Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 39 (2013) 7159–7166

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Effect of small-sized conductive filler on the properties of an epoxy composite for a bipolar plate in a PEMFC

Hendra Suherman[a,b,*], Jaafar Sahari[a,c], Abu Bakar Sulong[a,c]

[a]Fuel Cell Institute, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia
[b]Department of Mechanical Engineering, Universitas Bung Hatta, 25137 Padang, West Sumatera, Indonesia
[c]Department of Mechanical & Materials Engineering, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia

Received 13 December 2012; received in revised form 15 February 2013; accepted 15 February 2013
Available online 26 February 2013

Abstract

This paper focused on using a conductive polymer composite (CPC) as a potential replacement for the conventional graphite bipolar plate used in polymer electrolyte membrane fuel cells (PEMFC). Based on the requirements established by the US Department of Energy (DOE), the in-plane electrical conductivity and flexural strength are required to be greater than 100 S/cm and 25 MPa, respectively. The high filler loading is needed to satisfy the high in-plane electrical conductivity. However, the high filler loading reduces the flexural strength and manufacturability of the composite. In this study, the composites were prepared by compounding using an internal mixer followed by compression moulding. The combination of 10 vol% carbon black (CB) as the second filler with synthetic graphite/epoxy (SG/EP) resulted in the following composite properties: 150 S/cm (in-plane conductivity), 55 S/cm (through-plane conductivity), and 38.8 MPa (flexural strength). Used as the second filler, the CB, which had a small-sized diameter, formed conductive networks that filled the voids between the SG and polymer matrix. The in-plane electrical conductivity and flexural strength of the CB/SG/EP composites at the optimum composition exceeded the requirement for bipolar plate applications.

Keywords: Conductive polymer composites; PEMFC; Carbon black; Small-sized filler; Internal mixer

1. Introduction

Conductive polymer composites (CPCs) have numerous existing and potential applications [1–3]. Composites are designed, processed and fabricated based on the needs of the applications. The loading of the conductive filler in commonly used CPCs is below 10 vol% [4,5]. However, for applications, such as in bipolar plates used in polymer electrolyte membrane fuel cells (PEMFCs), a high loading of conductive fillers to fill the composites is necessary. The high filler loading is needed to satisfy the high electrical conductivity requirements. However, the high loading reduces both the mechanical strength of the composite and the manufacturability with conventional processing methods [6].

The primary challenge in designing a bipolar plate is choosing the materials and processing methods that would achieve the properties set by the US Department of Energy (DOE) for commercial viability [7]. A composite consisting of graphite (G) as the primary filler and carbon black (CB) as the second conductive filler in epoxy (EP) has the potential to be used as a bipolar plate material. The small particle size (30 nm) of CB allows it to fill the voids between larger graphite particle, thus increasing the conductivity network and the electrical conductivity of the composite [8,9]. The effect of the surface area of CB, where CB was used as conductive fillers in polypropylene/graphite (PP/G) composite bipolar plates, has been investigated by Mighri et al. [10]. It was observed that the electrical conductivity increased as the surface area of the CB increased. The maximum CB loading concentration obtained was at 18 vol%. Lee et al. also reported the

---

*Corresponding author at: Fuel Cell Institute, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia.
Tel.: +60 389216502, +60 389216038; fax: +60 389216024.
E-mail addresses: henmeubh@yahoo.com, hendraubh@gmail.com (H. Suherman).

0272-8842/$ - see front matter © 2013 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2013.02.059

advantage of CB used as the secondary filler in G/polymer composite bipolar plates [11]. They found that the amount of the conductive filler needed was less when CB was used as the secondary filler in the G/polymer composites. The small CB particles formed conductive paths between the G, the primary filler within the polymer matrix, which increased the electrical conductivity. However, when a critical loading of 7.5 vol% was reached, the electrical conductivity decreased because the wetting of the CB in the polymer matrix became poor. Dhakate et al. also used CB as the secondary filler in phenolic resin/G composite bipolar plates. They observed that the critical loading concentration of CB was 20 vol% [12]. The difference in the critical loading concentration of CB as the second filler within a polymer matrix is worthy of further study. For example, Lee et al. found that the critical loading concentration was 5 vol% [11], whereas Dhakate et al. determined that the critical loading concentration was 20 vol% [12]. In this study, synthetic graphite was chosen as the primary conductive filler combined with a small amount of electrically conductive carbon black as the secondary filler to achieve the bipolar plate requirements set by the DOE. The objectives of this study were to study the effect of small-sized conductive fillers in a synthetic graphite/epoxy polymer matrix and to develop a fabrication process for a CB/SG/EP composite suitable for a bipolar plate in a PEMFC.

2. Experimental

2.1. Material

Two conductive fillers were used in this study: SG and CB. The SG had a surface area of 1.5 m^2/gr with a 74-μm particle size. The CB had a surface area of 250 m^2/gr with a 30-nm particle size. The SG and the CB were supplied by Insutex Industries Sdn. Bhd., Malaysia, which is a local agent for Asbury Carbons Inc., US. The epoxy resin used was a bisphenol-A-based epoxy resin with a viscosity of 6 P, and the curing agent used, 4-Aminophenylsulphone, were obtained from Mid Western Lab Suppliers., Malaysia. The manufacturer recommended an epoxy curing temperature of 80 °C. The 4-Aminophenylsulphone is a diamine type (tetra functional), which facilitates rapid and dense cross-linking of the epoxy resins. An epoxy matrix with a low viscosity was selected to create better wetting conditions for the conductive fillers. Fig. 1 shows the SEM images of the SG and CB used in this study.

