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TENSILE, FLEXURAL AND IMPACT PROPERTIES OF ULTRASMALL TiO_2 NANOTUBES REINFORCED EPOXY COMPOSITES

Ultrasmall TiO_2 nanotubes (TiO_2NTs) of the length ~250±20 nm and diameter ~20 nm are synthesized and TiO_2NT reinforced (0.1 wt.%) epoxy composites are fabricated. The reinforcing effects are studied by means of tensile, flexural, and impact tests as per ASTM standards. TEM and XRD characterization techniques are used in this study. It is observed that TiO_2NTs greatly enhanced the tensile strength by 85%, elongation by 7%, flexural strength by 55%, and the impact strength by 8%. The mechanical properties of the epoxy nanocomposites indicate that TiO_2NTs are efficient fillers to enhance the performance of epoxy composites.

Keywords: **TiO_2 nanotubes, epoxy nanocomposites, mechanical properties, polymer nanocomposites**

INTRODUCTION

High performance and cost-effective designs for structural components are the top criteria of aerospace, automobile, civil, and alternative energy industries. These critical requirements of industries have led engineers to give high priority to designing high strength materials with reduced weight. The need for lightweight and strong materials has paved the way for polymer composites to industries. Most advanced polymer composites are made of epoxy, a thermosetting resin, due to the epoxy resin's outstanding characteristics like good adhesion to fiber reinforcements, compatibility with a variety of curing systems, better thermal, mechanical, electrical, and chemical properties [1-3].

The performance of epoxy-based composites is improved by dispersing second phase materials as fillers in epoxy resin systems. By using fillers at the nanoscale (10^{-9} m), several enhancements in the composite properties are observed, which are mainly due to the improved interface and result in an improved load transferring ability. An effective method to fabricate advanced composites is the incorporation of nanofillers in the epoxy, combining the benefits of both the epoxy and the nanomaterials [4, 5]. Because of their excellent properties, TiO_2 nanofillers have encouraged researchers to enhance the mechanical properties of epoxy nanocomposites [6]. As TiO_2 (3D) particles have a limited surface area, 1D TiO_2 nanotube-like structures are drawing attention due to their increased surface area. In this work, ultrasmall TiO_2 nanotubes are synthesized by the hydrothermal process. Epoxy composites are then fabricated with the obtained TiO_2 nanotubes (TiO_2NTs) (0.1 wt.%) and the reinforcing effects are investigated through tensile, flexural, and impact tests as per ASTM standards.

MATERIALS AND METHODS

Materials

TiO_2 (> 99, Sigma Aldrich), NaOH (98%, Alfa Aesar), epoxy (Araldite LY 556, Huntsman Advanced Materials), and hardener (Aradur HY 951, Huntsman Advanced Materials).

Synthesis of TiO_2 nanotubes

The synthesis of TiO_2NTs was carried out hydrothermally, which is a green synthesis route and it has several advantages of producing phase-pure nanostructures in a one-step reaction that is cost-effective and reproducible [7]. In the typical synthesis, it starts with an aqueous solution of NaOH (7 M) and TiO_2 powder (500 mg) kept in a pressure vessel of a Teflon-lined stainless steel autoclave and placed in a 120ºC preheated oven for 20 hours. The resulting nanostructures were washed with water several times to remove the impurities, finally washed with ethanol, and dried at 70ºC [8]. The schematic diagram of the TiO_2NTs synthesis process is presented in Figure 1.

