

# Mechanical and Corrosion Behaviour of Zn-27Al Based Composites Reinforced with Groundnut Shell Ash and Silicon Carbide

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## Keywords:

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## ABSTRACT

*The mechanical and corrosion behaviour of Zn-27Al alloy based composites reinforced with groundnut shell ash and silicon carbide was investigated. Experimental test composite samples were prepared by melting Zn-27Al alloy with pre-determined proportions of groundnut ash and silicon carbide as reinforcements using double stir casting. Microstructural examination, mechanical properties and corrosion behaviour were used to characterize the composites produced. The results show that hardness and ultimate tensile strength of the hybrid composites decreased with increase in GSA content. Although the % Elongation somewhat decreased with increase the GSA content, the trend was not as consistent as that of hardness and tensile strength. The fracture toughness of the hybrid composites however, increased with increase in the GSA content of the composites. In 3.5 % NaCl solution, the composites were resistant to corrosion with some of the hybrid composite grades containing GSA exhibiting relatively superior corrosion resistance to the grades without GSA. In 0.3M H<sub>2</sub>SO<sub>4</sub> solution, the composites were generally a bit more susceptible to corrosion (compared to 3.5 % NaCl solution), but the effect of GSA content on the corrosion resistance of the composites was not consistent for the Zn-27Al alloy based composites.*

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## 1. INTRODUCTION

In recent years, Zn-Al based composites are gaining wide spread importance in several high technological applications [1-2]. The Zn-Al alloy based matrices are designated ZA-8, ZA-12 and ZA-27 corresponding to the approximate aluminium content in the alloy [3]. These alloys are known to possess good combination of

physical, mechanical and technological properties (low melting point, excellent castability, high strength, good machining and tribological properties), as well as by low manufacturing costs [4-5]. The Zn-Al based alloys are suitable for a wide range of applications such as for manufacture of industrial fittings and hardware, pressure tight housings, sleeve bearings, thrust washers and

wear plates [6-7]. Of all members of ZA casting alloys, ZA-27 alloy has the highest strength and the lowest density, as well as excellent bearing and wear resistance properties [8]. This alloy also provides the highest design stress capability at elevated temperatures of all the commercially available zinc-based alloys [9]. However, the ZA-27 alloy as well as other ZA alloys are not applicable at operating conditions more than 80 °C, due to the deterioration of their mechanical properties at elevated temperatures [9]. Thus strengthening by the use of refractory ceramic particles or fibers has been explored to improve tensile strength, strength to weight ratio and creep resistance at higher working temperatures [10-11].

Hard reinforcements such as silicon carbide and alumina have been successfully utilized to enhance the hardness, strength, elastic modulus and abrasive wear resistance of ZA based composites while some properties like fracture toughness, impact resistance, damping capacity, corrosion resistance, machinability and conductivity have been improved with the use of graphite as complementing reinforcement to SiC or alumina [11-15].

Presently, there is increasing interest in developing low cost - high performance metal matrix composites (MMCs) using ashes processed from agricultural wastes as partial or complete replacements for conventional synthetic reinforcements such as SiC and alumina [16]. Very encouraging results have been observed from Aluminium matrix composites reinforced with hybrid mix of the agricultural waste ashes (such as rice husk ash, bamboo leaf ash) and the synthetic reinforcements (such as SiC and alumina) [17]. The development of Zn-Al based hybrid composites has been reported in literature but very little resource can be found for Zn-Al based composites developed with the use of agricultural waste ashes as single or hybrid reinforcements. These agro waste ashes are noted to contain reasonable amounts of silica (SiO<sub>2</sub>) and other refractory oxides such as alumina Al<sub>2</sub>O<sub>3</sub> and hematite (Fe<sub>2</sub>O<sub>3</sub>). They usually are of lower densities compared with conventional reinforcements such as SiC (3.18 g/cm<sup>3</sup>) and alumina (3.9 g/cm<sup>3</sup>), and can be processed cheaply using simple reactors/burners [16,18].

