

# Comparison of Compression Molding and Selective Laser Sintering Processes in the Development of Composite Bipolar Plates for Proton Exchange Membrane Fuel Cells

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## Abstract

Bipolar plates are key components of Proton Exchange Membrane (PEM) fuel cells. They carry current away from the cell and withstand the clamping force of the stack assembly. Therefore, PEM fuel cell bipolar plates must have high electrical conductivity and adequate mechanical strength, in addition to being light weight and low cost in terms of both applicable materials and production methods. In order to attain these goals, we have manufactured graphite-carbon-polymer composite plates using Compression Molding (CM), which is suitable for mass production, and Selective Laser Sintering (SLS), which is suitable for making prototypes. In this paper, the electrical conductivity and flexural strength of the bipolar plates fabricated using the CM process versus constitutive materials are experimentally studied. The properties of bipolar plates fabricated using the CM process are compared with those of plates fabricated using the SLS process. Natural graphite (NG), synthetic graphite (SG), carbon black (CB), and carbon fiber (CF) are used as the constitutive materials for both processes, with epoxy resin employed as the binder matrix. By varying the volume fraction of each constituent, the distribution of the electrical conductivity and flexural strength of parts made using the CM and SLS processes are obtained, and the similarities and differences of the effects of the various constituents between these two processes are compared.

Keywords: Bipolar plates; Graphite-carbon-polymer composite Compression molding; Selective Laser Sintering.

## 1. Introduction

Proton exchange membrane (PEM) fuel cells are attractive options for alternative energy production to fossil fuels due to promising features that allow them to generate electrical energy without undergoing combustion, such as their high power density, relatively low operating temperature, good start-up, ability to convert fuel to water as the only byproduct, longer lifetime, and shape modularity [1,2,3]. In a fuel cell stack, bipolar plates are key components as they serve the following functions [3,4,5]:

- (i) distribute the fuel and oxidant within the cell,
- (ii) facilitate water management within the cell,
- (iii) separate the individual cells in the stack,
- (iv) carry current away from the cell,
- (v) enable heat transfer,

- (vi) support thin membranes and electrodes,
- (vii) withstand the clamping forces of the stack assembly, and
- (viii) prevent leakage of reactant gases and coolant.

The bipolar plate is the heaviest component of the PEM fuel cell, accounting for about 80% of the total weight of a fuel cell stack. It is also a very costly component. According to a cost analysis study, about 45% of a fuel cell stack's cost is incurred by the bipolar plate [1]. Therefore, quality improvement and weight and cost reductions are critical issues in the development of PEM fuel cell bipolar plates, especially those fuel cells employed in automotive or mobile applications. The processing methods and materials used to manufacture bipolar plates determine the final properties of the products, so they are of great importance for any manufacturer or researcher of the bipolar plates.

Materials that have been used for making PEM fuel cell bipolar plates include non-porous graphite (both natural and synthetic), metals (both non-coated and coated), and polymer composites [1]. Graphite is the most commonly used material for fabricating PEM fuel cell bipolar plates because it has a suitable combination of thermal and electrical properties and excellent corrosion resistance in the highly-acidic PEM fuel cell environment. However, graphite is very brittle and has poor mechanical properties, machining graphite plates is very costly and time-consuming. Metallic bipolar plates are stronger and more conductive, and also can be fabricated more easily and at a lower cost than graphite bipolar plates. However, they suffer from low corrosion resistance in the PEM fuel cell environment. Graphite-carbon-polymer composites are promising alternatives to both graphite and metal because they have the advantages of good mechanical, thermal, and electrical properties; they are also light weight and have high corrosion resistance [6,7]. Conductive materials such as flaky natural graphite, synthetic graphite, expanded graphite, and carbon black have been used by many researchers to impart good electrical conductivity to composite bipolar plates [3,5,6,8-14]. Moreover, carbon fiber has been employed to improve the mechanical integrity of bipolar plates. The Department of Energy (DOE) proposed a technical target for bipolar plates for the year 2010 [15], in which the main requirements were to achieve electrical conductivity greater than 100 S/cm and flexural strength greater than 25 MPa.

