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ORIGINAL ARTICLE

Investigation on mechanical behaviour of Al–Mg-Si alloy hybridized with calcined eggshell and TiO_2 particulates

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Abstract

The development of hybrid agro-metallic alloy and its composites has increased in the last few years to overcome the shortcomings of monolithic alloys. Using hard ceramic reinforcements would enhance the strength of the alloys and its composites during component building. One such ceramic reinforcement is the Titania (TiO_2) powder, which possesses more strength than other ceramics materials, but the cost is a little higher. To overcome this, eco-friendly, calcined eggshell (CES) particulates are added to TiO_2 reinforcement to enhance the strength of the hybrid composite at a reduced cost. The main novelty of the present study is the employment of CES and TiO_2 particulates in the Al 6061 matrix during the development of hybrid Al 6061 composites. This increases the strength of the fabricated composites at a reduced cost and results in the development of eco-friendly agro-metallic composites. Samples were produced individually in groups with varying proportions of CES at 3, 6, 9 and 12 wt% and combined with fixed proportions of TiO_2 at 3, 6, 9 and 12 wt% individually with groups such as A (3 wt% of $TiO_2 + 3$, 6, 9 and 12 wt% of CES), B, C and C and D, respectively. Microstructural characterization through FESEM and phase identification through XRD analysis are conducted to justify the uniform dispersion of reinforcements in the matrix. Developed samples were subjected to tensile, flexural and hardness tests, and the results proved that the mechanical properties of composites were enhanced when combining 3, 6, 9 and 12 wt% CES with 3 and 6 wt% of TiO_2 compared with unreinforced Al 6061. The enhancement is linked to the uniform dispersion of the particles and good interaction between the particles. However, the 3, 6, 9 and 12 wt% CES with 9 and 12 wt% of TiO_2 yielded inferior strength performance relative to the reference mix due to particle clustering and agglomeration formation. This acts as a yielding point for stress concentration. Therefore, it was concluded that a combination of 3, 6, 9 and 12 wt% CES with TiO_2 should not exceed 6 wt% of TiO_2.

Keywords Agro-metallic · Calcined eggshell · Hybrid composite · Microstructure · Yield stress · Stress concentration

1 Introduction

Aluminium alloys have been noted to exhibit high-performance properties such as suitable mechanical properties at room temperature, high ductility, high casting tolerance, excellent castability and high strength [1, 2]. It has found a wide range of applications in aerospace, automobile, military, games-recreational sports equipment, chemical industries, and transportation industries, where these properties are essential [3]. The search for a lightweight, fuel-efficient, cost-effective transportation system that was absent in the early automobile produced led to the hunt for better materials to fulfil this yearning. The discovery of aluminium alloys for transportation applications was considered eco-friendly, reduced greenhouse gas emissions, fuel consumption efficiency, and lightweight and cost-effective. Moreover,

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aluminium and its alloy possess excellent corrosion resistance and improved ductility and are readily available [4, 5]. Amongst other light metals, pure aluminium is characterized by good castability, sound mechanical and chemical properties, and low processing cost [6, 7]. Aluminium has a ductile fracture property at all temperatures; this property changes when exposed to very low temperatures [8, 9].

Engineering practice allows incorporating other elements to boost further strength exhibited by pure aluminium at an elevated temperature, as long as inherent properties are improved. Nowadays, aluminium alloy composites are developed for better engineering performance of the alloy. The composites are often produced by incorporating particulate or whisker-type reinforcement to enhance the engineering properties further. Aluminium metal matrix composites (MMCs) combine aluminium matrix and reinforcement to achieve improved characteristics such as high strength, excellent thermal conductivity, abrasion resistance, creep resistance, enhanced ductility and toughness, and good corrosion resistance [10, 11]. The matrix is the based material in which the reinforcement is embedded, while reinforcement is the material such as particles, flakes, fibre and whiskers embedded in the matrix [12, 13].

Ceramics particle reinforcement (fibre, whisker, particle) [14, 15] is conventionally used in the development of aluminium-based composite for its improved properties like high strength, better elastic modulus, excellent mechanical and chemical properties, and relatively low processing cost [16]. Titanium dioxide (TiO_2) has been one of the major types of ceramic reinforcement due to its ability to yield good properties. Applying TiO_2 particles on ZA22 + TiO_2 MMCs successfully refined the inter-dendritic structure alloy, increasing UTS and hardness [17]. Seah et al. [18] noted that adding TiO_2 to the ZA27 alloy matrix significantly improved mechanical factors such as UTS, yield strength and hardness. The influence of residual thermal stresses developed due to intrinsic behaviour between the constituents of the composites and constrained plastic flow in the soft alloy matrix. The presence of hard and brittle particle reinforcement (TiO_2) resulted in improved strength. The hard TiO_2 particle serves as a barrier to dislocation movement. Ravindra et al. [19] reported that when the volume ratio of TiO_2 increases, the inter-particulate distance between the hard TiO_2 particles in an alloy matrix decreases, resulting in dislocation pileup and boosting the alloy matrix's strength. This study's adopted material design strategy uses the selected reinforcement to meet the composite's strengthening and toughening needs and cheap production costs. In contrast, the Al-6061 matrix meets the high elastic modulus capacity required.

On account of the reviewed literature, it was concluded that TiO_2 is an excellent reinforcing agent in Al matrix. However, the cost implications have led to the research for alternative or supplement particulate for the same purpose. Recently, studies have gone into the reuse and recycling of agro-based products in metal composite development. Calcined products of these agro-by-products have made a lot of impact in this area. Some of these calcined agro-based by-products are rice husk ash [20, 21], snail shell ash [22, 23], coconut shell ash [24, 25] and eggshell ash [26, 27], amongst others. These calcined products are cheap reinforcements in the matrix, yielding better quality. Few studies have combined the products with TiO_2 to supplement Al 6061. This study was conceived to develop a hybrid aluminium composite by combining Al 6061 with TiO_2 particulate and calcined eggshell (CES). The prime novelty of the present work is the use of CES particulates in the base aluminium alloy along with the TiO_2 particulates. Adding TiO_2 particles alone would be economically not feasible due to its increased cost. To overcome this, adding CES particles is highly recommended to obtain a high-strength hybrid composite at a reduced cost. CES being an eco-friendly reinforcement, the fabricated hybrid composite, would be an eco-friendly agro-metallic hybrid composite. The selected reinforcements were varied to observe the effect of reinforcements, and the variations in the mechanical properties and microstructural examination are studied in the present research article.

