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Mechanical, Thermal, and Photocatalytic Properties of TiO_2/ZnO Hybrid Composites Fabricated via Additive Manufacturing Method

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Abstract

This study explores the fabrication and characterization of TiO_2/ZnO hybrid nanocomposites using stereolithography (SLA), a cutting-edge additive manufacturing technique. Hybrid composites were prepared by incorporating 0.5 wt.% nano- TiO_2 and varying nano-ZnO concentrations (0.1 wt.%, 0.3 wt.%, and 0.5 wt.%) into an epoxy/acrylate-based resin. All composite samples were designed in SolidWorks, printed with an LCD-based SLA printer, and UV-cured for structural stabilization. A series of analyses were conducted to evaluate their morphological, mechanical, thermal, and photocatalytic properties. SEM analysis showed uniform particle dispersion at lower ZnO concentrations, while higher additions caused agglomeration. XRD confirmed the anatase phase of TiO_2 and the wurtzite structure of ZnO, ensuring their structural stability. TGA results showed improved thermal resistance for the hybrid composites compared to the pure resin, highlighting the synergistic effects of TiO_2 and ZnO in mitigating thermal degradation. Mechanical tests showed significant improvements in flexural strength and hardness, with the TZ5 composite (0.5% w/w TiO_2 and ZnO) showing the best performance due to optimum filler distribution. Photocatalytic tests showed superior Methylene Blue degradation for the hybrid composites, with TZ5 achieving the highest efficiency (80.9%) due to the synergistic effects of TiO_2 and ZnO. These results highlight the potential of SLA-manufactured composites for environmental and energy applications.

Keywords: Additive manufacturing, Stereolithography (SLA), TiO_2/ZnO hybrid composites, Material characterization.

Eklemeli İmalat Yöntemiyle Üretilen TiO_2/ZnO Hibrit Kompozitlerin Mekanik, Termal ve Fotokatalitik Özellikleri

Öz

Bu çalışma, son teknoloji bir eklemeli imalat tekniği olan stereolitografi (SLA) kullanılarak TiO_2/ZnO hibrit nanokompozitlerin üretimini ve karakterizasyonunu araştırmaktadır. Hibrit kompozitler, epoksi/akrilat bazlı bir reçineye ağırlıkça %0,5 nano-TiO_2 ve değişen nano-ZnO konsantrasyonları (ağırlıkça %0,1, ağırlıkça %0,3 ve ağırlıkça %0,5) eklenerek hazırlanmıştır. Tüm kompozit numuneler SolidWorks'te tasarlanmış, LCD tabanlı bir SLA yazıcı ile basılmış ve yapısal stabilizasyon için UV ile sertleştirilmiştir. Morfolojik, mekanik, termal ve fotokatalitik özelliklerini değerlendirmek için bir dizi analiz yapılmıştır. SEM analizi, düşük ZnO konsantrasyonlarında homojen parçacık dağılımı gösterirken, daha yüksek katkı maddeleri topaklanmaya neden olmuştur. XRD, TiO_2'nin anataz fazını ve ZnO'nun wurtzite yapısını doğrulayarak yapısal kararlılıklarını sağlamıştır. TGA sonuçları, hibrit kompozitler için saf reçineye kıyasla daha iyi termal direnç göstererek TiO_2 ve ZnO'nun termal bozulmayı azaltmadaki sinerjik etkilerini vurgulamıştır. Mekanik testler, optimum dolgu maddesi dağılımı nedeniyle en iyi performansı gösteren TZ5 kompoziti (%0,5 w/w TiO_2 ve ZnO) ile eğilme mukavemeti ve sertlikte önemli gelişmeler göstermiştir. Fotokatalitik testler, TiO_2 ve ZnO'nun sinerjik etkileri nedeniyle TZ5'in en yüksek verime (%80,9) ulaştığı hibrit kompozitler için üstün Metilen Mavisi degradasyonu göstermiştir. Bu sonuçlar, çevre ve enerji uygulamaları için SLA ile üretilmiş bu kompozitlerin potansiyelini vurgulamaktadır.

Anahtar Kelimeler: Eklemeli imalat, Stereolitografi (SLA), TiO_2/ZnO hibrit kompozitler, Malzeme karakterizasyonu.