In addition to materials, the manufacturing method and processing conditions of composites greatly influence the dispersion and inter-particle positions within the polymer matrix; therefore, they have significant effects on the final electrical and mechanical properties of the composite plates [7]. Compression molding (CM) is a common method for making polymer composite bipolar plates [16] and is very suitable for mass production. The literature reveals that it has been used widely for making graphite-carbon-polymer composites, either with thermosetting or thermoplastic resins. The effects of conductive and reinforcing particles on bipolar plate properties including electrical conductivity and flexural strength have been studied experimentally by various researchers [3,5,6,8-13].

Selective Laser Sintering (SLS), an additive manufacturing technique, has been studied in making graphite composite bipolar plates for PEM fuel cells [14,17-19]. In the SLS process, a mixture of graphite material and binder in a powder bed is scanned by laser, and the molten binder bonds graphite particles together to form 3D parts layer by layer. The major advantages

of the SLS process include its ability to build complex flow fields for bipolar plates and its consumption of less time and financial resources when making bipolar plates from each design, which reduces the time and cost of fabricating bipolar plates in the R&D stage as compared to conventional methods.

In the study described in the present paper, the effects of constitutive materials, including natural graphite (NG), synthetic graphite (SG), carbon black (CB), and carbon fiber (CF), on the electrical conductivity and mechanical strength of composite bipolar plates for PEM fuel cells are experimentally studied. The electrical conductivity and mechanical strength results obtained using the CM process are compared with the results previously obtained using the SLS process [14]. Variations in the electrical and mechanical properties versus changes in the bipolar plate constituents are investigated for the two processes.

## **2. Materials and Tools**

The materials and compositions used for making composite bipolar plates using the CM process are chosen to match those used previously in the SLS process [14] in order to allow more meaningful comparisons between the two processes.

### **2.1 Conductive and reinforcing constitutive materials**

Natural graphite (3610), synthetic graphite (4437), carbon black (5303) and carbon fiber (AGM99) are obtained from Asbury Graphite Mills, Inc. (New Jersey, USA). Properties of these materials, as provided by the manufacturer, are given in Table 1. Natural graphite is the primary electrical conducting material, but it has poor wettability with the liquid resin. Synthetic graphite has lower electrical conductivity than natural graphite due to its lower degree of crystallinity. Carbon black, manufactured by the combustion or thermal decomposition of hydrocarbon fuel under reducing conditions, has a very small particle size and thus a very large specific surface area. Carbon fiber is used to enhance the mechanical strength of composite bipolar plates.

### **2.2 Polymer resin**

The thermosetting epoxy resin is inexpensive and has good mechanical strength, hardness, and thermal and chemical resistance. Liquid epoxy EPON<sup>TM</sup> Resin 828, an undiluted, clear, difunctional bisphenol A/epichlorohydrin derived liquid epoxy resin, is used in the experiments. The density of this epoxy resin is 1.16 g/cm<sup>3</sup>, and EPIKURE<sup>TM</sup> 3230 is a good hardener for EPON<sup>TM</sup> 828 when employed in the compression molding processes, according to the information provided by the manufacturer (MOMENTIVE Inc.).