In this investigation the mechanical properties and corrosion behaviour of Zn-27Al alloy reinforced with varied weight ratios of ground nut shell ash and silicon carbide is reported. Groundnut is produced in large quantity in Nigeria and many other parts of the world [19-20]; and to date limited use of the groundnut shells after extraction of the seeds has been reported in literature. Conversion of these agricultural wastes to products suitable for use as reinforcements in composites will help extend the frontiers of knowledge of composite materials development and applications, and contribute in agricultural waste management.

## 2. MATERIALS AND METHOD

### 2.1 Materials and Preparation

Commercial pure Aluminium and Zinc (with chemical composition presented in Table 1) were selected for the production of the Zn-Al alloy matrix. Chemically pure silicon carbide (SiC) particles having average particle size of 30 µm and groundnut shell ash (<50 µm) derived from controlled burning and sieving of dry groundnut shell ash were used as reinforcement for the Zn-27Al based composites to be produced. Graphite particles having particle size of < 50 µm was also procured for addition in the composite mix to help improve machinability of the composites. The chemical composition of the groundnut shell ash is presented in Table 2.

**Table 1.** Elemental Composition of the Zinc and Aluminium used for the production of the Zn-27Al based Composite matrix.

Elements	Weight percentage
Al	99.92
Fe	0.003
Si	0.033
Mn	0.021
others	0.023

Element	Weight percentage
Zn	99.96
Fe	0.02
Si	0.006
Pb	0.004
others	0.01

**Table 2.** Composition of Groundnut Shell Ash.

Elements	Weight percentage
SiO <sub>2</sub>	41.42
Al <sub>2</sub> O <sub>3</sub>	11.75
Fe <sub>2</sub> O <sub>3</sub>	12.60
CaO	11.23
MgO	3.51
TiO <sub>2</sub>	0.63
Na <sub>2</sub> O	1.02
K <sub>2</sub> O	11.89
P <sub>2</sub> O <sub>3</sub>	1.71
MnO	0.23
SO <sub>3</sub>	0.44
*LOI	3.57

\*LOI represents loss on Ignition

A two step stir casting process as described by Alaneme and Aluko [20] was adopted for the production of the test composite samples. Charge calculation was used to determine the amount of groundnut shell ash (GSA) and silicon carbide (SiC) required to prepare 7 and 10 wt.% of the GSA-SiC reinforcements (in the Zn-27Al alloy matrix) consisting of 0, 20, 30 and 40 % GSA. 0.25 wt.% graphite was added to each charge to improve machinability of the composites after casting.

The groundnut shell ash, silicon carbide and graphite particles were initially preheated separately at a temperature of 250 °C to remove moisture and to help improve wettability with the molten Zn-Al alloy. The Aluminium billet was charged into a gas fired crucible furnace (fitted with a temperature probe), and heated to a temperature of 670 °C until the Aluminium melted completely. The temperature of the furnace was lowered to 500 °C before Zinc was introduced. After the Zinc has melted completely, the melt was then allowed to cool in the furnace to a semi solid state (at a temperature of about 450 °C) and it was stirred at 200 rpm for 5 minutes to achieve homogenization.

The preheated groundnut shell ash, SiC particles and graphite particles were then charged into the melt and stirring of the slurry was performed manually for 5-10 minutes. The composite slurry was superheated to a temperature of 530 °C, stirred mechanically at 400 rpm for 10mins and thereafter sand casted. The sample designations for the grades of Zn-27Al based composites produced are presented in Table 3.

**Table 3.** Sample Designations for the Composites produced.

Sample Designation	Weight percent GSA: SiC
7 wt% Reinforcement	
A0	0: 100
A20	20:80
A30	30:70
A40	40:60
10 wt% Reinforcement	
B0	0: 100
B20	20:80
B30	30:70
B40	40:60

## 2.2 Mechanical Testing

Hardness tests ( $H_{RC}$ ) were conducted on polished specimens, representative of each grade of composite produced using Indentec Hardness Testing Machine. Multiple hardness tests were performed on each sample and the mean of values within the range of  $\pm 2\%$  was taken as the hardness of the specimen.