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1. Introduction

Additive manufacturing, represents a transformative approach in modern manufacturing, enabling the creation of complex geometries and bespoke designs through layer-by-layer material deposition. Since its inception in the 1980s, this technology has undergone significant evolution, with various methods, including Stereolithography (SLA), Fused Deposition Modelling (FDM), and Selective Laser Sintering (SLS), becoming widely adopted for both prototyping and final product manufacturing (Xiao and Kan 2022; Güler et al. 2024). SLA is especially noteworthy for its capacity to produce high-resolution components with an excellent surface finish, rendering it a preferred option for applications requiring intricate details and smooth surfaces (Huang et al., 2020).

Stereolithography (SLA) employs a photopolymerization process in which liquid resin is cured layer-by-layer using ultraviolet (UV) light. This method enables the precise fabrication of complex structures by selectively curing cross-sectional layers of the resin in accordance with a digital model (Husna et al., 2024).

Manapat et al. (2017) demonstrated the successful 3D printing of polymer nanocomposites via SLA, thereby illustrating the method's versatility in producing functional materials with tailored properties. For example, this study demonstrated the successful 3D printing of polymer nanocomposites via SLA, thereby illustrating the method's versatility in producing functional materials with tailored properties. This technology offers unparalleled flexibility in design, material utilization, and cost-effectiveness compared to traditional manufacturing methods. Among the many material systems investigated for Additive manufacturing, composites have stood out for their exceptional mechanical, thermal and functional properties (Ikram et al., 2022).

Studies conducted SLA method in literature are as follows. For example, Zandinejad et al. (2022) examined the flexural strength and modulus of SLA-manufactured zirconia with varying porosities, demonstrating how porosity affects mechanical properties and the feasibility of bio-inspired dental restorations. Similarly, Arora et al. (2023) investigated the impact of building orientation on the mechanical properties of ceramic structures produced via SLA, with a particular focus on shrinkage compensation and the resulting mechanical performance of the final products. The incorporation of ceramic additives in nano-additive SLA methods has demonstrated significant improvements in material characteristics. Tian et al. (2020) examined the shrinkage, phase composition, and mechanical properties of β-SiAlON ceramics fabricated via stereolithography, demonstrating that the SLA technique efficiently generates intricate geometries while preserving favorable mechanical properties.

This study aims to fabricate and comprehensively analyse TiO_2/ZnO hybrid nanocomposites using stereolithography (SLA) to explore their mechanical, thermal, and photocatalytic properties. The integration of nano-TiO_2 and ZnO at precise ratios allows for the investigation of the synergistic effects of these materials on performance metrics, thereby offering novel insights into composite optimisation. The innovation resides in the utilisation of SLA for hybrid composite fabrication, which connects advanced manufacturing with environmental and energy applications.

2. Material and Methods

Commercial TiO_2 and ZnO nanopowders were purchased from Nanokar company. The TiO_2 and ZnO particles were dried in an electrical drying oven (Binder, ED53) at 80°C for 12 hours before use. A mixture of 0.5 wt.% of nano TiO_2 powder and varying amounts (0.1 wt.%, 0.3 wt.%, and 0.5 wt.%) of nano ZnO powder were prepared in a commercial epoxy/acrylate-based resin. The resulting mixtures were stirred at room temperature for approximately 1 hour and then dispersed using a sonicator.

Table 1. Sample identification based on the composition of TiO_2 and ZnO.

Sample Name	***Content(wt.%)***		
	Matrix	***ZnO***	***TiO_2***
Pure	100	-	-
T	99.5	-	0.5
Z	99.9	0.1	-
TZ1	99.4	0.1	0.5
TZ3	99.2	0.3	0.5
TZ5	99	0.5	0.5

SolidWorks and HALOT BOX software were utilized to design and print the geometries for production. 3D CAD models were produced for additive manufacturing using an LCD-based SLA printer (Creality Halot-One). Samples were printed with a layer thickness of 50 µm and a 4-second exposure time per layer. Post-processing involved IPA washing for 15 minutes and 60 minutes of curing. Structural analyses were performed using X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) to confirm the anatase phase of TiO_2 and the wurtzite structure of ZnO. Flexural modulus and hardness were evaluated using ASTM D790 and Shore D methods, providing average values from three measurements per sample.

