Prospects of graphite - polypropylene/epoxy blend composite for high performance bipolar plate in polymer electrolyte membrane fuel cell

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Abstract. Conductive polymer composites (CPCs) are very promising candidate materials for bipolar plates (BPs) in polymer electrolyte membrane fuel cells (PEMFCs). However, a major challenge facing application of CPCs in PEMFC BPs is the difficulty in achieving high electrical conductivity while maintaining adequate mechanical strength. Therefore, a good balance between electrical conductivity and mechanical strength is critical in the development of high-performance CPC BPs. In this study, CPCs consisting of polypropylene (PP)/epoxy blend filled with graphite were investigated for application as BP material, which will combine electrical conductivity and mechanical strength that meet the performance requirements for PEMFC BPs. The CPCs, with 30 – 80 wt% graphite powder, were produced by melt mixing followed by compression molding. The morphology, in-plane electrical conductivity, and flexural strength of the composites were investigated using the scanning electron microscopy, four-point probe method, and three-point bending test, respectively. The results obtained were compared with the technical targets for PEMFC BPs by the United States Department of Energy (DOE). All the PP/epoxy/graphite composites exhibited flexural strength that satisfies the DOE target of > 25 MPa while the composite with 80 wt% graphite content showed the best in-plane electrical conductivity.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have a huge potential for addressing the world’s energy needs and the environmental issues associated with the current fossil-dependent energy systems. Out of the currently available fuel cell technologies, the PEMFC is preferable, particularly for transportation and other mobile applications, due to its beneficial features such as convenient fuel supply, high energy efficiency, desirable power density, low temperature operation, and long lifetime [1-2]. The bipolar plate (BP) is a key component of the PEMFC, and its functionality and performance greatly impact on the overall performance and durability of the PEMFC stack. Key among the required properties for the BP to perform its functions effectively is good electrical performance.
For PEMFC BP application, conductive polymer composites (CPCs) have the potential to outperform other material options such as graphite and metals. This is due to their attractive properties such as low cost, good corrosion resistance, low density, and ease of forming gas flow channels [3-4]. However, a major drawback of CPC BPs is their low electrical conductivity, and the conductive filler loading in most commonly used CPCs is below 10 vol% [5], which is usually not enough to impart sufficient electrical conductivity for BP application. Despite their generally low conductivity, CPCs with remarkable electrical conductivity values have been reported in the literature [5-10]. However, the conductivities of several of the developed CPCs are still lower than the target set by the United States Department of Energy (DOE). In cases where the DOE target has been met, high filler content (70–80 wt%) was required [5, 11]. At such high filler concentrations, issues associated with difficulty in processing as a result of increased melt viscosity set in. This leads to degradation of the mechanical strength of the produced composites. To address this problem, some authors have employed the use of different filler combinations with the goal of achieving a good balance between electrical conductivity and strength [6, 10, 12]. However, the carbon black, carbon fiber, carbon nanotubes, and graphene, which are usually used as secondary fillers in addition to graphite in such multi-filler CPCs, often pose problems such as agglomeration and non-uniform dispersion. This results in detrimental effects on the electrical and mechanical properties of the composites [13]. Another possible approach to achieve CPC BPs with a good electrical conductivity and strength balance is the use of polymer matrices with inherently high strengths since they have the potential to yield composites with high electrical conductivity and satisfactory mechanical strength even at high filler loadings.

Epoxy resins are attractive matrix materials for producing CPC BPs due to their excellent mechanical properties and chemical resistance. However, they are brittle and extremely prone to impact-induced failure due to their highly crosslinked structure. If applied in PEMFC BPs, especially in transportation applications, cracking of the plates and leaking of reactant gases may occur as a result of poor resistance to mechanical shocks and vibrations. Polypropylene (PP) has lower mechanical strength compared to epoxy but it has good toughness and impact resistance [14]. A blend of PP and epoxy have been reported to exhibit improved combination of strength, toughness, and impact resistance [15]. Therefore, the potential exists for obtaining CPC PEMFC BPs with electrical conductivity and mechanical strength that meet the DOE targets, using PP/epoxy as the matrix. In this study, the prospect of PP/epoxy/graphite composite to yield high performance and durable PEMFC BPs was investigated. PP/epoxy blends filled with varying contents of graphite were produced by melt mixing and followed by compression moulding. After various characterization steps, the performances of the produced composites were compared to the DOE targets.

