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Polypropylene Composites for Polymer Electrolyte Membrane Fuel Cell Bipolar Plates

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Summary: The polymer electrolyte membrane fuel cell (PEMFC) holds tremendous promise for a variety of mobile and stationary power generation applications and is the cornerstone of the anticipated hydrogen economy. One of the major factors limiting fuel cell commercialization is the development of bipolar plates since bipolar plates account for approximately 70% of the PEMFC weight, and 60% of the stack manufacturing and materials cost. The objective of this research is to investigate a feasibility of a conductive composite family to be used as bipolar plates in a PEMFC, in order to get the highly conductive, light weight, and low cost bipolar plates. This work utilized a combination of a polypropylene and low cost conductive filler materials: graphite, conductive carbon black, and carbon fibers. The components were combined in a batch mixer and injection molded into samples for testing with loadings up to 65%wt of fillers. The novel blends were tested for electrical conductivity, hydrophobicity, rheology, and actual plates (16 cm^2) were tested in fuel cell testing trials. The impact of different types of fillers on the composite properties was evaluated, as well as the synergetic effect of mixtures of fill types within a polypropylene matrix. From the results, the highest conductivity, 1900 S/m (in-plane) and 156 S/m (through plane), was obtained with the 65% composite. Moreover, the effects of additives such as coupling agents, and intrinsically conductive polymer (polypyrrole) were observed in this work. The electrical conductivity was influenced by polypyrrole added to the polypropylene composite.

Keywords: composite bipolar plates; conductive plate; electrical conductivity; polymer electrolyte membrane fuel cell (PEMFC); polypropylene composite

Introduction

The development of alternative electricity generation technologies, such as fuel cells, has been stimulated by the desire for the reduction of pollutant and CO_2 emissions. Polymer electrolyte membrane fuel cells (PEMFCs) are attractive because they provide high reactant conversion efficiency,[1] no harmful emissions, quiet operation, rapid load response and low operation temperatures. Current designs are still considered to be too expensive, so cost reduction is an important area of PEMFC research.[2] The bipolar plates in a PEMFC stack are a relatively expensive component that may present opportunities for cost reduction. The bipolar plates typically fill a number of functions: to conduct electrons to complete the circuit (i.e. carrying electrons to and from the electrode), to provide a flow path for gas transport to distribute the gases over the entire electrode area uniformly, to distribute the fuel and oxidant within the cell, to facilitate water management within fuel cell, to connect the individual cells in the stack, to provide mechanical strength and rigidity to support a fuel cell stack, and to provide thermal conduction to help regulate fuel cell temperature and removing

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heat from the electrode to the cooling channels.[3,4] The bipolar plate material characteristic requirements include low-cost materials and processing, light weight, thin, sufficient mechanical integrity, high surface and bulk electronic conductivity, low permeability (i.e. boundary between fuel and oxidant), and corrosion resistance (in the moist atmosphere of the cell).[5] The currently available materials for fuel cell bipolar plate production are metals, graphite and composites based on graphite. Metallic bipolar plates could be attractive for use in automotive and transport applications but they also have corrosion problems, and they release of cations which can poison the electrode catalysts or the electrolyte, thus decreasing of cell performance.[6] Graphite bipolar plates possess good electrical conductivity, excellent corrosion resistance, and a lower density than metal plates. The problems of graphite plates are their brittleness and lower density than metal plates. The high cost of graphite bipolar plates is also associated with the machining of gas flow channels on the surface of plates and post processing requirement such as resin impregnation to make the plate impermeable to the fuel and oxygen.[2,7] Conductive composites as an alternative material have shown promise toward solving this problem due to strong compatibility with the fuel cell environment and low cost/high volume manufacturing options. Electrically conductive materials with thermoplastic matrices are considered to be an important group of relatively inexpensive materials for special applications. They are divided into two types: one is intrinsically conducting polymers such as polypyrrole, polyaniline, polythiophene; and the other is conducting composites in which some conducting fillers, such as carbon black, graphite, short carbon fibers.[8] Composite systems, consisting of conducting fillers (e.g., carbon black, graphite, metal powder, short carbon fibers) or conductive polymer in a polymer matrix, may create materials that are tough and flexible with high electrical conductivity.[9] Whatever the nature of particles, current circulation is obtained through ‘percolation’ of the conductive components through the polymer resin, forming conductive pathways throughout the bulk composite material. Bipolar plates made from polymer carbon composite are light in weight and have low gas permeability, and can reduce manufacturing cost by mass production.[10] Different bipolar plate production techniques like high performance drilling, compression moulding and injection moulding have been investigated to fabricate the required shape. Zentrum für BrennstoffzellenTechnik GmbH[11] has demonstrated the production of bipolar plates by injection moulding can become price competitive even for comparatively small series in the range of several thousand plates. Since injection molding has been identified as most promising and cost-effective production processes, this work focused on injection moulding as a mass production technique to manufacture bipolar plates, and selected resin materials capable of this manufacturing method. The purpose of this work is to investigate the feasibility of a specific conductive composite family to be used as bipolar plates in a PEMFC. In this paper, the study focused on the composites of polypropylene (PP), carbon black, carbon fiber and synthetic graphite. Furthermore, the effects of coupling agent and conductive polymer acting as an additive on the electrical conductivity are observed in this work. PEM stacks with injection moulded bipolar plates of 3 mm thickness and an electrical conductivity of up to 1900 S/m have been constructed and successfully operated.