The photocatalytic activity of 3D-printed samples was assessed through the degradation of methylene blue (MB) dye under UV-A and UV-B light sources. Samples were pre-conditioned in darkness for 30 minutes to achieve adsorption/desorption equilibrium, then exposed to UV light for 5 hours. UV/Vis spectrophotometry monitored MB degradation at 664 nm, with pure MB solutions used as controls.

3. Results and Discussion

In Figure 1. SEM analysis of the pure, TiO_2-added (T) and ZnO-added (Z) samples shows distinct variations in surface morphology and microstructure. The pure resin (a) shows a relatively smooth and homogeneous surface, as expected due to the absence of fillers. However, the TiO_2-added sample (b) shows scattered micro-scale particles, indicating the presence of TiO_2 which contributes to an increase in surface roughness. In contrast, the ZnO- based sample (c) shows larger agglomerates, suggesting that ZnO has a higher tendency for particle agglomeration.

Figure 2. depicts SEM images of the hybrid composites (TZ1, TZ3, TZ5) demonstrate that the dopants are distributed more well in the hybrid structures than in the composites doped with ZnO and TiO_2. For instance, sample TZ1 displays a relatively uniform matrix with homogeneously distributed particles, whereas TZ3 and TZ5 illustrate that the dopants are clustered and agglomerated, particularly at higher ZnO doping ratios. This behaviour can be attributed to the strong interparticle interactions of ZnO, as evidenced in analogous studies (Hayeemasae et al., 2017).

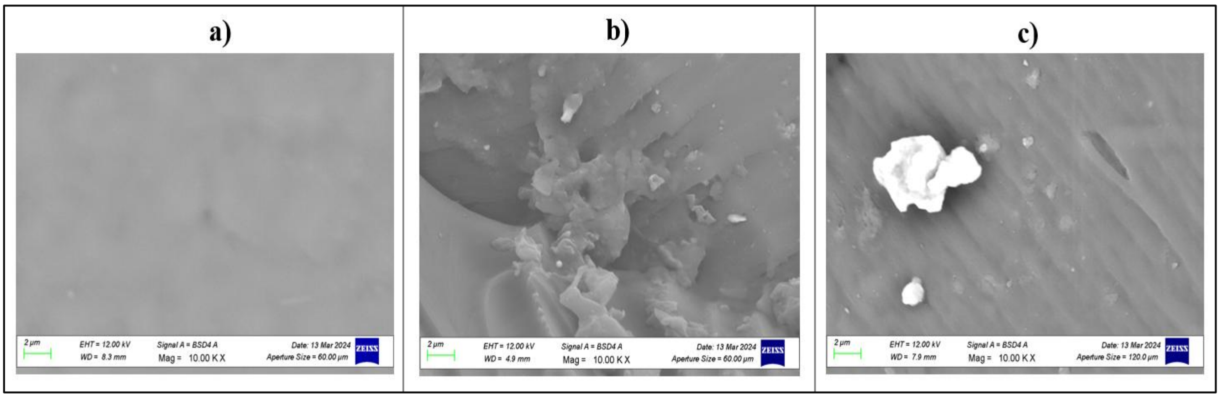

Figure 1. SEM analysis of the produced a) Pure, b) TiO_2-added, c) ZnO-added.