2.2. Fabrication of the CB/SG/EP composites

The liquid epoxy and curing agent were mixed at a weight ratio of 3:1. Mixing the SG/CB in the epoxy was performed in three steps. In the first step, the CB and SG were mixed at different vol% in a ball mill to obtain a homogenous mixture. The weight ratio of the balls and powder used was 4:1 with stainless steel balls (10 mm in diameter), which were mixed at 200 rpm for 1 h. In the second step, the EP and curing agent were mixed using a high-speed mechanical mixer (RW 20-KIKA-WERK) at 1200 rpm for 40 s. In the third step, the SG, CB and EP were mixed using an internal mixer (Haake Reomix) at 30 °C [13]. The rotational speed and the mixing time for all the mixings using the internal mixer were 25 rpm and 10 min, respectively. The compositions of the SG and CB were 55, 60, 65, and 70 vol% and 5, 10, 15, and 20 vol%, respectively. The composite mixtures were then poured into a steel mould to cure at various moulding temperatures (80, 110, 130, and 150 °C). The various moulding pressures (15, 20, 25 and 30 MPa) were applied for 1.5 h.

3. Characterisation

The in-plane electrical conductivity of the CB/SG/EP composites was measured using a Jandel Multi Height Four-point probe [14].The through-plane electrical conductivity of the CB/G/EP composites was measured using a through-plane electrical conductivity tester manufactured by Zentrum für BrennstoffzellenTechnik in Duisburg, Germany [15]. The mechanical properties were measured by the three-point bending test according to ASTM D790-03 at room temperature using a Universal Testing Machine Model Instron 5567 at a cross-head speed of 1 mm/min. The dimensions of the specimens for the three-point bending test were 100 (length) × 12.7 (width) × 2.5 mm (thickness), and the support span length of the specimens was fixed at 50.8 mm. The fractured surfaces of the composites plates from the three-point bending test were observed using scanning electron microscopy (FESEM, Model Supra 55/55VP) to observe the dispersion of the conductive fillers in the polymer matrix. The porosity of CB/SG/EP composite was determined according to the ASTM C20 test procedure. Thermal degradation at the optimal composition of the CB/G/EP composites was measured by thermal gravimetric analysis (TGA, NETZSCH STA449F3) from 31 °C to 900 °C at a heating rate of 20 °C/min in a nitrogen atmosphere.

4. Results and discussion

4.1. Electrical conductivity of the CB/SG/EP composites

The in-plane and through-plane electrical conductivities of the composites with different loading concentrations of SG (primary filler) and CB (secondary filler) are shown in Fig. 2. The in-plane and through-plane electrical conductivities sharply increased as the CB loading concentration increased from 5 vol% to 10 vol%. Then, the conductivities began to decrease as the CB loading concentration increased from 15 to 20 vol%. A similar trend for the in-plane and through-plane electrical conductivities at the optimum loading of 10 vol% CB can be observed. The highest in-plane and through-plane electrical conductivities of the CB/SG/EP composite were 150 S/cm and 55 S/cm at