Test specimens obtained from master composite alloys were subjected to tensile test using Instron Universal test machine in accordance with the ASTM 8M-91 standards [21]. Readings were taken to determine the ultimate tensile strength (UTS) and strain to failure (reported as % Elongation). Similarly, circumferential notched tensile tests were carried out on standard machined test specimens using the Instron Universal Test Machine in accordance with the test procedures described by Alaneme [22]. The load-extension plots obtained were used to determine the fracture toughness as described by Dieter [23].

In all test cases, multiple tests were carried out for each grade of the Zn-27Al based composites and average of the measurements taken to ensure repeatability and reliability of the generated data.

## 2.3 Microstructural Examination

A Zeiss Metallurgical Microscope with accessories for image analysis was used for optical microscopic investigation of the composites produced. The specimens for the test were metallographically polished and etched before microscopic examination was performed. The polished samples were etched in dilute aqua

regal solution (3HCl:1HNO<sub>3</sub>) before they were viewed under the microscope.

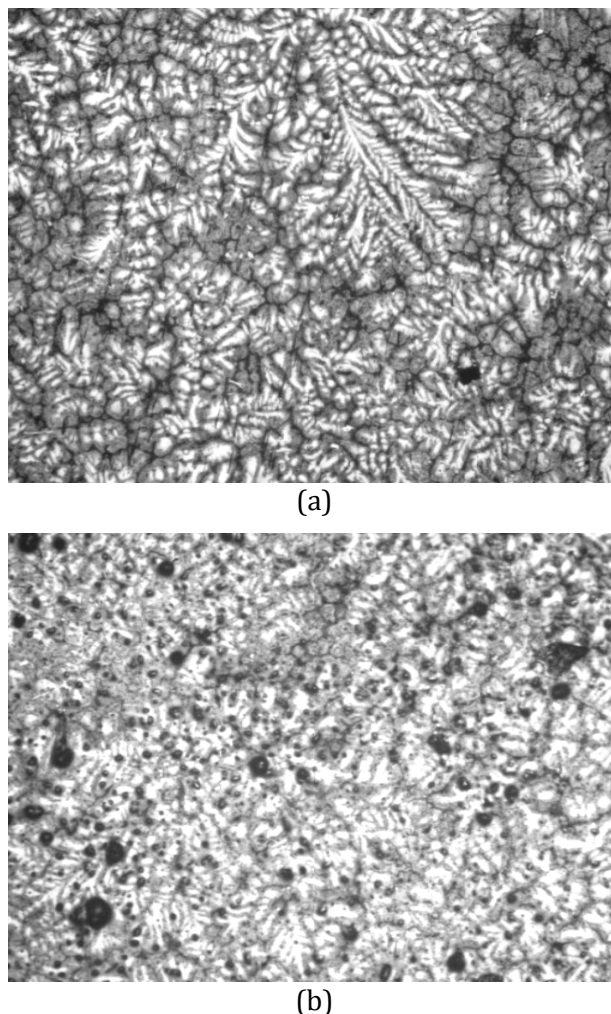
## 2.4 Corrosion Test

The corrosion behaviour of the composites was studied by weight loss method using mass loss and corrosion rate measurements as basis for evaluating the results generated. The corrosion test was carried out by immersion of the test specimens in 0.3M H<sub>2</sub>SO<sub>4</sub> and 3.5 % NaCl solutions which were prepared following standard procedures [24]. The specimens for the test were cut to size 15×15×10 mm and then mechanically polished with emery papers from 220 down to 600 grades to produce a smooth surface. The samples were de-greased with acetone, rinsed in distilled water, and then dried in air before immersion in still solutions of 0.3M H<sub>2</sub>SO<sub>4</sub> and 3.5 % NaCl at room temperature (25 °C). The solution-to-specimen surface area ratio was about 150 ml cm<sup>-2</sup>, and the corrosion setups were exposed to atmospheric air for the duration of the immersion test. The weight loss readings were monitored on two day intervals for a period of 42 days. The mass loss (g/cm<sup>2</sup>) and the corrosion rate (mmy) for each sample was evaluated in accordance with ASTM G31 standard recommended practice [25]. Three repeat tests were carried out for each grade of the Zn-27Al based composites produced, and the reproducibility and repeatability of the results from the triplicates were found to have no significant differences.

