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EVALUATION OF THE DEVELOPMENT AND CORROSION RESPONSE OF ZA-27/PERIWINKLE SHELL COMPOSITE EXPOSED TO 0.5 M HCl

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ABSTRACT

Materials science and engineering designs materials tailored for specific needs by manipulating the relationships between processing, structure, and performance. Zinc-based ZA-27 alloys are prized for high strength but suffer a decrease in properties at temperatures above 80°C. This research aimed to develop a metal matrix composite using ZA-27 as the matrix and periwinkle shell ash as a low-cost reinforcement. Composites were produced via green sand casting using varying percentages (2%, 4%, 6%, 8% and 10%) of periwinkle shell ash as reinforcement. and particle sizes (+45 µm, +53 µm, and +63 µm). Three different test samples were produced, and corrosion was evaluated at room temperature in 0.5M HCl over 240 hours (10 days) using the weight-loss technique at time interval of 48 hours. Results showed that the unreinforced ZA-27 alloy exhibited better corrosion resistance than all reinforced composites. However, within the reinforced group, samples with +45 µm particle size and 10% ash content showed the highest relative resistance compared to +53 µm, and +63 µm. Corrosion rates for all samples decreased as exposure time increased due to the formation of a passive layer. It was also established that increased percentage reinforcement resulted to increased corrosion resistance.

Keywords: ZA-27, Periwinkle Shell Ash, Metal Matrix Composite, Corrosion Penetration Rate and Green Sand Casting

INTRODUCTION

Materials Science and Engineering is the discipline concerned with the relationships among synthesis/processing, structure (at atomic and microstructure scales), material properties (mechanical, electrical, chemical, etc.), and performance enabling the design, development, modification and application of materials tailored for specific needs (Mitchell, 2023)

A composite material is a solid material formed by combining two or more chemically or physically distinct constituent materials (phases), each retaining its own identity, to create a new material whose properties are superior or not attainable by the individual constituents acting alone (Britannica, 2025). The core benefit of composite materials is their great strength and stiffness, for example carbon fibers have great specific strength, high modulus, and good in fatigue resistance, dimensional stability and lower density (Thori *et al* 2013). Furthermore, composites combine properties of different engineering materials for improved properties, hence engineers have placed high premium on high performance materials; materials with great deal of strength and lighter weight, reduced thermal elongation, increased fatigue strength, higher temperature applications, good corrosion resistance and wear properties. There are a lot of composite materials, basically classed based on their matrix phase-ceramic matrix composite (CMCs), metal matrix composite (MMCs), and polymer matrix composite (PMCs) (Brando, 2014).

Hashem (2024) states that MMCs "are composites consisting of a metallic matrix reinforced by a second phase engineered so that the resulting material exhibits properties not attainable by the base metal alone. In composite materials the reinforcing phase often in the form of fibres or particles is generally much harder, stronger and stiffer than the matrix, and is responsible for providing the composite with enhanced strength, stiffness, hardness and load-bearing capacity compared to the unreinforced matrix.

Zinc-based zinc–aluminum (ZA) alloys such as ZA-8, ZA-12 and ZA-27 provide high strength, hardness, wear- and bearing-resistant properties, often superior to bronze or conventional zinc alloys, making them suitable for structural, bearing, and wear-resistant applications (Retapure *et al* 2023). Zinc-based alloy with 27% (mass fraction) aluminum belong to Zn-Al foundry alloys with relatively high content aluminum (ZA alloy). The alloys are distinguished by exceptionally high wear resistance as well as favorable physical and mechanical properties (low density and melting point, high strength and hardness at ambient temperature, ease of machinability, good damping properties, good corrosion resistance) (Bobic *et al.*,2013).

However, the elevated temperature (> 100°C) properties of zinc-aluminum alloys are unsatisfactory and restrict their use in some applications. One promising approach to improve the elevated temperature properties was reinforcing the alloys with SiC fibers or particles, alumina particles and fibers, glass fibers etc. Notwithstanding, the use of this alloy is rather limited because of drastic decrease of strength and creep resistance at temperatures above 80°C. Strengthening by ceramic particles or fibers is destined to improve strength to weight ratio and to increase tensile strength and creep resistance at higher working temperatures. The results of tribological investigations of composites with ZA-27 alloy substrate reinforced by Al_2O_3 particles of different size or by graphite particles have been presented most recently. The investigated composite materials have shown significantly higher wear resistance than the matrix ZA-27 alloy. In general, corrosion behavior of aluminum

MMCs has been studied most extensively, while there has been hardly any information available on the corrosion behavior of zinc-aluminum based composites (Bobic *et al.,* 2009).

