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Characterization of Waste Eggshells and $CaCO_3$ Reinforced AA2014 Green Metal Matrix Composites: A Green Approach in the Synthesis of Composites

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Three AA2014 alloy metal matrix composites containing reinforcing particles of eggshell, carbonized eggshell and $CaCO_3$ (powder) were processed. The influences of different particle percentage of eggshell were compared with commercial calcium carbonate. The electromagnetic stir casting technique followed by hot extrusion was employed to fabricate metal matrix composite. The results revealed that the tensile strength, hardness and fatigue strength increased by the addition of eggshell particles up to 12.5 wt.% in AA2014 matrix alloy for both carbonized and uncarbonized reinforced composites. Toughness, ductility and corrosion rate decreased by the addition of eggshell particles up to 12.5 wt.% in AA2014 matrix alloy for both carbonized and uncarbonized reinforced composites. Mechanical properties decreased in the addition $CaCO_3$ in AA2014 matrix alloy. After the heat treatment process, mechanical properties further improved for both carbonized and uncarbonized eggshell particles reinforced composites. However, corrosion rate increased. These results showed that using the carbonized eggshell as reinforcement in the AA2014 alloy gave better physical and mechanical properties at lower cost as compared to uncarbonized ES particles and $CaCO_3$. Apparent interfacial reaction layer and minimum corrosion were observed at AA2014/12.5% carbonized eggshell particulate composite. No reaction product was observed at AA2014/$CaCO_3$ particulate metal matrix composite.

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1. Introduction

Metal matrix composites (MMCs) have been studied for some years now and their properties are becoming increasingly well known. Particle-reinforced metal matrix composites have found broad application in various industries, such as automotive, aerospace, marine, nuclear industries and the other applications where low density, high stiffness and good wettability are required. The aluminum matrix composites are used in various engineering applications such as aircraft structures, automobile structures, fuselage structures, under tension cylinder block liners, vehicle drive shafts and automotive pistons.[1-3]

A lot of environment pollution due to the waste of industries/ societies encourages our societies for utilizing these waste products in research areas. More recent advancements involved the use of waste or recycling materials like fly-ash, red mud, rice-hull ash, bagasse ash, basalt fiber, breadfruit seed hull ash, maize stalk waste and eggshells waste particle. These raw materials offer great opportunities because synthesized reinforcements can be produced in situ economically.

Each year, alone the US (united state) food industry generates 150,000 tons of eggshell waste a year. The disposal methods for waste eggshells are 26.6% as fertilizer, 21.1% as animal feed ingredients, 26.3% discarded in municipal dumps and 15.8% used in other ways. Many landfills are unwilling to take the waste because the shells and the attached membrane attract vermin. Together the calcium carbonate eggshell and protein rich membrane are useless. Further, eggshell waste disposal can be costly. Medium-sized egg-product processing plants can generate as much as 7 tons of wet eggshell waste daily in US alone. These eggshells typically are centrifuged, but still contain moisture in the 14-18% range. Many egg-processing plants must rely on the costly hauling of this waste to landfills. Moreover, while waiting for disposal, the messy holding containers exude an unpleasant odor affecting the work environment and neighboring community. It is also not at all unusual that as local landfill sites close, egg processors end up hauling the eggshell waste to ever-more-distant landfills. Eggshell dust can carry into the air (and your lungs, eyes...) whatever bacteria or microbes that have been associated with the egg or shell and may also carry airborne microbes that can therefore enter your lungs or eyes, etc. as you breathe. It is just as dangerous to breathe the dust after it has settled on clothing, furniture, hands, etc. Increased incidence of eye/eyelid infections, chronic sinusitis, lung problems, repeated, persistent or chronic congestion, coughs or colds, aggravation of asthmatic symptoms or emphysema-like symptoms, etc. are only some of the problems reported by eggers around the world.[4-6] Chicken eggshell waste is an industrial byproduct, and its disposal constitutes a serious environmental hazard. Chicken eggshell can be used in commercial products to produce new materials, and it has been highlighted in recent investigation because of its renovation prospective. Even though there have been several attempts to use chicken eggshell components for a variety of applications,[7-13] its chemical composition and accessibility make chicken eggshell a probable source of biofiller - reinforced composites giving additional or improved thermal and mechanical properties. The other advantages of using chicken eggshell are its availability in bulk quantity with lightweight and being economical and environmental friendly.

Although chicken eggshell is the waste product and very hazardous to our society having 94% $CaCO_3$, the question arises, if chicken eggshell contain 94% $CaCO_3$, then why we are not using directly commercial calcium carbonate containing 100% $CaCO_3$ in the fabrication of metal matrix composite.

S. B. Hassan et al.[7] studied the effects of eggshell particles (ES) on the microstructures and properties of Al-Cu-Mg/ES particulate composites. These results showed that using the carbonized eggshell as reinforcement in the Al-Cu-Mg alloy gives better physical and mechanical properties as compared to uncarbonized ES particles. Mechanical results concluded that ES particles upto 12 wt.% can be used to enhance the properties. Patricio Toro et al.[8] used different proportions of chicken eggshell as bio-filler in polypropylene (PP) composite with different particle sizes and proportions. Young's modulus (E) had been improved with the increment of ES content. Munlika Bootklad et al.[10] prepared thermoplastic starch (TPS) using compression molding and chicken eggshell. Libor Severa et al.[11] described the suitability and applicability of the nano indentation method for the determination of the micromechanical properties of a hen's eggshell. Tarig A. Hassan et al.[12] developed a novel combination of mechanochemical and sonochemical to produce high surface area, bio-based calcium carbonate ($CaCO_3$) nano particles from eggshells. Sivarao Subramanian et al.[18] prepared the eggshell by blending and sieving them into granule size of less than 160 μm. The ES filler had improved creep strain and creep modulus for the operating temperatures of 34 degrees Centigrade and 80 degrees Centigrade. M. C. Yew et al.[22] evaluated the effect of chicken eggshell (ES) as a bio-filler on the adhesion strength and thermal stability of acrylic coatings. The improvement in the properties of the coating was attributed to the even distribution of ES particles and better ES/matrix interface. Xia Chen et al.[23] carried out an investigation on solar photocatalytic activity of the TiO_2/Eggshell, TiO_2/Clamshell and TiO_2/$CaCO_3$. Sneha Lunge et al.[24] synthesized a new alumina supported carbon composite material called "Eggshell Composite" (EC) from eggshell waste as calcium source for selective fluoride adsorption from water. EC proved to be a potential, indigenous and economic adsorbent for fluoride removal. E. Mosaddegh[25] prepared the nano eggshell powder by ultrasound irradiation and used as a novel and biodegradable catalyst with high catalytic activity and reusability in green synthesis of 2-aminochromenes via condensation of α- or β-phathol, malononitrile and aromatic aldehydes at 120°C under solvent-free conditions.