Experimental Part

Composite Materials

In this study the materials used for composite development include polypropylene (PP) and various types of carbon based fillers. The matrix polymer used to prepare the ternary blend composite was an Equistar polypropylene with the melt flow index of 7 g/10 min. Three carbon fillers were used in conjunction with PP to form electrically conductive composites. The fillers include Fortafil's short carbon fiber (CF) whose particles are 7 μm in diameter, Cabot's Vulcan carbon black (VCB) which is 30 nm in size and 253 mg/g in surface area, Phillip's acetylene carbon black (ACB) which has particle size 42 nm and surface area is 90 mg/g, and Asbury carbons' synthetic graphite (SG) whose particle size is 44*250 μm and have a flake-like shape.

Composite Preparation

The processing procedures included design of experiment (DOE) sample design process, PP composites were prepared by the mixing of PP with conductive fillers in 270-mL mixing chamber at 80 rpm for 15 min 200 °C using Haake batch mixer, Bipolar plates were prototyped via injection molding (Engel 85 ton), and plate tested in a fuel cell. Material properties testing included investigation of conductivity, in-situ properties, microscopy and mechanical properties.

Three sets of experimental trails were conducted, which will be referred to as Trial 1, Trial 2 and Trial 3. *Trial 1* consists of a 'composite response' design was developed using Stat-Ease's design Expert 6.0 to determine an appropriate carbon black and to investigate a synergy for conducting composites. *Trial 2* explored the conductivity relationship between fill loadings using fillers (VCB, CF, and SG) of 1:1:1 mixtures, with overall fill loading ranged from 0 to 65%wt. The objective of the study in *Trail 2* was to attain the percolation "S-curve" for these blends. *Trial 3*, the influence of conductive polymer (577030 Aldrich Polypyrrole(PPy); conductivity 10–40 S/cm) and Titanate coupling agent powder (supported by Kenrich Electochemicals Inc.) on electrical conductivity were observed with overall coupling agent 1.8%wt of total weight of the composite and 1 and 3 %wt for coupling agent.

Property Characterization

In this work conductivity testing was performed with 2 methods. In-plane testing (Method 1), the current is flowing in the same direction as the injection molding direction but through-plane measurement (Method 2) takes place perpendicular to flow direction. From the results synergy advantage could not be observed in the Method 2 measurement. Method 1 was based on ASTM D-991.[12] Method 2 was developed from draft US Fuel Cell Council's recommended guidelines.[13] Two gold-nickel-copper electrode plates are used in a hydraulic press and a clamping pressure up to 10000 lbs-force was applied and both voltage and current were independently monitored on both electrodes to calculate the total resistance. Furthermore, in *Trial 2*, for in conductivity measurement, samples were tested in two directions: one test was in the sample direction which parallels to the injection molding direction, and another was the samples direction perpendicular to injection molding direction.

