Effects of Titanium Dioxide Nanoparticles on the Mechanical Strength of Epoxy Hybrid Composite Materials Reinforced with Unidirectional Carbon and Glass Fibers.

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Abstract. The present work describes the development of hybrid epoxy composite reinforced with unidirectional carbon, glass fibers and nano-TiO$_2$ powder in order to study some of its mechanical properties. Titanium dioxide (TiO$_2$) were dispersed in epoxy with different weight fractions (1, 3, and 5 wt. %) using sonication. Composite materials under study have been prepared by reinforcing the resulted nanocomposite by three different layers of unidirectional carbon fibers and glass bidirectional fibers using hand lay-up technique. Tensile and hardness tests as well as the surface roughness test have been performed during the experimental work. It has been observed that the tensile strengths of the fiber-reinforced polymer composites increase with fiber content, and TiO$_2$ nanoparticles up to a maximum value of 3 wt % after which it decreases. The value, modulus of elasticity, tension resistance, and hardness of the fiber-reinforced polymer composites increase with increasing fiber loading. The results obtained in this work show that the addition of TiO$_2$ nanoparticles at up to 3%wt to the epoxy composite reinforced with unidirectional carbon and glass fibers enhances the mechanical strength of such material.

Keywords. Nanocomposite, Nanoparticles, Glass fibers, Carbon fibers, Epoxy.

1. Introduction
Composite materials are recently grown and increasingly used in new applications. They are considered competitive to other materials in many applications such as airplanes, and automotive applications due to its higher stiffness to weight ratio [1]. Composite materials can be classified mainly to polymer matrix, metal matrix, and ceramic matrix composites. The addition of fiber improves the tensile properties of the composite material. This improvement is due to the higher strength and stiffness of the fibers than the matrices material [2]. Composite materials can be adapted to suit the individual needs to the desired specifications in a corrosive environment where it provides high resistance, weight light, lower product life cost, lower product life, a good combination of mechanical properties and thermal insulation. In addition, it offers the ability of monitoring the performance of these materials via an integral part of the composite sensors, and give them superiority over other materials [3]. Properties of composite materials are different even though the same materials are used and the same manufacturing process is used to produce the materials. Epoxy-nanocomposites are characterized by good mechanical performance, dielectric behavior, thermal stability properties, good corrosion resistance, adhesion to a moist substrate, good hardness, and
excellent tribological properties. Several potential applications led to broad interest in this type of materials [3, 4]. Using an inorganic filler to strengthen the epoxy resin is a common practice, since the nanoparticles fill the weak micro-regions of resin to enhance the interaction between the epoxy and the filler interfaces. The addition of the nanoparticles to the epoxy matrix leads to increasing the interfacial area between them and improves its properties. The reinforcement efficiency is strongly affected by particles size, dispersion of nanoparticles, and the volume faction of nanoparticles in epoxy matrix. Several methods were used to improve dispersion of nanoparticles in epoxy such as the sol-gel technique, shearing mixing, and ultrasonic homogenizing [4]. An ultrasonic homogenizer is suggested as an effective tool for the fabrication of epoxy nanocomposites [5,6,7]. It was found that every technique has a disadvantage in fabrication, such as decreased gelling time of epoxy resin in an ultrasonic homogenizer, and big agglomerations in shearing mixing. The main goal of the present work is to implement and test some of the mechanical properties of a hybrid composite material consisting of three materials to overcome the disadvantages of conventional composite materials.

2. Materials
The epoxy resin Quickmast 105 is used as a matrix material with suitable hardener. The mixing ratio of the epoxy and the hardener is 1.47:4, with gelling time of 40 minutes at 35°C, specific gravity of 1.1 g/cm³ and mixed viscosity of 1.0 poise at 35°C [8]. The titanium dioxide nanoparticles with 99% purity are used in the present work supplied by (MTI Corporation). It has specific surface area of 210 ± 10 m²/g, average particle size 50 nm and density 0.25 g/cm³. The fibers used are unidirectional carbon fibers provided by (Sika Wrap -300 Company, Switzerland), with the mechanical properties shown in table (1) [9], and bidirectional fabric glass fibers (GF) Woven Roving provided by (interweaving direct roving Fabrication Process china) and the mechanical properties are shown in table (1)[10].

