Comparing the Effects of ZnO and ZrO₂ Nanomaterials on the Mechanical, Chemical, and Crystalline Properties of Epoxy Resin (DGEBA)

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ABSTRACT

This research paper presents a comparative experimental study on the impact of zinc oxide and zirconium dioxide nanomaterials on the chemical, mechanical, and crystalline properties of epoxy resin (diglycidyl ether of bisphenol-A). Nanomaterials were incorporated into the epoxy resin at three different concentrations (4%, 6%, and 8%) by weight. Results indicated enhanced properties of the epoxy resin, including tensile and compressive strengths, as well as improvements in chemical and crystalline characteristics, assessed through scanning electron microscope (SEM) and Fourier-transform infrared spectroscopy (FTIR). Notably, zirconium dioxide exhibited superior performance across all properties, enhancing tensile and compressive strengths by 67% and 50%, respectively. Zinc oxide, at the same concentrations, led to a 50% increase in tensile strength and a 40% increase in compressive strength. These outcomes were observed at the highest concentration (8%wt) of both nanomaterials and the pure epoxy resin. The presence of nanomaterials at this ratio promoted greater cohesion within the composite, as evidenced by SEM images of selected samples. SEM analysis highlighted the pivotal role of ZrO₂ nanoparticles in improving epoxy integration, surface quality, crystallization, and imperfection removal, crucial factors for enhancing composite materials. FTIR analysis of the resin containing ZrO₂ nanoparticles revealed shifts and alterations in peaks, indicating successful nanoparticle-epoxy interaction, resulting in notable structural changes.

1. INTRODUCTION

Composite materials, amalgamations of two or more components, manifest properties surpassing those of their individual constituents. Epoxy resin, recognized for its robustness, endurance, and thermal attributes, finds widespread applications in automotive sectors, serving as an adhesive, in civil engineering, aerospace, coatings, and paints. However, the inherent fragility of this thermoplastic polymer resin is acknowledged [1-5].

The inception of nanotechnology dates back to 1959, marked by Richard Feynman's discourse titled "There is Room Plenty at Bottom." Although nanotechnology was not explicitly coined by Feynman, he envisioned the precision manipulation of molecules and atoms. Subsequently, in the 1980s, the field evolved with pivotal advancements, including the invention of a tunneling scanning microscope in 1981 and the discovery of fullerenes in 1985. Nanotechnology is anticipated to shape 21st-century technology, characterized by the ability to control matter at nanoscales, spanning from 1 to 100 nm [3, 6-10].

Over the preceding decade, there has been a conspicuous upswing in the fervor surrounding polymer nanocomposites, attributable to their striking progress beyond matrix polymers. Additive manufacturing has revolutionized intricate processes involved in fabricating polymer matrix composites.

Nanomaterials have secured noteworthy roles in photodetectors and photocatalysis, driven by their unique properties that facilitate heightened light absorption, efficient charge separation, and improved catalytic reactions. Their integration into nanocomposites augments coatings, offering unparalleled corrosion protection across diverse applications [6-8].

To craft nanocomposites for specific applications, extensive investigations have delved into the impact of nano fillers on crucial characteristics. Even a marginal weight-based escalation in nanofillers has demonstrated substantial enhancements in dielectric, mechanical, and thermal attributes. The amalgamation of metal oxide nanoparticles and polymers is a strategy employed to bolster mechanical strength [11-16].

Previous studies have accentuated the utilization of zinc oxide (ZnO) nanoparticles as a reinforcing agent for the epoxy resin system, specifically bisphenol A diglycidyl ether. Two modifications were explored: coating with polydopamine (PDA) and covalent activation using 3-aminopropyl triethoxysilane (APTES) and 3-glycidoxypropyl trimethoxysilane (GPTMS). To augment the bonding interface between the polymeric matrix and the reinforcement, four distinct types of nanoparticles—pristine ZnO, ZnO/PDA, ZnO/GPTMS, and ZnO/APTES—were employed. Tensile tests unveiled that the incorporation of pristine ZnO fortified the composite by 32.14%, whereas the addition of ZnO to the

reinforcement heightened the resin's fracture toughness by 9.40% [1].