Today, growing environmental awareness has triggered a paradigm shift from synthetic-fiber composites to composites made from natural reinforcing constituents (natural fibers or natural particulate fillers), which are more environmentally friendly, often with lower density, good specific strength, low cost, and biodegradability (Ngaraja *et al.,* 2024; Puttegawda *et ai.,* 2025). In recent times, many waste materials like fly ash periwinkle shell ash, and ashes produced from various agricultural wastes such as palm oil waste, rice husk ash, corncob ash, millet husk ash, groundnut husk ash have been tried as reinforcing materials in matrices of composites (Olutoge *et al.,* 2013). Also, periwinkles shell is use in applications such as concrete mixing and road maintenance in some localities (Onyechi *et al.,* 2015).

Investigation was carried on effect of mechanical properties on groundnut shell Ash reinforced Al6063. The results revealed that with the percentage reinforcement of groundnut shell ash will increase ultimate tensile strength, compressive strength and hardness of composite (Singh *et al.,* 2015). Furthermore, it was concluded that coconut shell ash can withstand a temperature up to 1500°C with a density of 2.05 g/cm^3 and it is suitable in production of light weight metal matrix composites component with good thermal resistance (Madakson *et al.,* 2012).

The present research work is aimed at using periwinkle shell as reinforcement for Zn-Al matrix composite.

MATERIALS AND METHODS

This section highlights the materials and equipment used for the experimental research together with the experimental procedures involved.

Materials

The materials utilized for the purpose of the experimental research are: - Zinc, Aluminum, Periwinkle shell, Hydrochloric acid and distilled water.

Equipment

Sieves (+45 µm, +53 µm, and +63 µm), wooden moulding flask, crucible furnace, digital weighing balance, hack saw, lathe machine, silicon carbide paper (320 µm, 400 µm, 600 µm and 800 µm), grinding machine and ball mill are used for the development of test samples. Other equipment used for the preparation of test sample include: electronic weighing balance, beakers, measuring cylinder, conical flask, thread, brush and clean cloth.

Production of the Composite

Periwinkle shell was sourced from a local market at Rivers state, Nigeria. The shell was washed with detergent using wire brush to remove the dirts, calcined to remove water. The treated periwinkle shell was ground using ball mill and sieved through three different sieve sizes of +45 µm, +53 µm and +63 µm. The test materials used for the production of the composite in the research are zinc ingot and aluminum and periwinkle shell ash serving as the reinforcement. The mould was made using green sandcasting method; the ZA-27 alloy was melted in crucible furnace together with periwinkle shell ash at temperature of 484^{0}C. The charge calculations for the mass of the materials used are given by these equations:

$$\text{Density} = \frac{mass}{volume} \quad (1)$$

Dimension of pattern used 10mm by 350mm

Density of ZA-27 = 4.73g/cm^3

$$\text{Volume of a bar} = \pi r^2 h \quad (2)$$

$$= \frac{22}{7} \times (5)^2 \times 350 \text{ mm}^3$$

Volume = 27500 mm^3 =27.5cm^3

$$\text{Mass} = \text{density} \times \text{volume} \quad (3)$$

Mass = 4.73 × 27.5

Mass = 130.075 g

200g of ZA-27 was used for casting the composite to take care losses during the production, with zinc having 73% and aluminum 27% of the total mass of the composite matrix. The reinforcing phase of the periwinkle shell ash was varied using five different percentages (2%, 4%, 6%, 8% and 10%) by weight of the matrix for three different sieve sizes of +45µm, +53µm and +63µm. The molten composite was stirred to reduce porosity, refine the microstructure, increased mixability and homogenized the distribution of the reinforcement. It was then poured into the mould and allowed to solidify after cooling.

Preparation of Test Sample for Corrosion Evaluation

The cast composite samples were machined into the required dimension of 9mm x 10mm using lathe machine. 50 samples were ground using different grades of Emery paper (320 µm, 400 µm, 600 µm and 800 µm) to smoothen the samples and remove scales.

