

Waste Epoxy Modified Iron Oxide-Polymer Composite Pellets: Green Strength Development and Oxide Reactivity in Ironmaking Technology*

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Abstract

The effect of waste epoxy blending with iron oxide-polymer composite pellets on mechanical compressive strength (crushing strength), nature of crushed pellets and extent of reduction of iron oxide in iron oxide-polymer composite pellet has been investigated in the laboratory. The mechanical compressive strength (crushing strength) of self-reduced pellets modified with and without waste epoxy was determined using a universal mechanical test equipment INSTRON 3369 operating at load cell 50 KN and crosshead speed 2mm/min. Gas analysis of the offgas was conducted on thermal decomposition products at 1600 °C using a continuous infrared gas analyser, followed by reduction studies at 1200 and 1600 °C. It was observed that incorporating waste epoxy into the green pellets results in significant improvement in the crushing strength from around 0.2 kN to over 4.0 kN. Additionally, green pellets with waste epoxy did not suffer from catastrophic pulverisation that was observed for pellets without epoxy. Gas measurements by continuous infrared gas analyser revealed significant amounts of the gaseous reducing agents CO and CH₄ and minor amounts of CO₂ as the major gaseous products from thermal decomposition at 1600 °C. Finally, the presence of waste epoxy in the pellet resulted in significant improvement in the extent of reduction of Fe₂O₃ by raw palm nut shell (PNS) and charred palm nut shell (CPNS), with measured extent of reduction increasing from 43.6% to 92.7% and from 63.3% to 96.9% at 35% replacement of PNS and CPS, respectively.

Keywords: Waste Epoxy, Palm Nut Shells, Composite Pellets, Compressive Strength, Extent of Reduction

1 Introduction

Pelletisation of iron ore was originally invented to make use of Blue dust and ultrafine concentrate generated in Iron ore beneficiation plants. Pelletising operations produce a "green" (moist and unfired) pellet or ball, which is then hardened through heat treatment. Pellets have the benefit of lower gangue, on account of beneficiated ore. They also produce fewer fines during transportation, in reduction furnaces like Blast Furnace/Corex and Direct Reduced Iron (DRI) besides their high reducibility. It has been proven that the benefits from pellets formation offset the associated costs and this is manifested in the fact that there are many Blast furnaces and DRI plants, running with 100% pellets.

In spite of the presumed advantages, the agglomeration of fine iron concentrates to produce pellets of high quality for blast furnace feed as well as self-reduced pellets is a major challenge for the Iron and Steel industry. It is an energy intensive process. Industrially acceptable pellets have a dry green strength greater than 22 N before firing and the acceptable strength is 2000 N for direct reduction baked pellets (at ~1300 °C). Mantovani and Takano (2000) investigated the use of composite pellets in various furnaces. They observed that compressive strength of above 300 N

per pellet is sufficient to charge composite pellets in rotary hearth or rotary kiln furnaces. For commercial applications, Sah and Dutta (2009) suggested a compressive strength higher than 300 N, porosity above 20% and shatter index lower than 1%. They measured maximum compressive strength values of 330 N and 362 N per pellet for two types of pellets ACP4 and BCP4, respectively, both having an Fe_{tot}/C_{fix} ratio of 4.0.

Epoxy (also known as polyepoxide) is a thermosetting polymer formed from the reaction of an epoxide 'resin' with a polyamine 'hardener' and is grouped into four types, namely, HN-2200 and HN-2000, both having the formula C₉H₁₀O₃ (3 or 4-methylhexahydrophthalic anhydride), HN-5500 with formula C₉H₁₂O₃ (3 or 4-methyl-1,2,3,6-tetrahydrophthalic anhydride) and MHAC, formula C₁₀H₁₀O₃ (methyl-3,6-endomethylene-1,2,3,6-tetrahydrophthalic anhydride).