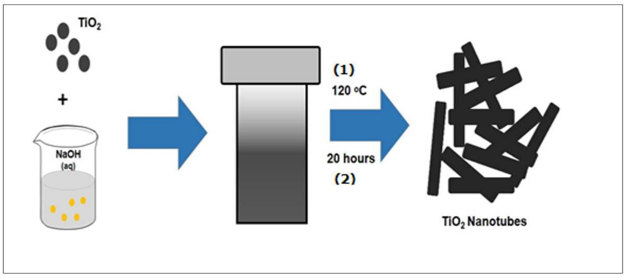

Fig. 1. Schematic diagram of TiO_2 nanotube synthesis process

Fabrication of epoxy nanocomposites

Aradur HY-951 epoxy was used to prepare the composite and Araldite LY-556 was used as the curing agent. The hand lay-up method was employed for epoxy composite fabrication. In the initial step, the epoxy was preheated to 100°C in a hot air oven, and then the synthesized TiO_2NTs were mixed with the epoxy at a weight ratio of 0.1% under constant mechanical stirring at 1200 rpm in ambient conditions. Subsequently, the composite was subjected to ultrasonication using a probe-type ultrasonicator (Vibra-Cell) for 10 minutes. During the mixing process, color of the epoxy varies from colorless to a uniform color, which specifies the formation of a homogeneous mixture of nanofillers and epoxy resin. The mixture was kept under vacuum for 20 minutes to eliminate air bubbles that were formed during mechanical mixing. Subsequently, at a 1:0.11 weight mix ratio, the hardener was gently added and the resultant mixture of epoxy was gently transferred into the mold. After curing at ambient temperature for 24 hours, the cured epoxy nanocomposite panel was removed from the mold for further studies. Using a computer numerical control (CNC) laser cutting machine, the epoxy nanocomposite panel was cut according to ASTM standards.

Instrumentation details

Powder XRD patterns of the samples were recorded using a PANalytical X'pert Pro diffractometer. The morphology of the nanostructures was examined using a JEOL-JEM 2100F transmission electron microscope (TEM). A CNC laser cutting machine was used to cut the fabricated composite panels to the standard test specimen sizes (Figs. 2 and 3).

Mechanical tests

The prepared test specimens were subject to the tensile test as per ASTM-D 638, the flexural test as per ASTM-D 790 using a universal testing machine (Zwick Roell, 2005, USA), and the impact test as per ASTM-D 256 using an impact test machine (Tinius Olsen 504--104, USA).

Fig. 2. TiO_2NTs/epoxy composite flexural test specimens

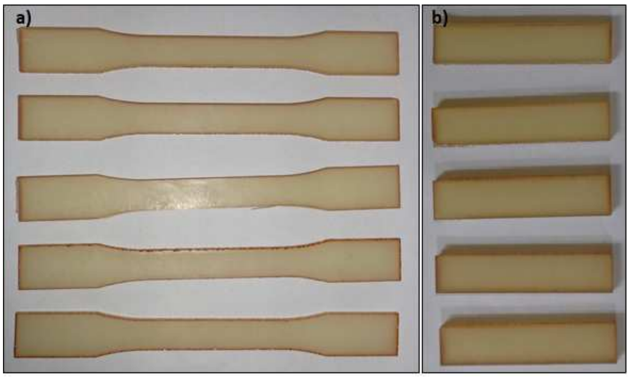

Fig. 3. TiO_2NTs/epoxy composites: a) tensile test specimens, b) impact test specimens

RESULTS

TiO_2 nanotubes

The synthesis of the TiO_2NTs was carried out hydrothermally starting with NaOH and TiO_2. The morphology of the resulting nanostructures (TiO_2NTs), examined by TEM (Fig. 4), revealed the presence of elongated tubular structures with an average length of 250±20 nm and a diameter of ~20 nm.

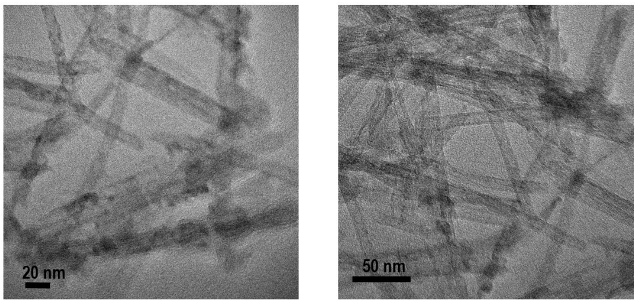

Fig. 4. TEM micrograph of synthesized TiO_2 nanotubes

Titanium dioxide (TiO_2) is a naturally available oxide of titanium also known as titania. Titania is available in various phases such as anatase, brookite, and rutile. XRD is the ideal characterization tool to find this nature of the phase. The XRD analysis of the synthesized TiO_2NTs (Fig. 4) confirmed that the formed TiO_2 is in the anatase form based on the diffraction peaks at 25° and 48° [9]. The XRD pattern of TiO_2NTs does not show any impurity diffraction peaks and it well agrees with JCPDS No. 21-1272. Furthermore, the intensity of the formed TiO_2 sample XRD peaks confirms that the synthesized nanostructures are crystalline. The very small crystallite sizes are represented by broad diffraction peaks, which is supported by TEM analysis.