Table 1 Chemical composition of AA2014 alloy (wt %)

Si	0.5-0.9
Fe	0.5
Cu	3.9 – 5.0
Mn	0.4-1.2
Mg	0.2-0.8
Zn	0.25
Ti	0.2
Ni	0.1
Cr	0.1
Al	Balance

Table 2 Measured properties of AA2014 alloy

Melting point	640°C
Density (g/cm^3)	2.8
Tensile strength (MPa)	185
Hardness (BHN)	60
Toughness (Joule)	12
Ductility (percentage elongation)	13
Fatigue strength (MPa) for 1×10^7 cycles	90

On the basis of literature review, it is found that very few researchers have compared the mechanical and physical properties of AA2014/eggshells green metal matrix composite with commercial reinforced metal matrix composite. Since, Presence of Mg (about 0.8%) in AA2014 alloy improves the wettability with eggshell particles ($CaCO_3$). Hence, in view of the above facts, an investigation was carried out to observe the feasibility to produce AA2014/carbonized eggshell green metal matrix composites by using electromagnetic stir casting process. For the comparison of the mechanical properties, microstructure (particles distribution and pores) and interface of AA2014/carbonized eggshell metal matrix composites, other two composites AA2014/uncarbonized green eggshell metal matrix composites and AA2014/commercial $CaCO_3$ metal matrix composites were produced by using the electromagnetic stir casting process.

2. Materials and Methods

2.1 Matrix material

AA2014 is a high strength and fully heat-treated (solution heat-treated & artificially aged) containing 4 to 5% copper. Machinability of AA 2014 alloy is very good. Typical applications of aluminium alloy 2014 are high strength components especially for use in the aerospace and defense industries.

AA2014 alloy reinforced with eggshell is, furthermore, exploited in high temperature applications for example in automobile engines and in other rotating and reciprocating parts such as brake- rotors, drive shafts, piston and in other structural parts which require light weight and high strength materials. Its chemical composition and mechanical properties

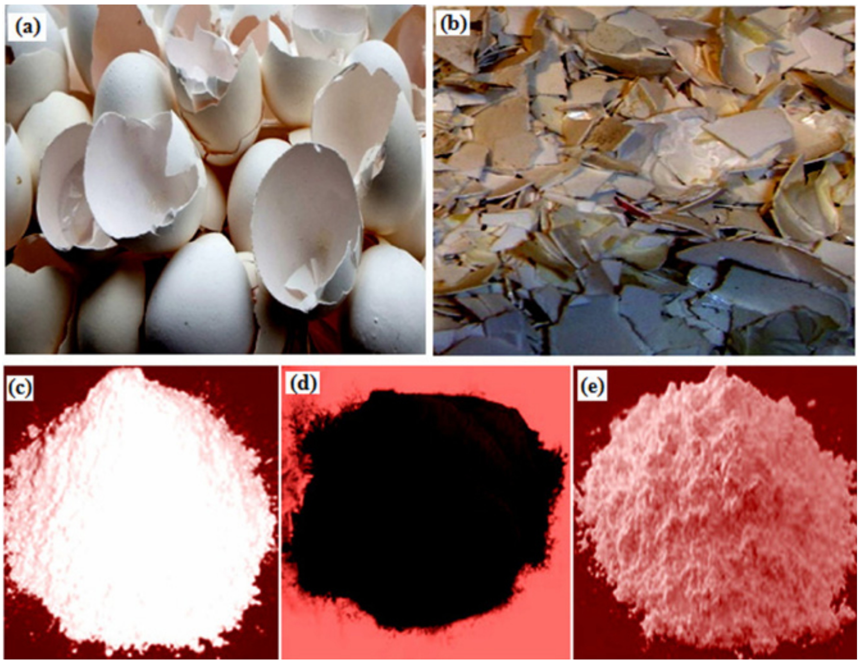

Fig. 1 Photograph of; (a) hen eggshells, (b) dried eggshells, (c) uncarbonized eggshells powder, (d) carbonized eggshells powder, (e) $CaCO_3$ powder

are given in Table 1 and 2 respectively:[14,15]

2.2 Reinforcement material

Three different particles commercial $CaCO_3$, uncarbonized eggshell and carbonized eggshell were used as reinforcement in AA2014 aluminium alloy matrix. For preparing the uncarbonized eggshell and carbonized eggshell reinforcements, hen eggshell was cleaned and dried in sun to eliminate the covering layer of eggshell as shown in Figs. 1(a)-(b). The dried eggshell was ball milled to obtain the eggshell powder (Fig. 1(c)). After that, it was carbonized to 500°C for 3 h to remove the carbonaceous materials as shown in Fig. 1 (d). Elemental analysis of carbonized powder shows a high level of Ca (39%), O (47%), and C (13%) with little quantity of Mg (0.62%), K (0.19%), Na (0.09%), and P (0.02%). The densities of uncarbonized and carbonized eggshell particles are 2.47 g/cm^3 and 2.0 g/cm^3.[16,17] The density of commercial $CaCO_3$ particles is 2.71 g/cm^3. Therefore, the waste eggshell can be considered carbonate based material from chemical and physical viewpoint. Photograph of commercial $CaCO_3$ powder was shown in Fig. 1(e).

SEM image of reinforcement particles morphology are shown in Fig. 2. Commercial $CaCO_3$ particles are of spherical morphology (Fig. 2(a)), uncarbonized eggshells particles are of spherical morphology (Fig. 2(b)) and carbonized eggshells particles are flake shaped (Fig. 2(c)). XRD pattern of the commercial $CaCO_3$ powder, uncarbonized eggshell powder and carbonized eggshell powder were carried out to identify the composition of reinforcement particles. The XRD analysis of commercial $CaCO_3$ in Fig. 3 confirms the presence of $CaCO_3$, while the XRD analysis of uncarbonized eggshell powder and carbonized eggshell powder in Figs. 4 and 5 confirms the presence of $CaCO_3$ and Mg. The amount of $CaCO_3$ is the highest about 94%, followed by little amount of Mg.

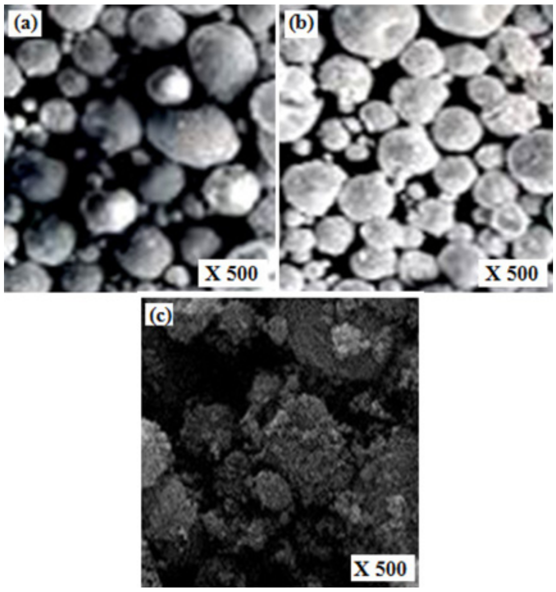

Fig. 2 SEM morphology of (a) commercial $CaCO_3$ powder, (b) uncarbonized eggshell powder and (c) carbonized eggshell powder

2.3 Experimental procedure

Three different particles commercial $CaCO_3$, uncarbonized eggshell and carbonized eggshell were used as reinforcement in AA2014 aluminium alloy matrix. The reinforcing particles uncarbonized eggshell and carbonized eggshell were preheated at 600°C for 1 in air, to increase their surface reactivity, while commercial $CaCO_3$ was preheated at 300°C for 1 h. The details of fabrication procedure of metal matrix composite by electromagnetic stir casting technique are given elsewhere.[18] The electromagnetic stir casting parameters are