Table 1. Mechanical properties unidirectional carbon and fiberglass [9][10].

| Material                     | Density g/cm³ | Young’s modulus E (GPa) | Poisson’s ratio |
|------------------------------|---------------|-------------------------|----------------|
| Unidirectional carbon fiber  | 1.81          | 230                     | 0.21           |
| Fiberglass woven roving fiber| 2             | 72.53                   | 0.22           |

3. Nanocomposite preparation

3.1. Mold preparation
A simple low-cost process (hand lay-up molding) was employed in this work to produce small sheets of composite materials. In the end, glass mold with dimensions (250× 250× 4) mm³ was used to ensure smooth surfaces. The base of the mold was coated with a clear Fablon film, while the inner walls were painted with Vaseline material to prevent sticking the molded part to the mold. Liquid matrix resin layers and reinforcing fibers were added sequentially to fabricated laminated sheets.

3.2. Preparation of nanocomposite materials
The nanocomposite material was prepared by TiO₂ addition to the epoxy resin. Since the nanoparticles of TiO₂ typically tend to agglomerate, therefore, the epoxy is diluted by mixing with acetone as a solvent by 10:2 weight percent ratio (resin: acetone) and manually stirred for 5 min [11]. The resulted mixture was sonicated with ultrasonic homogenizer (Ultrasonic Homogenizer FS-1200N) by applying full power for 10 minutes in impulse patterns of the 20s on and 10s off. The ultrasonic waves can break the agglomerated bodies and make them disperse in the liquid medium. The mixture was fully mixed using magnetic hotplate stirrer (Labtech Co. LTD) at a high speed for 30 minutes at room temperature to ensure vaporization of acetone. Finally, the hardening agent was included in the mixture by 1.47:4, at the room temperature (25°C). The mixture is now able to be used in the prepared mold [12].
4. Samples preparation

Various sheets of the composite material were manufactured using hand lay-up process. The mold was washed and its base was coated with a clear Fablon film while the inner walls were smeared with a thin Vaseline lubricant coat to prevent sticking to the mold parts. Woven fibers (GF and/or CF) had been cut to the same mold lengths and Weighted to measure their volume fraction used with the mixture law. The 1.47 g hardener was used for every 4 g of epoxy. The first layer of reinforcement material (glass fiber and/or carbon fiber) with dimensions (250 mm*250 mm) was placed over the resin in the mold and then inserted in the resin for complete wetting using a solid brush. Special brunches or rollers were used to prepare the sheets and avoid the trapping of air bubbles. The final lamina had been produced with a volume fraction of 30% for all layers (fibers + epoxy) sheets of composites. To avoid buckling and shrinkage, a heavy glass cover was added to the mold which also helps in eliminating any trapped air bubbles during the primary treatment process under the covering. Finally, the produced sheets were placed in a vacuum device to remove the air bubbles formed as a result of the interaction between the components. It consists of a container with air intake connected to an electric gas compressor with a single low pressure gauge. Each produced sheet was left for 24 hours for complete hardening at room temperature then transferred to an oven at (75˚C) for (3-4) hours for complete curing. This process is necessary for completing polymerization, relieving stresses induced during preparation process, and completing sheets hardening [10]. Testing samples were produced from these sheets using a CNC lathe machine (Suda ST1212 CNC router) to cut the laminates according to standard measurements.

5. Experimental testing procedure

5.1. Tensile test

In the present study, the tensile specimens are prepared according to ASTM D3039 [13] as shown in figure (1). Samples consisting of combination of woven roving fabric glass fibers and unidirectional carbon fiber with or without titanium dioxide nanoparticles (TiO$_2$) were prepared and tested. Four types of samples (Epoxy + three different types of fibers with or without TiO$_2$) have been tested. The test was carried out using a test machine type (LARYEE-50 KN) at room temperature until reaching the specimen fracture. The applied load is (5KN) with strain rate of (2 mm/min). A repetition of test for three times was ensured and the average values were adopted. The samples before and after testing are shown in figure (2).

![Figure 1. Tensile test specimen dimensions according to the (ASTM D3039).](image-url)
5.2. Hardness test
It was carried out according to (ASTM D2240-03) using Dorumeter hardness tester type (Shore D) with applied load of 50 N, and pressing time of (15 sec). The surface of specimens was prepared before testing. Specimen dimensions and distance from the edge are the most affecting parameters on the measured hardness. Specimens dimensions are shown in figure (3) [14]. The average value of seven readings of seven different tests is used as the final value of the hardness.