Research into the utilisation of postconsumer plastics, solely or in composite blends with other carbonaceous materials, as a source of carbon in metals production is gradually gaining momentum (Matsuda *et al.*, 2006; Nishioka *et al.*, 2007; Matsuda *et al.*, 2008; Ueki *et al.*, 2008; Dankwah *et al.*, 2011; Kongkarat *et al.*, 2011; Murakami *et al.*, 2009; Murakami and Kasai, 2011; Dankwah *et al.*, 2012; Dankwah *et al.*, 2013a; Dankwah and Koshy, 2014; Dhunna *et al.*, 2014; Mansuri *et al.*, 2013;

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Dankwah *et al.*, 2015a; Dankwah *et al.*, 2015b). However, none of these researchers has so far touched on the compressive strength or the nature of products obtained from the fragmentation of the iron oxide-composite pellets they utilised for their work. These two properties are part of the most important properties in Blast furnace iron making, which currently accounts for at least 90% of all iron making processes.

The aim of this work is therefore to investigate the utilisation of waste epoxy resin as a reductant and its effect on green strength development of iron oxide-waste polymer composite pellets.

2 Resources and Methods Used

Epoxy resin was obtained from the laboratory of School of Materials Science and Engineering, UNSW, Australia. The MSDS of the resin showed a molecular formula $C_{10}H_{10}O_3$, corresponding to 67.40 wt % C and 5.66 wt % H. Reagent grade hematite (96.89 wt % Fe_2O_3) procured from Sigma Aldrich, NSW, Australia was used as the source of iron oxide. The other carbonaceous material used was palm nut shells (PNS) from the Eastern Region of Ghana.

Three types of pellets were formed at room temperature without the need for induration. The first type of pellet (Fig. 1) consisted of a mixture of iron oxide with epoxy alone as reductant. This type of pellet did not require water or flour addition. In the second type of pellet, iron oxide was mixed with PNS alone as reductant. Flour was used as binder with no epoxy addition. In pellet type three (Fig. 2), epoxy replaced part of the PNS as a reductant.



Fig. 1 Iron Oxide-Epoxy Composite Pellet

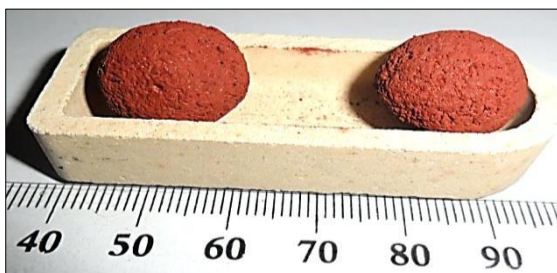


Fig. 2 Iron Oxide-PNS-Epoxy Composite Pellets

All the pellets were formed at room temperature and were allowed to cure for 72 hours. They were then subjected to compressive strength measurement test using a universal mechanical test equipment INSTRON 3369, operating at load cell 50 KN and crosshead speed 2mm/min. This was followed by reduction studies in a horizontal resistance tube furnace and also in a domestic microwave oven. Prior to the reduction process, the epoxy was subjected to high temperature thermal decomposition studies in a horizontal resistance tube furnace to ascertain the nature and concentration of gases evolved. A sample of the epoxy was administered into a LECOTM crucible and allowed to dry for about an hour. The LECOTM crucible with its content was then pushed into the hot zone of the HTF preheated at 1550 °C. The components of the emitted gas were measured continuously for 30 mins using a continuous infrared (IR) gas analyser with argon as carrier gas. Reduction studies in the HTF were done in a similar manner as the thermal decomposition process, except that composite pellets replaced the resin in the LECOTM crucible.

3 Results and Discussion

3.1 Compressive Strength Measurement

Fig. 3 shows the steps (a-d) involved in the measurement of the compressive strength of various iron oxide-epoxy composite pellets.