In cell testing is the ultimate measure of performance. In order to minimize the amount of material needed for in-situ testing a small fuel cell design was implemented (commercial fuel cells are very large, requiring large amounts of material). This approach required the design and construction of new fuel cell hardware in addition to a bipolar plate mold which could create plates that could be used in a fuel cell operating environment.

Rheological testing of the PP composites with and without coupling agent and processing agent (zinc stearate) was studied by the Dynisco Galaxy V Capillary Rheometer with 0.05 inch in die diameter and L/D ratio is 20. Further details regarding test procedures can be referenced in ASTM D3835-02.[14] The analysis of a material's microstructure is important in order to better understand the relationship between the filler loading and various other properties. In order to achieve this, the samples were viewed using a scanning electron microscope (SEM). The samples were prepared by cold fracturing using liquid nitrogen and sputter coated with gold. Moreover, surface property was measured by using contact angle tester.

Results and Discussion

Trial 1

The electrical conductivity enhancement in PP composites relates to percolation theory that has been initiated by Kirkpatrick.[15] The approach was found that the formation of the conductive network, leading to a substantial increase in conductivity. In *Trial1*, the electrical conductivity of injection molded polypropylene composites containing two types of conductive fillers, carbon black (CB) and carbon fibers (CF) were studied. From Figure 1, individually VCB shows the highest conductivity results, while the carbon fiber exhibits very low potential. To determine an appropriate carbon black two sizes of CB were investigated. From the results, VCB has higher impact on conductivity followed by ACB. It can be attributed to better dispersion of VCB in PP matrix due to VCB has smaller size and higher surface area. Then it could disperse better than ACB and could make better conductive path in composites. One of the goals in this work was to observe the synergistic effects then the PP composites filled with 2 types of carbon black and carbon fiber at 1:1:1 ratio (ACB:VCB:CF ratio). From the Figure 1, the conductivity seems quite attractive, the conductivity increases to 155 S/m on a wt% basis. It should be noted, thermal gravimetric analysis was used to determine the actual filler loading for each sample. The increasing conductivity increases can be attributed CF acts as long distance charge transporter, CB aggregates may serve as interconnections between the fibers by forming local conductive paths. Co-supporting conductive networks, synergistic effect, result in composites with enhanced conductivity and lower anisotropy. The comparisons between two conductivity

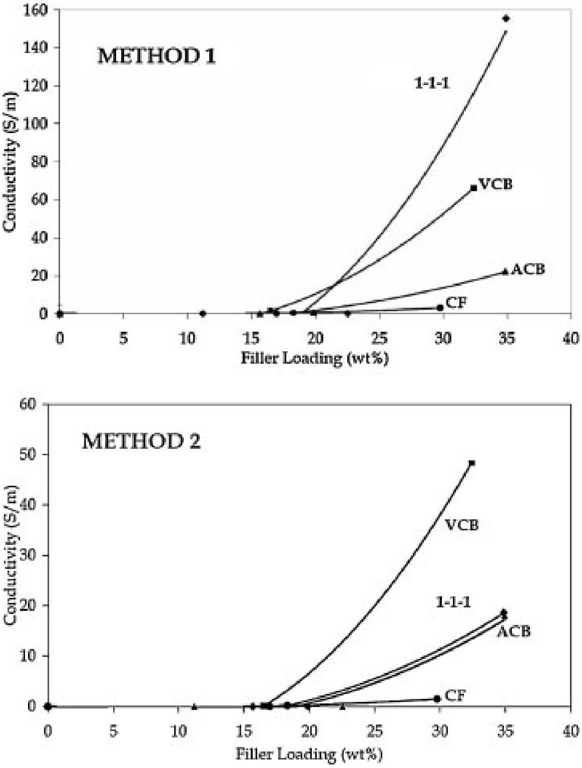

Figure 1.
Conductivity Trends in Trial 1 using Method 1 and 2 measurement technique.