2 Materials and methods

2.1 Material selection

Al 6061 ingot was procured from an aluminium smelting company. 97.6% pure grade of TiO_2 of 50 μm average particle size [28] and CES of average particle size 35 μm were utilized. The eggshell was calcined at calcination temperatures of 1000 °C and when the calcium carbonate was burned entirely in the open air into calcium oxide and carbon dioxide. The chemical reaction involved in the calcination process is given in Eq. 1.

$$CaCO_3 \xrightarrow{Calcination\ at\ 1000^{\circ}C} CaO + CO_2 \tag{1}$$

This calcined eggshell was used as reinforcement blended with TiO_2 particulates. The process steps involved in eggshell powder preparation are given in Fig. 1. The elemental composition of the CES particles is shown in Table 1.

2.2 Preparation of composite materials

In the present investigation, the stir casting route is utilized to develop the Al 6061 alloy/TiO_2/CES composite and the chemical composition of base matrix Al 6061 is presented in Table 2. TiO_2 and CES were introduced as reinforcing materials in particulate form with high elastic modulus and average

Fig. 1 Process steps involved in egg shell powder preparation

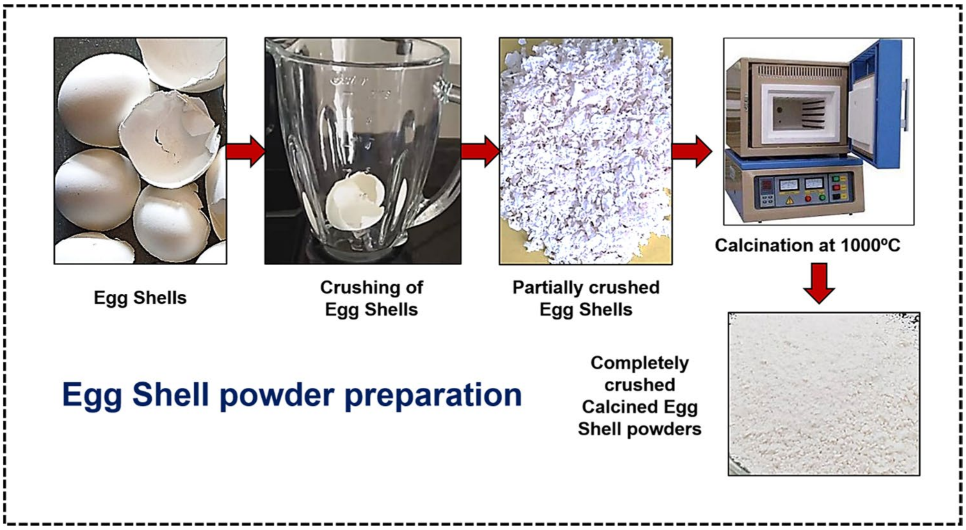

Table 1 Elemental composition of the CES particles

Element	C	Na_2O	MgO	P_2O_5	SO_3	K_2O	CaO	Fe_2O_3	SrO
Wt%	22.3416	0.2056	0.8694	0.5364	0.3952	0.0653	75.5184	0.0253	0.0428

Table 2 Elemental composition of Al 6061 alloy

Element	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Al
Wt%	0.54	0.22	0.33	0.09	0.90	0.08	0.05	0.12	Balance

particle sizes of 50 µm and 35 µm, respectively. TiO_2/CES particles were weighed, measured in varying steps of 4% between 3 and 12%, taken in a crucible furnace, and heated at a rate of 22.5 °C/min up to 750 °C. To remove moisture, reduce potential temperature gradients and increase wettability, TiO_2 particles were warmed at 500 °C and then injected into the molten alloy through a separate attachment at a rate of 10 g/min with a steady mechanical stirring of 574.2 rpm. An inert gas (Argon gas) atmosphere is maintained during the entire stir-casting process to prevent aluminium from oxidation and to increase the wettability between the matrix and reinforcements; magnesium are added to the matrix. To achieve uniform dispersion of the reinforcing element in the matrix alloy, stirring molten composite material was continued for 5 min and poured into the preheated mould (400 °C) of dimensions 100 mm in diameter and 175 mm in diameter length. The same procedure was adopted to cast the base matrix material and is labelled as a reference mix. The experimental setup used for the fabrication of composite material is shown in Fig. 2.

2.3 Mechanical characterization

2.3.1 *Micro-hardness analysis Al 6061/TiO_2/CES hybrid composites*

The hardness values of the Al 6061 alloy and composites were evaluated using a Vickers hardness tester. The 40-mm length and 15-mm thickness samples were machined with a polished plane parallel surface and subjected to 1 kN load for 15 s. The indentations were repeated four times to ensure consistency and reliability. The samples were put through its paces using the ASTM E92-17 standard [29].

2.3.2 *Tensile analysis Al 6061/TiO_2/CES hybrid composites*

Al 6061 alloy and its composites were tested for its tensile property by ASTM E8/E8M-21 standard [30] using a Universal Instron tensiometer model 3369 with 50-kN capacity.