Employing a combination of mechanical stirring and ultrasonication methods, epoxy composites reinforced with zinc oxide nanoparticles, alumina microparticles, and nano-clays were developed at concentrations of 1, 3, 5, and 8wt%. The results indicate that the inclusion of 8wt% alumina enhances the composite modulus by approximately 27%, while variations in particle weight concentration lead to fluctuations in flexural strengths, showing both increments and, in some cases, marginal decreases [16].

In a separate experimental investigation, optimal time intervals and quantities of ZnO particles were explored to fill high glass fibers (HGFs) and enhance the UV absorption of the composite. UV-vis absorption characteristics of samples with different ZnO/epoxy compositions were examined using a UV-vis spectrophotometer. The study revealed that HGFs exhibited favorable UVB and high UVA adsorption capabilities when filled with 4wt% and 5wt% ZnO at intervals of 0.2 mm and 0.5 mm. Notably, a ZnO sample with a 4wt% concentration maintained consistent UV absorption properties even with a continuous increase in the interval between HGFs [17].

Additionally, epoxy resin samples, produced by curing diglycidyl ether from DGEBA resin with a tertiary amine as a hardener, were experimentally tested for high strength. Various fillers were employed to create samples with diverse attributes, and subsequent mechanical tests were conducted to assess the samples' mechanical characteristics. The results demonstrated that glass fibers serve as an optimal filler for enhancing the mechanical qualities of epoxy resins [18].

Furthermore, an examination delved into the impact of a modified hyperbranched polymer on the tensile strength of epoxy resins at 77 K. In the DGEBA epoxy resin system, methyl nadec anhydride (MNA), treated with diglycidyl ether, was introduced as the modifier (H204). The impact strength at 77 K was investigated, revealing that the employed modifier enhanced impact strength at cryogenic temperatures. The addition of 10wt% H204 into the epoxy matrix led to a notable increase of 58.57%. Additionally, the fracture process and its strengthening effect were scrutinized using scanning electron microscopy (SEM) [19].

In other studies examined basalt fibers. The composites they created are made up of 3% and 6% Nano clay, 10% and 20% basalt fibers, and 0, 75, and 15% graphene Nano sheets. Samples were heated up in a medium before testing. The charpy impact tests were used to explore the impact strength, and the tension tests were used to research the tensile strength and elasticity. Basalt increases elasticity by 64%, impact strength by 18%, and tensile strength by 32%. The absolute elasticity modulus was increased by 66%, while the tensile and impact strengths were improved by 15% and 20%, respectively. This is accomplished utilizing graphene nanosheets. While the elasticity modulus and tensile strength rose by 59% and 17%, respectively, while the impact strength decreased by 19% with the addition of the nano clay. These mechanical characteristics matched those attained through the optimization of beauty [20]. Also other researchers investigated fiber-reinforced polymers (FRPs). The researcher emphasizes how incorporating alumina nanomaterials (Al_2O_3) and graphene Nano platelets (GNPs) into the FRPs used to make turbine blades may develop the blades fracture toughness and the vulnerable sections stiffness. The results of the tensile, bending, and hardness tests were compared in the case of the reinforced and unreinforced samples. The microscopic experiments revealed excellent scattering from both the FRP matrix of GNPs and Al_2O_3 and the reinforcing nanoparticles. The samples of free-defect are created when GNPs and Al_2O_3 nanoparticles are evenly dispersed throughout the FRPs matrix, and they display outstanding mechanical characteristics. This relates to fracture toughness and strength performance. Some researchers discovered a soft sensor comprised of a solid-state, nanofiber-based polymeric substance. The necessary extra hydroxyl sets for OP were created by hydrolyzing the electrospun fiber acetate nanocomposite fibrous assembly, and the polydiacetylene esters were employed as a binding substance. The material was characterized using scanning electron microscopy (SEM), Fourier-transform ultraviolet spectrometer (FT-IR), Instron® tensile tester, contact angle analyzer, and UV-Vis spectrophotometer. The polydiacetylene esters' ability to withstand hydrolysis in the cellulosic fiber matrix led researchers to conclude that the combinations would be ideal for OP sensing. The tension property of nanofibrous (NF) composites also allows for the manufacture of textiles. Last, the colorimetric OP sensing of the NF composites was discernible to the unassisted eye. The development of OP sensing in systems for protective gear depends on this important piece of research.