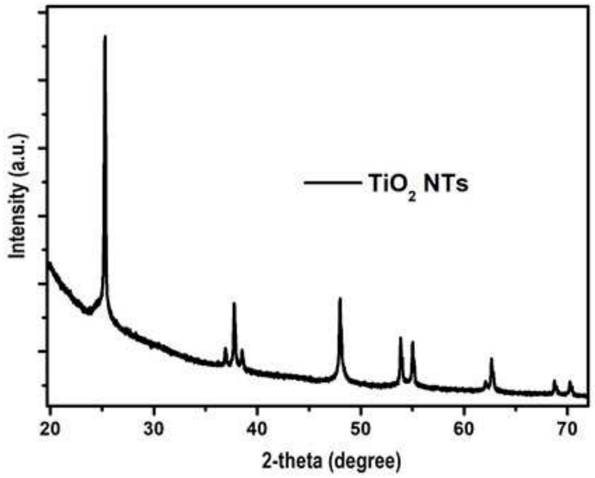

Fig. 4. XRD pattern of synthesized TiO_2NTs

Characterization of TiO_2NTs/epoxy nanocomposites

The uniform color of the epoxy nanocomposite panels confirms the uniform dispersion of the nanofillers. Although SEM, EDAX of the epoxy nanocomposites was performed (not shown in the current document), TiO_2NT could not be traced in the epoxy composite, as the nanofiller dimensions are very small (250 nm length and 20 nm diameter) and the nanofiller content also very little (0.1 wt.%).

Furthermore, XRD analysis of the epoxy nanocomposites was carried out; the XRD spectrum is presented in Figure 5. From the XRD data, the presence of a broad peak around 17-19° indicates the cured networks of pure and TiO_2NT/epoxy samples are amorphous due to the highly cross-linked structures. For the pure epoxy samples, a broad peak centered at $2\theta = 18.5°$ is observed, which is assigned to the amorphous structure of the epoxy. The absence of filler reflections in the TiO_2NTs/epoxy XRD spectrums is evidence for the uniform dispersion of the filler in the nanocomposites [10, 11]. The effect of the TiO_2NTs on the epoxy polymer is small on the XRD due to the highly amorphous nature of the epoxy polymer and the small amount of TiO_2NTs (0.1 wt.%). Importantly, the peak at 17.3 ($\approx 2\theta$) in the TiO_2NTs/epoxy samples is sharper in comparison to the pure epoxy samples, indicating the increase in the crystallinity of the epoxy structure upon the TiO_2NTs addition.

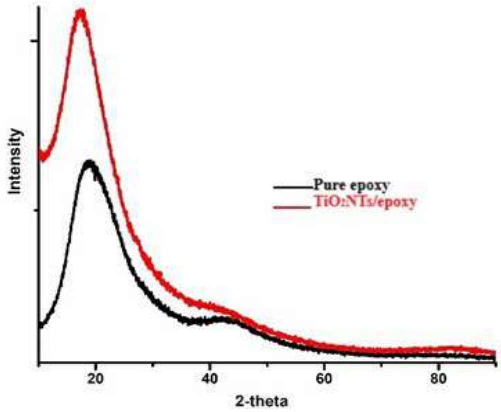

Fig. 5. XRD spectra of pure and TiO_2NTs/epoxy nanocomposite

Mechanical properties of TiO_2NTs/epoxy nanocomposites

The mechanical performance of TiO_2NTs/epoxy nanocomposites correlates highly with the homogeneity of the dispersion and the interfacial interactions. Because of the highly increased interfacial area in nanocomposites, improvement in the mechanical properties was predicted. The performance of the nanocomposites (TiO_2/epoxy) and pure epoxy samples were evaluated using tensile tests, flexural tests, and impact tests.

Tensile properties

The tensile test specimens were prepared and tested using a universal testing machine (UTM) as per ASTM D 638 standards at the crosshead speed of 2.5 mm/min. The results are presented in Figures 6 and 7. The pure epoxy has a tensile strength of 40.7 MPa, whereas the incorporation of TiO_2NTs resulted in an increase in tensile strength of the epoxy composite to 75 MPa. Thus, the tensile strength of the TiO_2NTs/epoxy composite improved by nearly 85%. The pure epoxy has a tensile modulus of 1.1 GPa; the tensile modulus decreased for the TiO_2NTs/epoxy to 0.9 GPa; a decrease of nearly 25%. The elongation of pure epoxy is 3.4%, while for TiO_2/epoxy it increased to 7%; it increased by nearly 108%.