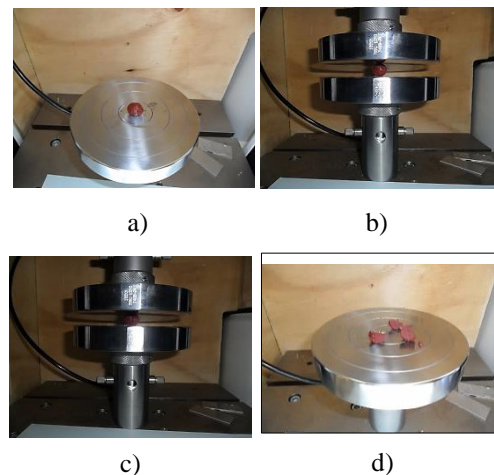


Fig. 3 Measurement of Compressive Strength of Iron Oxide-PNS-Epoxy Composite Pellets

3.1.1 Nature of Crushed Material

Fig. 4 shows the appearance of the epoxy modified composite pellets after the compressive strength test. It is apparent from the crushed samples on the plate that although the pellet failed after sometime, the crushed pellets did not show any signs of

pulverisation; instead they disintegrated into discrete particles. One crucial feature of the Blast furnace is that it does not tolerate pulverised samples in the cohesive zone, as such pulverised materials may clog the tuyeres. Accordingly, crushed particles in the Blast furnace must remain in non-pulverised discrete units to avoid clogging the tuyeres.



Fig. 4 Appearance of Iron Oxide-Epoxy Composite Pellets after Crushing Experiments

Epoxy modified composite pellets can therefore function effectively as charged materials in the Blast furnace based on the disintegrated crumbs demonstrated in Fig. 4.

In sharp contrast to the crushed samples observed for the epoxy modified composite pellets, Fig. 5 illustrates the nature of crushed materials obtained from the composite pellets without epoxy modification. The crushed products in this case show evidence of severe pulverisation, making such pellets unsuitable as charge material for the Blast furnace. These pellets may be suitable for the rotary hearth furnaces where particles are unlikely to undergo any crushing, since they are carefully arranged in a few layers on a hearth.



Fig. 5 Appearance of Composite Pellets without Epoxy after Crushing Experiments

3.1.2 Compressive Strength

Pellets that are to be fed in conventional Blast furnaces must have adequate mechanical strength

to avoid pulverisation in the cohesive zone. Fig. 6 shows a plot of the measured compressive strength as function of time for two samples of epoxy modified composite pellets formed at room temperature. The pellets are able to endure extreme compressive strengths above 3500 N (4331 and 3960 N) before failing. Combining these high compressive strengths with the fact that the particles broke down into discrete units without pulverisation, epoxy modified composite pellets are ideal charge materials for both rotary hearth and Blast furnace ironmaking.

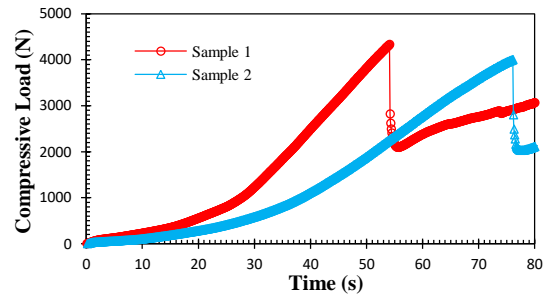


Fig. 6 Compressive Strength of Composite Pellets Modified with Epoxy

Figs. 7, 8 and 9 show the behaviour of three green composite pellets without epoxy modification. A sharp decline from an average of about 4145 N to about 135 N is observed when the composite pellets are formed without epoxy modification.