## 3. RESULTS AND DISCUSSION

### 3.1 Microstructure

Figure 1 shows the microstructural features of the Zn-27Al alloy and a representative Zn-27Al/GSA-SiC composite grade. It is observed from Fig. 1(a) that a somewhat feathery feature which is actually the dendritic pattern of the Zn-27Al alloy indicating the solidification pattern and grain morphology. Figure 1(b) on the other hand shows a partially concealed dendritic grain structure arising from the presence of the fairly homogeneous distribution of the GSA-SiC particles in the Zn-27Al alloy. A few pockets of particle clusters which are very common with stir casting processed MMCs are also observed in the microstructure.

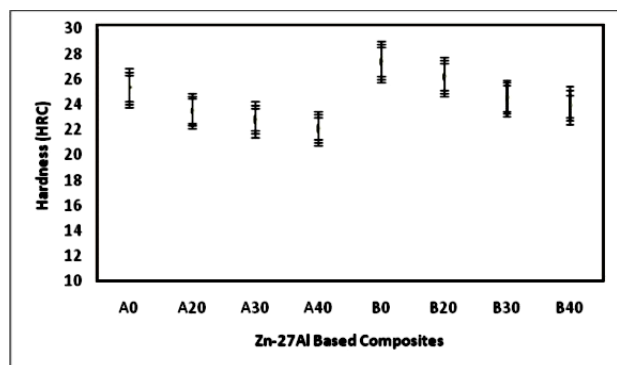


**Fig. 1.** Representative micrograph showing (a) the Zn-27Al alloy microstructure, and (b) the microstructure of the Zn-27Al based composite containing 7 wt% GSA-SiC in weight percent 30 % GSA: 70 % SiC.

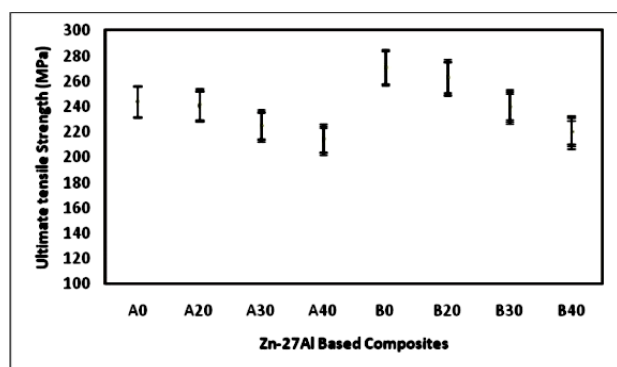
### 3.3 Mechanical Behaviour

The hardness values of the composites are presented in Fig. 2(a). There was little doubt that the hardness values of the composites would decrease with increase in the GSA content in the composites judging from the predominant silica, alumina, and haematite content of GSA (Table 2) which are less abrasive (harder) than SiC [18]. The interest was to ascertain if the percentage decrease in hardness was quite significant. For the 7 wt% GSA-SiC reinforced Zn-27Al composite grades, an average decrease in hardness of 7.1, 9.8, and 12.6 % was observed for the composites containing 20, 30, and 40% GSA (A20, A30, and A40) respectively. In the case of the 10 wt% GSA-SiC reinforced Zn-27Al composite grades, 4.56, 10.2, and 12.7 % reduction in hardness was observed for the