Corrosion Test

Prior to the experiment, each of the 45 coupons was weighed using digital weighing balance and tied with thread and accompanied with label on it. 0.5M solution of HCl electrolyte was prepared, stirred thoroughly poured into six (6) different beakers for 0%, 2%, 4%, 6%, 8% and 10% reinforcement. Five (5) coupons were immersed in each beaker with one (1) coupon being removed from each beaker after every 48 hours, washed thoroughly with brush, cleaned with a clean cloth, dried and weighed. The aforementioned procedure was repeated for the remaining four coupons. The test was replicated for three (3) different sieve sizes of +45 µm,+ 53 µm, +63 µm and control sample without reinforcement. In each case, the corrosion rates were computed using equation (3.4) below:

$$\text{CPR} = \frac{87.6\Delta m}{\rho AT} \text{ (mm/yr)} \quad (4)$$

Where:

87.6 = K: constant which depend on system of unit used

CPR: corrosion penetration rate (mm/yr)

ρ: density of the alloy (g/cm^3)

A: area of the coupons (cm^2)

T: exposure time (hours)

The set of data obtained were used to analyzed the corrosion behaviors Zn-Al reinforced periwinkle shell composite and that of unreinforced ZA-27.

RESULTS AND DISCUSSION

The results of the experiment are represented graphically in this section and subsequent discussion and analysis research findings.

Visual Examinations of the Test Coupons

Visual inspection of test coupons reveals the presence of black precipitate at the bottom of the beaker in the electrolyte, this precipitate was less for unreinforced sample compared to the reinforced composite. Furthermore, a reddish-brown precipitate was also observed in the electrolyte for the test samples reinforced with 53µm and 63µm periwinkle shell; this might likely be due to the presence of iron impurities. Visual examinations of the corroded samples suggest uniform corrosion, distributed over the entire surfaces of the samples. Pits were also observed which decreases as exposure time increases. Some gases were evolved immediately after immersing the samples in the electrolyte. The gas might likely be H_2 evolved from the cathodic region; in acid corrosion of substrates, H_2 gas is generally believed to be evolved at the cathode as in equation (7) and (8).

Anodic Reaction

$Zn \rightarrow Zn^{2+} + 2e^-$ (5)

Cathodic reaction

$HCl \rightarrow H^+ + Cl^-$ (6)

$2H^+ + 2e^- \rightarrow H_2$ (7)

Overall reaction

$Zn + 2H^+ \rightarrow Zn^+ + H_2$ (8)

Corrosion Behaviors of Control (Blank)

Generally, minimal corrosion rates were observed/recorded. This might be is due to the presence of aluminum which forms passive layer on the metal surface which inhibits further corrosion attack. As the exposure time was increased, the corrosion rate decreased as shown in Figure 1 below. This is in agreement with Bobic (2009) which states that ZA-27 alloy has excellent corrosion resistance in a variety of environment and corrosion rate decreases with increased exposure time in 0.5M solution HCl. From the Figure it could be seen that the highest corrosion rate was 32.27 mm/yr at 48 hours and the least was 8.45 mm/yr at 240 hours.

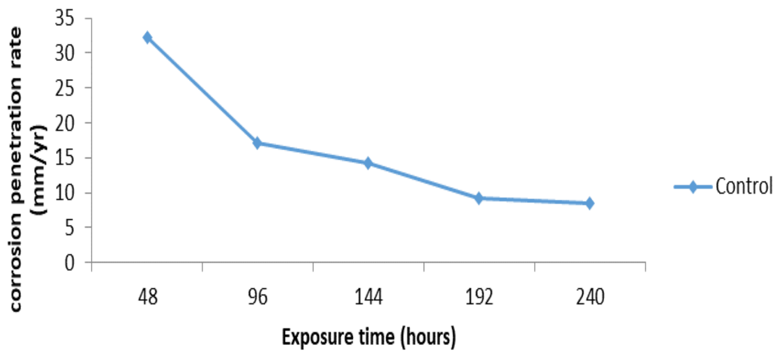

Figure 1: Variation of Corrosion Rate with Exposure Time for Control without Periwinkle Shell Reinforcement

Effect of Periwinkle Shell Ash on ZA-27

Figures 2, 3 and 4 show the effect of periwinkle shell addition on the corrosion rate and it could be seen generally from the Figures that the corrosion rate decreased as percentage reinforcement increases which is in agreement with Shehu (2015) that reinforcement enhance the properties of materials as well as corrosion resistant. From Figure 2, it was observed that decrease in corrosion rate as reinforcement was increased follows a uniform trend with 10% reinforcement deviating from the trend to give record a corrosion rate of 83.73 mm/yr. Similar trend was observed in Figure 4 for 53 µm at 10% reinforcement which might be due to impurities and other unforeseen sources of error. From Figure 4, it could be seen that corrosion rate decreased with increase in percentage reinforcement, samples exposed for 96 hours had the highest corrosion rate and while that exposed for 240 hours had the least corrosion rate. It was thus established that corrosion rate decreases as percentage reinforcement increased.