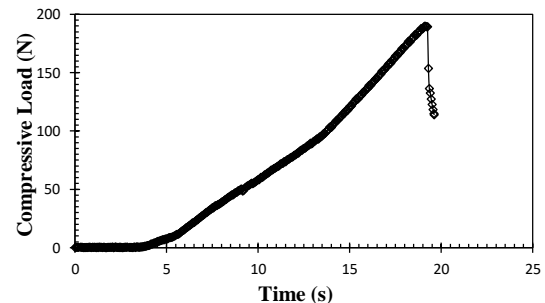


Fig. 7 Compressive Strength of Unmodified Composite Pellet 1

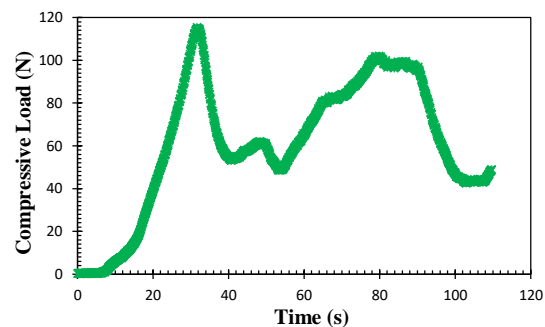


Fig. 8 Compressive Strength of Unmodified Composite Pellet 2

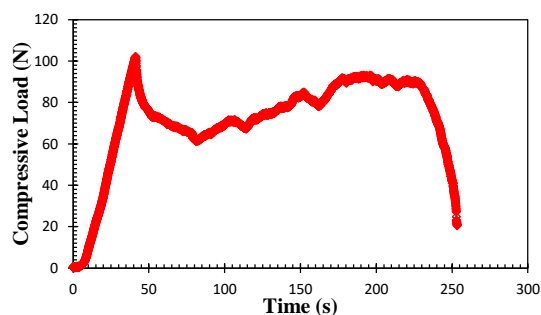


Fig. 9 Compressive Strength of Unmodified Composite Pellet 3

The observed difference in compressive strength between the pellets with and without epoxy modification could be attributed to the nature of bonding forces in these pellets. Whereas the bonding in the pellets without epoxy is physical the presence of epoxy introduces chemical bonding in the pellets, as illustrated in Fig. 10.

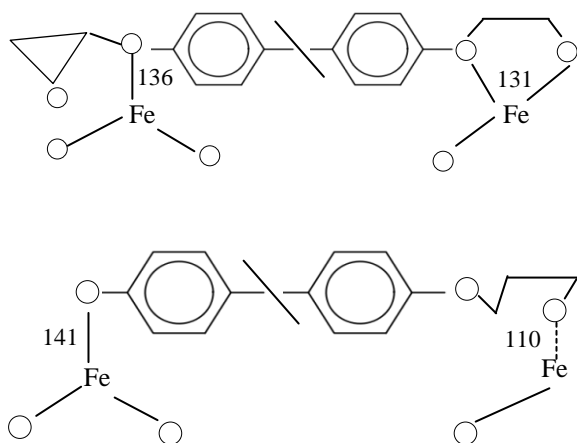


Fig. 10 Interfacial Chemical Bonding between Iron Oxide and Epoxy Resin. Numbers indicate binding energy in kJ/mol (Modified after Nakazawa, 1994)

3.2. Gas Emission Studies

3.2.1 Gas Emissions during Thermal Decomposition of Epoxy

The effectiveness of a polymer to function as a potential reductant in ironmaking technology depends on the type and amount of gases emitted into the furnace environment during thermal decomposition. Potential reductants often emit the reducing gases CH_4 , H_2 and CO into the furnace atmosphere leaving behind nanoscale solid carbon. Gaseous reduction of Fe_2O_3 is expected to follow the reactions in equations 1-3, below:

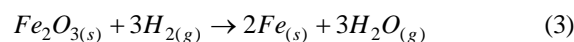
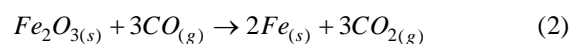
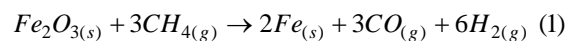


Fig. 11 illustrates the gas emission behaviour of the epoxy during thermal decomposition at 1550 °C. Gas emission commences almost immediately after inserting the polymer into the reaction zone of the horizontal tube furnace. The gas composition in the first 90 s is predominantly CO_2 which attains a maximum concentration of 3.43 vol% after 70 s and rapidly decreases to background concentrations of less than 0.250 vol% after about 450 s.