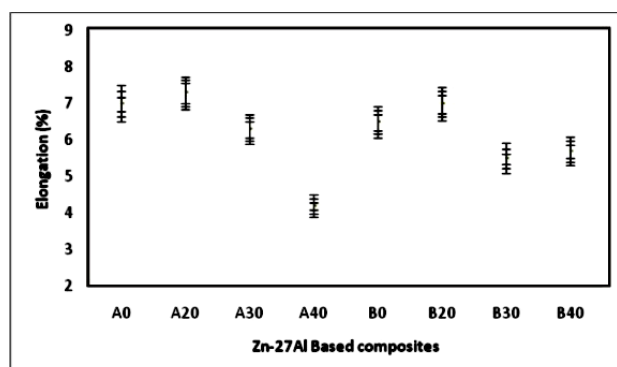
composites containing 20, 30, and 40 % GSA (B20, B30, and B40) respectively.



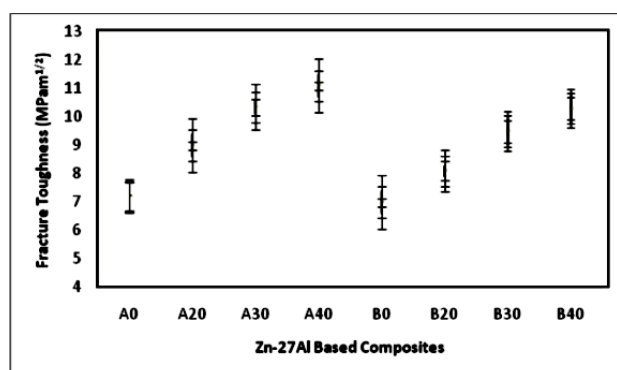
(a)



(b)



(c)



(d)

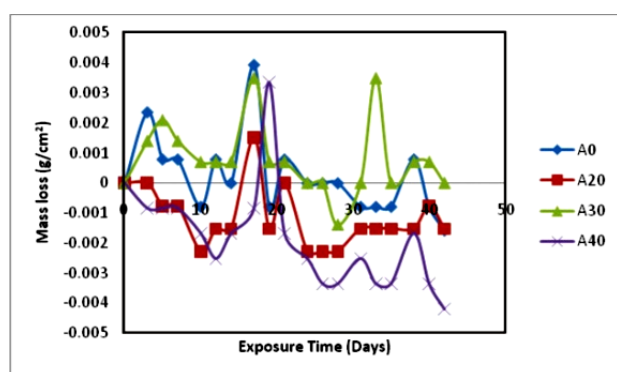
**Fig. 2.** Variation of (a) Hardness, (b) Ultimate Tensile Strength, (c) % Elongation, and (d) Fracture Toughness of the Zn-27Al based Composites Produced.

A similar trend was observed for the tensile strength values (Fig. 2b) in which the UTS decreased with increase in the weight percent of GSA. Reductions of 1.3, 8.1, and 12.3 % were obtained for the 7 wt% GSA-SiC reinforced Zn-27Al composite grades containing 20, 30, and 40 % GSA (A20, A30, and A40) respectively. For the 10 wt% GSA-SiC reinforced Zn-27Al composite grades 1.7, 9, 17.1 % were observed for the composites containing 20, 30, and 40 % GSA (B20, B30, and B40) respectively. The variation of % Elongation (Fig. 2c) with increase in the GSA content in the Zn-27Al based composites produced was not as consistent as was the case of the hardness (Fig. 2a) and tensile strength (Fig. 2b) discussed earlier. It is however noted that for both the 7 and 10 wt% reinforced composite series, the grades with little or no GSA (0 and 20 % GSA) appeared to be more ductile than the grades with higher content of GSA (30 and 40 % GSA). The fracture toughness results (Fig. 2d) are however noted to increase with increase in the weight percent of GSA in both the 7 and 10 wt% composite grades which is in contrast with the trend observed for the hardness and tensile strength. Significant increases of 25, 43, and 54 % were obtained for the 7 wt% GSA-SiC reinforced Zn-27Al composite grades containing 20, 30, and 40 % GSA (A20, A30, and A40) respectively. For the 10 wt% GSA-SiC reinforced Zn-27Al composite grades increase of 15, 36, and 47 % were observed for the composites containing 20, 30, and 40 % GSA (B20, B30, and B40) respectively. The improvement in the fracture toughness with increase in GSA content of the composites may be due to the reduced amount of relatively harder and brittle SiC particles in the Zn-27Al based composites produced [18]. The SiC particles like most hard and brittle ceramic particles have a higher tendency to undergo rapid crack propagation [17]. Thus it is noted that the addition of GSA in the Zn-27Al based composites results in improved resistance to crack propagation and fracture.

