Evaluation of the Mechanical Characteristics of Hybrid Nanocomposite Materials (TiO2-SiO2-ZrO2)

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Abstract. Hybrid nanocomposite materials have opened the way for more promising applications in the areas of optics, electronics, Ionics, mechanics, energy, environment, biology and medicine. In this work hybrid nanocomposite materials were synthesized, by mechanical stirring method, using SiO2+ZrO2+TiO2 nanoparticles with different percentages (4 wt.% to 10 wt.%), as a reinforcement material. The effect of the added nanoparticles on the mechanical properties was evaluated in terms of tensile strength, impact strength and hardness. The results revealed that the hybrid nanocomposite with 4 wt.% SiO2+ZrO2+TiO2 showed maximum tensile strength, hardness, and impact resistance. Further, the best development in the mechanical properties achieved in the literature, due to the addition of different Nano fillers (TiO2, SiO2, and SiO2 +ZrO2) with different percentages (4 wt.% to 10 wt.%), were compared with the achieved results in the present work. The results showed that the addition of hybrid nanocomposite SiO2+ZrO2+TiO2 provides significant mechanical properties development compared to the other materials addition.

Keywords: Hybrid, nanocomposite materials, mechanical characterization

1. Introduction
Composites are one of the most widely used materials because of their high strength-weight ratios, stiffness and cost effectiveness as a result of easy availability of raw materials which make them obvious choice for many applications. [1]. A composite material is made up of a combination of two or more constituents that are combined on a macroscopic level, and not soluble in each other. The matrix phase material is continuous in general. Another Phase is devoted to provide strength and stiffness which is stronger, and stiffer than the matrix. The fibers have a greater length compared to the diameter. Matrix carry out several important functions, including maintaining fiber in the correct orientation and spacing and protect them from abrasion and the environment. The type and quantity of reinforcement is determined the properties of the composite material [2]. Discovery of novel materials, processes and phenomena at the Nano scale, as well as the development of experimental techniques have provided new opportunities for the development of innovative nanostructured materials [3].
Nano-composite materials not only represent a creative alternative to design new materials, but also the characteristics they improved are allowing innovative industry application development [4]. Three basic reasons lead to changes in the properties of the materials when they are reduced to the level of Nano dimensions [5-8]:

1. Quantum confinement
2. High interface area
3. Closeness of the material lengths to the critical length scale of the property.

Many polymers today are compounded with fillers to modify their properties. This is usually done to improve mechanical properties such as stiffness or modify the performance, such as color, transparency, magnetic properties, and others. Often, quite large number of additives are required to obtain the desired property, which may result in increasing the density [9,10]. Nanocomposites have gained much interest recently. Researchers who considered these materials have investigated the effect of different nanomaterials on composites mechanical properties. Lu et al. [11] studied the effect of adding TiO$_2$ and SiO$_2$ Nano filler on the mechanical and wear properties of composites. The study observed that tensile strength, wear resistance and friction performance of the composites improve with the addition of the Nano fillers. Chen et al. [12] investigated the effect of the SiO$_2$ Nano filler on the mechanical properties of nanocomposites. It was found that the addition of 10 wt.% SiO$_2$ improves the modulus and fracture toughness by 25% and 30% respectively. However, a reduction in the strength fracture toughness were observed. Chowdhary et al. [13] dispersed aNano clay with different percentage in SC-15 epoxy. The results revealed significant improvement in the flexural strength and modulus.