### **2.3. Hot press**

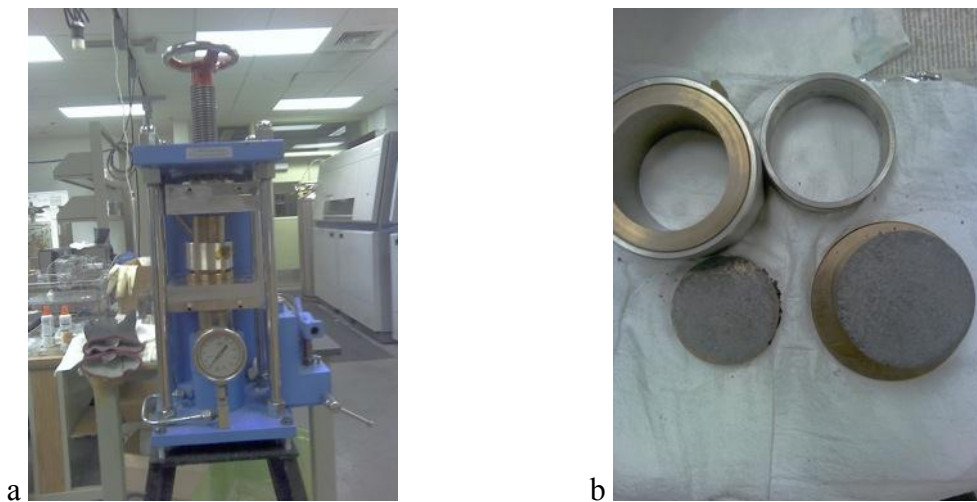
A 250 kN hydraulic press with hot platens is used to compress the composite powder in a circular mold. A temperature control unit on the apparatus digitally controls the temperature of the hot platens. Fig. 1(a) shows the hydraulic press with the heated platens between which the mold and dies are located, and Fig. 1(b) shows the dies.

## 2.4. Steel mold

Two cylindrical steel molds (of 3-inch diameter) and cylindrical punches are used to create the samples. With a band saw, the fabricated composite plates are cut into several specimens with dimensions according to appropriate ASTM standards, which will be described later.

**Table 1** Properties of graphite materials.

Properties	Natural Graphite (3610)	Synthetic Graphite (4437)	Carbon Black (5303)	Carbon Fiber (AGM99)
Particle size ( $\mu\text{m}$ )	75-150	10-45	<0.03	Diameter 7.4 Length 150
Theoretical density ( $\text{g}/\text{cm}^3$ )	2.26	2.26	1.8	1.75
Surface Area ( $\text{m}^2/\text{g}$ )	1.27	11.46	254	1.87
Typical Conductivity ( $\text{S}/\text{cm}$ )	27.78	17.24	2.93	-



**Fig. 1** (a): The 250 kN hydraulic press with heated platens, and (b): dies used in the experiments.

## 3. Manufacturing Process and Property Characterization

To reduce its viscosity, the epoxy resin is kept at  $100\text{ }^{\circ}\text{C}$  for several hours. The mold, which first is preheated until it reaches  $200\text{ }^{\circ}\text{C}$ , is thermally isolated inside the space between the two platens of the hot press to maintain this temperature with the help of thermally insulating fibers. A thermocouple is used to check the temperature of the mold before pouring the powder into it. Next, the hardening agent is added to the epoxy resin according to the prescribed volume percentage, and they are mixed until the liquid becomes clear. Because a 35 vol.% binder was used in all of the SLS experiments, a 35 vol.% resin is used in all of the CM experiments. The epoxy resin and hardener are added to an acetone solvent in a beaker and stirred by a mechanical stirrer for several

minutes. Next, the reinforcing constituents, i.e., natural graphite, synthetic graphite, carbon fiber, and carbon black, are added to the solution according to the specific composition data. The mixture is stirred for over one hour until the acetone evaporates. Then, the beaker is kept under a fume hood for several hours to evaporate the remaining acetone completely. Finally, the mixture is maintained inside an oven at 100 °C for half an hour to make sure that the graphite-carbon-polymer composite powder is completely dry and ready to be compression molded. Compression molding is performed by applying 54 MPa of pressure within 30 minutes of the molding time.