2. EXPERIMENTS

2.1 Materials

The materials used in this study are the zinc oxide (ZnO), the zirconium dioxide (ZrO_2) and Diglycidyl ether of bisphenol-A (DGEBA). The ZnO and ZrO_2 were used as nanomaterials added into an epoxy resin (DGEBA). All these materials were bought from local markets in Baghdad. They were checked to sure that they conform to the standard specifications. Both of the zinc oxide and the zirconium dioxide were added into the epoxy resin (DGEBA) with three percentages (4%, 6%, and 8%wt).

Figure 1 shows the zinc oxide (ZnO) powder and Figure 2 shows the zirconium dioxide (ZrO_2) powder.
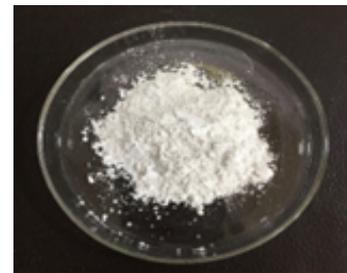
Figure 1. Zinc Oxide (ZnO)

Figure 2. Zirconium Dioxide (ZrO_2)

The diglycidyl ether of bisphenol-A (DGEBA) was used as a matrix material for the composite material. It is described as a transparent viscous liquid at the room temperature. 5 g of a hardener was added into 20 g of the resin to increase its hardness (Table 1).

Table 1. Specifications of the materials used in this study*

Material	Properties
Epoxy resin DGEBA	Two-component liquid, viscocity of 9000 to 13000 cps and density of 1.17 g/cm^3
Nano-ZrO$_2$	high purity ,White powder, with particles size 30 nm, apparent density of 5.68 g/cm^3, soluble in HF, and hot H$_2$SO$_4$
Nano-ZnO	high purity, White powder, with particles size 20 nm and density of 0.04 – 5 g/cm^3

* Supplied by the product data sheets.

2.2 Devices and equipment

Devices and equipment used in the completion of this work are described as follows:
1. Sensitive digital Balance,
2. Fume Hoods,
3. Molds for tensile and compressive testing samples made of wood
4. Universal Mechanical test machine, TINIUS OISEN H100KU for tensile and compressive tests.
5. Shimadzu IRAffinity-1S FTIR Spectrophotometer.
6. VEGA3/TESCANI Scanning Electron Microscope.
7. Facemask.
8. Gloves.

Figures 3 and 4 show the sensitive digital balance and fume hoods, Figure 5 Hydraulic press universal tester Figure 6 molds for tensile and compressive testing samples (made of wood), Figure 7 Universal tensile tester, Figure 8 Shimadzu IRAffinity-1S FTIR Spectrophotometer, Figure 9 Scanning Electron Microscopy Device final sample the pieces after tests. respectively. The Final sample as in the Figure 10, and the samples after tests as in Figure 11.