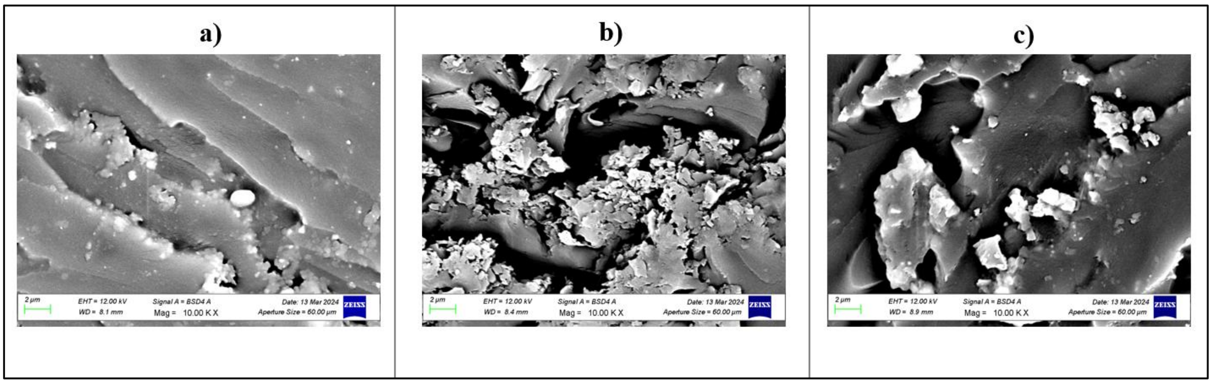

Figure 2. SEM analysis of the produced TiO_2/ZnO hybrid composites (a) TZ1, b)TZ3, c)TZ5).

The phase composition of the supplied TiO_2 and ZnO nanopowders was determined using XRD and the results are shown in Figure 3 and Figure 4. According to XRD analysis, the pattern in Figure 3 shows that the powder corresponds to TiO_2 anatase phase structure (JCPDS no 004-0477) with sharp peaks.

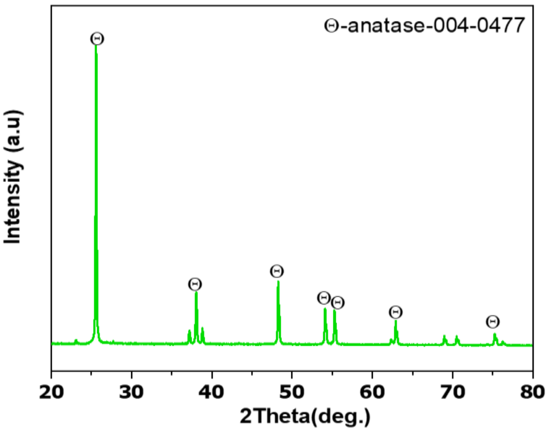

Figure 3. Phase analysis results of the TiO_2 additive used in the composite materials.

Figure 4 shows that the sharp peaks in the ZnO powder correspond to the ZnO phase structure (JCPDS no 01-089-7102).

The thermogravimetric analysis (TGA) results, as illustrated in Figure 5 depict the weight loss behavior of samples T, Z, TZ1, TZ3, and TZ5 as a function of temperature. All samples display considerable thermal degradation between approximately 300°C and 490°C, with the extent of weight loss varying in accordance with the composition. The nano-ZnO-doped sample (Z) exhibits a more pronounced weight loss in comparison to the hybrid samples (TZ1, TZ3, and TZ5). The incorporation of ZnO in varying proportions enhances the thermal stability of the composites, as evidenced by the diminished weight loss observed in the TZ samples. This behavior aligns with findings in similar studies, which report that ZnO and TiO_2 additives improve thermal stability in composite systems by mitigating oxidative degradation and enhancing structural resistance (Majeed and Aleabi, 2022). The TZ5 specimen, characterized by the maximal concentration of additives, exhibits the most consistent thermal performance, thereby suggesting that it possesses enhanced structural integrity when exposed to thermal stress.

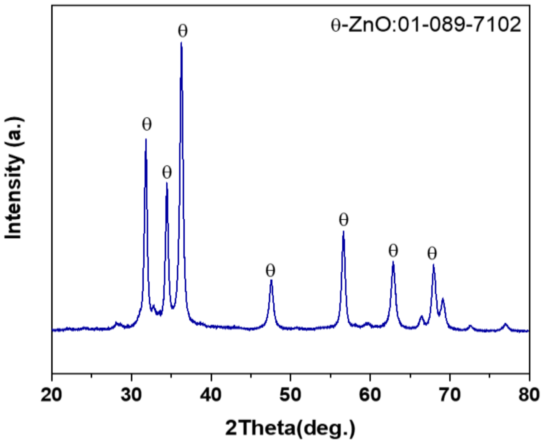

Figure 4. Phase analysis results of the ZnO additive used in the composite materials.