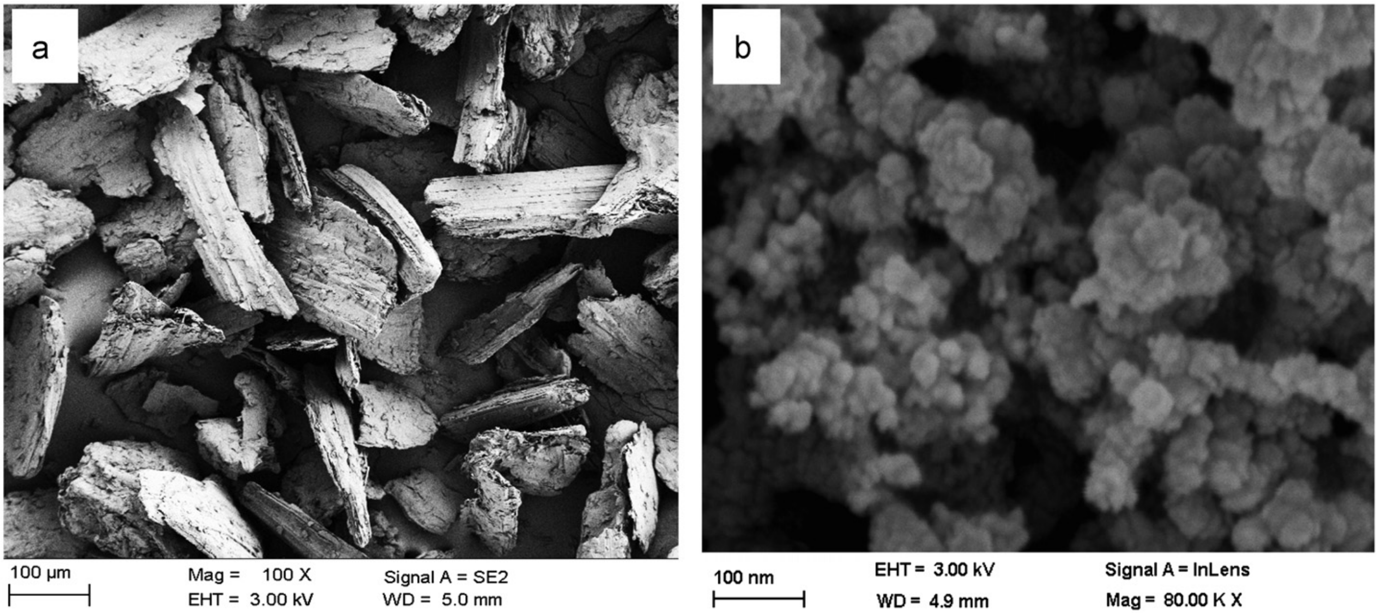

Fig. 1. (a) SEM images of the as-received CB and (b) SG.

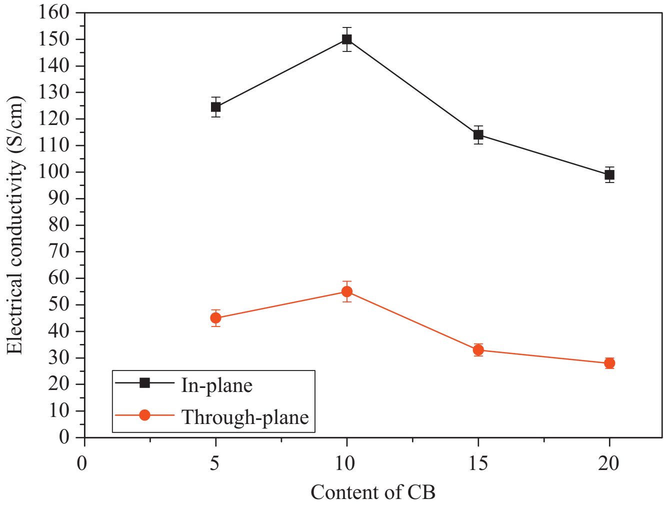

Fig. 2. Effect of the filler loading (vol%) on the in-plane and through-plane electrical conductivities of the CB/SG/EP composites.

10 vol% CB, respectively. These results can be explained by the synergistic effect of combining CB and SG as the primary and secondary fillers, which produces higher in-plane and through-plane electrical conductivities. The spaces between the SG particles, which exhibit a flake-like geometry, were filled effectively with CB, which are smaller in size and have a spherical geometry that improves the conducting path formation between the CB/SG and epoxy matrix, as shown in Fig. 3.

The in-plane electrical conductivity of the CB/SG/EP composite was greater than the through-plane electrical conductivity, which can be attributed to the arrangement of the conductive fillers on the surface being easier to form compared with that of the conductive fillers through the plate [16]. However, the in-plane and through-plane electrical conductivities decreased as the CB load increased due to the epoxy resin which did not fully wet the fillers. The agglomeration that occurred with a CB loading of 20 vol% deteriorated the in-plane and through-plane electrical conductivities [17]. Fig. 2 confirmed that incorporating conductive fillers with different geometries and sizes with CB loading (10 vol%) can create synergistic effects on the in-plane and through-plane electrical conductivities [17–19].

Fig. 4 shows the SEM images of the fractured surfaces of the CB/SG/EP composites. The images show that the CB was well-dispersed over the entire area between the SG particles at 10 vol%, but CB agglomerates were formed at 20 vol %. These agglomerates were responsible for the decreased in-plane and through-plane electrical conductivities [20–22].

4.2. *Effect of CB on the flexural strength*

Fig. 5 shows the effect of different CB concentrations on the flexural strength. The highest flexural strength obtained was 39 MPa at 10 vol% CB. The addition of CB at concentrations greater than 10 vol% caused the flexural strength to decrease sharply. Similar behaviour was also observed for the in-plane and through-plane electrical conductivities, as shown in Fig. 2.

Increasing the CB concentration beyond 10 vol% resulted in less available epoxy resin to bind to the conductive fillers, which decreased the flexural strength [6,23].

4.3. *Effect of the moulding temperature on the in-plane and through-plane electrical conductivities*

The effect of the moulding temperature on the in-plane and through-plane electrical conductivities is shown in Fig. 6.

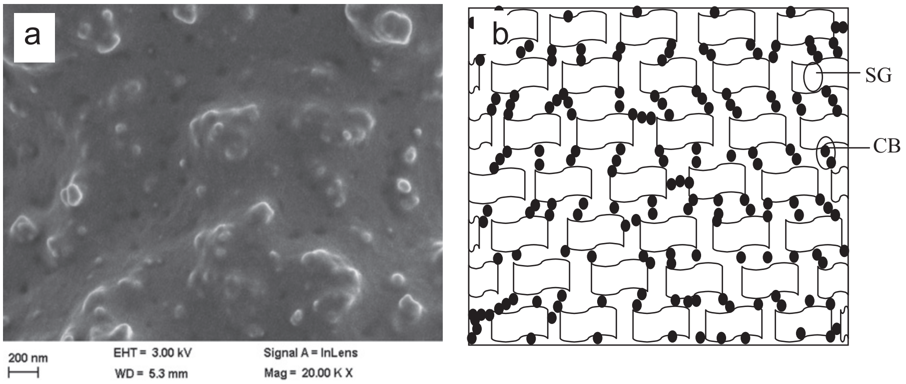

Fig. 3. (a) SEM fracture surface image of the CB/SG/EP composites and (b) schematic representation of the synergetic effect of combining CB and SG as conductive fillers.