Figure 3. Sensitive digital balance

Figure 4. Fume hoods
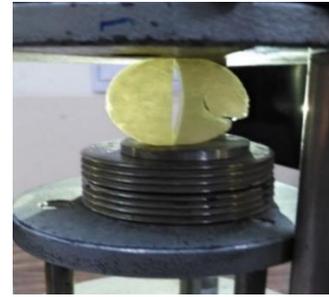
Figure 5. Hydraulic press universal tester

Figure 6. Molds for tensile and compressive testing samples (Made of Wood)

Figure 7. Universal tensile tester

Figure 8. Shimadzu IRAffinity-1S FTIR spectrophotometer

Figure 9. Scanning electron microscopy device

Figure 10. Final sample
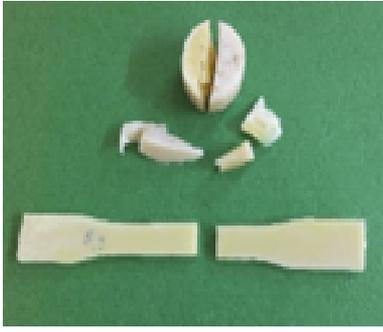
Figure 11. The samples after tests

2.3 Experimental tests

In this work, there are two types of tests namely the tensile and compressive test. Both tests were performed according to ASTM C1909-02 in Material Testing Laboratory at Materials Engineering Department / Al Mustansiriyah University for each test, while for the FTIR and SEM, both done in the University of Technology. there are seven samples with fourteen total samples (seven samples for the tensile test and the same number for the compressive test). In each test, the samples were prepared as follows as: -

The first sample is a reference (26 g of a pure epoxy resin without nanomaterials) consists of 20 g DGEBA matrix and three drops of the hardener (6 g). The 2nd, 3rd and 4th samples consist of an epoxy resin (26 g) and the zinc oxide. The zinc oxide was added with three percentages (4%, 6%, and 8% by weight) into the resin (one percentage for each sample). The same thing for the 5th, 6th and 7th samples, but the zirconium dioxide replaced by the zinc oxide. The sum of samples becomes seven for the tensile test, and the same thing for the compressive test.

3. RESULTS AND DISCUSSIONS

3.1 Tensile test

Figures 12 and 13 show results of the tensile strength of DGEBA with the presence of nanomaterials of zinc oxide (ZnO) and zirconium dioxide (ZrO_2) respectively. This Figure shows, this Figure shows that the tensile strength gradually increases with the percentage of nanomaterials of ZnO and ZrO_2 (from 4% to 8%). This retains to the good properties of these two materials (ZnO and ZrO_2) leading to improving the tensile property of DGEBA.
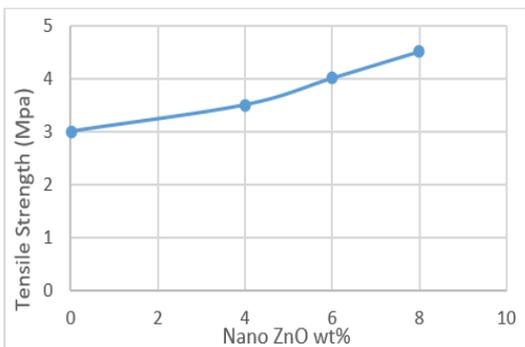
Figure 12. Tensile Strength of DGEBA with Different Percentages of Zinc Oxide
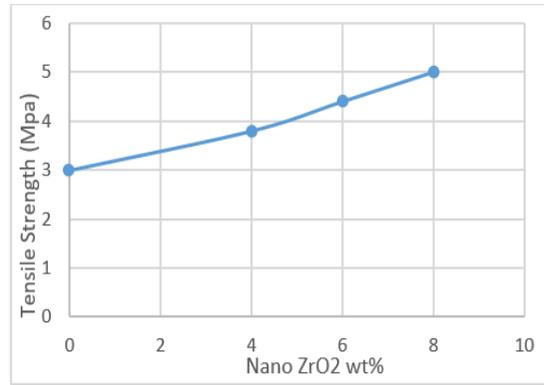
Figure 13. Tensile strength of DGEBA with different percentages of zirconium dioxide