Figure 6 presents the Shore D hardness analysis of TiO_2/ZnO-enhanced epoxy-based hybrid composites, based on the average of five measurements per sample. The results demonstrate a significant improvement in hardness with the inclusion of additives. Specifically, The TiO_2- and ZnO-free sample (pure) exhibited a hardness of approximately 77 Shore D, which increased to 79.6 Shore D with the addition of TiO_2, while the ZnO-added samples achieved a hardness of 79.8 Shore D. A gradual and significant improvement in hardness values was observed in the TZ1, TZ3 and TZ5 hybrid composites. This improvement can be attributed to the combination of metal oxide nanoparticles, including TiO_2 and ZnO, within the composite matrix. The TZ5 sample exhibited the highest hardness value, which clearly demonstrates the impact of the synergistic effect of metal oxides in enhancing the mechanical strength of the material. These findings are consistent with similar studies in the literature (Majeed and Aleabi, 2022).

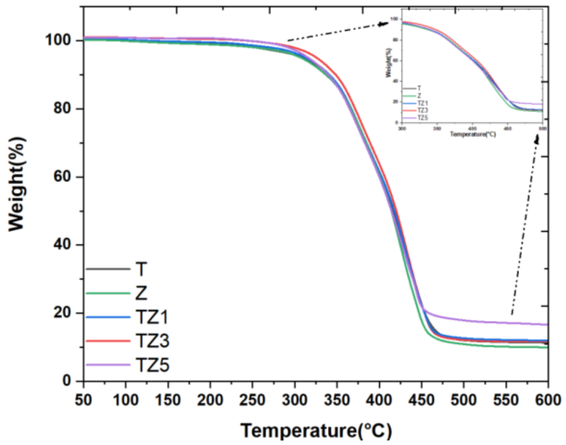

Figure 5. TGA analysis of the produced all samples.

Figure 7. shows the modulus of elasticity (E) values obtained from flexure tests. The pure polymer has the highest modulus (1287.58 MPa), indicating a homogeneous and continuous polymer chain structure. However, the incorporation of TiO_2(T, 1100.42 MPa) and ZnO (Z, 937.69 MPa) nanoparticles leads to a reduction in modulus. This reduction can be attributed to the disruption of the microstructure of the polymer matrix by the nanoparticles, which prevents efficient stress transfer and interrupts the continuity of the polymer network (Shubbar et al., 2023). This results from the nanoparticles disrupting the microstructure of the polymer matrix, inhibiting effective stress transfer.

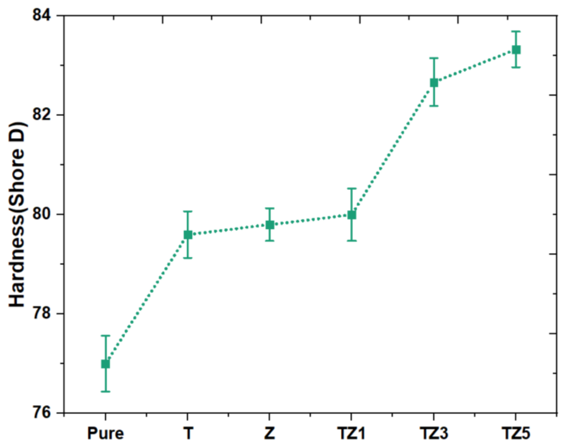

Figure 6. Hardness analysis of the produced all sample.

In the hybrid composites (TZ1, TZ3, TZ5), the combination of TiO_2 and ZnO at certain ratios shows a synergistic effect. Specifically, TZ3 (1071.25 MPa) shows improved modulus values, suggesting effective dispersion of the fillers and their positive contribution to the load bearing capacity. However, in TZ5 the higher concentration of ZnO leads to agglomeration resulting in a decrease in modulus (970.33 MPa). This suggests that excessive ZnO content has a negative effect on mechanical properties by reducing matrix integrity. These results are consistent with previous studies that have emphasised the critical influence of filler distribution and loading ratios on mechanical performance.

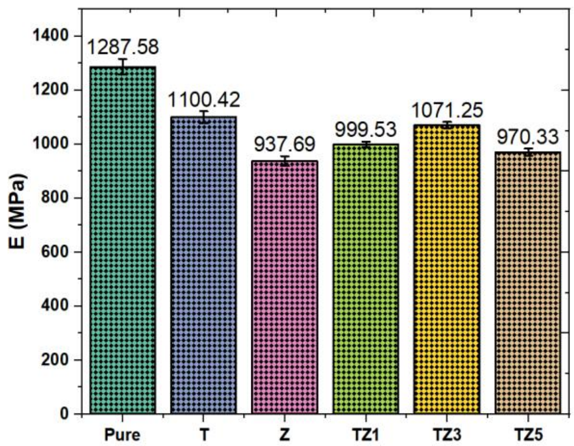

Figure 7. Elastic modules as a result of bending test of all produced samples.