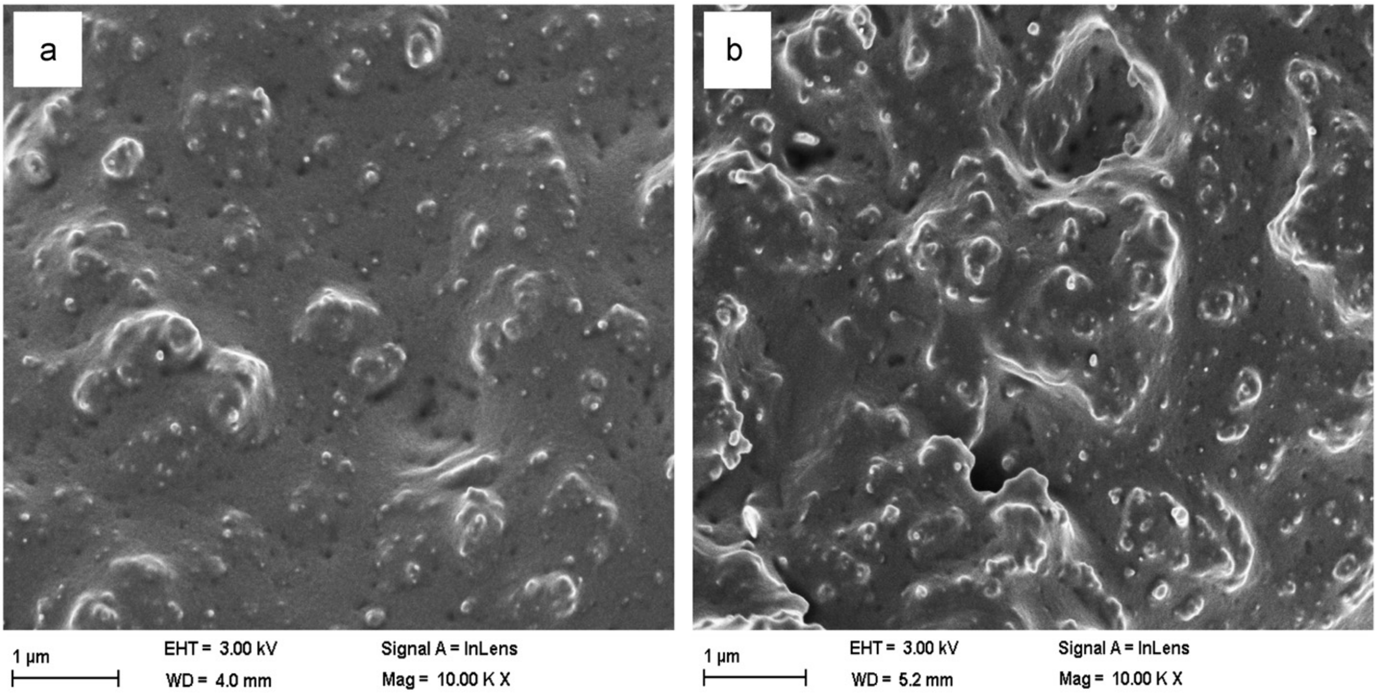

Fig. 4. SEM fracture surface images of the CB/SG/EP composites at (a) 10 vol% CB and (b) 20 vol% CB.

The CB/SG/EP composite with a composition of 10/65/25 vol% was selected to study the effect of the moulding parameters. Four different temperatures (80, 110, 130, and 150 °C) were used. The results show that the in-plane and through-plane electrical conductivities increased as the moulding temperature increased, where the highest electrical conductivities were achieved at a temperature of 150 °C.

The in-plane and through-plane electrical conductivities increased by 114% (150 S/cm) and 43% (45 S/cm), respectively, compared with when the composites were moulded at 80 °C. Increasing the moulding temperature from 80 to 150 °C enhanced the formation of the conductive network between the fillers in the polymer matrix, which progressively increased the in-plane and through-plane electrical conductivities of the composite [21,24].

4.4. The effect of the moulding pressure on the in-plane and through-plane electrical conductivities

The in-plane and through-plane electrical conductivities of the CB/SG/EP composites with 10/65/25 vol% composition moulded at different pressures are shown on Fig. 7. The results show that the in-plane and through-plane electrical conductivities increased gradually as the moulding pressure increased. The highest electrical conductivity was achieved at 30 MPa, which exhibited in-plane and through-plane electrical conductivities of 150 and 50 S/cm, respectively. The in-plane electrical conductivity increased by approximately 67% at a moulding pressure of 30 MPa compared with that at 15 MPa.

The high loading (75 vol%) of the conductive filler is needed to increase the electrical conductivity of the composites.