3.2 Compressive test

Figures 14 and 15 shows results of the compressive strength of DGEBA with presence of nanomaterials of zinc oxide (ZnO) and zirconium dioxide (ZrO_2) respectively. This Figure shows that the compressive strength gradually increases with the percentage of nanomaterials of ZnO and ZrO_2 (from 4% to 8%). This retains to the same cause mentioned in the section (3.1): the ZnO and ZrO_2 have good properties and adding them into DGEBA improves its compressive property.
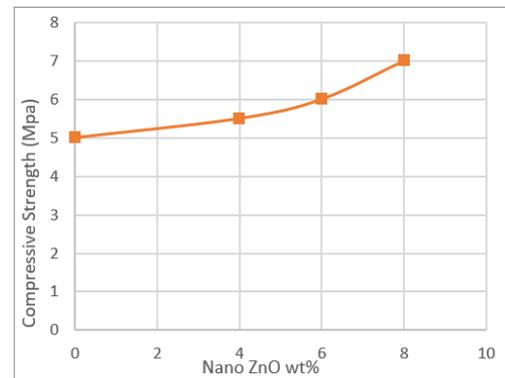
Figure 14. The compressive strength of DGEBA with different percentages of zinc oxide
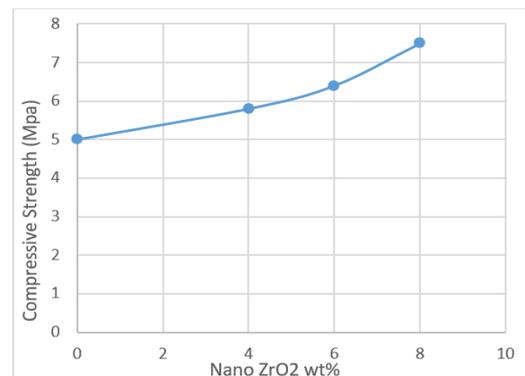
Figure 15. The compressive strength of DGEBA with different percentages of zirconium dioxide

To show the improvement ratio in the DGEBA properties after adding the (ZnO and ZrO_2), Figures 16 and 17 show results of these nanomaterials for the tensile and compressive

strengths respectively. As it is shown in these Figures, there is a priority for the zirconium dioxide where the higher value for both the DGEBA properties (the tensile and compressive) are achieved by using this nanomaterial (ZrO_2). Computationally, this nanomaterial improves these properties (the tensile and compressive) by 67% and 50% respectively compared to the pure epoxy. On the other side, the improvement ratio in these properties (the tensile and compressive) using the nanomaterial of ZnO cannot exceed 50% and 40% respectively. This is in the case of same nanomaterial percentage for both nanomaterials (ZnO and ZrO_2), and which is 8% by weight.
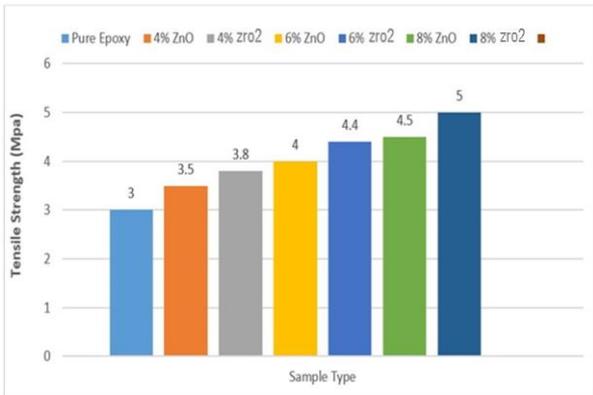
Figure 16. Comparison of DGEBA tensile strength results with different percentages of the zinc oxide and zirconium dioxide
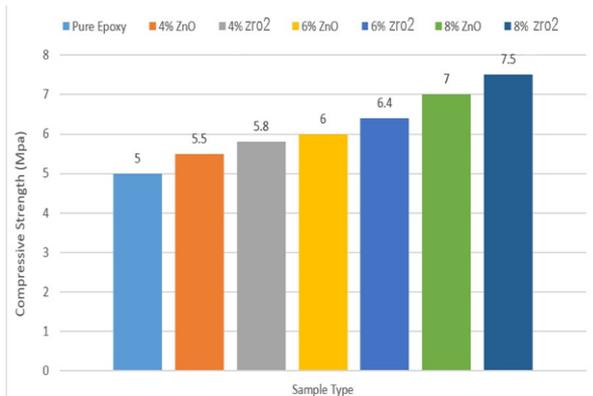
Figure 17. Comparison of DGEBA compressive strength results with different percentages of the zinc oxide and zirconium dioxide