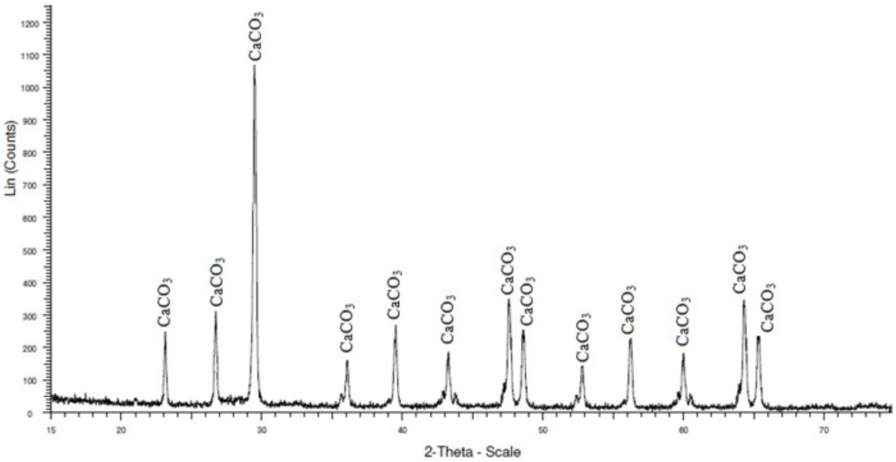

Fig. 3 Typical XRD spectrum of commercial $CaCO_3$ powder consisting of about 99 % $CaCO_3$

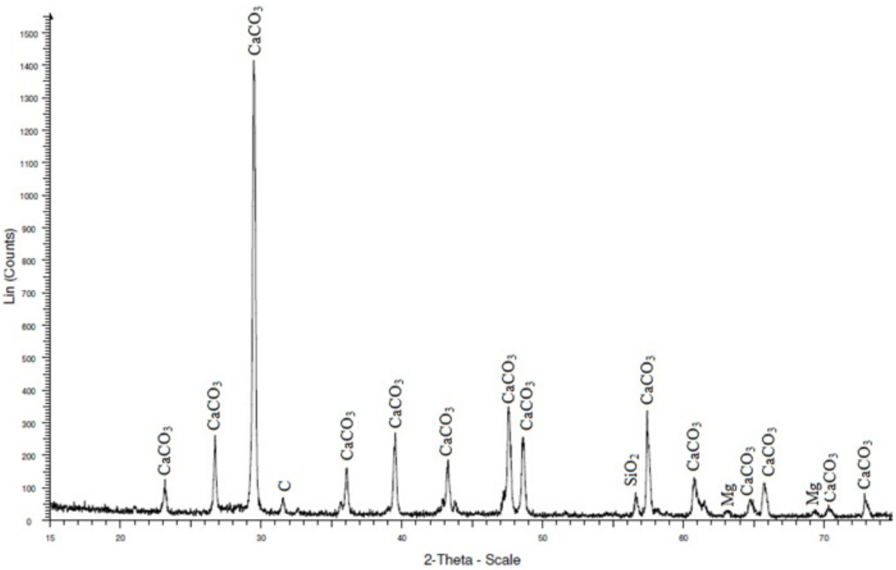

Fig. 4 Typical XRD spectrum of uncarbonized eggshell powder consisting of about 94 % $CaCO_3$

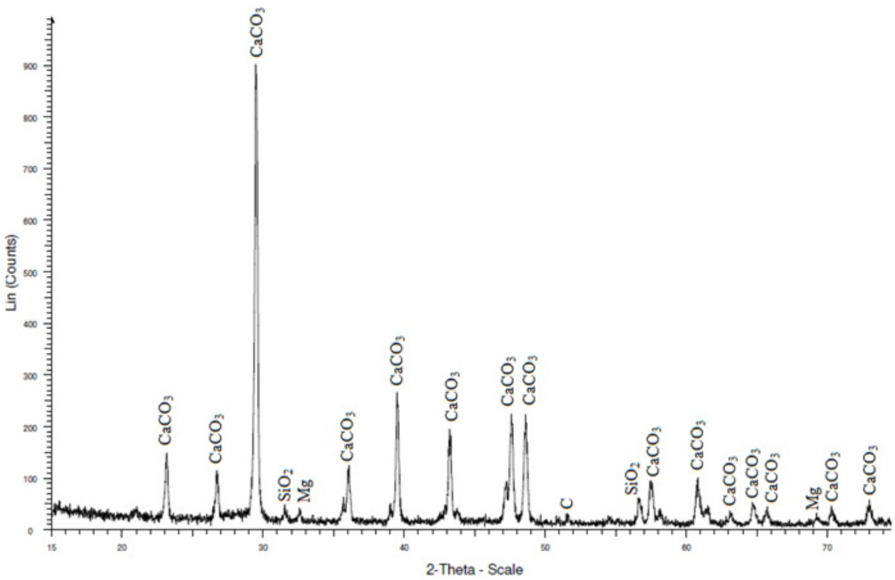

Fig. 5 Typical XRD spectrum of carbonized eggshell powder consisting of about 94 % $CaCO_3$

Table 3 Electromagnetic stir casting process parameters

S.No	Parameters	Values set as
1	Current	12 Ampere
2	Stirring time	180 seconds
3	Matrix pouring temperature	700°C
4	Percentage of commercial $CaCO_3$	0-15
5	Percentage of uncarbonized eggshell	0-15
6	Percentage of carbonized eggshell	0-15

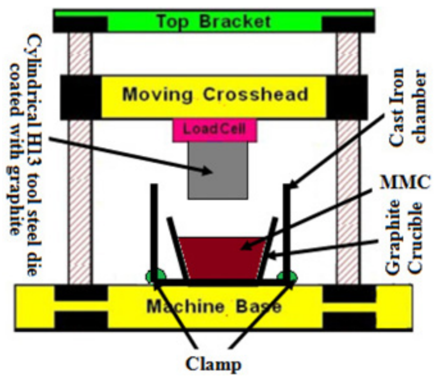

Fig. 6 Schematic diagram of squeeze casting process on UTM

presented in Table 3.

To reduce the porosity of the cast composites and to improve the particle distribution within Al matrix, the cast composites were subjected to hot extrusion. The melt composite was transferred to the cast iron chamber, which was clamped with machine base of universal testing machine (UTM). The cylindrical die punch was used to apply high squeeze pressure (60MPa) to the melt. The pressure was applied in mushy zone to eliminate the porosity and solidification shrinkage as shown in Fig. 6. Cylindrical H13 tool steel die coated with graphite (avoid any type of chemical reactions with MMC) was attached with load cell on the moving cross head of UTM. Before attaching to UTM, die was preheated about 3500°C. After the solidification, the prepared samples were removed from the crucible. Upper and lower regions of each sample were removed. The samples for further study were selected from the middle regions of the composites.

2.4 Precipitation hardening process

Precipitation hardening is a heat treatment technique used to increase the yield strength as well as other properties of composites. The process of precipitation hardening is actually a three step sequence. The orders of involved heat treatment process were solutionizing, hot bath quenching, aging and air-cooling as shown in Fig. 7.