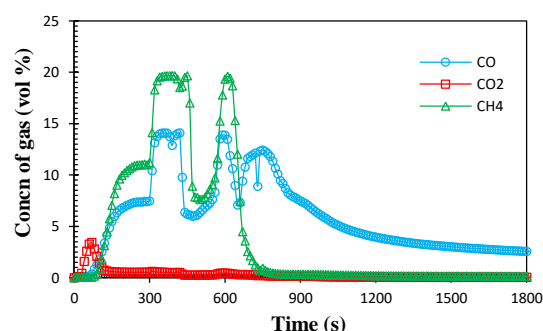
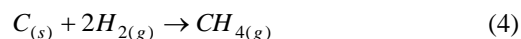


Fig. 11 Concentration of Exhaust Gas during Thermal Decomposition of Waste Epoxy

The decline in the concentration of CO_2 coincides with the commencement of CH_4 and CO concentrations. Epoxy emits large volumes of the gaseous reductants CO and CH_4 into the furnace environment, with each gas attaining multiple maxima of CH_4 (19.67 vol% and 19.32 vol%) and CO (14.08 vol%, 13.89 vol% and 12.34 vol%). The multiple maxima of CO is attributed to the Boudouard or water-gas reaction (Dankwah *et al.*, 2011), since epoxy contains atoms of carbon, hydrogen and oxygen. That of CH_4 may be attributed to the reaction of emitted hydrogen with nanoscale carbon (Dankwah *et al.*, 2011):



3.2.1 Gas Emissions during Reduction of Fe_2O_3 -Epoxy Composite Pellet

The gas emission behaviour during the reduction of Fe_2O_3 by epoxy is illustrated in Fig. 12. It is apparent from Fig. 12 that the concentration of CH_4 shows a rapid decline while the reverse is true for that of CO , which attains a maximum concentration of 22.58 vol%.

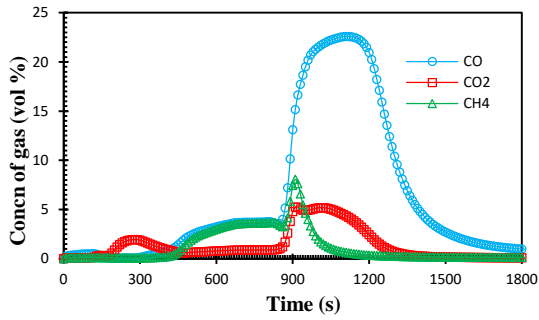


Fig. 12 Concentration of Exhaust Gas during Heating of Composite Pellet

The accumulated amounts of the three gases were plotted and are illustrated in Fig. 13. Similar amounts of CO₂ and CH₄ leave the furnace outlet and are considerably lower than the amount of CO which can be recovered with H₂ as syngas, as illustrated by Dankwah, 2013. The decline in the concentration of CH₄ along with the rise in that of CO, and presumably, H₂ were ascribed to equation (1) by Dankwah *et al.*, (2011).

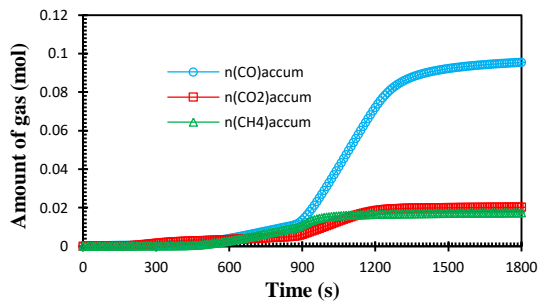
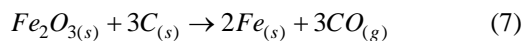
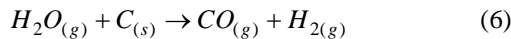
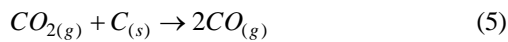


Fig. 13 Accumulated Amount of Various Gases in the Exhaust Gas during Heating of Composite Pellet

Other reactions mentioned in this respect are the Boudouard, water gas and solid reduction of Fe₂O₃ by nanoscale carbon, Dankwah *et al.*, (2011):



3.3 Nature and Characterisation of Reduced Metal

3.3.1 Nature of Composite Pellet before and after Reduction

Fig. 14 illustrates the nature of the reduced pellet before and after reduction at temperatures below 1200 °C in a horizontal tube furnace (HTF). As would be expected the pellet undergoes size reduction and colour change in the solid state but with no noticeable metal-slag separation.