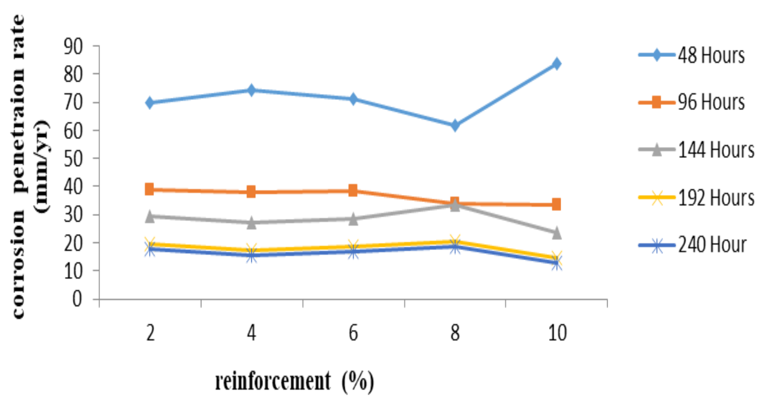

Figure 2: Variation of Corrosion Penetration Rate with Percentage Reinforcement for 45 µm Sieve Size at Various Exposure Times

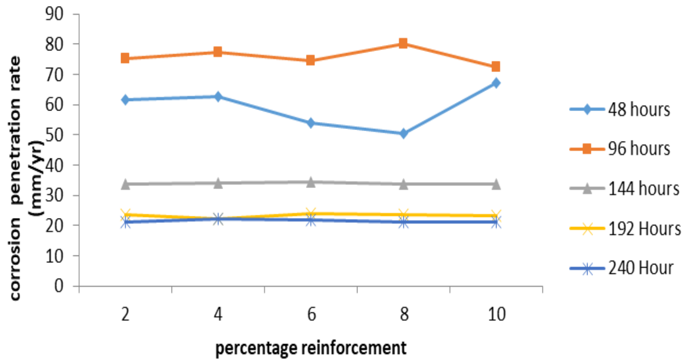

Figure 3: Variation of Corrosion Penetration Rate with Percentage Reinforcement for 53 µm Sieve Size at Various Exposure Times

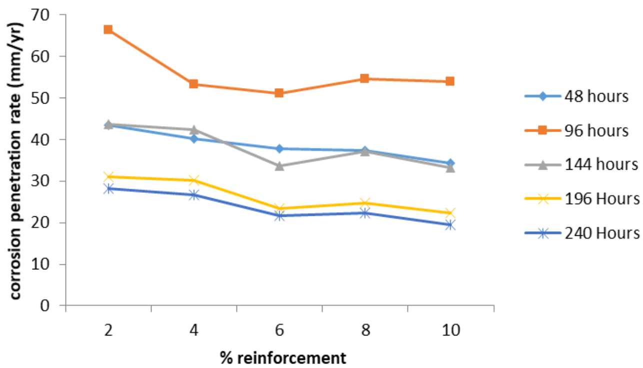

Figure 4: Variation of Corrosion Penetration Against Percentage Reinforcement for 63 µm Sieve Size at Different Exposure Times

Effect of Particle Size on Zinc-Aluminium/Periwinkle Shell Composite in 0.5m HCl

From Figures 5, 6, 7, 8 and 9 it could be observed that the smaller the sieve size the better the corrosion resistance; the finer the ash the greater the corrosion resistance and this might be improvements in other properties as reinforcement sieve size decrease. Results of Figure 6 are also in agreement with the fact that corrosion rate increases as sieves size increases; some deviations from the trend might be due to impurities, concentration of electrolyte or other unforeseen experimental source of error. Only results in Figure 5 deviated from the trend, which showed decrease in corrosion rate as sieve size was increased. It can thus be concluded that composite reinforced with 45 µm had better corrosion resistance than 53 µm and 63 µm sieve size.