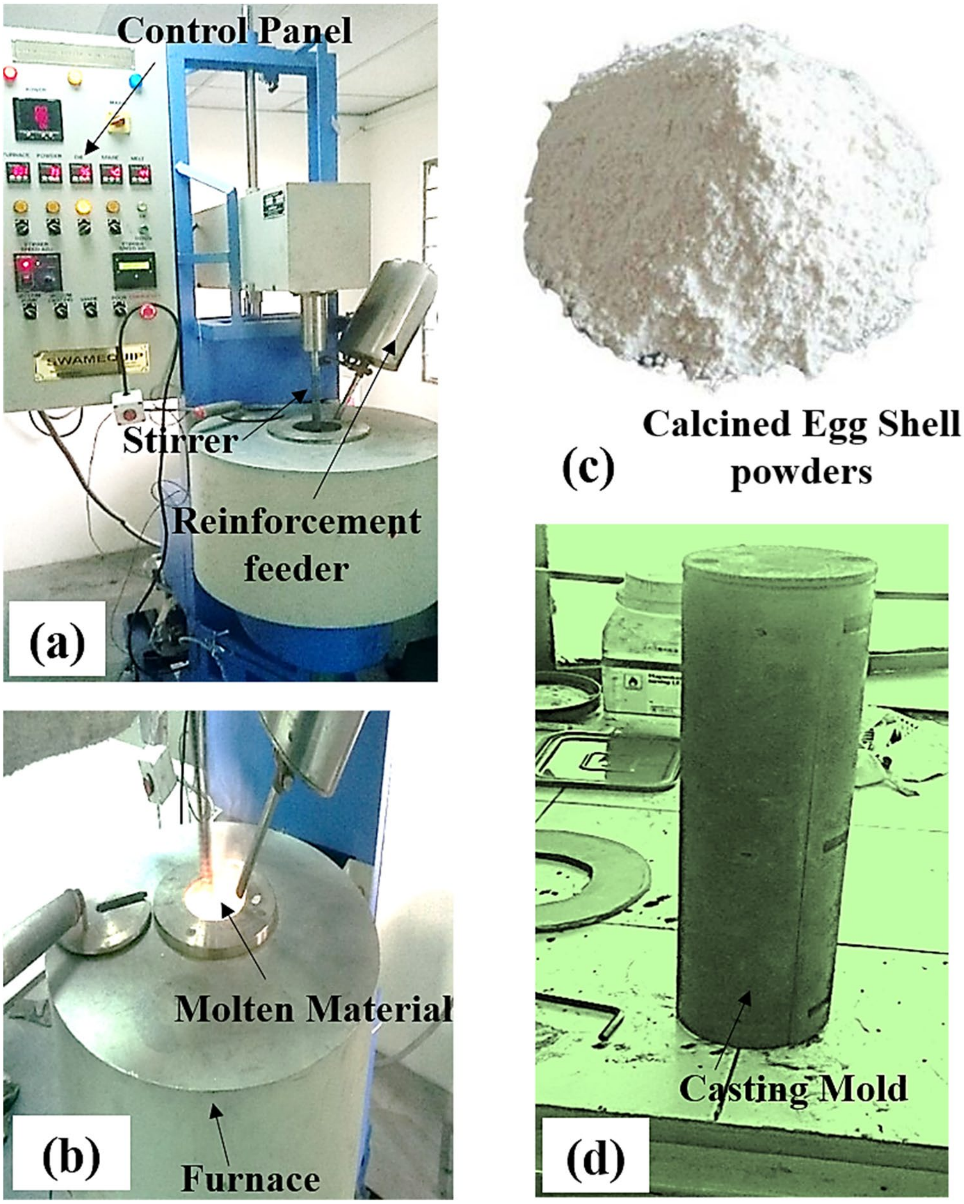

Fig. 2 **a** Stir casting setup with stirrer arrangement, **b** hot crucible with molten material, **c** reinforcement particulates, **d** mould used for casting

The samples of 90-mm diameter and 40-mm gauge length are prepared for the tensile study at a strain rate of 10^{-3}/s to fracture. The tests were repeated 5 times to ensure that the deviations in the results were below acceptable bounds.

2.3.3 *Flexural analysis Al 6061/TiO$_2$/CES hybrid composites*

The flexural testing was conducted with a three-point bending test on a Universal Testing Machine AGX-KN10 to calculate the flexural strength of the hybrid composites at fixed TiO_2 wt% and varying wt% of CES. The specimens were machined to 56′ 10 ‘6 mm at room temperature as per ASTM C-1161–18 standard [31]. The tests were conducted 5 times to reduce the deviations in the results below acceptable bounds.

2.4 Microstructural characterization

Zeiss low-powered metallurgical microscope JSM 7600F Joel, ultra-high-resolution field emission scanning electron microscope Philips/FEI XL 30S FEG-SEM, was employed for microstructural characterization. The as-cast samples were polished to a metallographic surface, finished and prepared for examination with different grades of grinding and polishing papers. Etched samples were swabbed adequately for 20 s in 0.5% hydrogen fluoride solution, rinsed and allowed to dry before the optical and scanning electron microscope examination at a magnification of 3000×.

2.5 X-ray diffraction analysis

By ASTM D 3906–19 standard, phase identification was performed using Bruker D2 Phaser XRD tester on Al 6061 alloy and composites of size 10 mm (diameter) QUOTE 5 mm (thickness). Using an AP Analytical Empyrean diffractometer and PIXcel detector, the specimens were scanned at a 2θ angle spectral range of 0° to 90° at a 2°/min scanning rate with the X-rays energy resolution of < 180 eV (CuKα). The XRD data were analysed to obtain phase parameters using X'Pert High score plus software.

The studies planned for the present examination are given in the form of the schematic in Fig. 3.

3 Results and discussion

3.1 Microstructural analysis of composites

The as-cast Al 6061 alloy and composites SEM micrographs are presented in Fig. 4, having 3, 6, 9 and 12 wt% TiO_2 blended with 3, 6, 9 and 12 wt% CES. The blended mixtures were added to enhance the microstructural behaviour of the hybridized composites. Continuous reinforcement dispersion resulted in the composite's strength enhancement from the microstructural analysis. A FESEM was employed for the microstructural characterization of the Al 6061 alloy and composites. It was inferred that the reinforcement addition resulted a refined grain structure from 3 wt% TiO_2/3, 6 wt% CES to 6 wt% TiO_2/3, 6 wt% with near absence/marginal presence of intermetallic compounds due to even dispersion of the particulates and the pores were filled to a large extent [32]. This is on account of solid interfacial bonding coexisting in the Al matrix. Further increments in the reinforcement's proportion by 9 and 12 wt% TiO_2/3.6 wt% CES agglomeration of particles within the Al matrix and lower ductility were observed. Notably, the interfacial bonding was strong, and porosities were reduced despite the agglomeration within the Al matrix [33, 34].