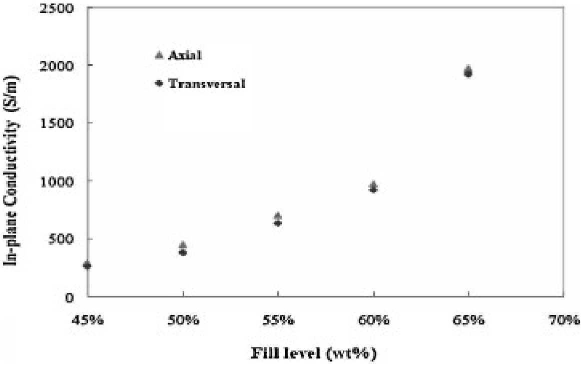

Figure 2.
In-plane conductivity of SG/VCB/CF composites measured in two directions.

measurements, the trough-plane conductivity measurement shows much lower conductivities and does not exhibit any synergy with the synergistic effects between the fillers. The results show a constructive interaction between ACB and VCB, and then the fiber contributes significantly to the conductivity with the measurement made using in-plane technique. According to the main challenge that was to keep blends with a low enough viscosity to enable successful processing while ensuring that there were sufficient conductive particles to provide good electrical conductivity. The conductivity of composites is limited by the high viscosity value at which the polymer blend can be compounded by the batch mixer, or twin-screw extrusion, or, more critically, injection molded to bipolar plates.

Trial 2

Then ***Trial 2***, synthetic graphite was used to replace ACB as one of conductive fillers since graphite not only has excellent conductivity but also possesses good lubricant effect in processing. Referring to percolation theory, a conductive blend will reach a threshold where the filler content will be high enough that the conductive filler can form a continuous network to allow for electrons to pass. From *Trial 1*, the blend with 35%filler was too low to reach to percolation threshold then the composites with loading up to 65%wt were prepared to get a high conductivity. From both of

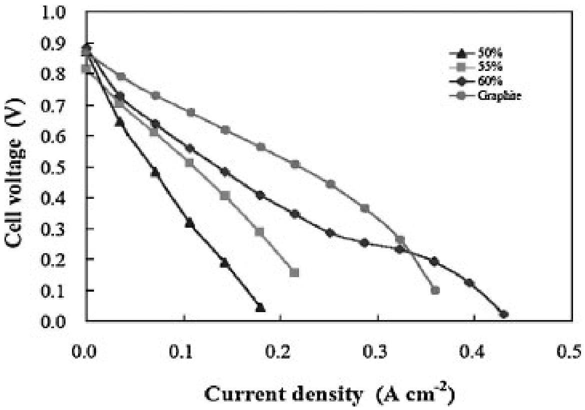

Figure 3.
I-V performance of graphite bipolar plate and 50% and 60% composite bipolar plates in a single cell test.

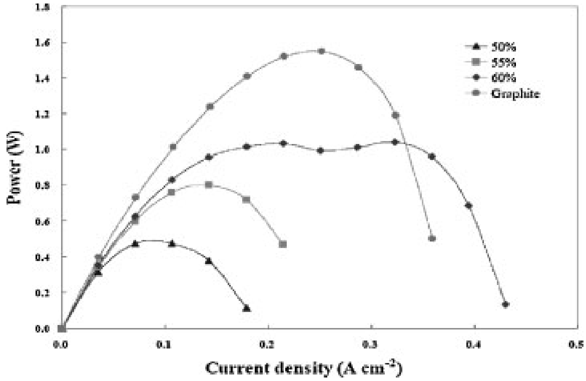

Figure 4.
Comparison of performance of graphite bipolar plate and 50% and 60% composite bipolar plates in a single cell test.

conductivity measurement techniques, the conductivities enhance with higher filler loading. For in-plane conductivity measurements, samples were tested in two directions: one test was in the sample direction which was parallel to the injection molding direction, and another was the sample direction perpendicular to the injection molding direction. As illustrated in Figure 2, in-plane conductivity of samples in injection molding direction was slightly better than that perpendicular to the injection molding direction. The reason for conductivity difference in two directions is that for samples having the same direction as injection molding, the fillers (specifically the fiber fill) are oriented in the direction of flow induced during the injection molding process. This is the same as the direction of electrical conductivity measurement, and oriented fillers allow electrons flow through easier than the direction perpendicular to injection process. Another explanation is the impact of fiber orientation with respect to the direction of conductivity measurement, which increases the in-plane conductively along the fibers.