The first step is known as solution treatment which was used to remove the room-temperature structure and redissolves any existing precipitate. Solutionizing process was done at a temperature of 530°C for 4.5 hour and then quenched in a hot bath about 70°C to keep away from warping of composite specimens. If the composite were slow cooled, the second – phase precipitate would nucleate and material would revert back to a structure similar to equilibrium. To prevent this from happening, the solutionized composites were quenched from their solution treatment temperature. Without delay (not more than 15

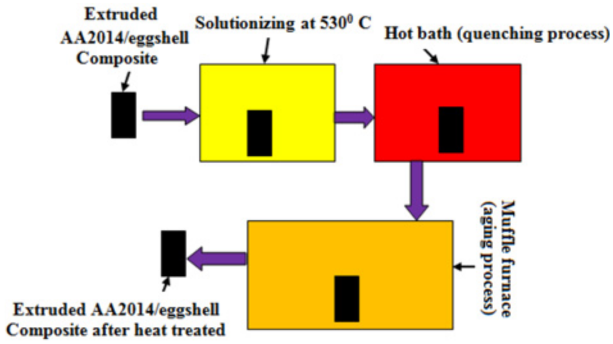

Fig. 7 Schematic diagram of precipitation hardening process

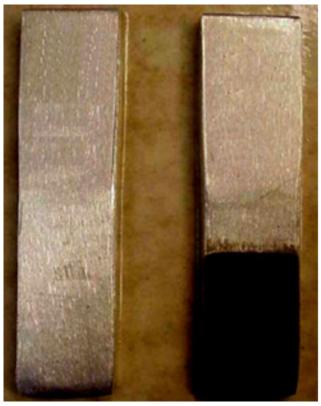

Fig. 8 Before and after corrosion test samples

seconds), artificially aging was carried out in a muffle furnace (250°C) for 13.5 hour.

2.5 Corrosion test

Corrosion test of all fabricated metal matrix composite were carried out in high alkalinity bath tub. All samples of composites were immersed in high alkalinity bath tub at room temperature for 120 hours in 3.5 wt.% NaCl aqueous solution. Corrosion rate was calculated assuming uniform corrosion over the entire surface of the composites. The corrosion rate in millimeters per year (mmy) was calculated from the weight loss using the given equation. The constant (K) could be varied to calculate the corrosion rate in Corrosion Rate (CR) = (Weight loss (g) * K) / (Alloy Density (g/cm^3) * Exposed Area (A) * Exposure Time (hr)) various units:[19,20]

Where, K = 8.75 × 10^4, Exposed area A = 9 cm^2, Exposure time = 120 hours

2.6 Porosity Analysis

The experimental densities of the composites were determined by means of the Archimedes principle. The theoretical densities of composites were calculated using a rule of mixtures. Porosity reflects the compactness of materials. Porosity and characteristics of pores (including size, connectivity, distribution, etc.) affect the properties of materials greatly. Porosity (P) is the percentage of the pores volume to the total volume with the volume of a substance.[18] It is defined by

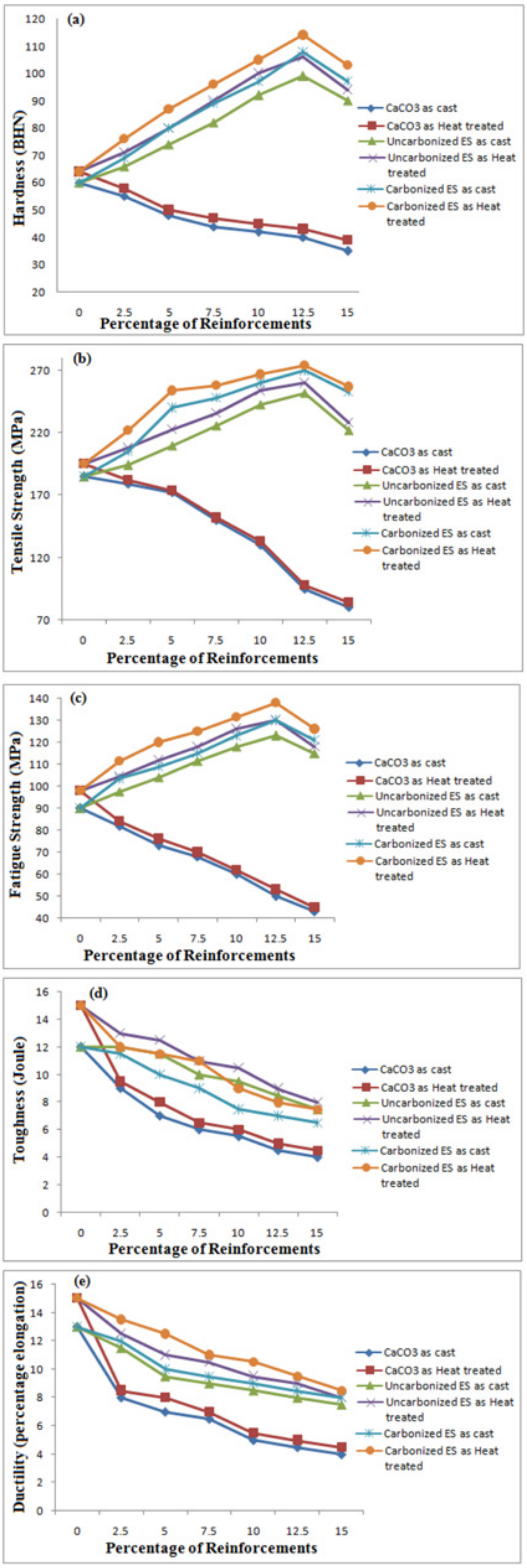

Fig. 9 Mechanical properties of metal matrix composites

$$P = (1 - \rho_{exp.} / \rho_{theo.}) \times 100\% \quad (1)$$

Where, P = Percent porosity, $\rho_{exp.}$ = Experimental density, $\rho_{theo.}$ = Theoretical density.

3. Results and Discussion

3.1 Evaluation of mechanical properties

The hardness of metal matrix composites increased up to 12.5 wt.% percentage of carbonized and non carbonized eggshell (ES) particles addition in the AA2014 alloy. The hardness values increased from 60 BHN at 0 wt.% to 99 BHN at 12.5 wt.% for uncarbonized eggshell particles and 108 BHN at 12.5 wt.% for carbonized eggshell particles respectively. These increments are certified to an increase of the weight percentage of hard and brittle phases of the eggshell particles in the AA2014 alloy. This hardness of the eggshell particles is obtained from $CaCO_3$, C and SiO_2 of the chemical made up of the particles (Figs. 4 and 5). The hardness values decreased beyond the 12.5 wt.% addition of eggshell particles for both carbonized and non carbonized metal matrix composites as shown in Fig. 9(a). As the amount of added eggshell particles increases (beyond 12.5 wt.%), the amount of trapped air increases thereby increasing the amount of pores resulting mechanical properties decrease. After the heat treatment process, hardness of the carbonized and non carbonized reinforced metal matrix composites is further improved. The hardness values of AA2014 aluminium alloy continuously decreases by the addition of commercial $CaCO_3$ powder as shown in Fig. 9(a). This result shows that $CaCO_3$ powder is not acceptable as a reinforcement material due to low wettability property of $CaCO_3$ powder with aluminium alloy while it containing about 99% $CaCO_3$.