3.3 SEM

Figure 18 offers a captivating peek into the dynamic interplay between ZrO_2, ZnO nanoparticles and the diglycidyl ether of bisphenol-A epoxy resin (DGEBA containing 8wt% of ZrO_2, ZnO nanoparticles). These nanoparticles exhibit a remarkable uniform distribution throughout the epoxy matrix, an accomplishment signifying their successful integration. A noteworthy transformation in the resin's surface structure is evident, an outcome that can be attributed to the nanoparticles' active role. The robust bond formed between the nanoparticles and the epoxy matrix likely contributes to an enhancement in the material's mechanical prowess. Fascinatingly, the SEM image hints at the nanoparticles possibly undertaking the role of nucleating agents, spurring epoxy crystallization and

potentially amplifying its thermal stability. By all indications, the nanoparticles seem to have played a part in ironing out surface imperfections, culminating in a more even-textured and condensed microstructure. It's prudent to consider that a more detailed quantitative analysis could unveil the full extent of nanoparticle dispersion and its consequent impact on the epoxy's mechanical and thermal attributes. These revelations hold utmost importance in tailoring composite design and bolstering overall performance across diverse applications.
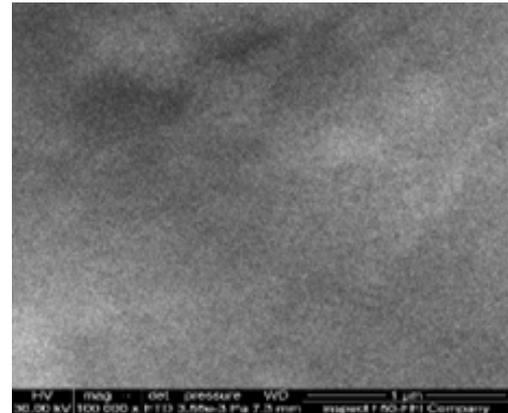
(a)
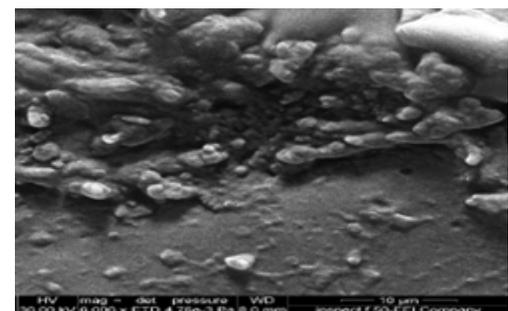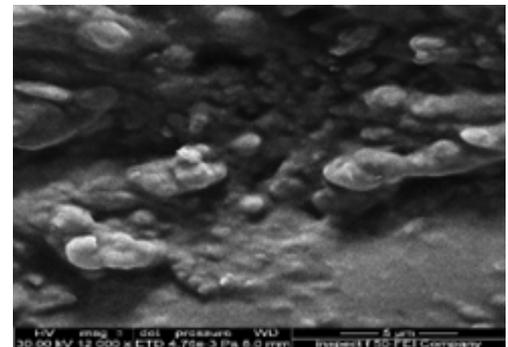
DGEBA+ZnO   DGEBA+ZrO2

(b)