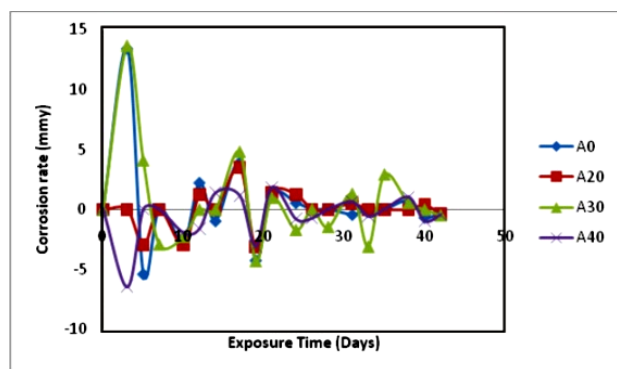
### 3.3 Corrosion Behaviour

Figures 3 and 4 show the variation of mass loss and corrosion rate with exposure time for Zn-27Al composite grades containing 7 and 10 wt.% GSA-SiC reinforcement respectively in 3.5 % NaCl solution. From Fig. 3(a), it is observed that the mass loss values for the composite grades

with 7 wt.% GSA-SiC reinforcement were generally very low indicating that the Zn-27Al/ 7 wt.% GSA-SiC composites are very stable and corrosion resistant in 3.5 % NaCl solution which is representative of a typical marine environment. The mass loss values for a good proportion of immersion period were negative – an indication of weight gain and affirmation of the protective nature of the passive film formed on the composites. Closer examination reveals that the hybrid composite grades A20 and A40 (which both contain 20 and 40 % GSA respectively), have superior corrosion resistance in comparison with the composite grade A0 (which does not contain GSA). The corrosion rate data (Fig. 3b) is consistent with the mass loss trend observed in Fig. 3(a).



(a)

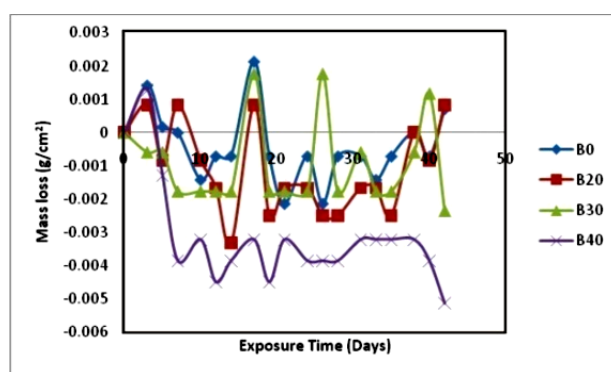


(b)

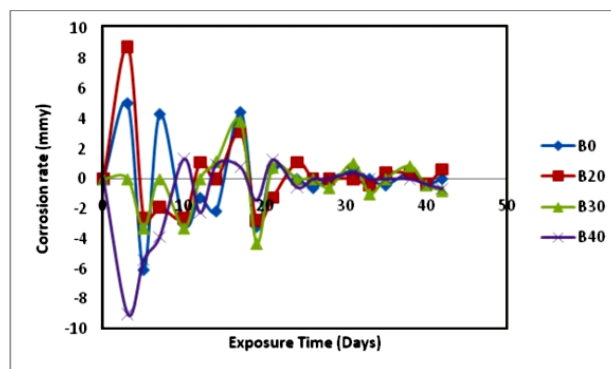
**Fig. 3.** Variation of (a) Mass loss, and (b) Corrosion rate of Zn-27Al based composites containing 7 wt% GSA-SiC in 3.5 % NaCl Solution.