2. Materials and Methods

2.1. Materials

The PP (density 0.9 g/cm³ and melt index 4) and maleic anhydride-grafted polypropylene (MAH-g-PP) used in this study were purchased from Sigma-Aldrich. Due to immiscibility of PP and epoxy, the MAH-g-PP (with melting point of 156 °C, density of 0.934 g/cm³ at 25 °C, and MAH content of 8-10 wt%) was used as a compatibilizer. The bisphenol-A epoxy resin (LR 30) and the amine-type hardener (LH 30) were purchased from AMT Composites, South Africa. The densities of the epoxy resin and hardener are 1.13 g/cm³ (at 25 °C) and 0.94 g/cm³ (at 20 °C), respectively. The graphite powder used was donated by Graftech South Africa (Pty) Ltd.

2.2. Composite Preparation

Before mixing, the PP and MAH-g-PP were dried under vacuum at 70 °C for 8 hours to remove any moisture that may be present. Different PP/epoxy/graphite composite samples with 30-80 wt% graphite were then prepared by melt mixing in a Haake Rheomix OS mixer at 190 °C and 60 rpm. The graphite powder, PP and MAH-g-PP were first manually mixed. The mixture was then transferred into the Rheomixer and mixed for
3 minutes. The epoxy resin was then added, and mixing was continued for another 4 minutes. The hardener was then added, and the mixing was continued. An epoxy-hardener weight ratio of 5:1 was used as recommended by the supplier. Also, epoxy-MAH-g-PP weight ratio of 3:1 was used for all the prepared composites. The total mixing time was 10 minutes. After mixing, the samples were compression moulded at 200 °C at 2 metric tonnes for 10 minutes.

2.3. Characterizations

The morphology of the graphite powder and the prepared composites was observed using a TESCAN VEGA3 scanning electron microscope (SEM). To analyze the morphology of the composites clearly, prior to SEM observation, some freeze-fractured samples were etched in dichloromethane for 30 min to remove the epoxy phase on the surfaces. Composite samples with 37 mm × 13 mm × 1.7 mm dimensions were used for the in-plane electrical conductivity measurements by means of the four-point probe method according to ASTM D4496. The electrical resistance (R) was measured by passing a constant current through the sample and measuring the voltage drop. The electrical resistivity (ρ) was calculated using equation (1):

\[
\rho = \frac{R}{I \times W} \times t \times f_1 \times f_2
\]

Where \(f_1\) and \(f_2\) are finite thickness and width correction factors, respectively, and \(t\) is the thickness of the sample. Based on the dimensions of the test specimens, the values \(f_1\) and \(f_2\) were obtained from data provided in literature [16-17]. Values of the in-plane electrical conductivity (\(\sigma\)) were obtained from the reciprocal of the resistivity values. The flexural properties of the composite samples were measured at room temperature by the three-point bending test using the Instron 5966 universal testing machining according to ASTM D790-03. The flexural specimens with dimensions 100 mm × 12.7 mm × 1.76 mm were cut from the compression moulded plaques using a thin diamond cutting disc. The support span was 30 mm, and the crosshead speed was 1 mm/min.

3. Results and discussion

3.1. Microstructure of the PP/epoxy/graphite composites

The morphology of the graphite filler used in the study shows a layered structure (figure 1). This type of structure has the potentials for achieving higher conductivity-CPCs compared to graphite particles with granular structure [18]. However, the larger surface area can result into lower degree of filling and processability. Figure 2 shows the SEM micrographs of the fractured surfaces of the neat polymer blend and composite. The microstructure of the PP/epoxy blend, as shown in figure 2a, shows a co-continuous morphology. Possible morphologies in binary immiscible polymer blends include lamellar structure, matrix-dispersed particle structure, matrix-fiber structure, and co-continuous structure. The formation of co-continuous structure is favoured by a symmetric or close to symmetric blend composition [19]. Therefore, the co-continuous morphology observed for the PP/epoxy blend can be attributed to the close to symmetric composition of the blend.