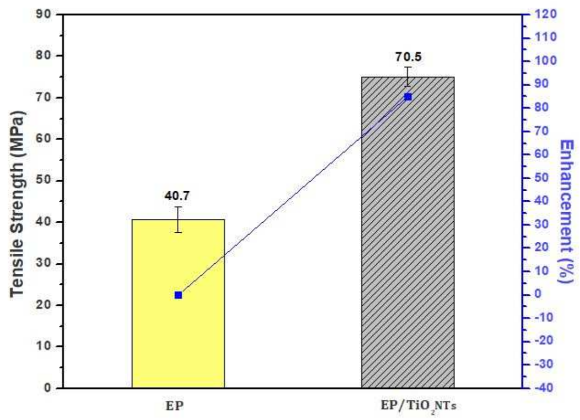

Fig. 6. Tensile strength values of pure epoxy, EP/TiO_2NTs composites

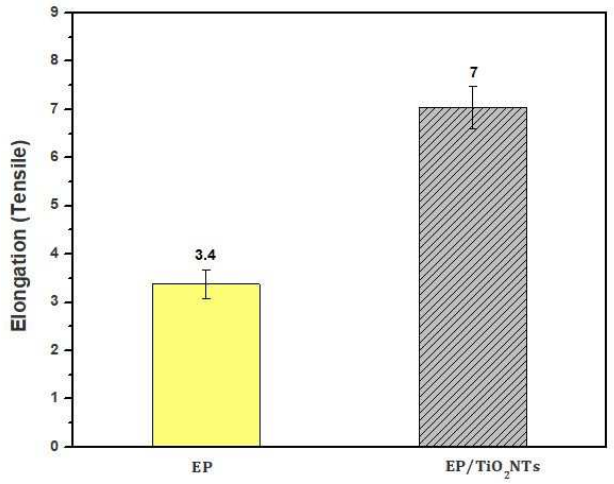

Fig. 7. Elongation (tensile) values of pure epoxy, EP/TiO_2NTs composites

Flexural properties

The flexural test specimens were prepared and tested using UTM operated at the crosshead speed of 2 mm/min as per ASTM D 790 standards. The flexural properties of pure epoxy and the TiO_2/epoxy nanocomposites are presented in Figure 8. The pure epoxy has flexural strength of 71.0 MPa. The incorporation of TiO_2NTs resulted in an increase in the flexural strength of the nanocomposites to 110 MPa. The flexural strength of the TiO_2NTs /epoxy composite improved by nearly 55%. The pure epoxy without any reinforcement has a flexural modulus of 3.1 GPa. The flexural modulus decreased for TiO_2/epoxy to 2.8 GPa. The flexural modulus of the TiO_2NT/epoxy composites decreased by nearly 9%. The elongation of pure epoxy is 9.9%; for TiO_2NT/epoxy it decreased to 4.7%; decreased by nearly 53%.

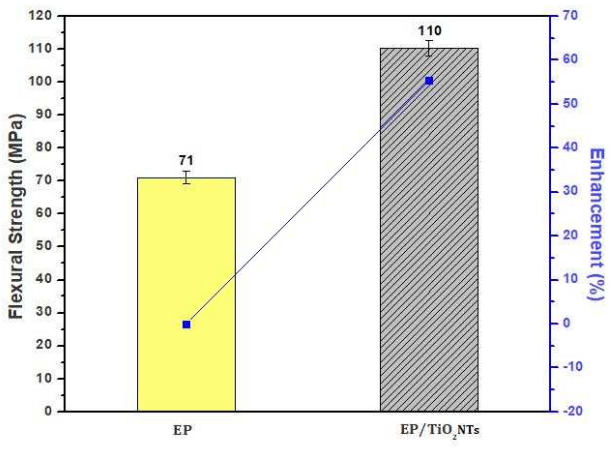

Fig. 8. Flexural strength values of pure epoxy, EP/TiO_2NT composites

Impact strength

The Izod impact test was conducted on pure and TiO_2/epoxy un-notched composites as per ASTM D 256 standards. Pure epoxy has a low impact strength of 4.4 kJ/m^2, whereas the TiO_2NTs/epoxy nanocomposites showed an impact strength of 4.78 kJ/m^2 (Fig. 9). Thus even with a very little amount of nanofiller (0.1 wt.%) reinforcement, the impact strength of TiO_2NT/epoxy increased by 8%.

