

ELECTRICAL AND MECHANICAL PROPERTIES OF GRAPHITE-BASED POLYMER COMPOSITES FOR BIPOLAR PLATES IN PEM FUEL CELLS

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Abstract

Graphite-filled phenolic resin composites (BBP4) are developed and characterized to be used as bipolar plates in Proton Exchange Membrane Fuel Cells (PEMFC). BBP4 has in plane electrical conductivity of 130 S/cm, thermal conductivity of 26 W/m K and flexure strength of 49 MPa. These values well exceed the US Department of Energy (DOE) requirements. In addition this work presents a comparative study of the effect of the polymer type on the thermal, electrical and mechanical properties. For this purpose four graphite-based thermoplastic composite are investigated using respectively four polymers matrix systems: Poly (vinylidene fluoride) (PVDF), poly (phenylene sulfide) (PPS), polypropylene Glycol (PPG86) and polypropylene (PPU). The effect of carbon black on the properties of the polypropylene/graphite composite is determined.

1. Introduction

Conductive polymer composites play a significant role in the application areas of conducting polymers as organic light emitting diodes, polymer photovoltaic cell or fuel cells [1,2].

A Proton Exchange Membrane Fuel Cell (PEMFC) converts the chemical energy into electrical energy by electrochemical reactions. Nowadays fuel cells represent an energy source of choice for stationary and mobile applications as electric vehicle network, speed cameras, telecommunications, and military communication installations.

PEMFC consists of the Membrane Electrode Assembly (MEA) (including the membrane, electrode and gas diffusion layer) and the bipolar plates. One of the most important components in the fuel cells is the bipolar plates. They are multifunctional components in a PEMFC stack. They separate gases between cells and provide a conductive medium between the anode and cathode, provide a flow field channel for the reaction gases and transfer heat out of the cell. Three types of material are used in bipolar plate, including metallic plates, pure graphite plates and polymer composites.

Metallic bipolar plates such as stainless steel show good mechanical stability as well as high electrical and thermal conductivity. The main disadvantage of metal plates is their susceptibility to corrosion. Pure graphite bipolar plates are already known for their excellent resistance to corrosion, and its low electrical contact resistance. The disadvantages of this type

of plates are their low mechanical properties, porosity and high costs. In order to solve this problem, the use of flexible graphite-based composite bipolar plates made from polymer/graphite composite are considered as an attractive option for PEMFC. They offer the advantage of lower cost, higher flexibility, reduced brittleness, lower gas permeability and they are lighter in weight [3,4].

There are two different types of materials to fabricate graphite -based composite plates: thermoplastic/filler composite and thermoset/filler composite. The composite is created by incorporating a filler or mixture of fillers like graphite (Gr) and/or carbon black (CB) [5].

The polymer matrix, which acts as binder in the material composite is insulating material with an electrical conductivity in the order of 10^{-15} S/cm. The incorporation of high graphite content creates the conductive network by increasing not only the electrical conductivity but also the mechanical properties of the composite [6,7]. The bipolar plates must have high electrical conductivity and sufficient mechanical properties to be used in fuel cell stack because of the constant compressive load.

US Department of Energy (DOE) defined requirements for ideal composite plates. These targets are summarised in Table 1 [8].

Property	Value
Electrical conductivity	> 100 S/cm
Contact resistance	0,1-0,2 Ω cm ²
Thermal conductivity	> 10 W/mK
Flexure strength	\geq 25 MPa
Compression strength	\geq 50 MPa
Tensile strength	\geq 41 MPa
Gas permeability	< 2×10^6 cm ³ s ⁻¹ cm ⁻²
Corrosion resistance	< 1 μ A cm ⁻²

Table 1. Required properties for ideal composites plates defined by US DOE [8].

In this paper both, high graphite-filled thermoplastic and thermosetting resin composites were developed and investigated as an alternative material for bipolar plates in order to meet the requirements shown in Table 1 on three most important properties: the in-plane electrical conductivity, the flexure strength determined by the three point flexural technique and the thermal conductivity. The thermal properties as glass transition and thermal degradation temperature were determined to get more information about the thermal stability of the material. The thermal conductivity measurement was performed within a large temperature range (20°C-150°C) where the operating temperatures of PEM fuel cell (80°C-120°C) are included. The in-plane electrical conductivity was determined at room temperature by using the 4 point-probe method. The flexure strength of the composite was measured at room temperature. Dynamic mechanical analysis (DMA) measurements were added in order to get a better understanding of mechanical properties of the material at high temperature.

The effect of CB of the polypropylene/graphite composite on the thermal, electrical and mechanical properties was investigated. Furthermore the effect of the polymer type on the previous properties of the graphite based thermoplastic composites was taken into account.

2. Experiment

2.1. Material

In this work two series of graphite polymer composite bipolar plates were developed. The polymer matrix used in first series was PPU X9067HS polypropylene from Basell with a density of 0.91 g/cm³. Three composites were prepared with 0% filler (PPU1), 70 wt% Gr (PPU2) and a mixture of CB and Gr (60 wt% Gr and 10 wt% CB, (PPU3)). The density of CB and Gr are respectively 1,6 g/cm³ and 2,2 g/cm³. The average particle sizes are 76 μm and 88 μm respectively. The polymer PPU and the fillers were first dry mixed in a kneader at 230 °C for 15 min and then placed in hydraulic compression press and heated to 260 °C. A pressure of 5 MPa was applied and held for 12 min to completely melt the PPU.