As shown in Figure 8., the elongation at break results highlights the ductility behavior of the pure polymer and its TiO_2, ZnO and hybrid composites. The brittle structure of the pure epoxy material shows a limited elongation of 6 mm. When added in the T sample, ductility improves significantly and reaches a value of about 9 mm due to the role of TiO_2 in enhancing energy absorption during deformation. However, in samples with only ZnO addition, the elongation value decreases to 6 mm, probably due to agglomeration and stress concentration points.

Hybrid composites (TZ1, TZ3, TZ5) significantly improve elongation, especially in TZ1, reaching 10 mm. Here, an optimum filler distribution indicates that a synergistic interaction between TiO_2 and ZnO was observed to improve the mechanical properties. The slight decrease in elongation for TZ3 and TZ5 suggests that higher ZnO content leads to agglomeration. This behavior is in line with previous studies that emphasize the effect of filler distribution and agglomeration on mechanical properties (Hayeemasae et al., 2017).

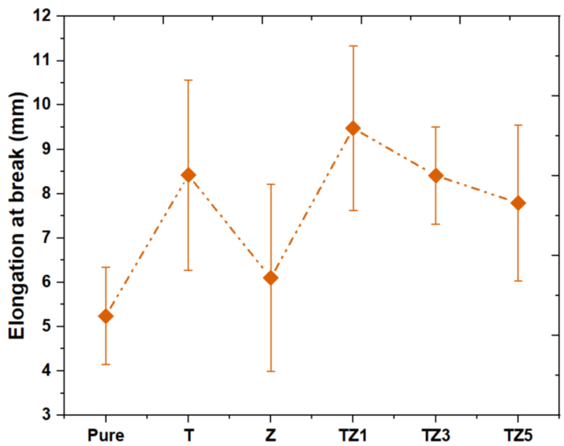

Figure 8. Elongation at break analysis of the produced TiO_2/ZnO nano-added hybrid composites.

Figure 9 shows the detailed increase in the performance of TiO_2/ZnO hybrid composites over time during the photocatalytic degradation of methylene blue (MB) solution. In the photocatalytic process, samples TZ1, TZ3, and TZ5 showed obvious superiority over other samples by rapidly increasing their degradation rates. In particular, sample TZ5 reached the highest degradation rate within 5 h. This increase can be explained by the high photocatalytic activity of TiO_2 combined with the wide band gap and strong oxidation ability of ZnO. The increasing ratio of ZnO (TZ5) provided a larger surface area, increased light absorption and increased the formation of reactive oxygen species. TiO_2/ZnO composites demonstrate superior performance in methylene blue degradation under UV light due to the complementary characteristics of the two oxides, which optimize electron-hole pair separation (Nasir et al., 2017).

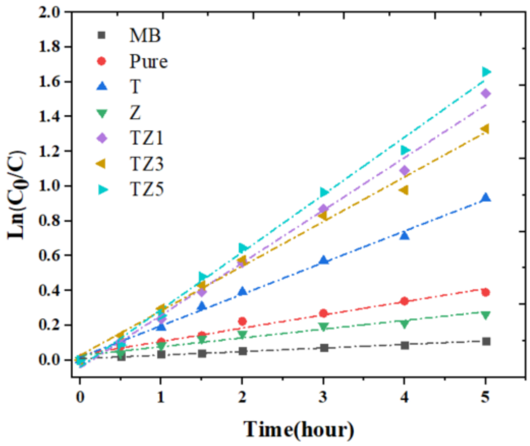

Figure 9. All samples kinetics of photocatalytic degradation.

Table 2 presents the reaction rate constants (K) and R^2 values, which quantitatively evaluate the photocatalytic performance of the samples. Methylene blue (MB) degradation without catalysts shows the lowest reaction rate (K = 0.0205 h^{-1}). The modest improvement in degradation rate of the pure resin (K = 0.0762 h^{-1}) can be attributed to its ability to absorb UV light, facilitating limited photodegradation. This is consistent with the findings of Iqbal et al. (2020) who noted that certain materials can enhance the photodegradation of dyes by improving light absorption and promoting the generation of reactive species.