The tensile strength increased with increasing percentage of eggshell particles up to 12.5 wt.% in the AA2014 alloy (Fig. 9(b)). Tensile strength increased from 185 MPa at 0 wt.% to 252 MPa and 270 MPa for uncarbonized and carbonized eggshell particles, respectively. The increases in tensile strength with percent eggshell particles additions up to 12.5 wt.% are due to the formation of nearly uniform distribution of eggshell particles in the AA2014 aluminium alloy matrix. It was observed that after 12.5 wt.% of eggshell powder, tensile strength of metal matrix composite began to decrease. This may also account for the poor distribution and dispersion of the eggshell particles in the AA2014 alloy matrix resulting in weak particles- matrix interaction for 15 wt.% of eggshell reinforcement. This poor particles distribution reduces the particles-matrix interaction and as a result decreases the tensile strength. After the heat treatment, tensile strength of uncarbonized and carbonized reinforced metal matrix composites is further improved. It is found that the addition of eggshell particles has a significant effect on the tensile properties. Improvement in tensile strength after heat treatment may be due to the AA2014/eggshell composite strengthening that might have occurred following a reduction in composite grain size and the generation of a high dislocation density. Tensile strength decreased from 185 MPa to 80 MPa due to low wettability property of commercial $CaCO_3$ powder as shown in Fig. 9(b).

Fatigue strength also increased up to 12.5 wt.% of eggshell particles for both uncarbonized and carbonized reinforcement particles as shown in Fig. 9(c). After the heat treatment, tensile strength increased from 90 MPa at 0 wt.% of eggshell to 130 MPa and 138 MPa for uncarbonized and carbonized eggshell particles, respectively. The Toughness and Ductility decreased as the percent eggshell particles and commercial CaCO3 powder addition increases in the composites as shown in Fig.

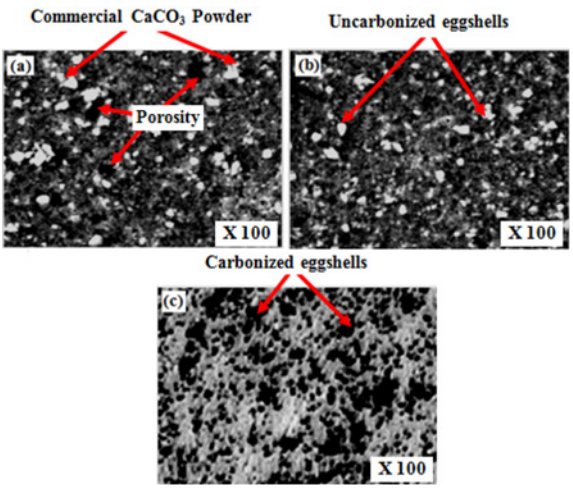

Fig. 10 Microstructure of reinforced; (a) 12.5 wt.% commercial $CaCO_3$ powder, (b) 12.5 wt.% uncarbonized eggshell powder and (c) 12.5 wt.% carbonized eggshell powder

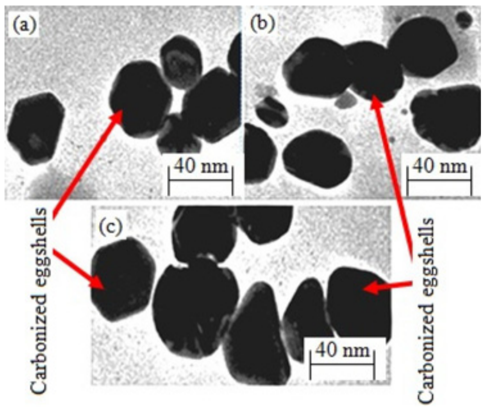

Fig. 11 TEM image of AA 2014/12.5 wt.% carbonized eggshells MMCs

9(d) and Fig. 9(e). The brittle character of the eggshell particle plays a significant role in reducing the toughness and ductility of the composites.

3.2 Analysis of MICROSTRUCTURE

The maximum mechanical properties of AA2014/eggshells particulate metal matrix were observed at 12.5 wt.% for both carbonized and uncarbonized eggshells. Fig. 10 displays the microstructures of AA2014 matrix composites reinforced with 12.5 wt.% commercial $CaCO_3$ powder, 12.5 wt.% uncarbonized eggshell powder and 12.5 wt.% carbonized eggshell powder respectively. The microstructure of AA2014/12.5 wt.% uncarbonized eggshell particulate metal matrix composite looks similar to that of AA2014/12.5 wt.% commercial $CaCO_3$ metal matrix composite in terms of distribution, with slightly lower amount of overall porosity. The microstructure of AA2014/12.5 wt.% carbonized eggshell particulate metal matrix composite presented a better result with respect to porosity than both above composites. Since carbonized eggshell particles is very good reactive to air at elevated temperature, the air trapped with carbonized eggshell particles reacts with carbonized eggshell inside the AA2014 melt. Resulting very few amounts of porosity develop in AA2014/carbonized eggshell particulate metal matrix composite. Among the three composites, particle distribution in AA2014/carbonized eggshell particulate metal matrix composite is found to be better.

Since, maximum mechanical properties were observed for AA2014/12.5 wt.% carbonized eggshell metal matrix composite. Hence, in view of the above facts, a TEM image was also carried out to observe the distribution and wettability of carbonized eggshells in matrix alloy. TEM image (Fig. 11) of AA 2014/12.5 wt.% carbonized eggshells metal matrix composite shows proper wettability between AA2014 aluminium alloy and carbonized eggshell particles.

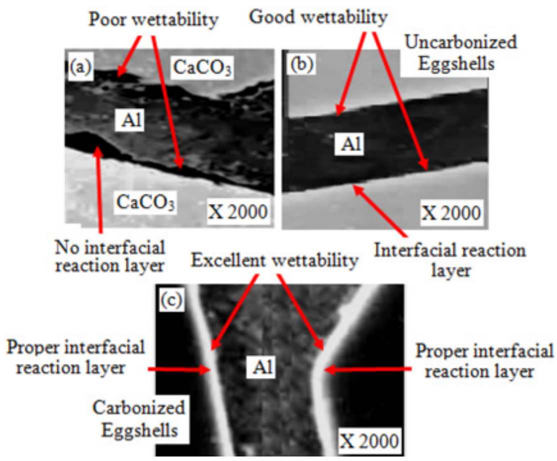

Fig. 12 Interfacial reaction layer of reinforced; (a) commercial $CaCO_3$ powder, (b) uncarbonized eggshell powder and (c) carbonized eggshell powder

3.3 Interface characteristics

Fig. 12 shows the interfacial reaction layer of AA2014 matrix composites reinforced with commercial $CaCO_3$ powder, uncarbonized eggshell powder and carbonized eggshell powder respectively. An interaction layer was found at the interface of AA2014/uncarbonized eggshell and AA2014/carbonized eggshell composites, while none was found at the interface of AA2014/commercial $CaCO_3$ powder. Since carbonized eggshell particles are very good reactive to air at elevated temperature, the air trapped with carbonized eggshell particles reacts with carbonized eggshell inside the AA2014 melt. As a result, excellent wettability can be observed at the interface of AA2014/carbonized eggshell particulate metal matrix composites.

3.4 Density and porosity analysis

Table 4 shows the theoretical and experimental density of composites. Theoretical density was calculated with the help of rule of mixture. Theoretical density of AA2014/12.5 wt.% carbonized eggshell was calculated as given below.