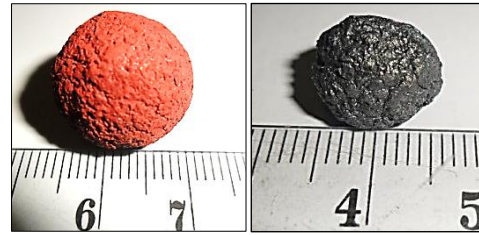


Fig. 14 Composite Pellet a) Before and b) After Reduction (T < 1200 °C)

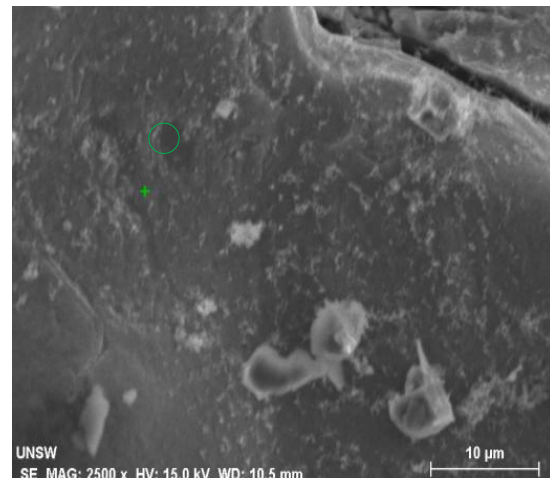
At temperatures above 1200 °C, spherically shaped premium grade iron nuggets are produced and are clearly separable from unreduced mass and the slag, as illustrated in Fig. 15.



Fig. 15 Samples of Reduced Metal obtained after Reduction at 1550 °C

3.3.2 Point and Line Scans on Scanning Electron Micrograph of Reduced Metal 1

A point scan analysis on the scanning electron micrograph of reduced pellet 1 at 1200 °C is shown in Fig. 16.



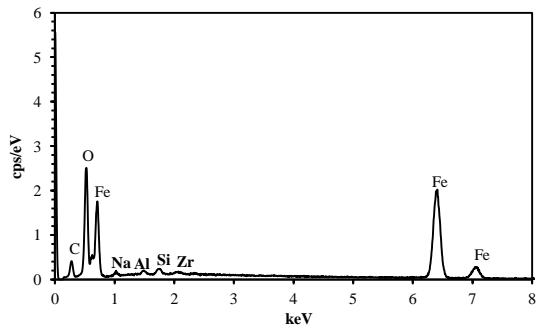


Fig. 16 Point Scan of Reduced Metal obtained after Reduction at 1200 °C

It shows a fairly reduced pellet with distinct peaks of Fe and some O. Minor peaks of C, Na, Al, Si and Zr are also observed. The minor but well-defined peak of carbon may be attributed to unreacted carbon, suggesting that reduction is incomplete. Na, Al and Si could be from the slag whilst Zr could be attributed to the LECOTM crucible that was used for the reduction in the HTF.

Line scan analysis over a distance of 100 μm from the bottom left corner on the SEM micrograph of reduced metal 1 at 1200 °C is shown in Fig. 17. A consistent increase in the major element Fe is observed along the distance. However, the variation in O is significant, suggesting that reaction is incomplete.