From the investigation of single cell performance, this picture shows the assembled single cell and the components of the cell. The polarization curve for single cells illustrates that the current density of the cells using composite plates increase with higher filler concentrations. However they are still lower than graphite plate. The interesting phenomenon is the performance of single cell using 60% composites BP. When the current density reached

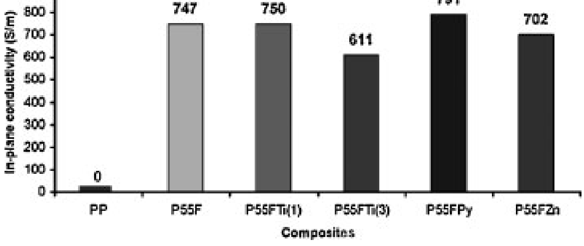

Figure 5.
In-plane conductivities of PP, PP/55%filler (P55F), PP/55%filler/1%coupling agent (P55FTi(1)), PP/55%filler/3%coupling Agent (P55FTi(3)), PP/55%filler/1.8% Polypyrrole (P55FPy), PP/55%filler/1%processing agent (P55FZn).

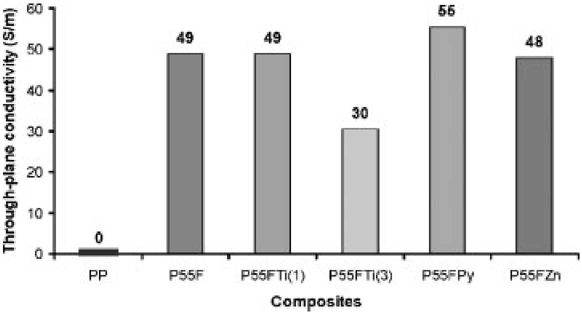

Figure 6.
Through-plane conductivities of the composites.

0.25 A cm^{-2}, the voltage of single cell decreased with a slower rate than before, and the maximum current density of 60% composite is higher than graphite plate. It may indicate that the PP composite plate has better water removable. The curve of distribution power and current density (Figure 4)shows that the maximum power output of composite plate is 1.04 W, while the graphite plate is 1.55 W.

Although equivalent performance to the graphite plates was not achieved, successful in-situ fuel cell testing was achieved. As expected the high fill composites (i.e. with better conductivity) performed better for the in-situ testing.

Trial 3

During this study blends were also produced similar blend with an intrinsically conductive polymer included as an additive, specifically polypyrrole (PPy) at level of 1.8%wt. The conductivity of the 55%wt composite with with PPy was 6% higher than with those blends without PPy. The results (Figure 5) showed that there is a distribution of PPy which increase the conductive pathways between the conductive fill materials, thus increasing the overall conductivity of the composite material.

The coupling agent does not much affect the electrical conductivity. Furthermore, the conductivity decreased with concentration of coupling agent increased. The addition of processing agent (zinc stearate) diminished conductivity. Through-plane conductivity has the same trend as in-plane as displayed in Figure 6. The influence of coupling agent on the conductivity of composites could not be investigated by through-plane measurement.

Figure 7 indicates the capillary flow properties of polypropylene composites 215 °C. The apparent viscosity decreased

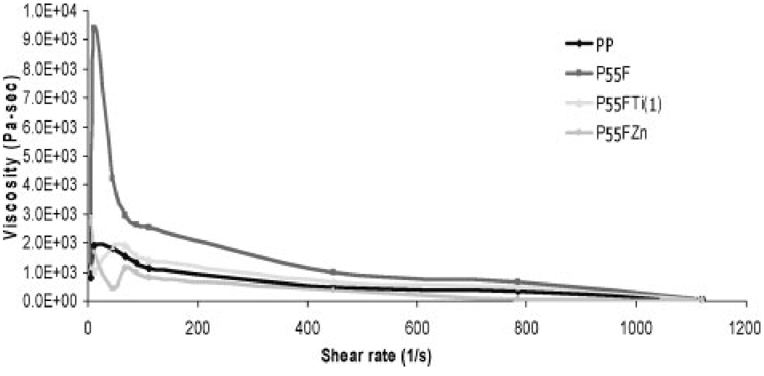

Figure 7.
The relation of viscosity and shear rate of the composites.