Density of AA2014/12.5wt.%carbonized eggshell

$$= 0.875 \times \text{density of AA2014} + 0.125 \times \text{density of eggshell}$$
$$= 0.875 \times 2.8 + 0.125 \times 2 = 2.7 \text{ g/cm}^3$$

Table 4 Theoretical and experimental density of Commercial $CaCO_3$, Uncarbonized Eggshell and carbonized Eggshell

Percentage of reinforcement	Commercial $CaCO_3$		Uncarbonized eggshell		Carbonized eggshell	
	Theo. density	Expe. densiy	Theo. density	Expe. densiy	Theo. density	Expe. densiy
0	2.8	2.78	2.8	2.78	2.8	2.78
2.5	2.798	2.66	2.792	2.74	2.78	2.75
5	2.796	2.65	2.784	2.73	2.76	2.74
7.5	2.793	2.62	2.775	2.71	2.74	2.72
10	2.79	2.58	2.767	2.70	2.72	2.70
12.5	2.789	2.56	2.759	2.69	2.70	2.69
15	2.787	2.50	2.751	2.65	2.68	2.60

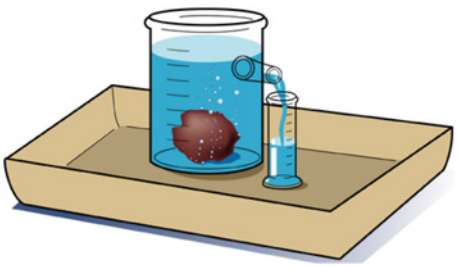

Fig. 13 Volume measurement of composites

Same course of action was conducted to calculate theoretical density of other compositions. Experimental density was calculated by Archimedes principle. To calculate the experimental density, first mass of the composite was measure. Volume of the composite was measure as shown in Fig. 13. After calculating the both values, experimental density was calculated by given formula.

Experimental density of composite = mass of composite/Volume

Porosity (P) is the percentage of the pores volume to the total volume with the volume of a substance. It is defined by

$$P = (1 - \rho_{exp.} / \rho_{theo.}) \times 100\%$$

Where, P = Percent porosity, $\rho_{exp.}$ = Experimental density, $\rho_{theo.}$ = Theoretical density

Porosity of AA2014/12.5wt.%carbonized eggshell (P)
= (1 − 2.69/2.70) × 100 = 0.37%

Same course of action was conducted to calculate porosity of other compositions. In the present investigation, black deviation bars between theoretical density and experimental density are showing percent porosity as shown in Fig. 14. Figs. 14(b) and 14(c) show that both the theoretical and the experimental densities decreased with increasing percentage additions of uncarbonized and carbonized eggshell particles. Theoretical densities of uncarbonized and carbonized eggshell particles were 2.47 and 2 g/cm^3, respectively. The overall theoretical density of AA2014/Eggshell particulate composites decreased with wt.% additions of eggshell particles e.g., the theoretical density of the composites decreased from 2.8 g/cm^3 at 0 wt.% to 2.759 g/cm^3 and 2.70 g/cm^3 at 12.5 wt.% for uncarbonized and carbonized ES particles, respectively.

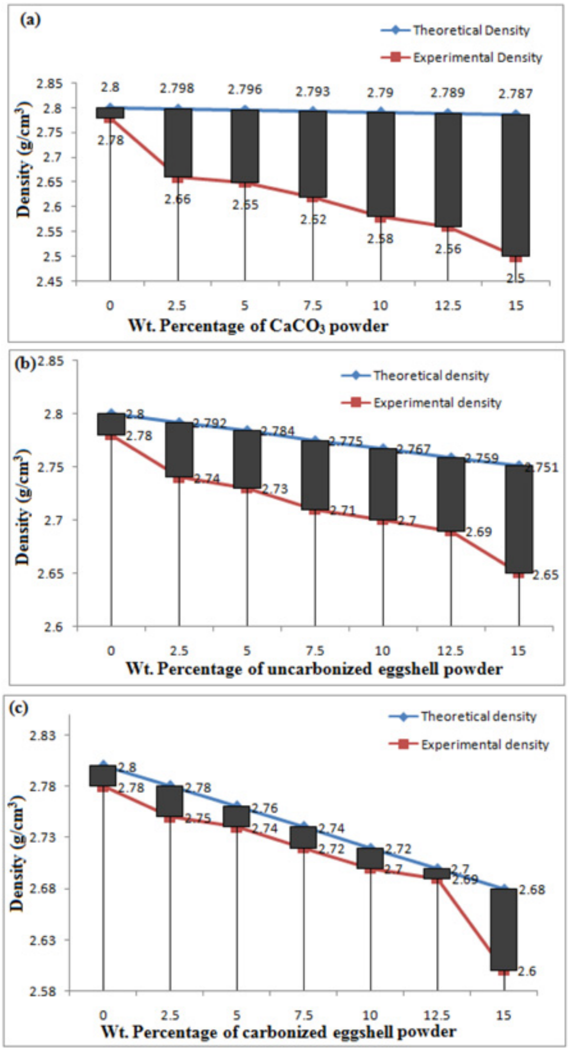

Fig. 14 Density and porosity analysis of reinforced; (a) commercial $CaCO_3$ powder (b) uncarbonized eggshell powder and (c) carbonized eggshell powder

The experimental density of the composites decreased from 2.78 g/cm^3 at 0 wt.% to 2.69 g/cm^3 and 2.69 g/cm^3 at 12.5 wt.% for uncarbonized and carbonized ES particles, respectively This shows that composites with light weight can be made with eggshell particles.

The composition AA2014/12.5% carbonized eggshell particulate metal matrix composite shows better mechanical properties as discussed above. Percent porosity for different compositions is shown in Fig. 13

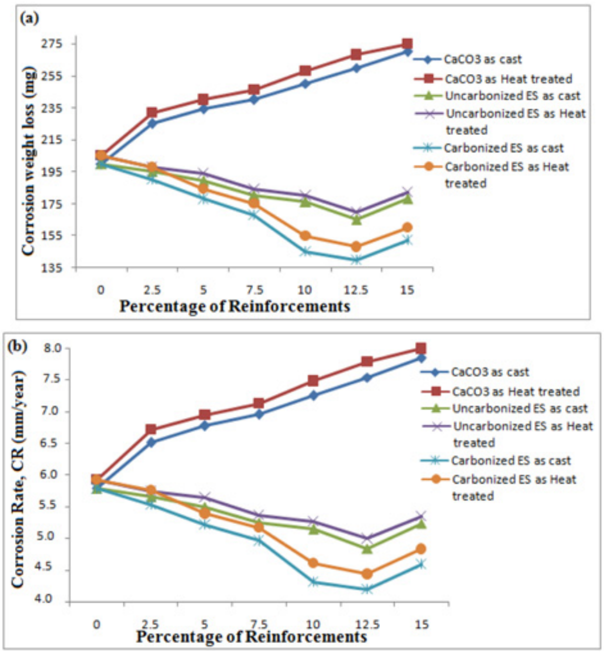

Fig. 15 Corrosion behaviour of metal matrix composites

with down bars. Based on porosity measurement, it can be concluded that porosity content increases linearly with increasing wt.% of $CaCO_3$ powder. Higher percentage of porosity produced inhomogeneous cast MMC consisting particle clusters which lead to specimen failure. Minimum porosity was found to be 0.37% for AA2014/12.5% carbonized eggshell particulate metal matrix composites as shown in Fig. 14(c).