The Zn-27Al alloy composite grades of the 10 wt.% GSA-SiC reinforced series also exhibited a very high resistance to corrosion in 3.5 % NaCl solution (Fig. 4). The negative mass loss values of the composites (Fig. 4a) are reflective of the stable and protective nature of the passive films formed on the surfaces of the composites. It is also noted that the corrosion resistance of the

composites improves with increase in the GSA content in the composites. The composite grade without GSA (B0) is observed to have the highest mass loss (least corrosion resistance) in 3.5 % NaCl solution. The improvement in corrosion resistance observed with the addition of GSA may not be isolated to the presence of silica which is the major constituent of GSA (Table 2) as is the case with Aluminium based composites with similar hybrid reinforcement compositions [26]. The nature and protective characteristics of passive films formed on Zn-Al based composites immersed in NaCl environments has been reported to depend on a complex relationship of the alloys and composite composition, structure and the surface area exposed to the corrosive environment [27].



(a)



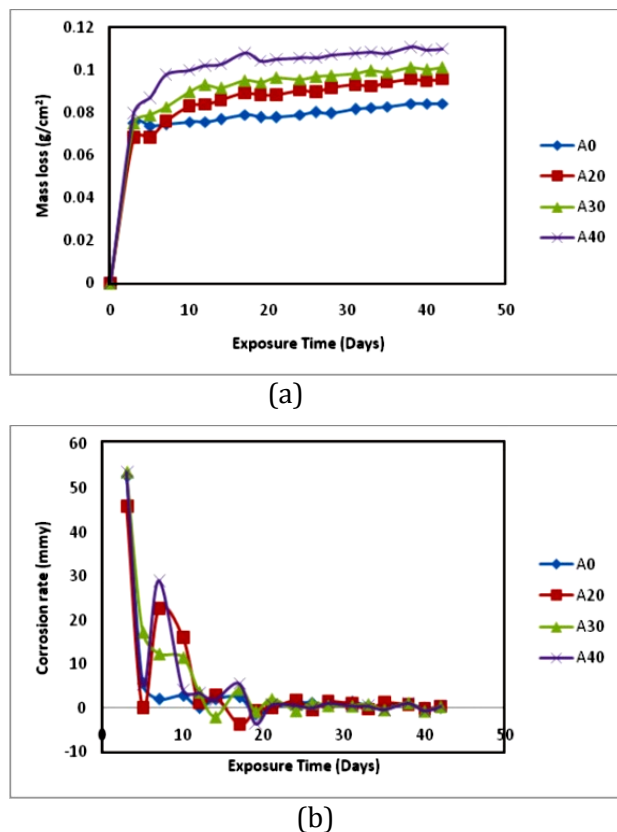
(b)

**Fig. 4.** Variation of (a) Mass loss, and (b) Corrosion rate of Zn-27Al based composites containing 10 wt % GSA-SiC in 3.5 % NaCl Solution.

Figures 5 and 6 show the variation of mass loss and corrosion rate with exposure time for composite samples with 7 and 10 wt.% of reinforcements respectively immersed in 0.3 M H<sub>2</sub>SO<sub>4</sub> solution.