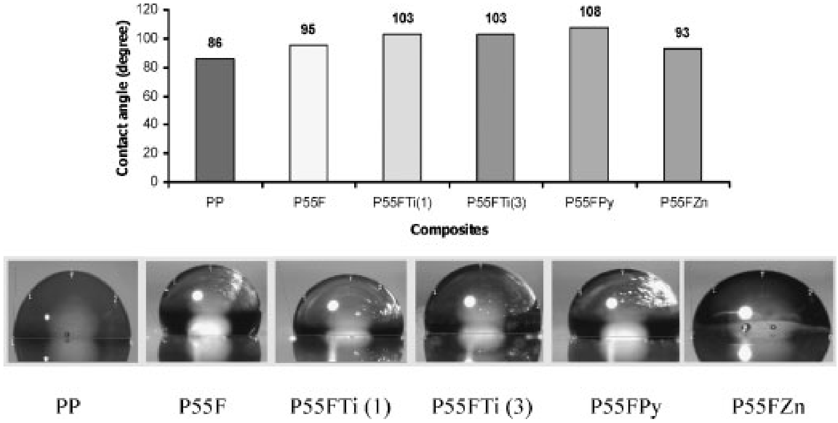

Figure 8.
Contact angles of composites.

quite sharply with increasing shear rate for filled and unfilled polypropylene, which implies a shear-thinning behavior of the materials. At a fixed shear rate, the apparent viscosity increased with addition of fillers. The flow properties are influenced by the addition of coupling agent and processing agent. The curves show that viscosity value of the composite with titanate coupling agent is close to neat PP, and the value of the composite with zinc stearate is lower than PP. Those could be affected by better interaction between fillers and the polymer melt and zinc stearate acts as lubricant. It is noted that at relative low shear rate the variation of the apparent viscosity was more significant than the viscosity at higher shear rate.

The surface hydrophobicity gets stronger with adding additive as showing in the Figure 8. The increasing is due to the strong hydrophobic properties of graphite and the additive can change sure face energy of composites. It was found that the hydrophobic of composites are higher than a graphite bipolar plate whose water contact angle is 100°.[13] This property may be important in a fuel cell as if facilitates water removal. This fact indicates that a water droplet in the gas flow channels of composite bipolar plates can be swept away more easily by the gas stream under relatively low flow rate conditions. In other words, cells can exhibit higher performance even at low flow rates. In a practical fuel cell stack with a large electrode area, blocking of the gas

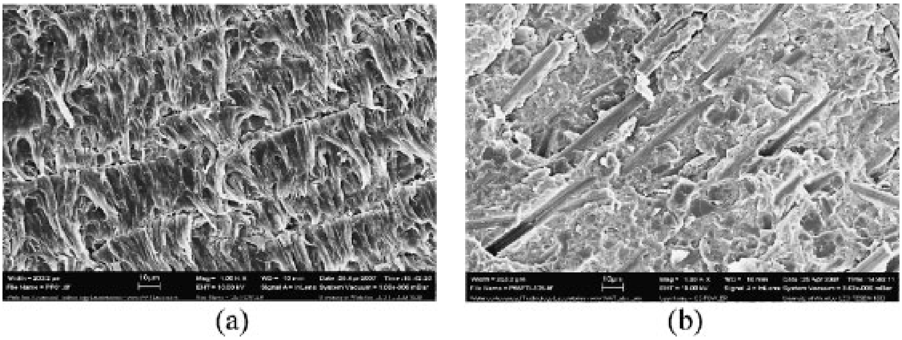

Figure 9.
SEM micrographs of virgin PP (a) and PP composite with 55%filler (b).