T sample demonstrates a significantly higher reaction rate (K = 0.1814 h^{-1}), attributed to its superior photocatalytic efficiency under UV exposure. Conversely, Z sample (Z, K = 0.0504 h-

[1]) shows lower performance due to faster recombination of electron-hole pairs, consistent with previous findings on ZnO photocatalysts(Nasir et al., 2017).

Hybrid samples (TZ1, TZ3, TZ5) show synergistic effects between TiO_2 and ZnO, with reaction rates progressively increasing with increasing ZnO content, peaking at TZ5 (K = 0.3306 h^{-1}). This improvement is due to enhanced charge separation and light absorption in the hybrid structure, as confirmed by studies on ZnO-TiO_2 systems(Haghighatzadeh et al., 2019). The high R^2 values (x>0.94) confirm the reliability of the kinetic model and show consistent performance across all samples.

Table 2. The reaction rates and R^2 values of all samples have been analyzed.

Sample Name	*K(h^{-1})*	*R^2*
MB	0.0205	0.9784
Pure	0.0762	0.9695
T	0.1814	0.9963
Z	0.0504	0.9419
TZ1	0.3022	0.9922
TZ3	0.2566	0.9920
TZ5	0.3306	0.9934

In Figure 10, illustrates the photocatalytic degradation of methylene blue (MB) over time, expressed as the normalized concentration ratio (C_0/C), under UV irradiation for pure,T,Z,TZ1, TZ3, and TZ5 samples. The degradation curve of MB without catalysts shows the slowest decline, indicating minimal photolysis in the absence of catalytic activity. The pure resin exhibits moderate photocatalytic activity, as evidenced by its gradual decrease in MB concentration, likely due to limited UV light absorption by the polymer matrix. This aligns with the work of Che Ramli et al. (2014), who noted that the photocatalytic performance of materials can be influenced by their ability to absorb UV light, which contributes to the degradation process, albeit at a lower efficiency compared to dedicated photocatalysts.

However, the TiO_2-added sample (T) demonstrates a significantly steeper decline in MB concentration, attributed to TiO_2's high photocatalytic efficiency under UV light. TiO_2 is well-known for its ability to generate reactive oxygen species (ROS) effectively, which are crucial for the degradation of organic dyes like MB. Joo et al. (2010) confirmed that the photoinduced holes in TiO_2 oxidize methylene blue molecules, leading to their decomposition into simpler, less harmful compounds.

On the other hand, the ZnO-added sample (Z) exhibits slower degradation rates compared to TiO_2, likely due to higher recombination rates of photogenerated electron-hole pairs, which limits its overall photocatalytic efficiency. Research by Rashad et al. (2016) has shown that although ZnO can act as a photocatalyst, its effectiveness is often hindered by rapid electron-hole recombination, which reduces the availability of reactive species required for dye degradation. This limitation is further supported by the findings of Farhan et al. (2018), who noted that the photocatalytic activity of ZnO is generally lower than that of TiO_2 due to similar recombination issues.

The hybrid composites (TZ1, TZ3, TZ5) demonstrate enhanced degradation performance compared to individual TiO_2 or ZnO samples, with TZ5 achieving the most rapid reduction in methylene blue (MB) concentration. This improvement is attributed to the synergistic effects between TiO_2 and ZnO, where ZnO extends the light absorption range and facilitates electron transfer, thereby reducing charge recombination. The progressive increase in photocatalytic activity from TZ1 to TZ5 correlates with the higher ZnO content, optimizing the interaction between the two oxides. Similar findings in previous studies highlight that TiO_2/ZnO composites exhibit superior photocatalytic activity due to their complementary properties, enabling efficient charge separation and enhanced degradation rates. For example, Dhiman et al. (2018) demonstrated that ZnO-based semiconductor composites significantly improved the degradation of MB, confirming the potential of hybrid catalysts for environmental remediation applications. Furthermore, Andrade Neto et al. (2018) reported that incorporating of ZnO into TiO_2 matrices enhances the photocatalytic properties, leading to more effective degradation of organic pollutants.