3.2 Phase characterization of composites

Figure 5 a and b present the XRD spectrum of the Al 6061 hybrid composites with 3% and 6% CES. It was observed that the Al 6061 phase was dominant in both compositions and had the highest peak. The peaks of TiO_2 and CES were also evident; this confirms that it is a hybridized Al 6061 composite. It was observed that peaks of the blended reinforcement increased as the weight percent of the reinforcement increased, as seen in Fig. 5. However, from the XRD spectrum, intermetallic compounds had a marginal presence with no resolvable peaks for the selected work material. The intermetallic compounds formed are due to solidification dynamics and had no consequential effect on the material behaviour [35]. Different groups of varying compositions of composites are given in Table 3.

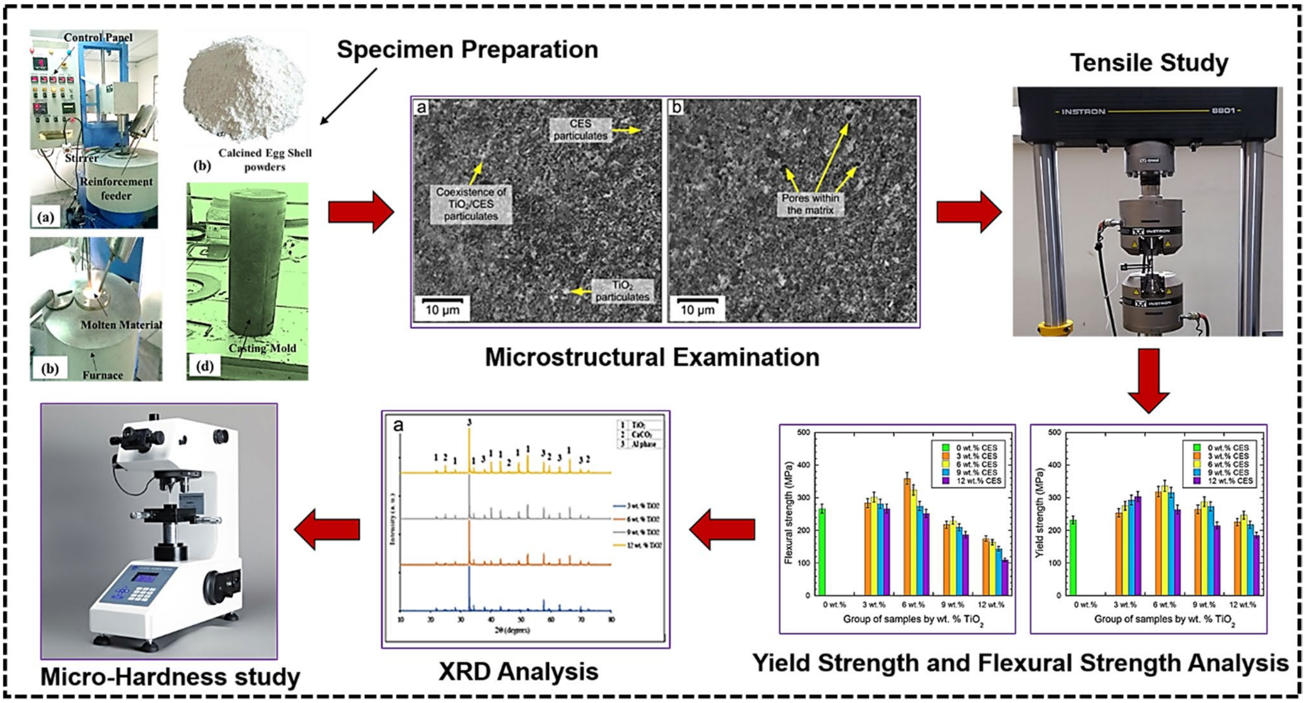

Fig. 3 Schematic representation of the studies planned for the present examination