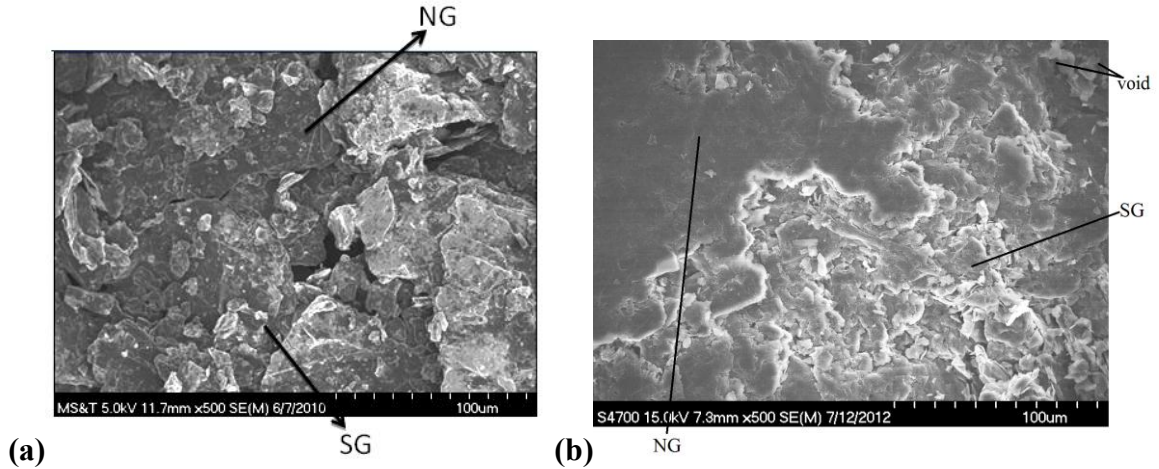
The four-probe technique is employed for measuring electrical conductivity according to the ASTM C611 standard. The KEITHLEY 220 programmable current source is used to apply a constant current of 10 mA between the two outermost current probes, and the KEITHLEY 181 NANO-VOLTMETER is used to measure the dropped voltage within a 20 mm distance between the two innermost voltage probes. Six specimens are selected for data measurement, and the average values are reported for the conductivity. The three-point bending test is performed to measure flexural strength. In accordance with ASTM D790-10, four tests are conducted using the INSTRON 4469 testing machine. The microstructures of the samples are obtained using the Hitachi S-4700 FE-SEM.

## **4. Results and Discussion**

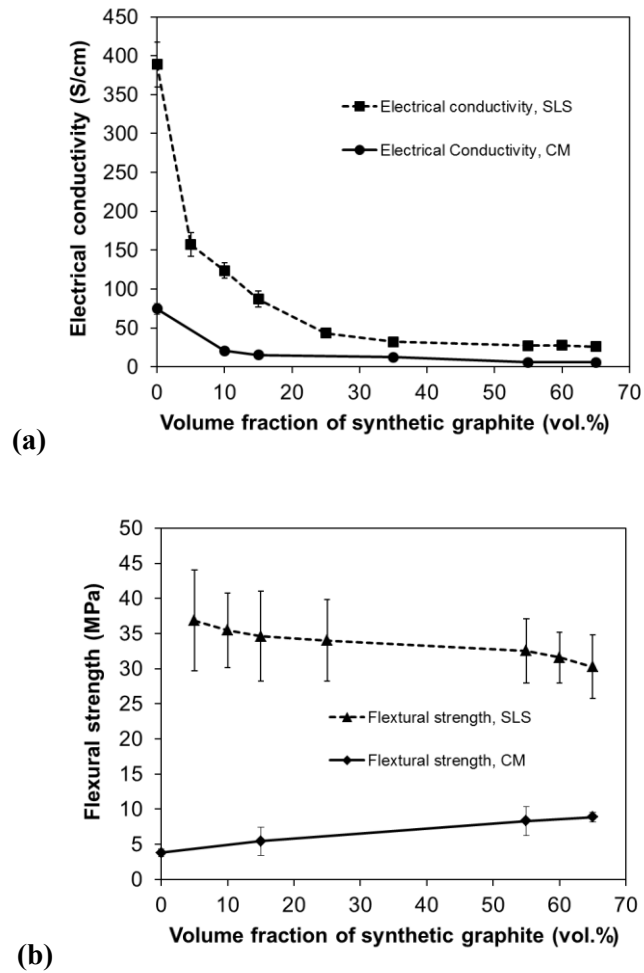
The influences of the constitutive materials on the electrical conductivity and flexural strength of the composite bipolar plates are presented and discussed below.