In conclusion, the synergistic effects observed in the TiO_2/ZnO hybrid composites highlight their potential as effective photocatalysts for environmental applications, particularly in the degradation of hazardous dyes such as methylene blue.

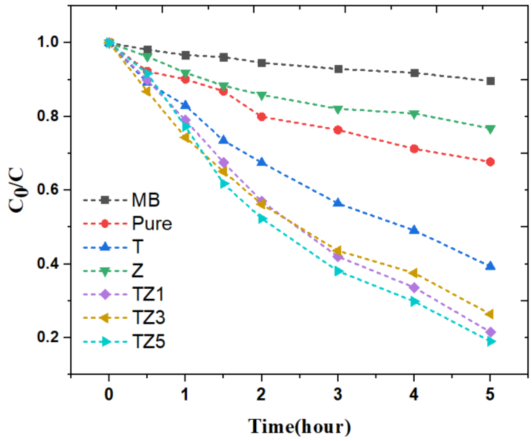

Figure 10. Photocatalytic removal curves for all samples.

In Figure 11. illustrates the photodegradation efficiency of methylene blue (MB) under UV light for various samples. MB without any catalyst demonstrates the lowest degradation efficiency (10.3%), confirming minimal natural photolysis. Sample ZnO-added composite sample (23.2%) has a lower photocatalytic activity than TiO_2-added composite sample (60.6%). This is mainly due to the higher electron-hole recombination rates of ZnO, which limits the formation of reactive oxygen species and reduces the photocatalytic activity. In contrast, TiO_2 in sample T can separate electron-hole pairs more effectively and provides higher photocatalytic activity under UV light (Nasir et al., 2017).

The hybrid composites (TZ1, TZ3, TZ5) exhibit significantly have been enhanced photodegradation efficiencies, peaking at TZ5 (80.9%), due to the synergistic interaction between TiO_2 and ZnO. These results are consistent with previous research showing that TiO_2/ZnO hybrids effectively enhance photocatalytic performance through complementary mechanisms (Nasir et al., 2017; Haghighatzadeh et al., 2019). The superior performance of TZ5 underscores the importance of optimising filler ratios in hybrid photocatalysts for environmental remediation applications.

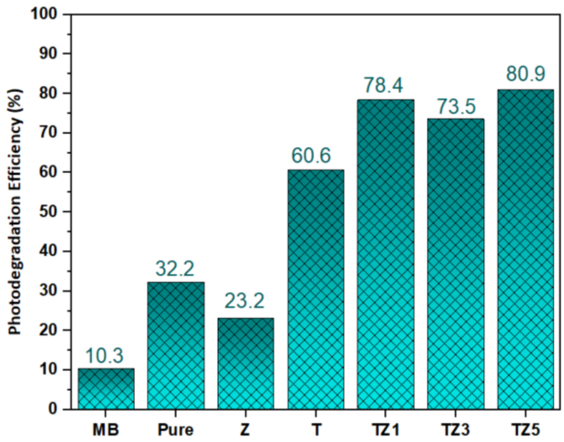

Figure 11. Photodegradation efficiency of methylene blue (MB) under UV light using different samples, including pure resin, ZnO (Z), TiO_2 (T), and hybrid composites (TZ1, TZ3, TZ5).

4. Conclusions

In this study, TiO_2/ZnO hybrid nanocomposites were successfully fabricated and analyzed using additive manufacturing techniques. The main findings and recommendations are as follows:

The incorporation of TiO_2 and ZnO improves both the photocatalytic and mechanical properties of the composites. TiO_2 improves the photocatalytic activity under UV light, while ZnO provides additional synergistic effects, improving light absorption and charge separation efficiency.

TiO_2/ZnO hybrid nanocomposites fabricated via additive manufacturing exhibit outstanding mechanical, thermal, and photocatalytic properties. These have been attributes that establish them as highly promising materials for advanced and special applications.

These composites demonstrate significant potential in environmental remediation, energy-efficient systems, and other sustainable technologies requiring high performance and durability.

Author contribution

Güler, S contributed to all sections of the article.

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Conflict of Interest Statement

The author declare that they have no conflict of interest.

Ethical Standards:

No Ethics Committee Approval is required for this study.

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