Figure 2b shows the morphology of the PP/epoxy/80 wt% graphite composite. At such high filler loading, the microstructure of the composite is largely influenced by the morphology of the graphite filler. This is as a result of the larger concentration and volume fraction of the graphite filler compared to the polymer matrix. The composition of such highly filled composite is more likely to represent that of graphite particles with a polymer binder rather than that of graphite filler dispersed in a polymer matrix. Therefore, the morphology of the PP/epoxy/80 wt% graphite composite revealed several micrometers size flakes of graphite protruding from the polymer matrix. The graphite flakes are present throughout, and no large, noticeable distinct polymeric features can be seen. Also, the SEM image (figure 2c) revealed presence of some voids (red arrows) within the material. This can be due to insufficient amount of resin to completely wet the graphite flakes.
Figure 1. Morphology of the graphite filler used in the study.

Figure 2. SEM micrograph of (a) neat PP/epoxy blend, (b) PP/epoxy/80 wt% graphite composite, and (c) PP/epoxy/80 wt% graphite composite at higher magnification showing presence of voids (red arrows).

3.2. Electrical properties of the PP/epoxy/graphite composites

The variation of in-plane electrical conductivity of the composite samples with graphite contents is shown in figure 3. The in-plane electrical conductivity of the composites increased as the graphite content increased from 30 to 80 wt%. The electrical conductivity of polymer/graphite composites depends on the electrical conductivity and concentration of the graphite filler and can be explained by the percolation theory. According to classical percolation theory, the electrical conductivity ($\sigma$) of polymer/graphite composites above the percolation threshold ($\Phi_c$) is related to the filler concentration according to the following equation [20]:

$$\sigma = \sigma_0 (\Phi - \Phi_c)^t$$  \hspace{1cm} (2)

Where $\sigma_0$ is the electrical conductivity of the filler, $\Phi$ is the weight fraction of the filler, and $t$ is a critical exponent related to the dimension of the filler. Therefore, at $\Phi > \Phi_c$, electrical conductivity of the composite will increase with increase in filler content. Also, the electrical conductivity of CPCs depends on mutual contact of the conductive filler materials to generate conductive paths throughout the composites [21-22]. Therefore, increasing the graphite filler content would result in more electrically conductive paths for flow.
of current carrier within the composites. The composite with 80 wt% graphite exhibited the highest in-plane electrical conductivity (68.03 Scm\(^{-1}\)) as a result of having the highest graphite content for formation of conducting networks. Although, the conductivity values obtained in this study are still below the DOE target of >100 Scm\(^{-1}\), the range of in-plane electrical conductivity obtained in this study is higher than the values reported for several filled single-polymer composites in previous studies [23-24]. The relatively high conductivities obtained for the PP/epoxy/graphite composites can be attributed to the formation of a co-continuous morphology, which would favor the dispersion of the graphite filler in one of the polymer phases and promote formation of more continuous electrical conducting networks.

3.3. Flexural properties of the PP/epoxy/graphite composites
The flexural test results for the neat epoxy, neat PP/epoxy blend, epoxy/50 wt% graphite composite, PP/50 wt% graphite composite, and PP/epoxy/50 wt% graphite composite are shown in figure 4. The PP/epoxy blend exhibited a flexural strength of 58.43 MPa, which is lower than that of the neat epoxy resin with flexural strength of 67.11 MPa. This can be attributed to the inherent lower strength of PP compared to cured epoxy resin. However, since the flexural strength of the PP/epoxy blend is still much higher than the DOE target (>25 MPa), the blend is a promising matrix material for CPC BP for PEMFC. Also, the epoxy/50 wt% graphite composite exhibited a higher flexural strength of 61.78 MPa compared to 39.27 MPa for the PP/50 wt% graphite composite. This can be due to the effects of the lower strength of PP as well as the lower viscosity of the epoxy resin during processing at the elevated temperature, compared to PP, which would result into better wetting of the filler and improve the filler-matrix bonding strength [25].

The PP/epoxy/50 wt% graphite composite exhibited flexural strength of 50.43 MPa, which is lower than that of epoxy/50 wt% graphite composite but is approximately 22% higher than that of the PP/50 wt% graphite composite. For immiscible polymer blend such as PP/epoxy, low strength would be expected due to high interfacial tension. However, the compatibilizing effect of the MAH-g-PP led to good flexural strength in the PP/epoxy blend. The interaction between the carbonyl groups of the maleic anhydride (MAH)
in the MAH-g-PP and the hydroxyl groups of the epoxy resin enables the penetration of the MAH-g-PP into the polymer blend constituents. The interfacial adhesion that results from the entangled compatibilizer between the constitutive chains within the blend would offer effective stress transfer from one polymer phase to another and hinders crack initiation at the interface. Therefore, CPC BPs for PEMFC with better mechanical performance can be achieved by using MAH-g-PP compatibilized PP/epoxy blend as the matrix compared to using PP as the matrix.