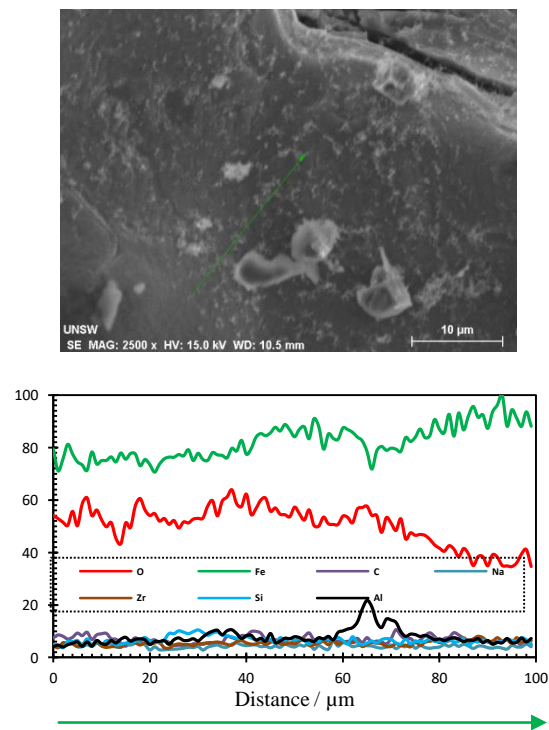
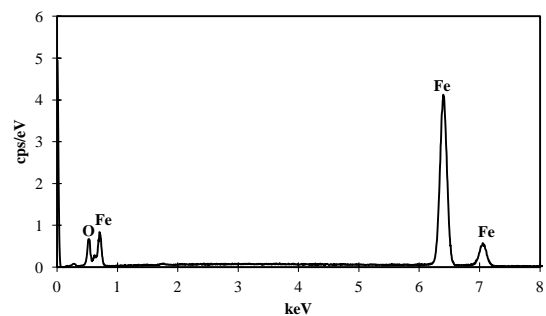
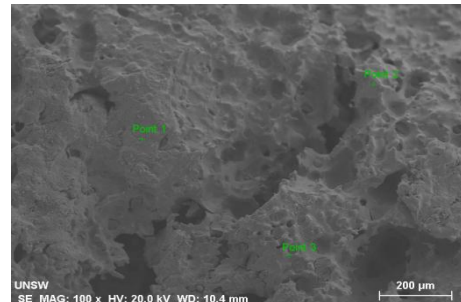


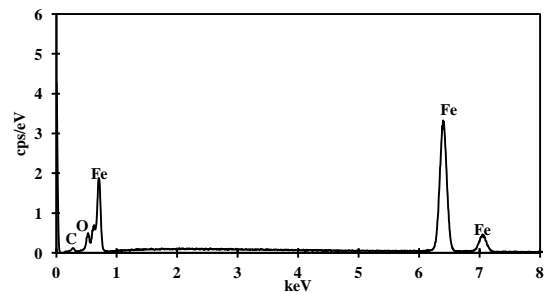
Fig. 17 Line Scan of Reduced Metal obtained after Reduction at 1200 °C

3.3.3 Point and Line Scans on Scanning Electron Micrograph of Reduced Metal 2

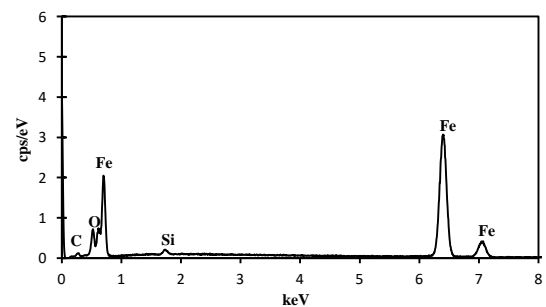
Point scan analyses on the scanning electron micrograph of reduced pellet 2 at 1600 °C are shown in Fig. 18. Intensification and attenuation of the peaks corresponding to Fe and O, respectively, are evident from Fig. 18. Coupled with the near disappearance of peaks corresponding to C, reduction of the oxide by epoxy can be said to increase as the temperature increases from 1200 to 1600 °C.



a) Point 1



b) Point 2



c) Point 3

Fig. 18 Point Scan Analyses of Reduced Metal obtained after Reduction at 1600 °C

Line scan analysis over a distance of 200 μm from the mid left corner on the SEM micrograph of reduced metal 2 at 1600 $^{\circ}\text{C}$ is shown in Fig. 19.