Zhou et al. [14] conducted thermal and mechanical investigations of the carbon Nano fiber (CNF) filled epoxy. The optimal CNF content was found to be 2.0 wt.%, which produces the highest improvement in tensile strength compared to the neat epoxy resin. Khan et al. [15] studied the effect of Nano clay inclusion on cyclic fatigue behavior and residual properties of carbon fiber reinforced composites. It was shown that fatigue life significantly extends with the incorporation of Nano clay to CFRP composite. The maximum improvement was about 74% with 3 wt.% clay content. Osman Asi [16] studied the bearing strength behavior of pinned joints of glass fiber reinforced composite which was filled with different percentage of Al$_2$O$_3$ (7.7, 10, 15%). From their result it was shown that bearing strength of composite increases with the increase of the added Al$_2$O$_3$ percentage. The highest bearing strengths were obtained for composite specimens with 10 wt.% Al$_2$O$_3$ particle content. Khan et al. [17] have investigating the impact fracture toughness and quasi-static fracture toughness chirpy impact test and compact tension test on clay-epoxy Nano composites and clay-carbon fiber reinforced polymer (CFRP) hybrid composites. The result revealed that the properties were increased in both the material with addition of clay up to 3 wt% but decrease after further addition of clay. Zeng et al. [18] studied the effect of addition rubber and silica Nano particles on the fracture toughness of epoxy matrix. It was observed that fracture toughness is improved by the presence of these Nano-particles. Nano rubber was more effective than Nano silica. It is observed from the literature that significant efforts have been directed, in the recent years, toward the reinforcement with nanoparticle materials. Most of the studies considered the task using different single material. However, due to the great interaction between the different materials on the nano scale, it is anticipated that mixes of these materials could provide properties development different from that achieved using single material. Hence, in the present work a new hybrid epoxy Nano composite material was synthesized using TiO$_2$, SiO$_2$ and ZrO$_2$ Nano fillers. The mechanical stirring method was used to manufacture the composites. The effect of the nanoparticle additives on the mechanical properties of the hybrid nanocomposite material was investigated.

2. Materials and Methods

Two types of material were used in the manufacturing of the nanocomposites. First was the matrix material which is a Diglycidyl ether of bisphenol (DGBA) (Epoxy Resin L-2, Hardener K-12,
Accelerator K-13). The second was the reinforcement material which included nano particles of TiO$_2$, SiO$_2$ and ZrO$_2$. Table 1 below provides the physical data of the reinforcement materials.

| Material | Description | Particle Size |
|----------|-------------|---------------|
| SiO$_2$  | White powder, 99.5% purity. | 15-20 nm |
| TiO$_2$  | Surface area of 50+15 m$^2$/g and is 99% purity. | 30 nm |
| ZrO$_2$  | White powder, 99.9% purity. | 70-80 nm |

To get a proper dispersion of the Nano filler in the epoxy material, mechanical stirring was done at 2000 rpm for 2 hours. Different hybrid nanocomposite materials were prepared by adding different percentage of (SiO$_2$,ZrO$_2$) and (SiO$_2$+ZrO$_2$+TiO$_2$) at (4 wt%, 6 wt%,8 wt% and 10 w%) to the epoxy resin. Ref. [11,12] have investigated the impact of mixtures of different portion of TiO$_2$, SiO$_2$ and ZrO$_2$ nano-particles on the mechanical properties of the nanocomposites. Thus, in the current work the authors decided to investigate the impact of mixture of equal portion of TiO$_2$, SiO$_2$ and ZrO$_2$ nano-particles.

These additives materials have been selected due to their wide range of applications especially in armor, aerospace industry and biological application [4]. They are characterized by lightweight and high strength which make them ideal reinforcing materials most of the modern designs. Further, the investigated additives percentages were selected based on studies available in the literature [11-13]. To reduce the viscosity of epoxy solution, it was preheated to 60°C for 30 minutes. Then, an ultrasonication bath was used to agitate particle in a mixture for two hours, it acts to break the intermolecular interaction and speed up the dissolution. After that, the solution was mixed with the hardener with a mixing ratio of 1:1 by weight and then 1 wt.% accelerator was added as per the instructions of the epoxy system resin supplier. A mechanical stirrer was then used for 15 minutes followed by 15 minutes of ultrasonication which result in good dispersion of nanoparticles. Consequently, a large amount of bubbles appeared in the solution which must be removed to avoid defects in the test specimens that may affect the accuracy of the testing results. To get a rid of the trapped air bubbles, the solution was put in a degassing beaker and placed in vacuum oven for 2 hours. After that, the bubble free mixture was poured in a Teflon mold and left in ambient temperature for 24 hours to cure. The samples were then interred to an electric oven at 500 C for 1 hour for post curing. Figure 2 shows the Teflon mold that has been used to cast the tensile test samples according to (ASTM D638) standard.