### **4.1 Effect of synthetic graphite**

The microstructures of parts with variations in natural graphite (NG) and synthetic graphite (SG) are shown in Fig. 2, in which the larger flaky particles are NG and the smaller spherical ones are SG. Electrical conductivity and flexural strength variations with different volume fractions of SG are shown in Figs. 3(a) and 3(b), respectively. As the volume fraction of SG increases, the conductivity of the bipolar plate decreases for both the CM and SLS processes because the conductivity of SG particles is lower than that of NG. The current conduction among NG particles is reduced by the presence of SG particles when the two types of particles are mixed together. Increasing the SG content increases the flexural strength of the samples made using the CM process but decreases that of the samples made using the SLS process. In the CM process, the stress distribution around small spherical SG particles is more uniform and the strain is smaller, so the mechanical strength improves. On the other hand, in the SLS method, adding smaller SG particles fills up the big pores among larger flaky NG particles, which reduces the porosity, so less resin can infiltrate, leading to lower mechanical strength.



**Fig. 2** SEM images showing the microstructures of (a): a brown part made using the SLS process and (b): a part made using the CM process with 15 vol.% SG, 50 vol.% NG and 35 vol.% binder.



**Fig. 3** Variations in (a) electrical conductivity, and (b) flexural strength versus changes in the volume fraction of SG for the CM and SLS processes.

The experimental results indicate that the electrical conductivity and flexural strength obtained when using the CM process are much lower than the SLS results and are below the DOE target values. The maximum electrical conductivity value with the CM process is approximately 74 S/cm, while the maximum value with SLS is approximately 380 S/cm. The low electrical conductivities in the CM parts have been observed by previous researchers. Dweiri and Sahari [9] used synthetic graphite, carbon black, and polypropylene with the melt compounding preparation method. Their composite bipolar plates fabricated using the CM process had a maximum electrical conductivity of 36 S/cm. Lee et al. [8] also developed compression molded bipolar plates using powder epoxy resin, graphite, and carbon black, obtaining an electrical conductivity below the DOE target. Bhlapibul and Pruksathorn [20] achieved a maximum electrical conductivity of only 4.52 S/cm when they employed polyester resin and graphite powder to fabricate bipolar plates using the CM process.

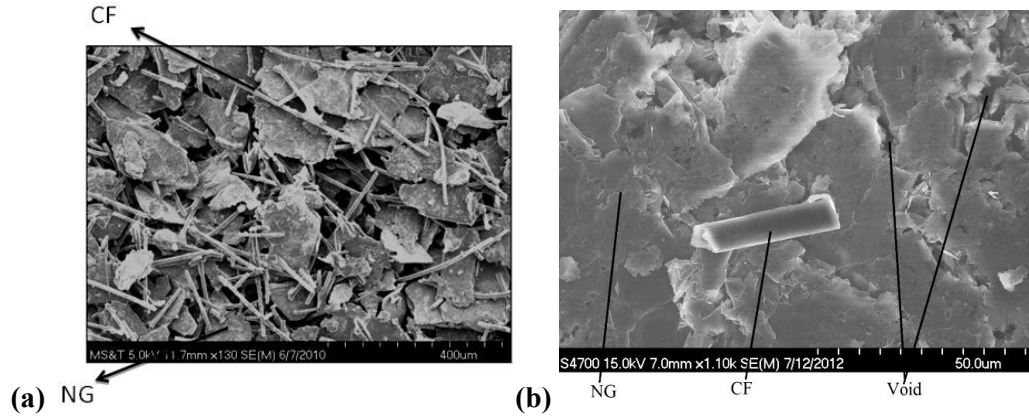
The measured electrical conductivity and flexural strength in the bipolar plates made using the CM and SLS processes can be attributed to the materials and preparation methods employed in these processes. In the CM process, the liquid resin covers the surface of the graphite particles during mixing and thus hinders the electrical connection between the graphite particles. In the SLS process, the phenolic binder in the form of particles is mixed with the graphite particles, and the polymer resin is infiltrated into the brown part, imparting mechanical strength to the composite plate. The phenolic binder does not remain inside the part after sintering; instead, it is converted to carbon ashes during sintering. The carbon ashes fill up the pores and help to increase the electrical conductivity. On the other hand, in the CM process, the mixture does not contain sufficient epoxy resin to impart mechanical strength to the fabricated parts. Moreover, there is local mixing of the liquid epoxy resin with the composite plate particles (rather than with the overall powder constituents uniformly), so agglomerates form inside the mixture after the acetone solvent is incorporated and the mixture is dried because of the accumulation of epoxy resin in some regions. As a result, the electrical conductivity and flexural strength decrease as the agglomerates introduce inhomogeneity inside the structure. Based on the previous research results of CM manufactured bipolar plates with high electrical conductivity [3,5,6,7], mixing ‘solid’ epoxy resin with the filler powder or using graphite particles with longer aspect ratios may help resolve the problem of low electrical conductivity and flexural strength of CM manufactured bipolar plates.