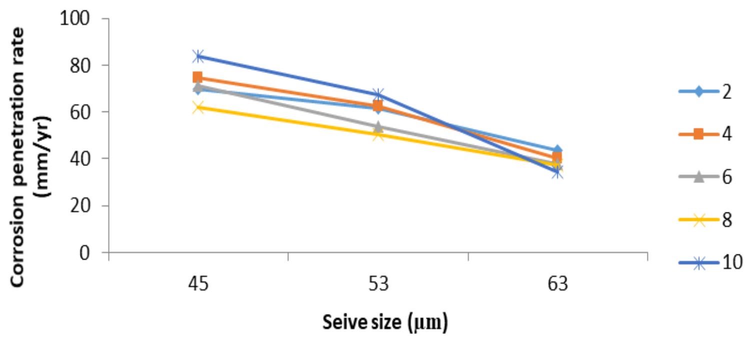

Figure 5: Variation of Corrosion Penetration Rate against Sieve Size at 48 Hours of Exposure Time for Different Percentage Reinforcement

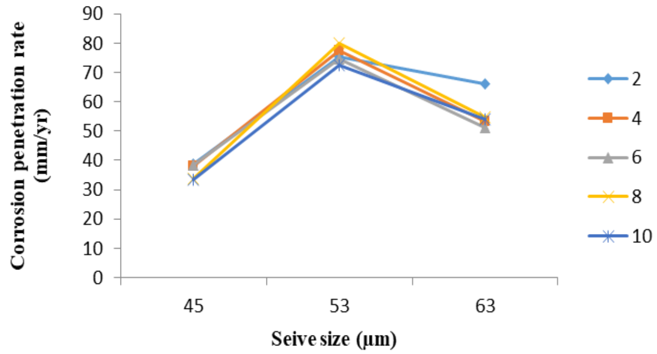

Figure 6: Variation of Corrosion Penetration Rate against Sieve Size at 96 Hours of Exposure Time for Different Percentage Reinforcement

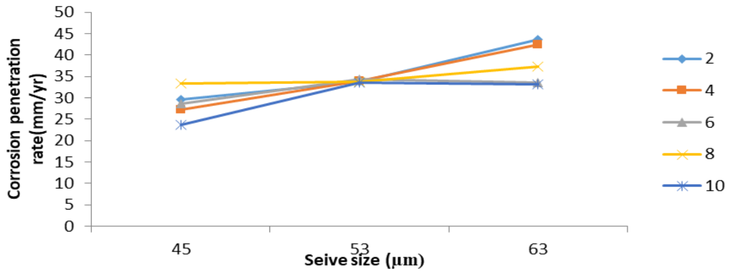

Figure 7: Variation of Corrosion Penetration rate against Sieve Size at 144 Hours of Exposure Time for Different Percentage Reinforcement

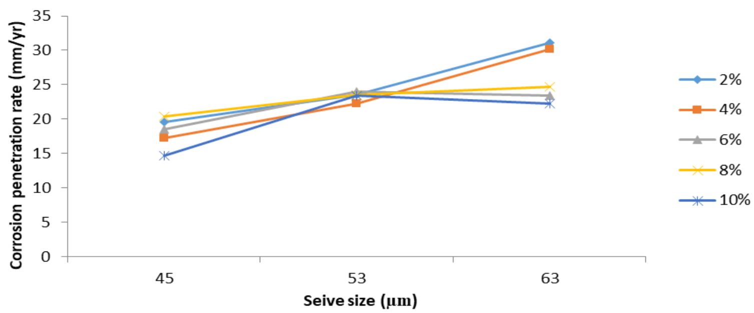

Figure 8: Variation of Corrosion Penetration Rate against Sieve Size at 192 Hours of Exposure Time for Different Percentage Reinforcement

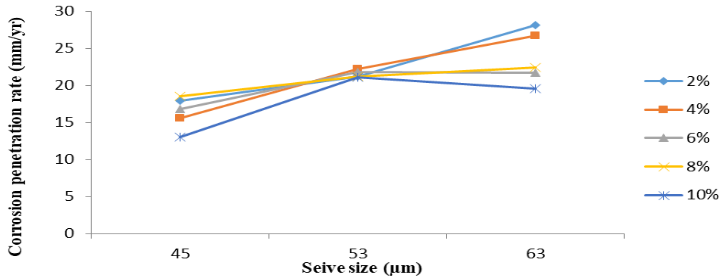

Figure 9: Variation of Corrosion Penetration Rate against Sieve Size at 240 Hours of Exposure Time for Different Percentage Reinforcement