The tensile test was performed using universal testing machine (LARYEE TECHNOLOGYCO, LTD, China), according to (ASTM D638) standard. Vickers microhardness testing equipment (Gewicht Shore D, Germany) was used to determine specimen’s hardness. Moreover, Izod impact testing equipment (XJU-22) was used to determine the specimens' toughness.
3. Results and Discussion

The results of investigating the synthesized nanocomposite were discussed in this section in terms of tensile properties, hardness and impact strength.

3.1. The tensile properties

Figure 3 shows the effect of different percentage of SiO$_2$+ZrO$_2$+TiO$_2$ mixture on the tensile properties. This mixture was prepared by mixing the same amount of each nanomaterial. The addition of (SiO$_2$+ZrO$_2$+TiO$_2$) nanoparticles reinforcement to epoxy matrix increased the tensile strength of hybrid nanocomposite materials to the maximum value at 4wt% for (SiO$_2$+ZrO$_2$+TiO$_2$) nanoparticles. Which is attributed to strong interface between the phases that distributes and transfers the load from the matrix to the reinforcement resulted in tensile strength improvement. After maximum value the tensile strength decrease that may be an interaction between Nano partials may have occurred, with an increase in proportions, leading to adverse reactions.

![Figure 3](image.png)

**Figure 3.** Effect of weight percentages of nanoparticles additives (SiO$_2$-ZrO$_2$-TiO$_2$) on tensile strength of hybrid nanocomposite material.

Figure 4 shows the effect of the added (SiO$_2$+ZrO$_2$+TiO$_2$) nanoparticles weight percentages on the elongation of hybrid nanocomposite material. The results revealed a linear proportion between the maximum elongation and the nanoparticles percentage, and the maximum elongation was at the percentage of 10 wt.%. 

Figure 4. Effect of weight percentages of nanoparticles additives (SiO₂-ZrO₂-TiO₂) on the elongation of hybrid nanocomposite material.

3.2. The hardness

Figure 5 shows the effect of weight percentages of nanoparticles additives (SiO₂+ZrO₂+TiO₂) on the hardness of the synthesized Nanocomposite. An average value of three measurements was calculated. There was a gradual decrease in hardness from 4 wt% to 6 wt% of (SiO₂+TiO₂+ZrO₂), and the maximum value of the hardness at 4 wt% of (SiO₂+ZrO₂+TiO₂). The decrease is due to the possibility that increasing the ratios of nanoparticle leads to a conglomerate and distribution of heterogeneous and soften the mixture. However, compared to pure epoxy, a considerable improvement in the hardness has been achieved due to the addition of the reinforcement particles. Which is attributed to the effective development in the indentation restriction caused by the added nanoparticles.

Figure 5. The effect of weight percentages of nanoparticles additives (SiO₂-ZrO₂-TiO₂) on the hardness of hybrid nanocomposite material.
3.3. The impact strength

Figure 6 shows the effect of weight percentages of nanoparticles additives (SiO2+ZrO2+TiO2) on the impact strength of hybrid nanocomposite material. A variation in the impact strength was observed as the percentage of the (SiO2+ZrO2+TiO2) in the epoxy are is changed. A gradual decrease from 0.25 J at 4% (SiO2+ZrO2+TiO2) approximately to value given by the epoxy matrix are observed at 10% (SiO2+ZrO2+TiO2). This variation can be explained in terms of hybrid nanocomposite elongation

![Figure 6](image)

**Figure 6.** The effect of weight percentages of nanoparticles additives (SiO2+ZrO2+TiO2) on the impact strength of hybrid nanocomposite material.

The addition of nanoparticles (SiO2+ZrO2+TiO2) resulted in better distribution of particles with minimum defects, the nanoparticles have significantly large specific surface area, which greatly facilitates the transfer of load from polymer matrix to nanoparticles which leads to increase in impact strength.