3.5 Corrosion behaviour

Corrosion weight loss and corrosion rate of metal matrix composites increased up to 15 wt.% percentage of commercial $CaCO_3$ particles addition in the AA2014 alloy. The corrosion weight loss increased from 200 mg at 0 wt.% to 270 mg at 15 wt.% for commercial $CaCO_3$ particles and corrosion rate increased from 5.79 mm/year at 0 wt.% to 7.85 mm/year respectively. Corrosion weight loss and corrosion rate of AA2014 aluminium alloy continuously decreases by the addition of uncarbonized eggshell particles and carbonized eggshell particles powder as shown in Fig. 15. The corrosion rate decreased from 5.79 mm/year at 0 wt.% to 5.24 mm/year at 12.5 wt.% for commercial uncarbonized eggshell particles and corrosion rate decreased from 5.79 mm/year at 0 wt.% to 4.6 mm/year respectively for carbonized eggshell particles. After the heat treatment process, corrosion weight loss and corrosion rate of metal matrix composites reinforced with $CaCO_3$ powder, uncarbonized eggshell powder and carbonized eggshell powder further increased.

3.6 XRD analysis

Figs. 16 and 17 show XRD analysis results for AA2014/12.5 wt.% uncarbonized eggshells particulate composite and AA2014/12.5 wt.% carbonized eggshells particulate composite respectively. XRD analysis was carried out to recognize the different elements and phases present in the composites. The XRD analysis of the AA2014/12.5 wt.% uncarbonized eggshells and AA2014/12.5 wt.% carbonized eggshells show the presence of $CaCO_3$, Al_2O_3, Al, MnO_2, Cu, $CaSiO_3$ and Mg_2SiO_4 phases.

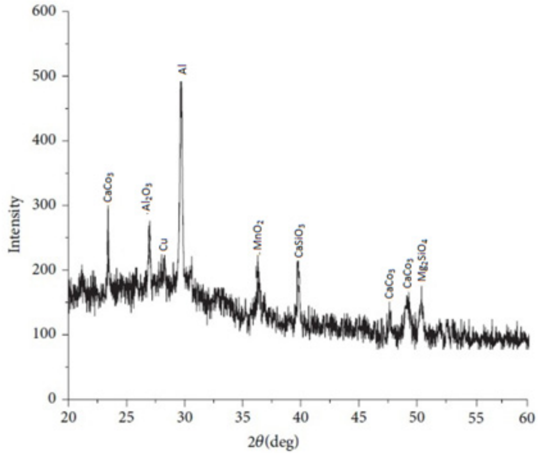

Fig. 16 XRD Analysis of AA2014/12.5 wt.% uncarbonized eggshell composites

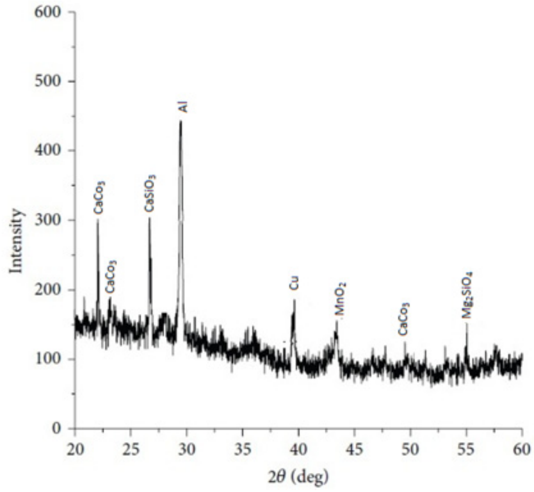

Fig. 17 XRD Analysis of AA2014/12.5 wt.% carbonized eggshell composites

Table 5 Cost of metal matrix composite in Indian Rupees (INR)

Percentage of reinforcement	Commercial $CaCO_3$	Eggshell particles
0	300	300
2.5	293.75	292.5
5	287.5	285
7.5	281.25	277.5
10	275	270
12.5	268.75	262.5
15	262.5	255

3.7 Cost estimation

The cost of AA2014 is about 300 INR, while the cost of commercial $CaCO_3$ powder is 50 INR. The eggshell particles are available as a waste, so the eggshell particles are available free of cost. Cost of AA2014/

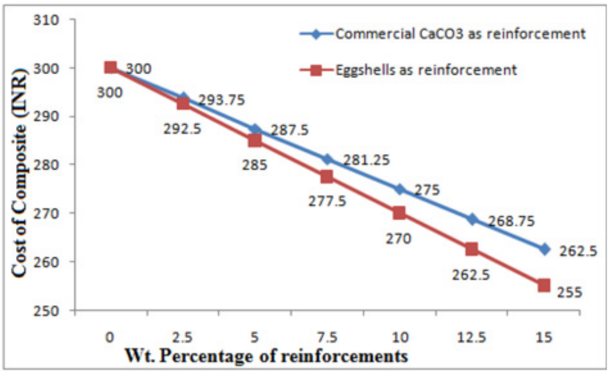

Fig. 18 Cost estimation of metal matrix composites

12.5 wt.% eggshell composite is estimated 262.5 INR. Cost of metal matrix composite with 12.5 wt.% eggshells particulate was found about 12.5% lower than the AA2014.

4. Summary and Conclusions

Eggshell particles are dangerous to breathe the dust after it has settled on clothing, furniture, hands, etc. Increased incidence of eye/eyelid infections, chronic sinusitis, lung problems, repeated, persistent or chronic congestion, coughs or colds, aggravation of asthmatic symptoms or emphysema-like symptoms, etc. are some of the other problems occurs due to eggshell particles. Further, eggshell waste disposal are very costly. For utilizing these eggshell particles, in the present investigation, eggshell waste particles were used for the fabrication of green aluminum metal matrix composites. AA2014/ $CaCO_3$ and AA2014/eggshell metal matrix composites with different weight fractions of reinforcement particles were prepared using electromagnetic stir casting technique followed by squeeze pressure. From the results, following conclusions may be derived.

1. Eggshell particles can be adapted favorably for the fabrication of green AA2014/ eggshells particulate metal matrix composites as a reinforcement material, while commercial $CaCO_3$ powder cannot be used as a reinforcement material in aluminium alloy matrix.

2. Particles distribution was found to be better in AA2014/ uncarbonized composites and AA2014/carbonized composites as compared to AA2014/$CaCO_3$ composites. A clear interfacial reaction product was found at AA2014/carbonized composites interface, while no reaction product was observed at AA2014/$CaCO_3$ composites interface.

3. Results of XRD showed the presence of $CaCO_3$, Al_2O_3, Al, MnO_2, Cu, $CaSiO_3$ and Mg_2SiO_4 phases in MMC.

4. Hardness, tensile strength and fatigue strength were improved about 80%, 45.94% and 53.33% respectively by addition of 12.5 wt.% carbonized eggshells particles in AA2014 alloy, while toughness and ductility were reduced. Further, increasing the weight fraction of eggshells particles in AA2014 alloy, mechanical properties (hardness, tensile strength and fatigue strength) keep decreasing and it is the lowest at 15% weight fraction, while mechanical properties were reduced continuously by addition of commercial $CaCO_3$ powder. Corrosion rate continuously decreases with the addition of eggshell particles in AA2014 aluminium alloy. However, after the heat treatment process, mechanical properties and corrosion rate further increase.