Figure 18. SEM image after the addition of nanoparticles to epoxy

3.4 FTIR spectrum

Figure 19 gives us valuable insights into how ZrO_2, ZnO nanoparticles and diglycidyl ether of bisphenol-A epoxy resin (DGEBA resin with (8wt% ZrO_2, 8wt% ZnO) nanoparticles are interacting. FTIR analysis was performed in the range of 400 to 4000 cm^{-1}. The shifts in characteristic peaks strongly suggest that there might be a chemical interaction going on between the nanoparticles and the epoxy matrix. The emergence of new peaks or alterations in peak intensity

indicates that changes have occurred in the molecular structure. This suggests that successful mixing of the nanoparticles into the epoxy has taken place. Changes in functional groups crucial for epoxy curing, such as hydroxyl and epoxy groups, could be observed. These alterations may provide insights into the manner in which the linkage of epoxy molecules is influenced by the nanoparticles. Discrepancies in the vibration patterns of epoxy molecules are also being observed, shedding light on potential modifications in the arrangement of the epoxy facilitated by the nanoparticles.
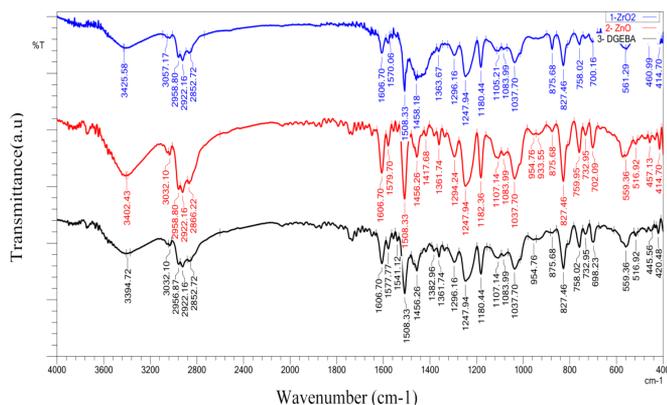
Figure 19. FTIR Spectrum of a. Epoxy Resin, b. Epoxy Resin with ZnO, c. Epoxy Resin with ZrO_2

4. CONCLUSION

The research reveals the significant potential of integrating nanomaterials like zinc oxide and zirconium dioxide to enhance the mechanical attributes, particularly tensile and compressive strengths, of the DGEBA resin. This augmentation in material performance not only demonstrates a direct correlation with the escalation in nanomaterial content but also underscores the ability to finely adjust material characteristics. Notably, optimal outcomes were achieved when employing a heightened content (8% wt) of both ZnO and ZrO_2, because the presence of nanomaterials at this ratio within the sample structure led to greater coherence between the parts of the composite, this is illustrated by SEM images for selected samples, promising novel directions for future composite formulation.

Furthermore, a comparative evaluation accentuates zirconium dioxide's exceptional efficacy in enhancing both tensile and compressive strengths, resulting in enhancements of approximately 67% and 50%, respectively. In contrast, the utilization of zinc oxide led to enhancements of about 50% and 40% for tensile and compressive strengths, respectively. These findings not only provide valuable insights for immediate applications but also lay the groundwork for subsequent research endeavors. The examination via scanning electron microscope illustrates that the introduction of ZrO_2, ZnO nanoparticles plays a pivotal role in bolstering epoxy integration, refining surface quality, promoting crystallization, and addressing imperfections. These attributes collectively contribute to the advancement of composite materials. Moreover, Fourier-transform infrared spectroscopy applied to the resin containing ZrO_2, ZnO nanoparticles showcases observable shifts and adjustments in peak patterns, indicating an efficacious interaction between nanoparticles and epoxy, resulting in conspicuous modifications to the overall structure.

Remarkably, the incorporation of ZnO nanoparticles into the epoxy resin yielded effects non akin to those observed with ZrO_2 nanoparticles in both the scanning electron microscope and Fourier-transform infrared spectroscopy tests. Prospective investigations may delve into the nuanced mechanisms underlying the superior influence of zirconium dioxide, potentially illuminating innovative approaches to engineer tailored nanocomposite systems for enhanced material performance. This study introduces novel insights, laying the foundation for broader avenues of exploration and applications.

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