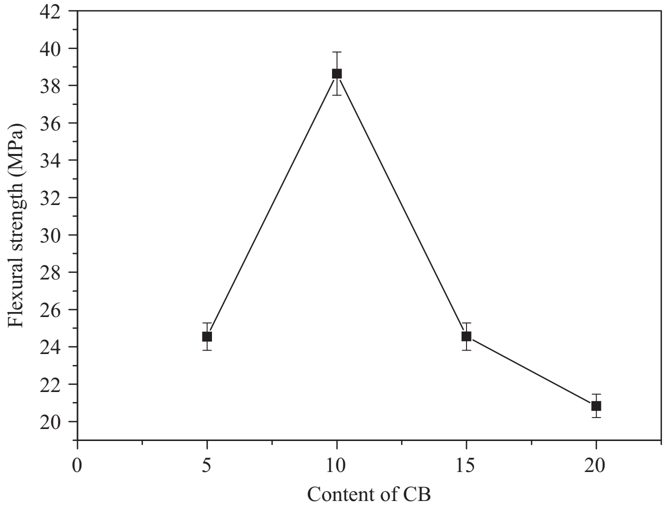

Fig. 5. Effect of the filler loading (vol%) on the flexural strength of the CB/SG/EP composites.

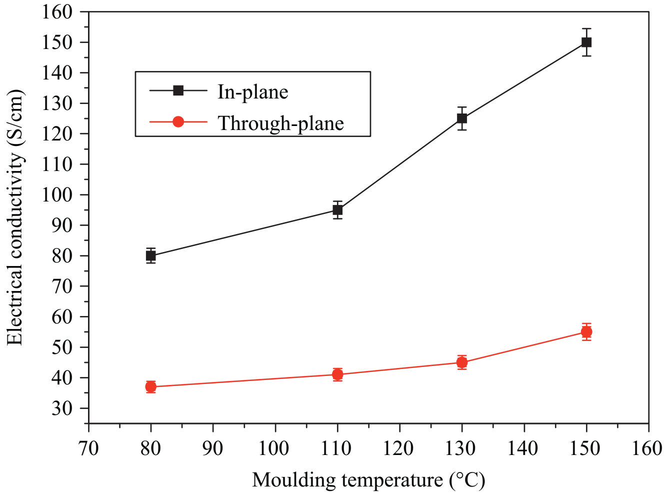

Fig. 6. Effect of the moulding temperature on the in-plane and through-plane electrical conductivities of the CB/SG/EP composites.

However, a greater filler loading results in a greater mixture viscosity, and subsequently, the fabrication process of the composites becomes more difficult. This condition caused voids in the composites, particularly when the filler loading exceeded the composition of the critical pigment volume concentration [25]. Theoretically, increasing the moulding pressure would produce denser composites, and the in-plane and through-plane electrical conductivities of the composites would increase. An increased moulding pressure can reduce voids in the composites.

Fig. 8 shows that the CB/SG/EP composite required a higher moulding pressure to reduce void formations during the fabrication process. Incorporating a primary filler (flake shape) with a secondary filler (spherical shape) effectively filled the voids; however, a higher moulding pressure is required to reduce the distance between the conductive fillers with different shapes and sizes, as shown in Fig. 8. It is evident that voids are only eliminated at the highest moulding pressure.

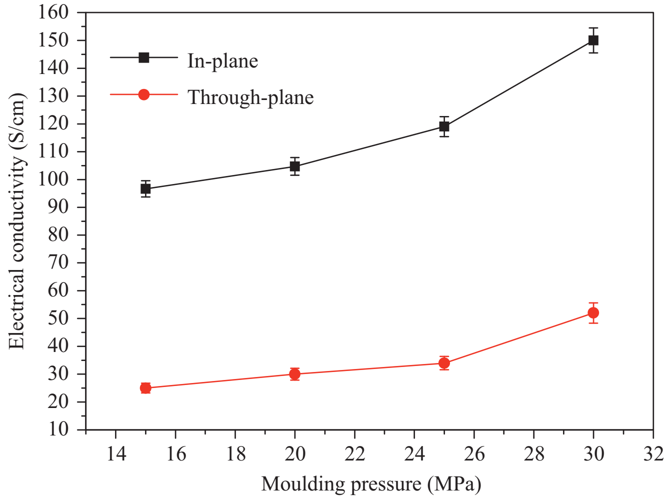

Fig. 7. Effect of the moulding pressure on the in-plane and through-plane electrical conductivities of the CB/SG/EP composites.

Boey and Lye used a hot press machine to reduce voids [26]. Increasing the moulding pressure can reduce voids in composites [26–28]. When the filler loading exceeds the percolation threshold, the electrical conductivity improves as the contact between the conductive fillers increases. Then, the electrical conductivity of the composites can be controlled by the electrical conductivity of the conductive filler and the contact between them [29,30].

