.5 wt%, from a low of 31.75 MPa for pure epoxy bonded assemble, increasing by 42.9%. With further increase in silica content, the shear strength decreased gradually. The remarkable increase in the shear strength with 2.5 wt% silica addition should be attributed to the improved wettability between epoxy and Ti surface, which resulted in much higher bonding strength between them.

1. Introduction

High-performance tubular riser materials are indispensable in the field of offshore oil and gas exploration, and steel risers have been widely applied in transporting these oil/gas/sea water mixtures from subsea wellhead to the production plat-form on the surface. However, it is reported that more than 20% of new reserves are located in the seabed deeper than 2500 m, and at such depth, steel risers encounter serious problems [1]. On one hand steel risers suffer from disadvantage of brittleness at low temperature of deep sea; on the other hand, we have to build much bigger and heavier platform to support their heavy weight caused by the high density of steel. Composite materials, especially glass-epoxy and carbon-epoxy composites, have drawn substantial attention from the offshore industry primarily due to their high specific strength as well as the tailorability of strength and stiffness, thermal conductivity and damping properties. Meanwhile, combined with the impermeable metal liner, fiber-metal laminate risers would be the most promising candidate which offer considerable weight savings, lower operational costs, higher production capacities and greater explorations depths over metallic risers. However, as to the fiber-metal laminate riser, one question is imperative: interfacial bonding between metal and polymer, which is a critical issue in determining the overall performance including mechanical properties, failure mode and anti-permeability of the integrated risers [2–4].

In previous studies, Ti alloy has been used as the liner material due to its ease of manufacturability, impact and corrosion resistance, and reasonable impermeability. In order to get an excellent interfacial bonding strength, various kinds of surface modification methods on Ti have been done, including sandblasting, shock peening, anodizing, etching, microarc oxidation, among others [2,5–17]. In our recent investigation, we tuned Ti alloy surface through concurrent treatments of sandblasting, anodization, etching and annealing, and high shear strength of epoxy bonded Ti assembles were achieved, together with main epoxy cohesive failure mode. Therefore, in this case bonding strength mainly depended on the properties of epoxy [3,18,19].

Inorganic particles are frequently employed to improve the mechanical performances of epoxy for engineering applications [20–22]. Both stiffness and toughness can be improved by the

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presence of nano-sized inorganic particles due to its unique features of higher specific surface area, modulus and hardness. Meanwhile, the required loadings of nanoparticles in epoxy matrices are usually much lower. Therefore, many intrinsic merits of neat epoxy, such as low weight, ductility and good processability will be retained after the addition of nanoparticles. It is also well known that dispersion state of nanoparticles is a crucial factor in determining the final properties of the nanocomposites. Compared with conventional processing approaches, e.g. mechanical mixing and melt compounding, a sol–gel technique introducing nanoparticles into pre-polymers by chemical reaction has been proved to be very effective in breaking down the clusters or agglomerates [23,24].

In this paper, epoxy nanocomposites containing various contents of nano-silica particles (0–20 wt%) prepared in situ by a special sol–gel process were applied to bond Ti alloy. Nano-silica was almost homogeneously distributed in an epoxy matrix even at 20 wt%. The static and dynamic mechanical properties of the nanocomposites were investigated. Effects of the presence of nano-silica on the wettability between Ti6Al4V adherends and epoxy, shear strength of the Ti6Al4V-epoxy assembled specimens together with failure modes are systematically investigated.

2. Materials and experimental procedures

2.1. Materials

Grade 5 Ti alloy (90% Ti, 6% Al, and 4% V) with thickness of 1.62 mm was considered as adherend after concurrent surface treatments of sandblasting, anodization, etching and annealing. Bisphenol-F epoxy resin (D.E.R. 354, Dow Chemical) was used as polymer adhesive hardened by an amine based curing agent (EPOLAM 5015, Huntsman). A nano-silica modified resin—Nanopox A510 was supplied by Nanoresins with 40 wt% nano-silica of ~20 nm in size. Nanocomposites were prepared by mechanically mixing D.E.R. 354 and A510 at 40 °C for 2 h, and then hardener were added into the mixture. After degassing in a vacuum oven, they were applied to prepare the single-lap-joints. The silica contents in the nanocomposites were 0, 1.25, 2.5, 5, 10, 15 and 20 wt%.