## **5.2 Effect of carbon fiber**

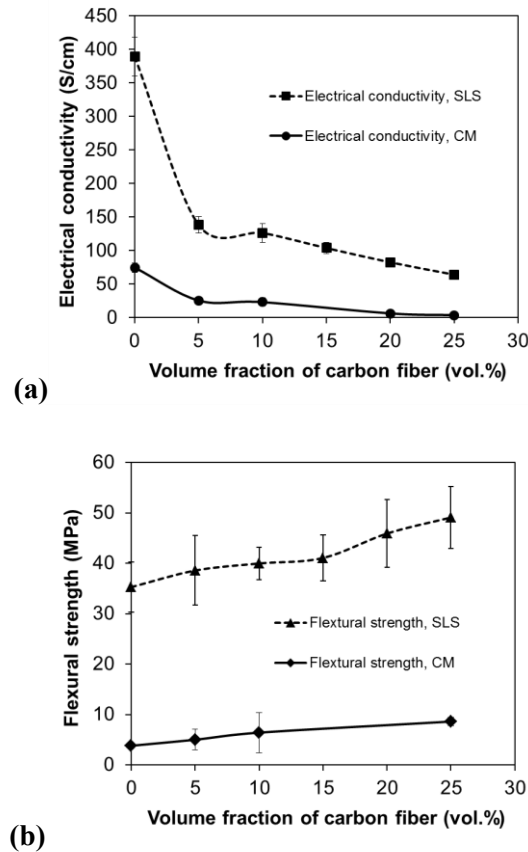
Carbon fiber is used widely in composite materials to increase mechanical strength. Fig. 4 shows the microstructures of a sample made using the CM process and a brown part made using the SLS process, with CF and NG as their constituents, in which long, thin carbon fibers are uniformly mixed with natural graphite particles.

Variations in electrical conductivity and flexural strength versus changes in the CF volume fractions are shown in Figs. 5(a) and 5(b), respectively. Both CM and SLS processes show the same trend in electrical conductivity and flexural strength. Adding CF into NG reduces the electrical conductivity because the dispersion of CF among NG

particles lessens the contacts of NG particles, while CF itself has much less conductivity. Increasing the CF ratio increases the flexural strength of the composite samples, as expected. In Fig. 5 the electrical and mechanical properties of the CM fabricated parts using these NG, CF, and epoxy resin materials are lower than those of the SLS fabricated parts and the DOE targets. This is due to the lack of homogeneity in the mixture of materials and the formation of polymer agglomerates inside the plate structure during preparation for the CM process, as explained before.