4.5. The effect of the moulding pressure on the porosity and the thermogravimetric analysis (TGA)

The effect of the moulding pressure on the porosity of the CB/SG/EP composite is shown in Fig. 9. Increasing of the moulding pressure during the compression moulding process from 15 MPa to 30 MPa decreased the porosity of the CB/SG/EP composite. The lowest porosity of CB/SG/EP composite was 1.52% at the highest moulding pressure (30 MPa) because increases in moulding pressure of the mixture cause the distance between SG and CB as conductive fillers to decrease, therefore eliminating the porosity of the CB/SG/EP composite. This value is lower than porosity of SG/EP composite at the same moulding pressure (30 MPa), namely 7%. These data confirm that, CB as secondary filler with small-size has potential to fill the distance between conductive fillers at higher moulding pressure. The TGA curve for the composite and pure epoxy polymer is shown in Fig. 10. The temperature degradation shift of the pure epoxy was approximately 280 °C and increased up to 370 °C for the CB/SG/EP composite at 10/65/25 vol%. A larger temperature shift is needed if the bulk composite is to be used as a bipolar plate in low-temperature and high-temperature PEM fuel cells that operate at 80 °C and 130–200 °C, respectively [5,31]. The TGA curves in Fig. 10 show that the fabricated

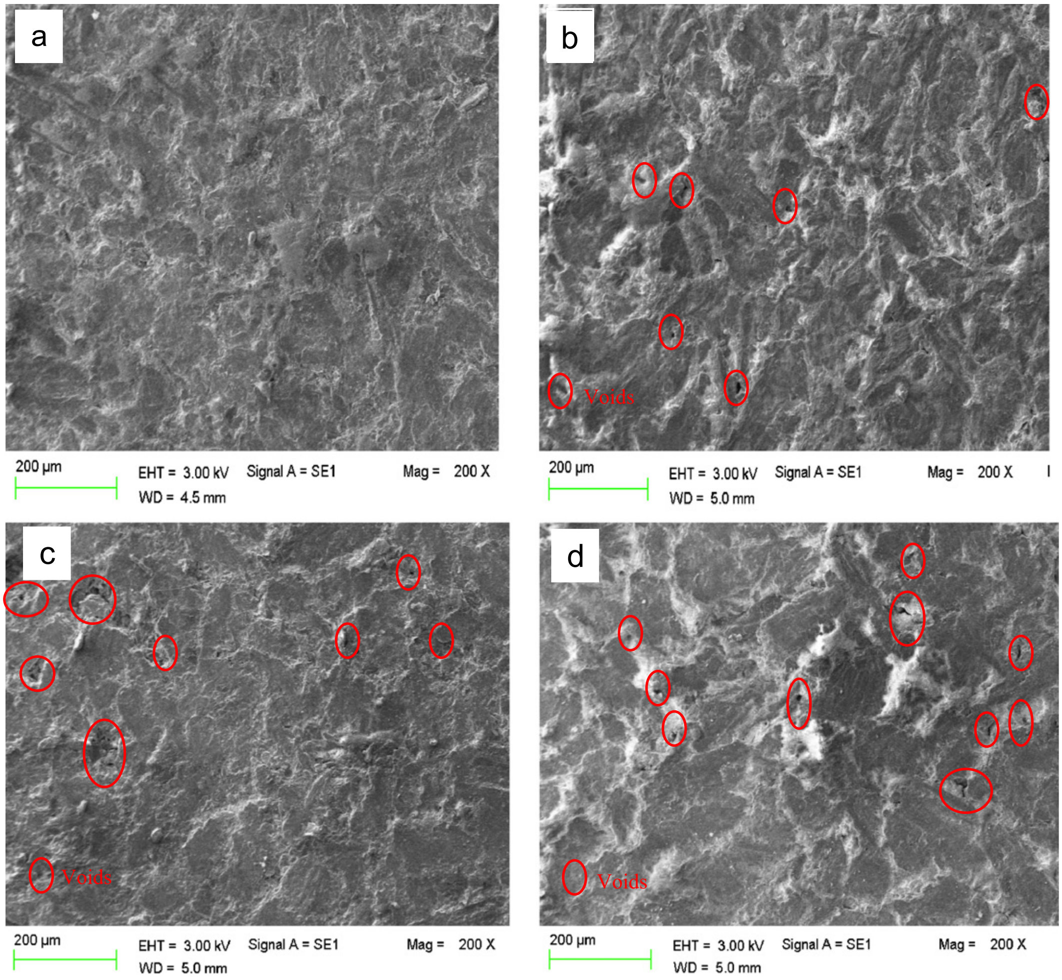

Fig. 8. SEM surface images of the CB/SG/EP composite at moulding pressures of (a) 30 MPa, (b) 25 MPa, (c) 20 MPa and (d) 15 MPa.

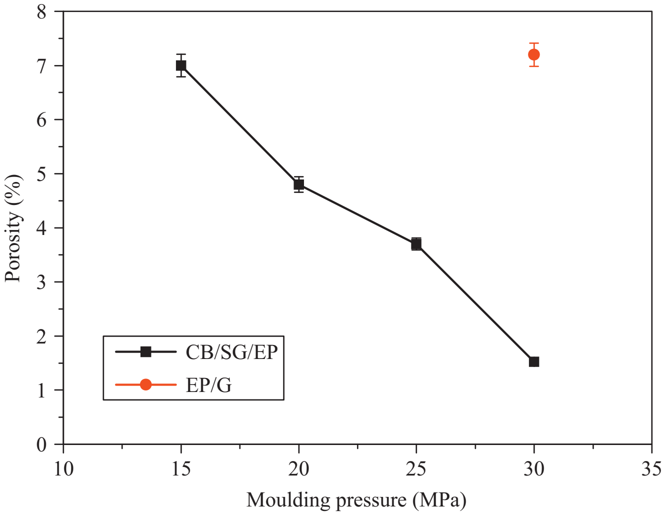

Fig. 9. Effect of the moulding pressure on the porosity of the CB/SG/EP composites.