2.2. Preparation of single-lap-joint specimen

Surface treated Ti specimens with size of 25.4 mm × 101.6 mm × 1.62 mm were used to prepare single-lap-joints. Nanocomposite resin was carefully spread on the Ti adherends without introducing air bubbles and the adherends were aligned well to fix the overlap of 12.7 ± 0.25 mm. After cleaning away the excess resin, the Ti-nanocomposite assembled specimens were cured at 25 °C for 24 h, 80 °C for 24 h and 120 °C for 4 h in the oven. The thickness of the epoxy layer in the cured specimen is ~0.4 mm. The nanocomposite bonded Ti alloy assembles were denoted as TN0, TN1.25, TN2.5, TN3.5, TN5, TN15, corresponding to the nanocomposites with different nano-silica contents of 0, 1.25, 2.5, 3.5, 5, 15 wt%.

2.3. Characterization methods

Dynamic mechanical thermal analysis (DMTA) was performed using TA Q400 with the tension configuration, raising the temperature from 30 to 140 °C at a heating rate of 1 °C/min. Tensile lap shear strengths were measured using a universal testing machine (Instron 5569) according to ASTM D1002 with sample size of 25.4 mm × 101.6 mm × 1.62 mm and overlap of 12.7 ± 0.25 mm. Work of fracture was calculated by the area in the load–displacement curve during tensile lap shear test. Flexural (three-point bending geometry) tests were also conducted according to the standards DIN-ISO-178 with modified sample size of 40 mm × 2 mm × 5 mm and span length of 32 mm. Young's modulus was calculated in accordance with the deflection-compensated stress–strain curves. WC ceramic was used to establish the stress–strain curves in the range of 0–100 MPa to compensate the tool deflection during actual tests. Quasi-static fracture toughness tests were carried out using compact tension (CT) specimens with dimensions of 3.4 mm × 36 mm × 36 mm. A pre-crack was made by lightly tapping a fresh razor blade into the bottom of the saw slot in the specimen. The crosshead speeds for tensile lap shear, flexural and fracture toughness tests were 1.3, 1 and 0.1 mm/min, respectively. Six specimens were used for each testing condition and average values with standard deviations were finally reported. The fractographs of the nanocomposites after flexural tests and Ti-epoxy joints after tensile lap shear tests were examined by field emission gun scanning electron microscopy (FEG-SEM, JEOLJSM7600F) equipped with an EDX-S detector. The contact angle between epoxy and Ti adherends were measured by a contact angle measurement with photo intervals of 10 s. A rheological meter HAAKE MARS (Thermo Fisher Scientific, Germany) was used to test the viscosity of the epoxy.

3. Results and discussion

3.1. Properties of epoxy nanocomposites with different nano-silica contents

3.1.1. DMA of nanocomposites

Fig. 1 shows the DMA results for the materials. Two obvious features were noted. Firstly, with the increase in the nano-silica contents, modulus significantly rose, which was more pronounced at lower testing temperature. This phenomenon can be explained from the point of view of thermal mismatch between epoxy matrix and nano-silica [24]. Since the coefficient of thermal expansion of silica was much lower than that of epoxy resin ($0.5 \times 10^{-6}/^{\circ}C$ vs. $60 \times 10^{-6}/^{\circ}C$), nano-silica would be surrounded by residual compressive stress, which facilitated the stress transfer from the matrix to silica, and thus a notable stiffening effect was obtained. However, at higher temperature, relaxation of residual stress occurred, resulting in worse stress transfer and lower stiffening effect. Secondly, glass transition temperature of nanocomposites showed declined trend with the increase in silica content, which was due to the plasticizing effect of nano-silica as reported by other researchers [24].

3.1.2. Mechanical properties of the nanocomposites

Fig. 2 presents the mechanical properties of the nanocomposites with different nano-silica contents. It can be noted that with the increase in silica content, except for Young's modulus, all other mechanical properties including flexural strength, fracture toughness and hardness rose first, reached their peak values at 15 wt%, and then declined when nano-silica content was 20 wt%. At nano-silica content of 15 wt%, the nanocomposite exhibited the best mechanical performances. For example, flexural strength, fracture toughness and hardness were 198.6 MPa, 0.72 MPa $m^{1/2}$ and 21.0 H V, which were 31.3%, 53.2% and 20.2% higher than those of neat epoxy, respectively. However, with further increase in silica content to 20 wt%, flexural strength, fracture toughness and hardness declined slightly, which were 1.0%, 8.3%, 4.8% lower than their respective peak value. Meanwhile, as expected, Young's modulus