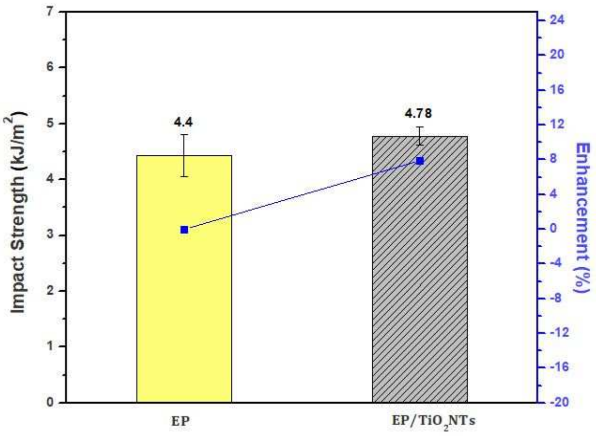

Fig. 9. Impact strength values of pure epoxy, EP/TiO_2NT composites

DISCUSSION

The enhancement of the mechanical properties of the epoxy composite by reinforcing with a small amount of TiO_2NTs may be attributed to the increased interfacial interaction due to good nanofiller-matrix adhesion, and the higher specific surface area of the TiO_2NTs.

A similar trend of enhancement of the tensile strength, elongation, and flexural strength were reported [12]. A maximum of 14% enhancement of the tensile strength and 72% in elongation was achieved at 3 wt.% TiO_2 nanoparticles (17 and 50 nm) and the maximum enhancement of the flexural strength by 22% was achieved at 1 wt.% TiO_2 nanoparticles. The reinforcing effects were attributed to the good dispersion of nanofiller and improved interface area between the epoxy and nanofiller. Nanoparticles can act as a crack growth inhibitor when the material yields under specific conditions.

The tensile strength and elongation of epoxy composites improved with TiO_2 nanoparticle reinforcement (6 wt.%) around 10 and 72%, respectively. The reinforcing effects are attributed to the quality of the interface and improved interfacial interactions between the nanofiller and the epoxy [13]. TiO_2 nanoparticles 30 nm in size improved the tensile strength of the epoxy composite by ~7% at a 0.5 wt.% reinforcement level [14]. It was reported that TiO_2 nanoparticles are effective in improving the elongation of epoxy nanocomposites [15].

The flexural strength of an epoxy composite improved by 18% with the addition of TiO_2 nanoparticles (10 nm) at 10 wt.% [16]. This reinforcing effect is attributed to homogeneously distributed TiO_2 nanoparticles and which lead to toughening mechanisms like shear yielding, bridging of the crack by the nanoparticles, and particle debonding.

It was demonstrated that the anisotropic long tubular structures of nanotubes substantially modify the mechanical properties of epoxy composites [17]. Higher interactions at the epoxy-nanotube interface due to the large aspect ratio of nanotubes were reported. Higher levels of interactions among the polymer matrix and nanotubes at the interfaces lead to higher quantities of stress transfer from the matrix to the nanofiller [18].

In this present study, it was demonstrated that TiO_2NTs improved the flexural strength and impact strength; similar reinforcing effects of TiO_2 nanofillers are reported elsewhere [19]. It has been stated that TiO_2 particles can block and divert crack propagation in the composite.

It was shown that long tubular unique nanotubes, when mixed with a polymer, can combine with the surrounding polymer chains and form 3-D network structure, resulting in improved flexural properties [20]. Nanofillers with large surface areas can serve as connecting bridges to prevent the matrix from fracturing upon mechanical deformation [21]. It was reported that the dispersion of the nanotubes confined the polymer chain mobility under loading conditions and enhanced the mechanical performance of the epoxy composite [22].

The mechanical properties of TiO_2N/epoxy nanocomposites indicate that TiO_2NTs are better fillers to enhance the properties of epoxy composites. The reason for these great reinforcing effects of TiO_2NTs can be ascribed to the improved interface in the epoxy due to their nanoscale length and diameter as well as tube-like structure with improved surface area (outer and inner), better dispersion of TiO_2NTs in the epoxy, robust interaction between the TiO_2NTs and epoxy, as well as physiochemical interactions between the nanofiller and epoxy [12, 14, 17, 18].

CONCLUSIONS

1D titanium nanotubes were synthesized and characterized for their morphology and dimensions using the TEM technique. TiO_2NT reinforced epoxy composites were prepared to investigate the reinforcing effects on the mechanical properties of epoxy composites by means of tensile, flexural, and impact tests.

The mechanical performance investigations of TiO_2NT reinforced epoxy composites revealed that the maximum enhancement in tensile strength of 85%, maximum enhancement in flexural strength of 55%, and maximum enhancement in impact strength of 8% were achieved due to TiO_2NT reinforcement. The reinforcement of TiO_2NTs as the filler resulted in significantly increased tensile and flexural properties, even with the very low addition level (0.1 wt.%).

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