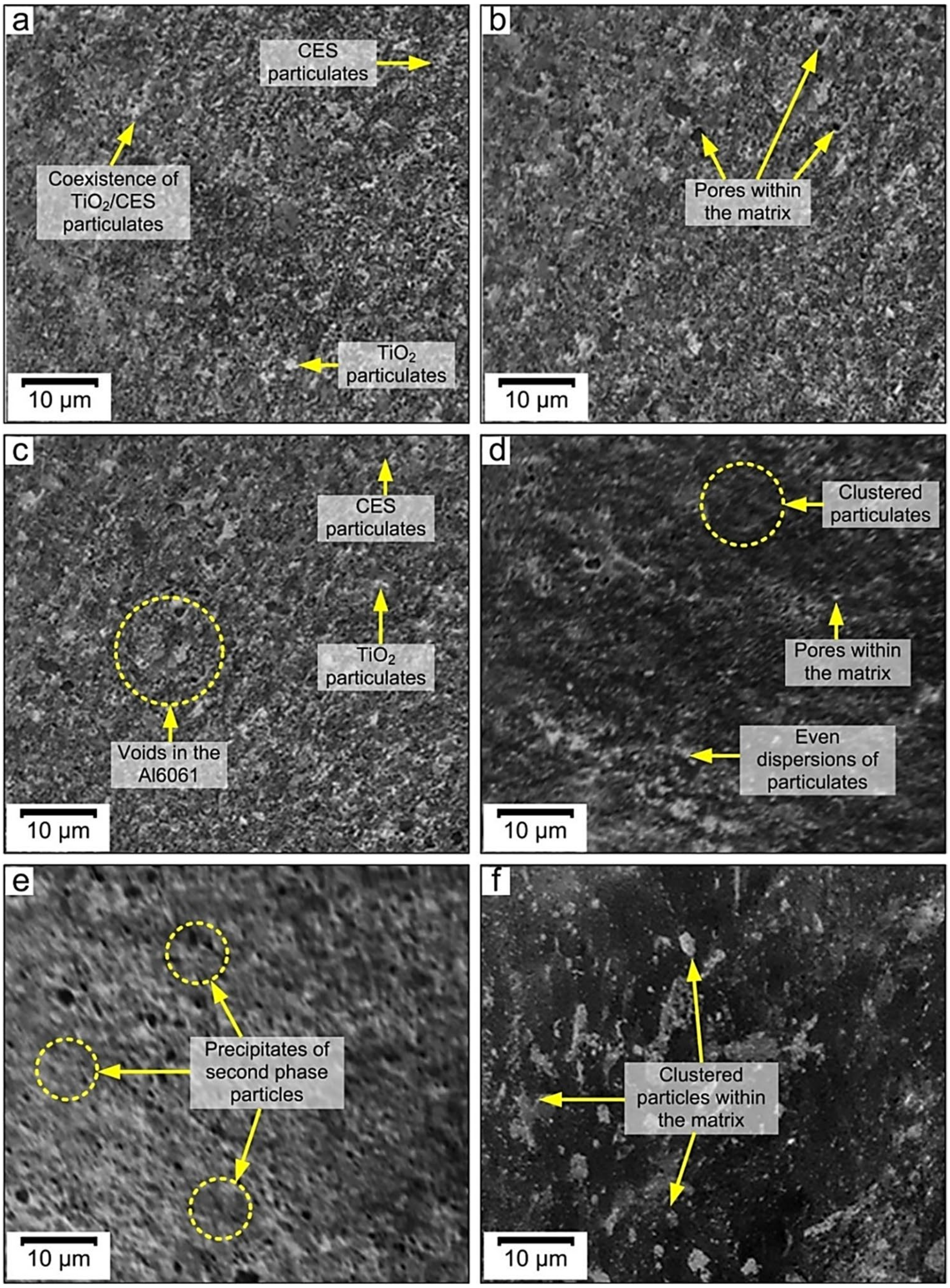

Fig. 4 SEM micrographs of the Al 6061 alloy and hybridized composites: **a** 3wt% TiO_2/3wt% CES, **b** 3wt% TiO_2/6wt% CES, **c**, 6wt% TiO_2/3wt% CES, **d** 6 wt% TiO_2/6wt% CES, **e** 9 wt% TiO_2/3 wt% CES, **f** 9 wt% TiO_2/6 wt% CES, **g** 12 wt% TiO_2/3wt% CES, **h** 12 wt% TiO_2/6 wt% CES

3.3 Mechanical characterization

3.3.1 Ultimate tensile strength

The ultimate tensile strength of the developed composite is presented in Fig. 6. Group A samples contained a fixed proportion of 3 wt% TiO_2. It was observed that there was an improvement in UTS with varying proportions of CES (3 wt%, 6 wt%, 9 wt% and 12 wt%) compared with the unreinforced alloy. The composite sample was prepared with 3 wt% TiO_2/6 wt% CES which displayed the highest strength improvement compared with the other hybrid composites in the group. Three, 6, 9 and 12 wt% CES brought about 15.66%, 21.70%, 16.01% and 9.6% improvement in the strength of the developed composite relative to the reference mix. Some other authors [36, 37] reported that the addition of TiO_2 to the ZA27 alloy resulted in a significant improvement in mechanical properties. The increase in strength is attributed to residual stresses that develop due to the intrinsic behaviour of the thermal coefficient of expansion between the reinforcement and matrix of the composites, which is a constraint to plastic flow and triaxiality in the soft alloy matrix due to the brittle and hard reinforcement particles. TiO_2/CES act as a barrier to dislocation movement in the

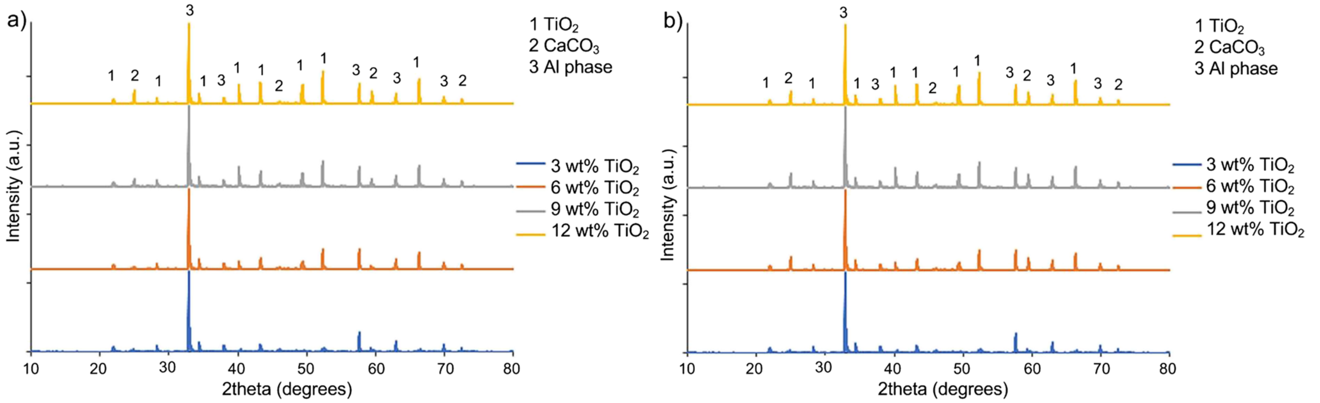

Fig. 5 **a** X-ray diffraction spectrum of Al 6061 composite with 3% CES, **b** X-ray diffraction spectrum of Al 6061 composite with 6% CES

Table 3 Different groups of composites with varying composition

Sl. no	Base matrix	Wt% composition of TiO_2	Wt% composition of CES	Group name
1	Al 6061	3	3, 6, 9, 12	A
2		6	3, 6, 9, 12	B
3		9	3, 6, 9, 12	C
4		12	3, 6, 9, 12	D

matrix, thereby causing dislocation to pile up, decreasing the inter particulate distance and improving the strength of the composite. The addition of TiO_2/CES increases ductility, resulting in lower ductility [38]. In the case of group B samples, constant 6wt% TiO_2 and varying wt% of CES at 3, 6, 9 and 12% revealed that 3 and 6 wt% of the CES ensued 32.74%, 40.93% strength enhancement than 9, 12 wt% of CES. Optimum UTS was realized by the collage of 6 wt% TiO_2 and 6 wt% CES yielded a 40.93% improvement over the reference mix. The 3 and 6 wt% CES is traceable to the excellent interaction between the CES and TiO_2 particulate and the formation of continuous interfacial bonding between the matrix and reinforcement. Also, even dispersion of the particulates with the matrix engendered even stress distribution, promoting strength [39].