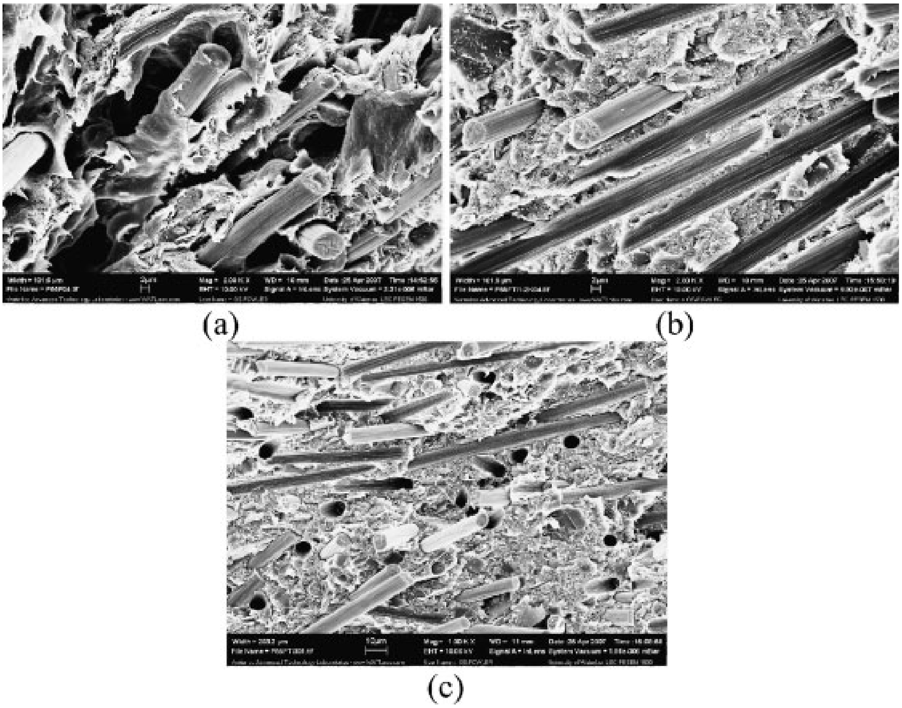

Figure 10.
SEM micrographs of virgin PP composite without coupling agent (a), PP composite with 1%wt coupling agent (b) and PP composite with 3%wt coupling agent (c).

flow channels by condensed liquid water tends to occur and results in serious degradation as electrode area, reactant utilization and humidifying temperature increases.

SEM micrographs of the cross section of virgin PP and PP composite with 55%filler are shown in Figure 9. These images show a certain degree of contact among filler particles, within polymer matrix. With this contact, more electron flow paths are formed so electrons can pass, forming an electrical conductive circuit.

By introducing coupling agent, conductivity has been slightly improved in composite sample. It is due to increasing wettability and dispersion of particle filled composites. The micrographs of PP composite with and without coupling show that the coupling agent has the potential to improve significantly the interface fillers/polymeric matrix as illustrated in Figure 10.

The SEM images show the poor interfacial adhesion between the fillers (especially CF) and PP matrix that is due to addition of higher coupling agent concentration. 1%wt of processing agent was added during melt blending. Even the

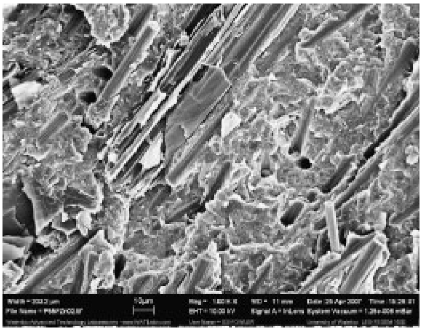

Figure 11.
SEM micrographs of virgin PP composite with processing agent.

processabilility was better due to reduction of viscosity; the conductivity was not achieved since agglomeration of graphite particles can still be observed in the micrograph. Moreover, a poor interfacial adhesion of CF and PP can be observed clearly (Figure 11).

Conclusion

Polypropylene based formulations using PP matrix with carbon black, graphite, and carbon fibers as conductive fillers were developed for producing blends for use as fuel cell bipolar plates. Electrical conductivities around 1900 S/m (in-plane) and 156 S/m (through plane), were obtained with the 65% composite. From the investigation of single cell performance, the results are promising for future opportunities with composite materials within PEMFC even though the developed materials are currently inferior to the performance of graphite. Using polypyrrole as conducting additive was successful in further improving electrical properties of the composites. Finally conductive injection moldable thermoplastic composites can be achieved although equivalent performance to graphite plates has not yet been achieved.

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