3.4. Mechanical characteristics of hybrid nanocomposite materials (TiO2+SiO2+ZrO2) over other nanocomposite materials.

In our previous work [20,21], hybrid nanocomposite materials were synthesized, by mechanical stirring method, using different Nano fillers (TiO2, SiO2, and SiO2 +ZrO2) with different percentages (4 wt.% to 10 wt.%). The best development achieved in the tensile strength, impact strength and hardness, due to these materials, were compared with the achieved development using TiO2+SiO2+ ZrO2 hybrid nanocomposite materials.

3.4.1 Tensile test

Figure 7 shows a comparison between the best development in tensile strength due to adding TiO2, SiO2, (SiO2 +ZrO2) and (TiO2+SiO2+ZrO2) nanocomposite materials.
Figure 7. A comparison between the best achieved tensile strength development by using TiO2, SiO2, (SiO2 +ZrO2) and (TiO2+SiO2+ZrO2) nano particles materials.

The tensile strength due to adding of (TiO2+SiO2+ZrO2) nanocomposite materials have compelling value to max tensile strength recorded as a result of adding of TiO2 nanocomposite materials. This development is attributed to the increased ratio of the particles to matrix interface. Consequently, more load transfer exists, which accordingly increases the strength, this conforms with the results provided by Saiful Islam et al. [19]

Figure 8 shows a comparison between the best development achieved in elongation due to the addition of TiO2, SiO2, (SiO2 +ZrO2) and (TiO2+SiO2+ZrO2) nanoparticle materials. It is observed that the addition of SiO2 resulted to maximum elongation value while the addition of hybrid Nanocomposite materials (SiO2+ZrO2) and (TiO2+SiO2+ZrO2) resulted to lower elongation.

Figure 8. A comparison between the best development in elongation due to the attrition of TiO2, SiO2, (SiO2 +ZrO2) and (TiO2+SiO2+ZrO2) Nanoparticle materials.

3.4.2 Hardness Test

Figure 9 shows a comparison between the best development achieved in hardness due to the addition of TiO2, SiO2, (SiO2 +ZrO2) and (TiO2+SiO2+ZrO2) nanoparticle materials. It is observed that the addition of TiO2 resulted to maximum hardness value while the addition of
hybrid Nanoparticle materials (SiO2 +ZrO2) and (TiO2+SiO2+ZrO2) resulted in lower development. This is due to the coagulation of the hybrid nanoparticle materials as result of poor homogeneity of mixed material.

Figure 9. A comparison between the best development in hardness due to the addition of TiO2, SiO2, (SiO2 +ZrO2) and (TiO2+SiO2+ZrO2) nanoparticle materials

3.4.3 Impact Strength
Figure 10 provides a comparison between the best development achieved in the impact strength due to the addition of TiO2, SiO2, (SiO2 +ZrO2) and (TiO2+SiO2+ZrO2) nanoparticle materials. It is observed that the addition of hybrid nanoparticle materials (SiO2+ZrO2) and (TiO2+SiO2+ZrO2) resulted in higher impact strength which could be due to the solid solution strengthening effect of the hybrid nanoparticle materials.

Figure 10. A comparison between the best development in the impact strength due to the addition of TiO2, SiO2, (SiO2+ZrO2) and (TiO2+SiO2+ZrO2) nanoparticle materials
4. Conclusions
Characterizations of the mechanical properties for hybrid nanocomposite materials have been presented in this study. A mixture of equal portions of TiO2, SiO2 and ZrO2 nano particles was prepared and used in different percentage to produce reinforced nanocomposites. The mechanical stirring method was used to prepare the composites and the mechanical characteristics were evaluated in terms of tensile strength, elongation, hardness, and toughness. The results revealed that the hybrid nanocomposite with 4 wt.% SiO2+ZrO2+TiO2 showed maximum tensile strength, hardness, and impact resistance. Further, the best development achieved, in our previous work, in the tensile strength, impact strength and hardness, due to addition of different Nano fillers (TiO2, SiO2, and SiO2 +ZrO2) with different percentages (4 wt.% to 10 wt.%), were compared with the achieved development in the current study. The results showed that addition of hybrid nanocomposite (SiO2+ZrO2+TiO2) resulted in good mechanical properties compared with other materials.

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