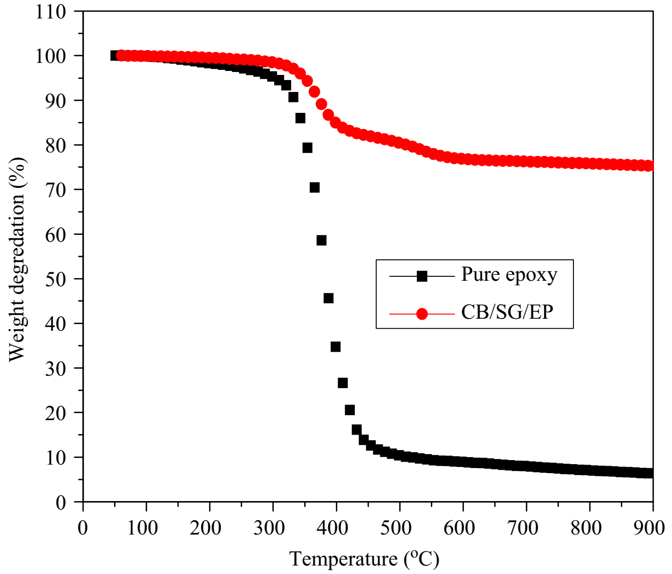

Fig. 10. TGA curve of the CB/SG/EP composite at the optimal concentration.

composite plate has the potential to be used in low- and high-temperature PEM fuel cells. The pure epoxy exhibited essentially the same behaviour as that of the composite until approximately 140 °C, which is when the pure epoxy began to degrade, whereas the composite plate was stable until 280 °C. Fig. 10 shows that the weight loss due to degradation at 100 °C was only 0.2%. The low weight degradation of the composite plate was due to the small amount of CB, which increased the thermal stability of the composite plate. This result confirms that the CB/SG/EP composite plate with a 10/65/25 vol% composition is suitable for bipolar plate applications in low- or high-temperature PEMFCs.

5. Conclusion

The effects of CB on the properties of a polymer composite plate were investigated. Based on the results, the following conclusions were reached:

1. The combination of SG and CB as the primary and secondary fillers produced higher in-plane and through-plane electrical conductivities.
2. The addition of CB at loadings above the critical filler loading (10 vol %) decreased the electrical conductivity and flexural strength.
3. Increasing of the moulding pressure during the compression moulding process decreased the porosity of the CB/SG/EP composite.
4. The results of the electrical conductivity, flexural strength, porosity and thermal gravimetric analyses indicated that 10/65/25 vol% is a suitable composition of CB/SG/EP composites for use as bipolar plate material in low- and high-temperature PEMFCs.

Acknowledgements

The authors gratefully acknowledge the financial support given for this work by the Malaysian Ministry of Higher Education (MOHE) Universiti Kebangsaan Malaysia under the UKM-GUP-TK-08–17-063 project.

References

[1] Q.H. Zhang, D.J. Chen, Percolation threshold and morphology of composites of conducting carbon black/polypropylene/EVA, Journal of Materials Science 39 (2004) 1751–1757.

[2] C.K. Leong, Y. Aoyagi, D.D.L. Chung, Carbon black pastes as coatings for improving thermal gap-filling materials, Carbon 44 (2006) 435–440.

[3] C. Li, E.T. Thostenson, T.W. Chou, Sensors and actuators based on carbon nanotubes and their composites: a review, Composites Science and Technology 68 (2008) 1227–1249.

[4] S. Chunhui, P. Mu, H. Zhoufa, Y. Runzhang, Aluminate cement/graphite conductive composite bipolar plate for proton exchange membrane fuel cells, Journal of Power Sources 166 (2007) 419–423.

[5] S. Radhakrishnan, B.T.S. Ramanujam, A. Adhikari, S. Sivaram, High-temperature, polymer–graphite hybrid composites for bipolar plates: effect of processing conditions on electrical properties, Journal of Power Sources 163 (2007) 702–707.

[6] X.S. Yi, G. Wu, D. Ma, Property balancing for polyethylene-based carbon black-filled conductive composites, Journal of Applied Polymer Science 67 (1998) 131–138.

[7] 〈http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/fuel_cells. pdf〉.

[8] R.B. Mathur, S.R. Dhakate, D.K. Gupta, T.L. Dhami, R.K. Aggarwal, Effect of different carbon fillers on the properties of graphite composite bipolar plate, Journal of Materials Processing and Technology 203 (2008) 184–192.

[9] P.H. Maheshwari, R.B. Mathur, T.L. Dhami, Fabrication of high strength and a low weight composite bipolar plate for fuel cell applications, Journal of Power Sources 173 (2007) 394–403.

[10] F. Mighri, M.A. Huneault, M.F. Champagne, Electrically conductive thermoplastic blends for injection and compression molding of bipolar plates in the fuel cell application, Polymer Engineering and Science 44 (2004) 1755–1765.