[Figure 3. Standard hardness test specimen.]

5.3. Surface roughness test
It was executed by using (TR 200) tester equipped with a detector that proceeds linearly along the considered length. The detector moves according to the profile of the surface and this movement converted into electric signals which is amplified and converted into digital signals via A/D converter. The surface irregularities are characterized by surface scales. Each test was repeated three times at various positions of each specimen and the average value was taken. The testing device appears to have an excellent feature that gives a direct estimated value of surface roughness [15-16]. This study investigates the effect of reinforcement materials on the surface micrometry of the test surface of the composite material specimens using this tester.

6. Results and discussion
The tensile test is performed on the specimens of composite materials to obtain the load– elongation, and stress-strain curves. The general trend of stress-strain curves for the composite material was produced by adding TiO₂ with different weight fractions (1, 3, and 5 wt.%) to the epoxy (EP) composite material reinforced by the glass and carbon fibers as shown in Figures (4-7). These figures illustrate that the stress increases with increasing the strain in a nonlinear relationship for all types of the considered materials. Many factors affect the tensile properties of the tested materials before and
after (TiO$_2$) addition like the type and volume fraction of fibers and the weight fraction of TiO2. Figure (4) shows a comparison for the tensile test results of (EP+C/C/C) with that obtained when adding TiO$_2$ with different weight fractions (1%,3%,5%wt). It can be shown that the resistance of the composite material to the tensile loading increases with the implementation of TiO$_2$ in epoxy up to 3%wt. This can be attributed to the increasing surface area associated with quantum effects revealed by a decreased size of the nano particles. The number of atoms on the surface will be more as compared to the atoms present in the bulk form. The nano fillers have a high specific surface area which reduces the effects of applied mechanical stresses. It is also shown in this figure that using TiO$_2$ with (5 wt.%) results in a decrease in the resistance of the composite material to the tensile loading and the failure occurs at lower values of tensile strain. The agglomeration of the nanoparticles inside the matrix seems to be the main reason for the decrease in elastic modulus when adding higher percentage of TiO$_2$ nanoparticles (5%wt%). The agglomeration of the nanoparticles is the main reason of forming weaker interface bond between the filler and the matrix. It is also observed in this figure that (EP+C/C/C+3%TiO$_2$) laminated composite has the maximum tensile strength in comparison with the other types since there is an increase in the maximum tensile stress by 3.2 % and strain reduction by 9.5% in comparison with laminated composite without nano-TiO$_2$.

![Figure 4](image_url)

**Figure 4.** Stress-strain curves of hybrid EP composite reinforced with Carbon fibers and TiO$_2$ nanoparticles.

Figures (5) shows that addition of TiO$_2$ nano powder has little effect on the tensile strength of EP, CGC composite material with a decrease in material strain. The maximum decrease in strain has been recorded for (EP, CGC, TiO$_2$ by 3%). Figures (6) and (7) clearly show that laminated composites cause an increase in the maximum tensile stress by 19.4% and 21.5% and a decrease in the strain by 5% and 13.5% for (EP+G/C/G+3%TiO$_2$), and (EP+G/G/G+3%TiO$_2$) laminated composites, respectively.

![Figure 5](image_url)

**Figure 5.** Tensile stress-strain curves of EP resin reinforced with Carbon, glass fibers and TiO$_2$ nanoparticles.
Figure 6. Tensile stress-strain curves of EP resin reinforced with Carbon, glass fibers before and TiO\textsubscript{2} nanoparticles.

Figure 7. Tensile stress-strain curves of EP resin reinforced with glass fibers(3ply) and TiO\textsubscript{2} nanoparticle.

6.1. Tensile strength

The variation in tensile strength of composite and hybrid composite material specimens when adding different weight fractions of TiO\textsubscript{2} and different fiber types are presented in figure (8). This figure shows that when adding TiO\textsubscript{2} nanoparticles with (3 wt. %) to the composite material, the values of the tensile strength increased. The tensile strength of hybrid composite material consisting of epoxy reinforced by 3ply of unidirectional carbon fabric and 3% wt TiO\textsubscript{2} (EP+C/C/C+TiO\textsubscript{2}), increased by about 13% when adding TiO\textsubscript{2} compared with (EP+C/C/C) laminated composite, while it increased by 9.6%, 9.9% and 7.2% for the (EP+C/G/C+TiO\textsubscript{2}), (EP+G/C/G+TiO\textsubscript{2}), and (EP+G/G/G+TiO\textsubscript{2}) hybrid nanocomposite, respectively. This can be attributed to higher contact surfaces due to the existence of TiO\textsubscript{2} nanoparticles which increases the resistance of the material to the applied load.