5. The experimental density and cost of metal matrix composite with 12.5 wt.% carbonized eggshells particulate were found to be 3.92% and 12.5% respectively lower than the matrix material (AA2014). The minimum porosity is observed for AA2014/12.5 wt.% carbonized eggshell particulate metal matrix composites.

REFERENCES

1. Kumaran, S. T. and Uthayakumar, M., "Investigation on the Dry Sliding Friction and Wear Behavior of AA6351-SiC-B_4C Hybrid Metal Matrix Composites," Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology, Vol. 228, No. 3, pp. 332-338, 2014.

2. Peng, Z. and Fuguo, L., "Micro-Macro Unified Analysis of Flow Behavior of Particle-Reinforced Metal Matrix Composites," Chinese Journal of Aeronautics, Vol. 23, No. 2, pp. 252-259, 2010.

3. Alaneme, K. K., Akintunde, I. B., Olubambi, P. A., and Adewale, T. M., "Fabrication Characteristics and Mechanical Behaviour of Rice Husk Ash-Alumina Reinforced Al-Mg-Si Alloy Matrix Hybrid Composites," Journal of Materials Research and Technology, Vol. 2, No. 1, pp. 60-67, 2013.

4. Hecht, J., "Eggshells Break into Collagen Market," New Scientist, Article No. 2170, 1999.

5. Daengprok, W., Garnjanagoonchorn, W., and Mine, Y., "Fermented Pork Sausage Fortified with Commercial or Hen Eggshell Calcium Lactate," Meat Science, Vol. 62, No. 2, pp. 199-204, 2002.

6. Wei, Z., Xu, C., and Li, B., "Application of Waste Eggshell as Low-Cost Solid Catalyst for Biodiesel Production," Bioresource Technology, Vol. 100, No. 11, pp. 2883-2885, 2009.

7. Hassan, S. B. and Aigbodion, V. S., "Effects of Eggshell on the Microstructures and Properties of Al-Cu-Mg/Eggshell Particulate Composites," Journal of King Saud University-Engineering Sciences, Vol. 27, No. 1, pp. 49-56, 2015.

8. Toro, P., Quijada, R., Yazdani-Pedram, M., and Arias, J. L., "Eggshell, a New Bio-Filler for Polypropylene Composites," Materials Letters, Vol. 61, No. 22, pp. 4347-4350, 2007.

9. Rath, M. K., Choi, B.-H., Ji, M.-J., and Lee, K.-T., "Eggshell-Membrane-Templated Synthesis of Hierarchically-Ordered NiO-$Ce_{0.8}Gd_{0.2}O_{1.9}$ Composite Powders and their Electrochemical Performances as SOFC Anodes," Ceramics International, Vol. 40, No. 2, pp. 3295-3304, 2014.

10. Bootklad, M. and Kaewtatip, K., "Biodegradation of Thermoplastic Starch/Eggshell Powder Composites," Carbohydrate Polymers, Vol. 97, No. 2, pp. 315-320, 2013.

11. Severa, L., Němeček, J., Nedomová, Š., and Buchar, J., "Determination of Micromechanical Properties of a Hen's Eggshell

by Means of Nanoindentation," Journal of Food Engineering, Vol. 101, No. 2, pp. 146-151, 2010.

12. Hassan, T. A., Rangari, V. K., Rana, R. K., and Jeelani, S., "Sonochemical Effect on Size Reduction of $CaCO_3$ Nanoparticles Derived from Waste Eggshells," Ultrasonics Sonochemistry, Vol. 20, No. 5, pp. 1308-1315, 2013.
13. Chaithanyasai, A., Vakchore, P. R., and Umasankar, V., "The Micro Structural and Mechanical Property Study of Effects of Egg Shell Particles on the Aluminum 6061," Procedia Engineering, Vol. 97, pp. 961-967, 2014.
14. Senthilkumar, R., Arunkumar, N., and Hussian, M. M., "A Comparative Study on Low Cycle Fatigue Behaviour of Nano and Micro Al_2O_3 Reinforced AA2014 Particulate Hybrid Composites," Results in Physics, Vol. 5, pp. 273-280, 2015.
15. Durmuş, H. K. and Meriç, C., "Age-Hardening Behavior of Powder Metallurgy AA2014 Alloy," Materials & Design, Vol. 28, No. 3, pp. 982-986, 2007.
16. Mosaddegh, E., Hassankhani, A., Pourahmadi, S., and Ghazanfari, D., "Ball Mill-Assisted Preparation of Nano-$CaCO_3$ as a Novel and Green Catalyst-based Eggshell Waste a Green Approach in the Synthesis of Pyrano [4, 3-b] Pyrans," International Journal of Green Nanotechnology, Vol. 1, DOI No. 10.1177/1943089213507160, 2013.
17. Ghabeer, T., Dweiri, R., and Al-Khateeb, S., "Thermal and Mechanical Characterization of Polypropylene/Eggshell Biocomposites," Journal of Reinforced Plastics and Composites, Vol. 32, No. 6, pp. 402-409, 2013.
18. Dwivedi, S. P., Sharma, S., and Mishra, R. K., "Microstructure and Mechanical Behavior of A356/SiC/Fly-Ash Hybrid Composites Produced by Electromagnetic Stir Casting," Journal of the Brazilian Society of Mechanical Sciences and Engineering, Vol. 37, No. 1, pp. 57-67, 2015.
19. Aziz, I., Qi, Z., and Min, X., "Corrosion Inhibition of SiC p/5A06 Aluminum Metal Matrix Composite by Cerium Conversion Treatment," Chinese Journal of Aeronautics, Vol. 22, No. 6, pp. 670-676, 2009.
20. Zakaria, H. M., "Microstructural and Corrosion Behavior of Al/SiC Metal Matrix Composites," Ain Shams Engineering Journal, Vol. 5, No. 3, pp. 831-838, 2014.
21. Salleh, M. R., Kamely, A., and Tajul, A., "Characterizing Chicken Eggshell Reinforced Polypropylene (PP)," Advanced Materials Research, Vols. 264-265, pp. 871-879, 2011.
22. Yew, M. C., Ramli Sulong, N. H., Yew, M. K., Amalina, M. A., and Johan, M. R., "Fire Propagation Performance of Intumescent Fire Protective Coatings using Eggshells as a Novel Biofiller," The Scientific World Journal, Vol. 2014, Article ID: 805094, 2014.
23. Chen, X., Li, C., Wang, J., Li, J., Luan, X., et al., "Investigation on Solar Photocatalytic Activity of TiO_2 Loaded Composite: TiO_2/Eggshell, TiO_2/Clamshell and TiO_2/$CaCO_3$," Materials Letters, Vol. 64, No. 13, pp. 1437-1440, 2010.
24. Lunge, S., Thakre, D., Kamble, S., Labhsetwar, N., and Rayalu, S., "Alumina Supported Carbon Composite Material with Exceptionally High Defluoridation Property from Eggshell Waste," Journal of Hazardous Materials, Vol. 237-238, pp. 161-169, 2012.
25. Mosaddegh, E., "Ultrasonic-Assisted Preparation of Nano Eggshell Powder: A Novel Catalyst in Green and High Efficient Synthesis of 2-Aminochromenes," Ultrasonics Sonochemistry, Vol. 20, No. 6, pp. 1436-1441, 2013.