[11] J.H. Lee, Y.K. Jang, C.E. Hong, N.H. Kim, P. Lee, H.K. Lee, Effect of carbon fillers on properties of polymer composite bipolar plates of fuel cells, Journal of Power Sources 193 (2009) 523–529.

[12] S.R. Dhakate, R.B. Mathur, B.K. Kakati, T.L. Dhami, Properties of graphite-composite bipolar plate prepared by compression molding technique for PEM fuel cell, International Journal of Hydrogen Energy 32 (2007) 4537–4543.

[13] H. Suherman, J. Sahari, A.B. sulong, Electrical properties of carbon nanotubes-based epoxy nanocomposites for high electrical conductive plate, Advanced Materials Research 264–265 (2011) 559–564.

[14] R. Dweiri, J. Sahari, Electrical properties of carbon-based polypropylene composites for bipolar plates in polymer electrolyte membrane fuel cell (PEMFC), Journal of Power Sources 171 (2007) 424–432.

[15] A. Heinzel, F. Mahlendorf, O. Niemzig, C. Kreuz, Injection moulded low cost bipolar plates for PEM fuel cells, Journal of Power Sources 13 (2004) 35–40.

[16] W. Chen, Y. Liu, Q. Xin, Evaluation of a compression molded composite bipolar plate for direct methanol fuel cell, International Journal of Hydrogen Energy 35 (2010) 3783–3788.

[17] B.K. Kakati, D. Sathiyamoorthy, D.A. Verma, Semi-empirical modeling of electrical conductivity for composite bipolar plate with multiple reinforcements, International Journal of Hydrogen Energy 36 (2011) 14851–14857.

[18] R.A. Antunes, C.L. Mara, D. Oliveira, E. Gerhard, E. Volkmar, Carbon materials in composite bipolar plates for polymer electrolyte membrane fuel cells: a review of the main challenges to improve electrical performance, Journal of Power Sources 196 (2011) 2945–2961.

[19] P.C. Ma, M.Y. Liu, H. Zhang, S.Q. Wang, R. Wang, K. Wang, Y.K. Wong, B.Z. Tang, S.H. Hong, K.W. Paik, J.K. Kim, Enhanced electrical conductivity of nanocomposites containing hybrid fillers of carbon nanotubes and carbon black, ACS Applied Materials and Interface: American Chemical Society 1 (2009) 1090–1096.

[20] V. Causin, C. Marega, A. Marigo, G. Ferrara, A. Ferraro, Morphological and structural characterization of polypropylene/conductive graphite nanocomposites, European Polymer Journal 42 (2006) 3153–3161.

[21] N. Hu, Z. Masuda, G. Yamamoto, H. Fukunaga, T. Hashida, J. Qiu, Effect of fabrication process on electrical properties of polymer/mwnt nanocomposite, Composites Part A 39 (2008) 893–903.

[22] H. Suherman, A.B. Sulong, J. Sahari, Effect of filler loading concentration, curing temperature and molding pressure on the electrical conductivity of CNTs/graphite/epoxy nanocomposites at high loading of conductive fillers, International Journal of Mechanical and Materials Engineering (IJMME) 5 (2010) 74–79.

[23] Q. Yin, K. Sun, A. Li, L. Shao, S. Liu, C. Sun, Study on carbon nanotube reinforced phenol formaldehyde resin/graphite composite for bipolar plat, Journal of Power Sources 175 (2008) 861–865.

[24] C.A. Martin, J.K.W. Sandler, M.S.P. Shaffer, M.K. Schwarz, W. Bauhofer, K. Schulte, A.H. Windle, Formation of percolating networks in multi-wall carbon-nanotube–epoxy composites, Composites Science and Technology 64 (2004) 2309–2316.

[25] V. Mehta, J.S. Cooper, Review and analysis of PEM fuel cell design and manufacturing, Journal of Power Sources 114 (2003) 32–53.

[26] F.Y.C. Boey, S.W. Lye, Void reduction in autoclave processing of thermoset composites: part 2: void reduction in a microwave curing process, Composites (1992) 266–270.

[27] P. Olivier, J.P. Cottu, B. Ferret, Effects of cure cycle pressure and voids on some mechanical properties of carbon/epoxy laminates, Composites 26 (1995) 509–515.

[28] I. Sudarisman, J. Davies, The effect of processing parameters on the flexural properties of unidirectional carbon fibre–reinforcement polymer (CFRP) composites, Materials Science and Engineering A 498 (2008) 65–68.

[29] S.I. Heo, J.C. Yun, K.S. Oh, K.S. Han, Influence of particle size and shape on electrical and mechanical properties of graphite reinforced conductive polymer composites for the bipolar plate of PEM fuel cell, Advanced Composite Materials 15 (2006) 115–126.

[30] H. Suherman, A.B. Sulong, J. Sahari, Effect of the compression molding parameters on the in-plane and through-plane conductivity of carbon nanotubes/graphite/epoxy nanocomposites as bipolar plate material for a polymer electrolyte membrane fuel cell, Ceramics International 39 (2013) 1227–1284.

[31] T. Derieth, G. Bandlamudi, P. Beckhaus, C. Kreuz, F. Mahlendorf, A. Heinzel, Development of highly filled graphite compounds as bipolar plate materials for low and high temperature pem fuel cells, Journal of New Materials for Electrochemical Systems 11 (2008) 21–29.