Figure 4. Flexural strength of the neat epoxy resin and polymer blend filled single polymers, and 50 wt% graphite filled polymer blend.

High mechanical strength is required by BPs to be able to provide rigidity to support the membrane electrode assemblies within the PEMFC and withstand the clamping forces within the stack assembly. The effect of graphite content on the flexural properties of the PP/epoxy/graphite composites is shown in figure 5. The flexural strength of the composites increased with increasing graphite content from 46.5 MPa at 30 wt% graphite to a maximum value of 54.36 MPa at 70 wt% graphite. Increase in the graphite content from 70 to 80 wt% led to a decrease in the flexural strength of the composite to 40.16 MPa. This can be due to reduced filler-matrix adhesion and presence of voids (figure 2c) as a result of insufficient amount of resin to wet and bind the graphite powders within the composite. Voids act as potential points of failure within composite materials and their detrimental effect on the mechanical strength of the material becomes significant when their content reaches a certain level [25]. All the PP/epoxy/graphite composites exhibited good flexural strength even at high filler loadings. This can be attributed to the good interfacial bonding between the polymer phases as a result of the compatibilization effect of the MAH-g-PP. Also, increase in the load-bearing capacity of graphite filled CPCs with increasing graphite content as a result of good interfacial bonding and filler-matrix adhesion within the composites has been reported by some authors [26-27]. Increase in graphite content from 30 to 40 wt% resulted in decrease in the flexural modulus from 4177.4 MPa to 3385.9 MPa. Further increase in the graphite content led to an increase in the flexural modulus up to 11,472.8 MPa at a graphite content of 80 wt%. The increase in flexural modulus is due to the higher stiffness of graphite compared to the polymer matrix. All the flexural strength values obtained in this study meet the DOE target of >25 MPa. Therefore, all the PP/epoxy/graphite composites exhibited good flexural properties for PEMFC BP application.
4. Conclusion
Different PP/epoxy/graphite composites with 30-80 wt% graphite were prepared by melt mixing followed by compression moulding, and the morphology, electrical conductivity, and flexural properties were investigated. SEM micrograph of the PP/epoxy blend revealed a co-continuous morphology. This could be due to the immiscible nature of PP and epoxy resin, and the close to symmetric composition of the blend. The results also showed that the in-plane electrical conductivity of the composites increased with increase in graphite content from $12.09 \text{ Scm}^{-1}$ at 30 wt% to $68.03 \text{ Scm}^{-1}$ at 80 wt% graphite. The increase in conductivity with graphite content can be attributed to formation of more conducting networks as the graphite concentration increased. Also, the composite exhibited relatively high electrical conductivities due to formation of a co-continuous morphology, which would favor the distribution of the filler in one of the polymer phases and promote formation of more continuous conducting networks. The in-plane conductivity range obtained in this study is higher than that for several graphite filled-single polymer composites reported in literature. Achieving this level of conductivity shows the potentials of graphite-PP/epoxy composites for meeting the US DOE target for in-plane electrical conductivity for PEMFC BP. The flexural modulus of the composites initially decreased with increase in graphite content and then increased with increase in graphite content from 40 wt% to 80 wt%, while the flexural strength increased with increase in graphite content up to 70 wt% and then decreased with further increase in graphite content. However, all the PP/epoxy/graphite composites exhibited flexural strength that meet the DOE target of $>25 \text{ MPa}$. This can be attributed to good interfacial bonding between the polymer phases as a result of the compatibilizing effect of the MAH-g-PP, and good filler-matrix adhesion. Among the produced composites, the PP/epoxy/80 wt% graphite composite has the best combination of in-plane electrical conductivity and flexural strength with respect to the DOE targets. The results obtained in this study showed that graphite-PP/epoxy blend composite has a good potential for application in CPC BPs for PEMFC.

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