However, it was noted that the 6wt% TiO_2 interacting with 9 and 12 wt% CES led to a 19.93% and 1.78% decrease in strength, respectively, for strength value obtained at 6 wt% TiO_2/6 wt% CES. The reduction associated with this observation is due to discontinuous site formation within the matrix and reinforcement, which serve as stress risers deleterious to the behaviour of the composite material when subjected to tensile loading, thereby impacting lower ductility at such region. A combination of 6 wt% TiO_2 and 12 wt% CES yielded a 1.78% marginal increment compared with the reference mix. This shows that the interaction between 6 wt% TiO_2 and 12 wt% CES had inconsequential improvement in the strength of the composite [5].

At 9 wt% constant TiO_2 and 3, 6, 9 and 12 wt% CES in group C, the UTS strength of Al 6061 reinforced with 3 wt% and 6 wt% CES increased by 15.30% and 22.78%, respectively, relative to the reference mix. On inclusion of 9 wt% CES, there was 2.49% marginal increase in strength over the reference mix. At 12 wt% CES, a 16.01% reduction in UTS was observed over the reference mix due to the matrix's clustering of particles. Hence, it is deduced that combination of 9 wt% TiO_2 and 9 wt% CES has no significant effect on UTS, whereas the blend of 9 wt% CES/12 wt% TiO_2 in Al 6061 matrix is deleterious to the performance of the hybrid composite [15].

The performance of group D samples, involving the blend of 12 wt% constant TiO_2 and varying weight percent of CES at 3, 6, 9 and 12%, is presented in Fig. 6. It was noted that there was a corresponding decrement in the UTS of 3, 6, 9 and 12 wt% CES, with 12 wt% TiO_2. This depicts that the

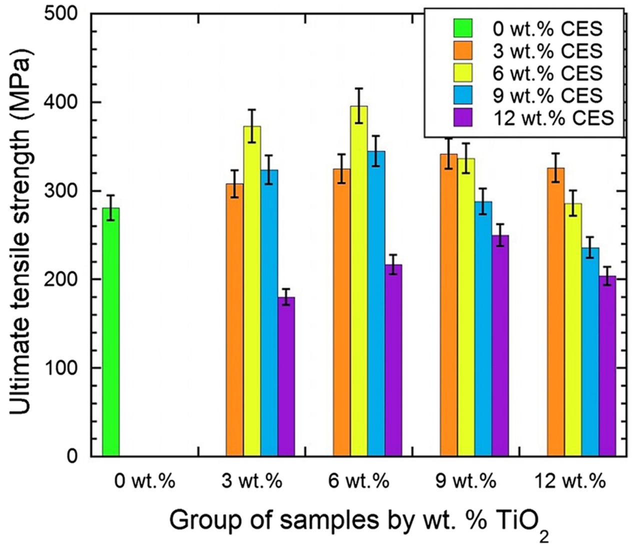

Fig. 6 Ultimate tensile strength of the Al 6061 alloy and hybrid composites

blended mixtures of reinforcement negatively affected the performance of developed Al 6061 matrix composites due to the presence of clustering of the particulates within the matrix, serving as an avenue for crack propagation when subjected to tensile loading [40].

3.3.2 Yield strength

Figure 7 presents the yield strength of developed Al 6061 composites. It was noted that the yield strength was improved due to the increased weight percent of the reinforcement. Specifically, for 3wt% TiO_2/and varying proportions of CES (3, 6, 9, 12 wt%) as in the case of group A samples, corresponding increments of 9.48%, 18.97%, 26.29% and 31.03% yield strength were observed, respectively. Al 6061 reinforced with 3 wt% TiO_2/12 wt% CES displayed higher yield strength than the unreinforced Al matrix because of even dispersion and strong interfacial bonding between the particulate and the matrix.

Group B with a constant 6 wt% TiO_2 blended with varying wt% of CES is presented in Fig. 7. Increased yield strength of 37.5%, 45.26% and 36.21% compared with the reference mix were observed for 3wt% CES to 6wt% CES and 9 wt% CES, respectively. The Al 6061 reinforced with 12 wt% CES had a marginal increment of 13.79% in yield strength relative to the reference mix. The 6 wt% TiO_2/6wt% CES had the highest yield strength compared to another hybrid of the composites, while the 6 wt% TiO_2/12 wt% CES had the least yield strength than the reference mix. The improvement in yield strength relative to the reference mix can account for strong interfacial bonding between wt% TiO_2/wt% CES and the matrix.

In this study, group C presented a constant of 9 wt% of TiO_2 with varying wt% of CES. It was observed that the 9 wt% CES/6 wt% TiO_2 displayed the highest yield strength having a 24.14% increment, while the 9wt% CES/12 wt% TiO_2–reinforced Al 6061 had the least yield strength of 7.33% lower than the unreinforced Al matrix. The lower yield strength exhibited by the 9 wt% CES/12 wt% TiO_2–reinforced Al 6061 may be attributed to the formation of discontinuous sites within the matrix due to the clustering of the blended reinforcement within the reference mix.

Group D presented the yield strength of the blended mixture in the Al 6061 matrix. It was observed that there was a marginal increment in yield strength of the 12 wt% TiO_2/6 wt% CES with a 6.47% increment. The other grades of the hybrid-reinforced composites significantly decreased yield strength (3, 9 and 12 wt% have − 2.59%, − 6.03%, − 20.26% decrement) except the 12 wt% TiO_2/6 wt% CES with 6.47% increment in yield strength. The decrease in yield strength of Al 6063–reinforced 12 wt% TiO_2/3, 9 and 12 wt% CES can be linked to the formation of discontinuous sites and interfacial bonding. This depicts using 12 wt% TiO_2/(3, 9 and 12) wt% CES will lead to unhealthy Al 6061 composites [14].