**Fig. 4** SEM images showing the microstructures of (a): a brown part made using the SLS process, and (b): a part made using the CM process with 25 vol.% CF, 40 vol.% NG and 35 vol.% binder.



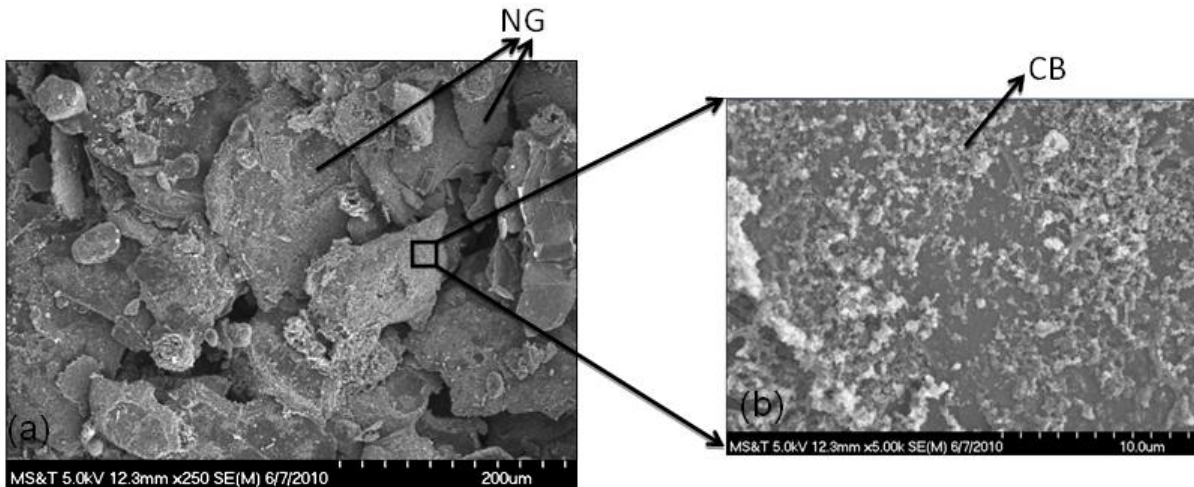
**Fig. 5** Variations in (a) electrical conductivity, and (b) flexural strength versus changes in the volume fraction of CF for the CM and SLS processes.