Effect of Exposure Time on Zinc- Aluminium/Periwinkle Shell Composite

The effects of exposure time on the corrosion rates of the test samples are shown in the Figures 10, 11 and 12. It was observed that the corrosion rate decreased with increased exposure time and the un-reinforced (control) had better corrosion resistance than the reinforced composite. Composite reinforced with 45 µm sieve size has the highest corrosion rate of 83.73 mm/yr at 48hours for 10% reinforcement and least corrosion of 8.45 mm/yr for control at 240 hours. Similar trend was observed in Figures 11 and 12 but, with corrosion rate increasing at 96 hours and finally decreasing with increasing exposure time. In all the cases, the control samples had better corrosion resistance than the reinforced composite. Conclusively, corrosion rate decreased with increased in exposure time in 0.5 M HCl electrolyte.

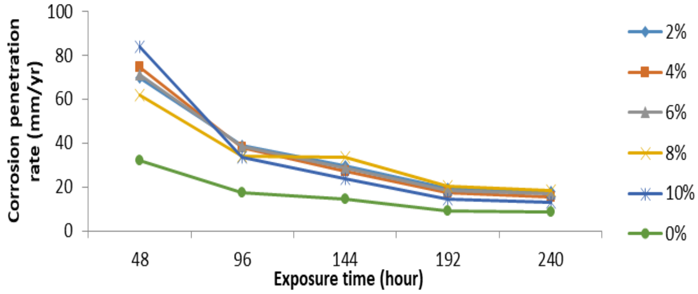

Figure 10: Variation of Corrosion Penetration Rate against Exposure time for 45µm Sieve Size at Different Percentages of Reinforcement

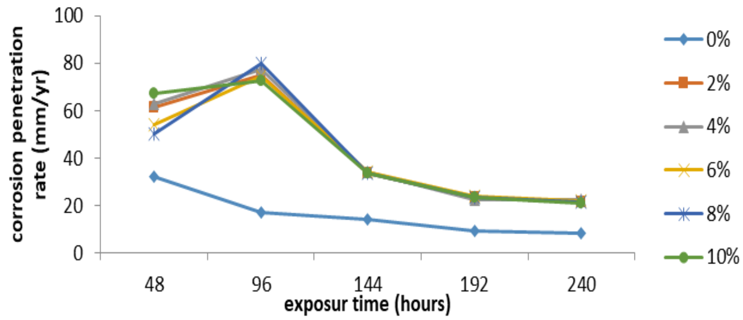

Figure 11: Variation of Corrosion Penetration against Exposure Time for 53 µm Sieve Size at Different Percentages of Reinforcement

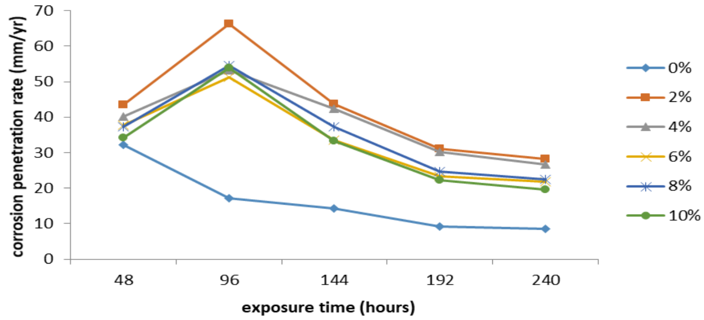

Figure 12: Variation of Corrosion Penetration Rate Against Exposure time for 63 µm Sieve Size at Different Percentages of Reinforcement

CONCLUSION

The corrosion behavior of zinc-aluminum reinforced periwinkle shell composite in 0.5M solution HCl using three different sieve sizes of +45 µm, +53 µm and +63 µm with 2%, 4%, 6%, 8% and 10% reinforcement was evaluated by weight loss. From result obtained, it was concluded that base Alloy (unreinforced ZA-27 alloy) maintains better corrosion resistance than the reinforced composites under the tested conditions. Additionally, within the composite samples, increasing the percentage of periwinkle shell ash from 2% to 10% resulted in a decrease in the corrosion rate and particle Size significantly influences the corrosion behavior; composites produced with +45 µm particles exhibit better resistance than those with +53 µm or +63 µm particles. Finally, the corrosion rate for both the alloy and the composites decreases as exposure time increases in the 0.5 M HCl electrolyte.

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