3.3.3 Flexural strength

The flexural strength of the reference mix and developed composite is presented in Fig. 8. In group A, samples containing a fixed proportion of TiO_2 (3 wt%) improve the flexural strength of 3wt% and 6wt% of CES with percentage increments of 6.37% and 9.54%. The 6 wt% CES displayed the highest flexural strength of 9.54% increment compared with the other hybrid. This is because even dispersion of the reinforcement with the Al 6061 matrix impinges dislocation

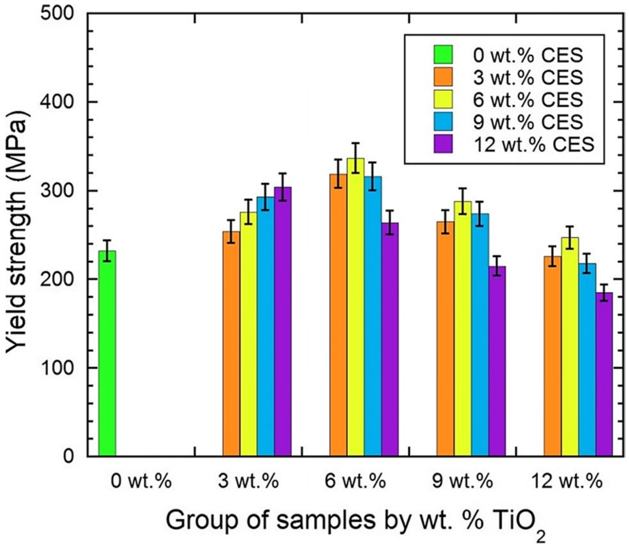

Fig. 7 Yield strength of the Al 6061 alloy and hybrid composites

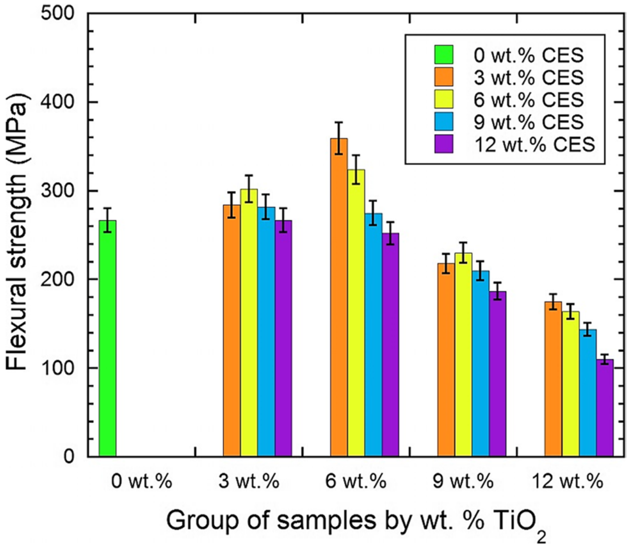

Fig. 8 Flexural strength of the Al 6061 alloy and hybrid composites

movement and a solid interfacial bonding [41]. A marginal increment in flexural strength was observed for the 9 wt% CES compared to the 3 wt% and 6 wt% CES blended with a fixed ratio of 3wt% of TiO_2. The 12 wt% CES–reinforced Al 6061 depicts flexural strength within the same range as that of the reference mix with no effect on the material behaviour. As the weight percent of the reinforcement increases above 6 wt% CES inclusions, there was a progressive decrement in the flexural strength of 9 wt% and 12 wt% CES having 5.62% and 0%, respectively, compared to the reference mix. This is due to intermetallic compounds within the matrix, resulting in lower ductility, which aids a faster dislocation movement on loading [34, 35]. This deduction is traceable to Saravana Kumar et al. [42]. They investigated the flexural behaviour and microstructure of hybrid metal matrix composites. It was reported that, as the wt% of reinforcement increased, the flexural strength decreased and attributed to the presence of uniform residual stresses and possible differences in the potential temperature gradient of the composite.

In group B, samples containing a fixed ratio of 6 wt%-TiO_2 and varying wt% of CES at 3, 6, 9 and 12 wt% were revealed that 3 and 6 wt% of the CES ensued a significant increment of 34.46% and 21.35% flexural strength enhancement relative to reference mix, beyond which a progressive reduction at 9 and 12 wt% of CES compared to the other hybrid. As the weight percent of CES increases, there is a progressive decrease in the flexural strength of the composites with optimum flexural strength realized by the collage of 6 wt% TiO_2 and 3 wt% CES yielded a 34.46% improvement over the reference mix. The increment between 3 and 6 wtCES is palpable to the excellent interaction between the CES and TiO_2 particulate and the formation of continuous interfacial bonding between the matrix and reinforcement. However, it was noted that as the 9 wt% of CES inclusions were added, there was a marginal increase of 2.97% in the flexural strength of the composite relative to the reference mix. In contrast, the 12 wt% CES inclusion brought flexural strength below the reference mix. This is attributed to second-phase particles resulting in discontinuity within the matrix and lower ductility facilitating dislocation movement on loading.

The production of sound Al 6061-based composites with groups C and D is not visible as they depict flexural strength below the reference mix. Group C has fixed 9wt% TiO_2 and 3, 6, 9 and 12 wt% CES recorded a decrement of 18.35%, 13.86%, 21.35% and 29.96%, respectively, and group D with fixed 12 wt% TiO_2 and 3, 6, 9 and 12 wt% CES resulting to 34.46%, 38.58%, 46.07% and 58.80% decrement compared to the reference mix. The decrease may be associated with the formation of discontinuous sites within the matrix and reinforcement, which serve as stress risers deleterious to the behaviour of the composite material when subjected to loading, thereby resulting in rapid crack propagation and lower ductility in the composites resulting in dislocation movement of the particles upon loading. Since the properties obtained in group C and group D are lesser than the reference mix, the said compositions of composite material are not recommended for extreme applications.

3.3.4 Vickers micro-hardness analysis

Figure 9 presents the Al 6061 reference mix's hardness and composites. It was observed that group A samples that contained a fixed proportion of TiO_2 (3 wt%) improved hardness with varying proportions of CES (3 wt%, 6 wt%, 9 wt% and 12 wt%) as compared with the reference mix. The composite sample was prepared with 3 wt% TiO_2/3, 6, 9 and 12 wt% CES possess improved hardness, specifically with 6.52%, 13.04%, 23.91% and 18.48%, respectively, compared with the reference mix. A progressive increment in hardness was observed as the wt% of CES inclusions increased from 3 to 9 wt%.

In contrast, a further increase to 12 wt% CES inclusions decreased in hardness of the composite relative to the other hybrid. Optimum hardness was observed for the 9 wt% CES inclusions. Seah et al. [18] reported the presence of hard dispersoids TiO_2, also known as a hard element, was associated with an increase in the hardness of Al- and Zn-based MMCs, which had positively contributed to the enhanced hardness of AMCs. The increment in wt% of TiO_2/CES can be linked to the particle hardening effect, which is a barrier to dislocation movement. The reduction in hardness exhibited by a further increase of reinforcement addition results from the clustering of particulates within the matrix, thereby resulting in the brittleness of the composite [43] and on compressive loading, the crack propagates rapidly [44].