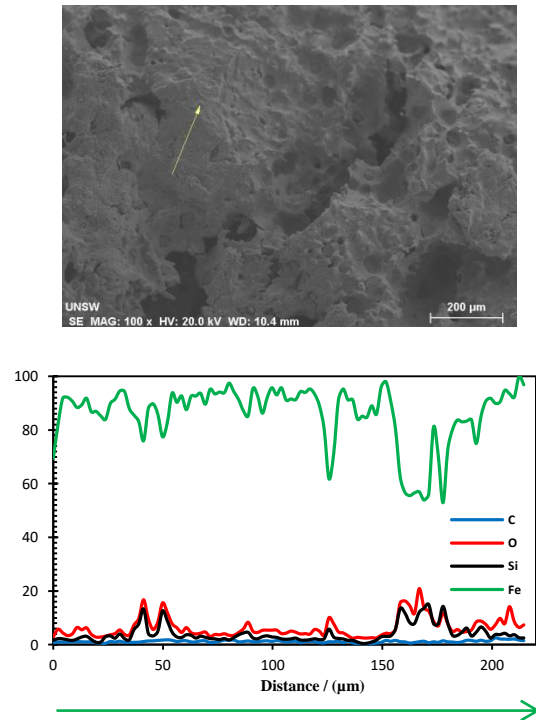


Fig. 19 Line Scan of Reduced Metal obtained after Reduction at 1600 $^{\circ}\text{C}$

Wide variation in the content of Fe is observed along the distance. Iron is the dominant element with minor amounts of O, Si and C. Of particular interest is the content of C which appears to be very low compared to the levels at 1200 $^{\circ}\text{C}$, suggesting that more carbon is consumed at high temperatures. Reduction of Fe_2O_3 is therefore more active at higher temperatures.

3.4 Effect of Epoxy on Reduction of Fe_2O_3 by Palm Nut Shells

Table 1 shows the effect of epoxy on the reduction of Fe_2O_3 by various compositions of raw palm nut shells (RPNS) and charred palm nut shells (CPNS).

Table 1 Extent of Reduction of Epoxy Modified Iron Oxide-Biomass Composite Pellets

SAMPLES	% Reduction
A (100% RPNS)	43.6
B (100 CPNS)	63.3
C (100% Epoxy)	85.8
D (65% CPNS + 35% Epoxy)	96.9
E (65% RPNS + 35% Epoxy)	92.7
F (50% CPNS + 50% Epoxy)	87.9
G (50% RPNS + 50% Epoxy)	82.5

It is seen from Table 1 that charring as well as epoxy addition (up to 35% epoxy addition) has beneficial effect on the reduction of Fe_2O_3 by PNS. Incorporation of epoxy in the pellet increases the extent of reduction of Fe_2O_3 by PNS from 43.6% to 63.3%. Replacement of 35% of RPNS and CPNS by epoxy increases the extent of reduction of Fe_2O_3 from 43.6% to 92.7% and from 63.3% to 96.9%, respectively. Beyond 35% replacement, the extent of reduction decreases; for this set of compositions, a blend composition of 65% (C)PNS + 35% Epoxy appears to be the optimum. The observed increase in the extent of reduction with epoxy addition may be due to a more compact composite pellet that is able to improve gas holdup resulting in improved reduction.

4 Conclusions

This work investigated the effect of waste epoxy addition on green iron oxide-polymer composite pellet formation, compressive strength development, nature of crushed pellets and the extent of reduction of Fe_2O_3 by PNS. Major findings of this investigation can be summarized as follows. The addition of epoxy results in:

- (i) Improved compressive strength of the green pellets:
- (ii) Reduced pulverisation of the crushed pellets after failing under compression:
- (iii) Significant improvement in the extent of reduction of Fe_2O_3 by PNS

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