From Fig. 5(a), it is observed that all the composite grades with 7 wt.% reinforcement are

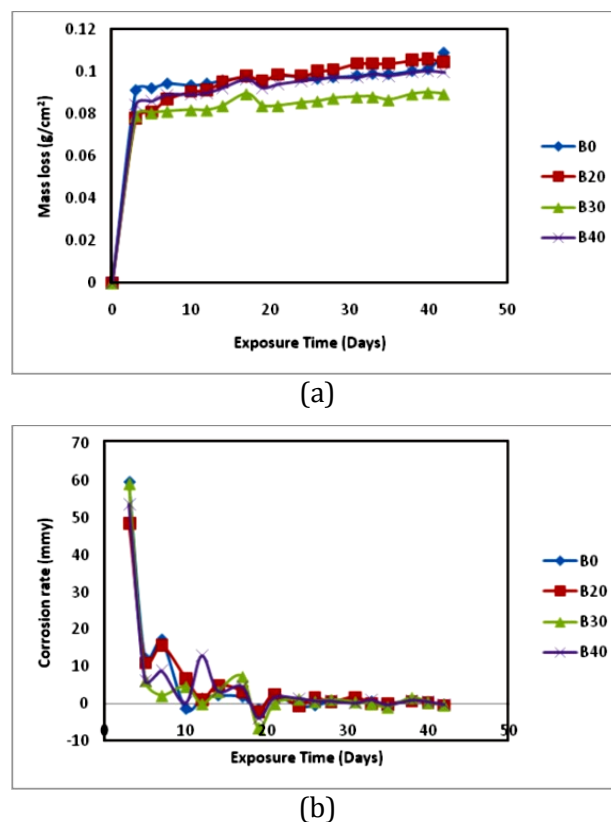
susceptible to corrosion in 0.3M H<sub>2</sub>SO<sub>4</sub> with A0 (the sample with 0% GSA) exhibiting the least mass loss in comparison with other composites in this series. In addition, the mass loss and corrosion rate (Fig. 5b) increased gradually for all the composite grades after the initial sharp rise observed during exposure in the acidic solution. The progression in the corrosion of the composites is an indication that the passive film formed on the composites was unable to give adequate protection to the substrates.



**Fig. 5.** Variation of (a) Mass loss, and (b) Corrosion rate of Zn-27Al based composites containing 7 wt% GSA-SiC in 0.3M H<sub>2</sub>SO<sub>4</sub> Solution.

In the case of the Zn-27Al composite grades with 10 wt.% GSA-SiC reinforcement, it is observed from Figure 6(a) that the mass loss for most of the composites are comparable with the exception of the composite grade B30 (containing 30 % GSA) which was relatively more resistant to corrosion in the 0.3M H<sub>2</sub>SO<sub>4</sub> solution. Just as in the case of the composite grades with 7 wt.% reinforcement, It is noted that the mass loss increased steadily throughout the immersion period after an initial sharp increase at the start of the immersion test. The corrosion rate results (Fig. 6b) are consistent with the mass loss observation presented in Fig. 6(a). The corrosion

trends observed for the Zn-27Al based composites in 0.3M H<sub>2</sub>SO<sub>4</sub> solution is supported by the investigation of Sharma et al. [28].



**Fig. 6.** Variation of (a) Mass loss, and (b) Corrosion rate of Zn-27Al based composites containing 10 wt% GSA-SiC in 0.3M H<sub>2</sub>SO<sub>4</sub> Solution.

#### 4. CONCLUSIONS

The mechanical and corrosion behaviour of Zn-Al hybrid composites containing 7 and 10 wt.% of varied weight ratios of GSA and SiC was investigated. The results show that:

- Hardness and ultimate tensile strength of the hybrid composites decreased with increase in GSA content.
- Although the % Elongation somewhat decreased with increase the GSA content, the trend was not as consistent as that of hardness and tensile strength.
- The fracture toughness of the hybrid composites however, increased with increase in the GSA content of the composites.
- In 3.5 % NaCl solution, the composites were resistant to corrosion with some of the hybrid composite grades containing

GSA exhibiting relatively superior corrosion resistance to the grades without GSA.

- In 0.3M H<sub>2</sub>SO<sub>4</sub> solution, the composites were generally a bit more susceptible to corrosion (compared to 3.5 % NaCl solution), but the effect of GSA content on the corrosion resistance of the composites was not consistent for the Zn-27Al alloy based composites belonging to the 7 and 10 wt.% series.

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