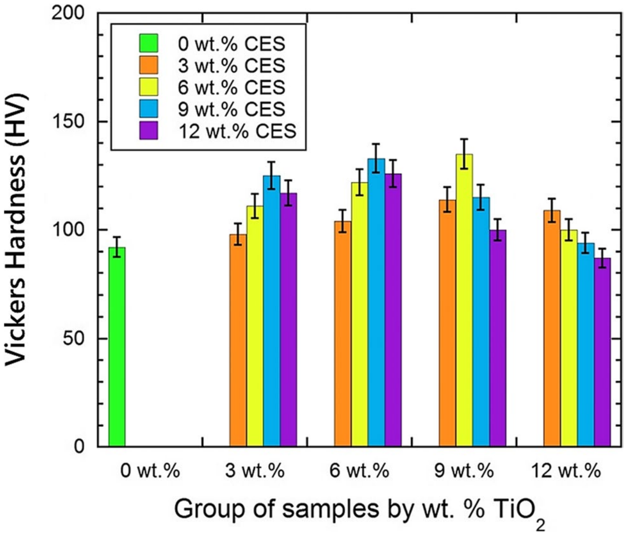

Fig. 9 Hardness behaviour of the Al 6061 alloy and hybrid composites

In the case of group B samples, which contained constant 6wt%-TiO_2 and varying wt% of CES at 3, 6, 9 and 12%, it was observed that 3, 6, 9 and 12 wt% of the CES ensued 20.65%, 32.61%, 46.74% and 8.69% hardness enhancement compared to the reference mix. Beyond the hardness of 9 wt% CES, there was a decrease in hardness of the 12 wt% CES relative to the other hybrid with the 9 wt% CES exhibits the highest hardness with a 46.74% increment. This increase in hardness of the composites than the reference mix can be linked to even dispersion of particles in the matrix, thereby resulting in the formation of continuous sites, resulting in enhanced hardness preventing dislocation navigation through the composites [45]. The decrease exhibited by the 12 wt% CES relative to the other hybrids was triggered by agglomeration within the matrix, a stress concentration area during loading [27].

At 9 wt% constant TiO_2 and 3, 6, 9 and 12 wt% CES in group C, the hardness of the Al 6061 matrix reinforced with 9wt% TiO_2 and varying 3, 6, 9 and 12 wt% CES shows an equivalent improvement in adding the inclusions into the matrix with an increment of 35.87, 44.57, 25 and 2.17%, respectively, to the reference mix. The optimum hardness percentage increment of 44.57% was obtained for the 6 wt% CES, followed by 35.87% hardness for 3wt% CES inclusion; this enhanced hardness of the composite may be ascribed to particle hardening effect relative to the reference mix. As the wt% of CES inclusions increased, there was a decrement in hardness of 9 wt% CES which has a 25% increment relative to the reference mix but decreases compared to the hybrid of 3 wt% and 6 wt% CES. The 12 wt% CES reinforced the Al 6061 matrix and displayed a marginal increment of 2.17% in hardness relative to the reference mix resulting in a marginal effect in the hardness behaviour of the composite. The decrement in hardness of 9 wt% and 12 wt% CES relative to the other 3 wt% and 6 wt% was triggered by agglomeration in the matrix deleterious to the performance of the hybrid composite.

The performance of group D samples, involving the blend of 12 wt% constant TiO_2 and varying weight percent of CES at 3, 6, 9 and 12%, is presented in Fig. 9. It was noted that there was an enhancement in the hardness of the 3 wt%, 6 wt% and 9 wt% CES-reinforced Al 6061 matrix with 36.96%, 27.17% and 8.69% relative to the reference mix. Three wt% CES-reinforced Al 6061 displayed optimum hardness with a 36.96% increment relative to the reference mix, while the 12 wt% CES had hardness 5.43% below the reference mix. This resulted from more particles of the reinforcement clustering around the grain boundary, which caused the non-uniform distribution of the particles. It shows a consequential effect on the material behaviour due to the reinforcement's brittle nature and the presence of clustering of the particulates within the matrix, serving as an avenue for crack propagation when subjected to tensile loading.

4 Conclusions

The mechanical and microstructural analysis of Al 6061 alloy hybridized with calcined eggshell and TiO_2 particulates were investigated. The main novelty of the research is the addition of the CES as a reinforcement/partial replacement for TiO_2 which is a very expensive material. Hence, the research should encourage the use of higher wt% of CES in combination with lower wt% TiO_2 in order to produce cost-effective hybrid composites. The significant outcomes of the current research showed that:

1. with the exemption of segregated preferential particle reinforcement around the grain boundary area, the production of healthy and low-cost processing of Al 6061 alloy and composites is visible via the stir casting route adopted. This is on account of the inconsequential presence of intermetallic compounds;
2. hardness, UTS, flexural strength and yield strength showed that significantly adding reinforcement to the matrix is detrimental for some engineering applications. This analogy is a result of agglomeration formed within the composite, thereby affecting the strength parameters;
3. the increased matrix/reinforcement particle interphase bonding and the intrinsic brittle character of TiO_2/CES were cited as key drivers in the Al 6061 composites' improved strength balance;
4. from the SEM micrographs, it was seen that the composite with the composition of 6 wt% TiO_2/6 wt% CES had the best balance of UTS and Y.S due to the uniform dispersion of the reinforcement particles, which improved the composite's strength parameters;
5. incorporating 3, 6, 9 and 12 wt% of TiO_2 with 6 and 9 wt% of CES triggered the enhancement of the composite hardness behaviour. This is because of the dislocation pileup created by the increased volume ratio of hard TiO_2/CES particles added to the matrix alloy, acting as a barrier to dislocation movement; and
6. combination of 3, 6, 9 and 12 wt% CES with not more than 6 wt% of TiO_2 would result in good and enhanced property hybrid composites for various structural applications.

Author contribution All the authors contributed equally to the manuscript.

Data availability All data employed in support to the outcomes in the study are included in this article.

Declarations

Ethics approval and consent to participate Not applicable.

Consent for publication Not applicable.

Competing interest The authors declare no competing interests.

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