Figure 8. Tensile strength of composite and hybrid composite before and after adding TiO\textsubscript{2}.
6.2. Tensile modulus
The variation in the tensile modulus of composite and hybrid composite material specimens when using different weight fractions of TiO$_2$ addition and various stacking sequence of the fibers is presented in Figure (9). It can be observed that the tensile modulus increases when adding TiO$_2$ nanoparticles with (3 wt. %) to composite materials. The modulus of elasticity of TiO$_2$/3ply of unidirectional carbon fabric/epoxy (EP+C/C/C+TiO$_2$) laminated nanocomposite increased by about 11.77% when adding TiO$_2$ compared with (EP+C/C/C) laminated composite. For (EP+C/G/C/TiO$_2$) hybrid nanocomposite, the tensile modulus increased by about 14.1%, while it increased by 19.6% for (EP+G/C/G+TiO$_2$) hybrid nanocomposite, and 17.1% for (EP+G/G/G+TiO$_2$) hybrid nanocomposite. This behavior reflects the homogeneous pattern of TiO$_2$ nanoparticles into the hybrid composite material which is caused across linking between the matrix and nanomaterial causing a resistance to the chain movement and hence increasing Young’s modulus. Also, the nature of the bonding between the matrix and the Nanofillers particles with fibers plays an important role due to the good ability of the liquid epoxy to spread on the TiO$_2$ and fibers which causes increasing bonding between such materials. Hence, the resultant hybrid nanocomposite will require high stress to break their physical bonding.

![Figure 9. Tensile modulus of the composite and hybrid composite materials.](image)

6.3. Hardness test results
The hardness test results for different composite and hybrid nano composite materials prepared in the present work are shown in figure (10). It is observed in this figure that hybridization of the composite materials by adding TiO$_2$ nano particles with different particle concentrations leads to increase in the hardness of the composite material. This figure obviously shows that the best percentage of addition of TiO$_2$ is 3%wt. The percentage increases in hardness of the hybrid nanocomposite with 3%wt TiO$_2$ in comparison with that without TiO$_2$ addition as presented in table (2).

![Figure 10. Hardness of composite and nanohybrid composite materials.](image)
Table 2. Percentage increase of hardness of nanohybrid composite materials.

| Material                  | % Hardness Increase |
|---------------------------|---------------------|
| EP+G/C/G+3%TiO$_2$       | 29.8                |
| EP+C/G/C+0.3%TiO$_2$     | 25.3                |
| EP+C/C/C+3%TiO$_2$       | 24                  |
| EP+G/G/G+3%TiO$_2$       | 27.9                |

6.4. Surface roughness test results
Surface roughness tests show that all prepared testing samples have an average roughness ranging between 0.024 and 0.140 µm. The addition of the nanoparticles to the composite material makes smoother surfaces and this results are consistent with these of [17].

7. Conclusions
The experimental investigation of the behavior of composite and hybrid nanocomposite material consists of epoxy resin as a matrix reinforced by the woven glass and unidirectional carbon fibers with various weight fractions of Titanium dioxide (TiO$_2$), leading to the following conclusions:

1. The fabricated nanocomposite properties are directly influenced by weight fractions of (TiO$_2$), increasing the weight concentrations of (TiO$_2$) up to 3%wt and improving the mechanical properties of such material.
2. An enhancement in tensile strength by 7.2% for (EP+C/G/C+TiO$_2$) up to 13% for (EP+C/C/C+TiO$_2$) was obtained when adding 3%wt of TiO$_2$.
3. The tensile modulus of hybrid nanocomposite materials enhances by 11.7% for (EP+C/C/C+3wt%TiO$_2$) up to 19.6% for (EP+G/C/G+3wt%TiO$_2$).
4. Hardness increases with weight percentage of TiO$_2$ by 24% for (EP+C/C/C+3%TiO$_2$) up to 29.8% for (EP+G/C/G+3%TiO$_2$)
5. Surface roughness is smaller in the specimens with nanofillers than those without nanofillers.

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