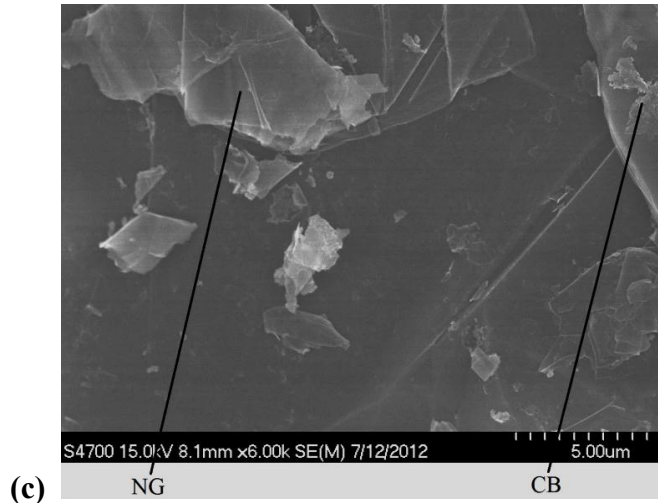


### 5.3 Effect of Carbon Black

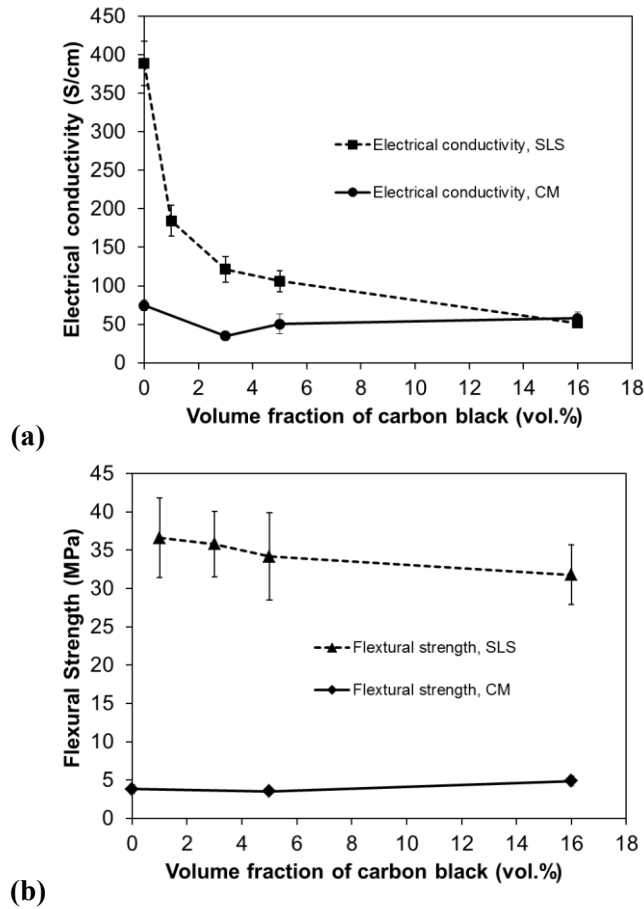
Fig. 6 shows the microstructure of a brown part made using SLS and a part made using CM, both with 16 vol.% CB, 49 vol.% NG and 35 vol.% binder. The surface of NG particles is covered by the nano-size CB particles in the SLS sample shown in Fig. 6(b); however, CB particles are present between NG particles but do not cover the surface of NG particles in the CM sample shown in Fig. 6(c).

Fig. 7 shows variations in electrical conductivity and flexural strength with different volume fractions of CB. In the CM process, adding CB to NG decreases the electrical conductivity because CB has less intrinsic electrical conductivity than NG. However, when the CB volume fraction continues to increase, the electrical conductivity increases because nano-size CB particles fill the voids between NG particles. Likewise, increase in CB can enhance the flexural strength after a certain volume fraction. In the SLS process, as the CB content increases, electric conductivity decreases. This is because CB has lower intrinsic conductivity than NG. During the ball-milling process, CB particles with large surface areas tend to agglomerate and cover the whole surface of NG particles, as shown in Fig. 6(b), which impedes contact between NG particles. This is different from the CM process, in which CB particles fill the small voids between NG particles rather than covering their surface; thus, electrical conduction can pass through these small CB particles in CM made bipolar plates.





**Fig. 6** SEM images showing (a) microstructure of a brown part made using SLS; (b) detailed view of the surface of NG particle; (c) microstructure of a part made using CM (16 vol.% CB, 49 vol.% NG and 35 vol.% binder).



**Fig. 7** Variations in (a) electrical conductivity, and (b) flexural strength versus changes in the volume fraction of CB for the CM and SLS processes.

## 5. Conclusion

The compression molding (CM) and selective laser sintering (SLS) processes are compared in terms of their fabrication of composite bipolar plates for PEM fuel cells. The effects of these two processing methods on the electrical conductivity and flexural strength of the graphite-carbon-polymer composite bipolar plates are evaluated. For purpose of meaningful comparison, the same materials and compositions are used in both manufacturing processes. Different volume fractions of NG, SG, CF, and CB, with a constant amount of epoxy resin as the binder, are used for comparison in the experimental study. The results show that the trends of electrical conductivity variations versus changes in the volume fractions of SG and CF are the same for the CM and SLS processes; however, increasing the volume fraction of nano-size CB increases electrical conductivity in the CM process but decreases electrical conductivity in the SLS process. The flexural strength improves significantly by adding SG and CF and increases slightly by increasing the CB ratio in the CM process. For SLS-fabricated parts, only CF can improve the mechanical strength, while SG and CB reduce the flexural strength of the composite plates.

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