In the second series, 4 compounds were developed with approximately the same graphite content (~ 80 wt%): Poly (vinylidene fluoride) (PVDF)/Gr BMA5, poly (phenylene sulfide) (PPS)/Gr, polypropylene Glycol/Gr PPG86 and phenolic resin/Gr BBP4. All the samples were prepared using a compression molding machine.

2.2. Thermal properties

The thermogravimetric analyser (TGA Q5000, TA Instrument) was used to determine the thermal degradation temperature T₁. The temperature T₁ was obtained at 5% weight loss [5]. The measurements were carried out under nitrogen atmosphere with a heating rate of 10 K/min. In addition the glass transition T_g and the melting temperature T_m were determined by using differential scanning calorimetry (DSC Q2000, TA Instrument) technique. The measurements were carried out under nitrogen atmosphere with a heating rate of 20 K/min.

2.3. Measurement of in-plane electrical conductivity

The in-plane (bulk) electrical conductivity was measured with a conventional four probe method. The measurements were performed at room temperature using a cylindrical four point probe head and RM3000 Test Unit from Jandel Engineering Limited. The RM3000 can supply constant currents between 10nA and 99.99mA, and measure voltages from 0.01mV to 1250mV. The electrical conductivity σ of the sample was calculated according to [9]:

$$\sigma = \left[2\pi \times \frac{U(V)}{I(A)} \times G \left(\frac{w}{s} \right) \right]^{-1}$$

where s is the probe spacing (s = 1 mm), w is the thickness of the sample, U is the voltage, I is the current and G is the correction factor. The measured samples have a thickness of about 3 mm.

2.4. Measurement of thermal conductivity

In this work the thermal conductivity of the materials was not directly determined. A first, two parameters were measured: the specific heat parameter by using modulated DSC and the thermal diffusivity parameter by using the equipment of Laser Flash technique from Netzsch (427). The thermal conductivity λ is related to the thermal diffusivity D according to:

$$\lambda(T) = D(T) \times C_p(T) \times \rho$$

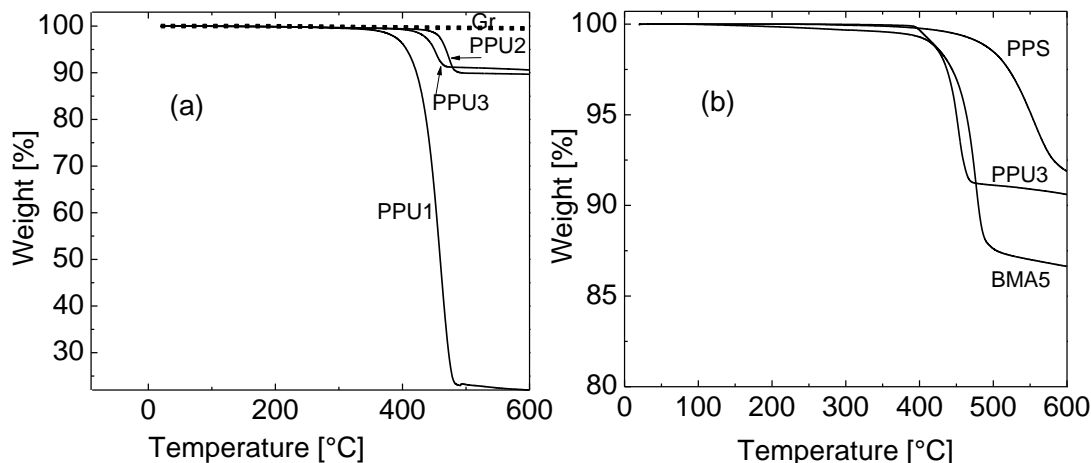


Figure 1. TGA curves for PPU1, PPU2, PPU3 and pure graphite (dashed line) (a) and for PPS, PPU3, BMA5 (b).

where C_p is the specific heat and ρ is the volume density. The density is supposed to be independent of the temperature. Both measurements were performed over the temperature range 20 °C - 150 °C with a heating rate of 3 K/min. The measurements of the thermal diffusivity were carried out on samples with cylindrical shape having a diameter of 12,7 mm, while the diameter of the cylindrical shape of samples for the C_p - measurement is 5 mm.

2.5. Mechanical properties

The three -point bending flexural technique according to DIN EN ISO 178 was performed at room temperature in order to obtain the flexure strength of the materials. The operating temperature of the PEMFC is between 80 °C and 120 °C. To gain more information of mechanical properties in this range Dynamic mechanical analysis (DMA Q800, TA Instrument) technique was performed under the three-point bending mode. A scanning temperature range from 22 °C to 120 °C and a heating rate of 3 K/min were employed.

Both the storage modulus E' as well loss modulus E'' were determined. In this paper only the results of E' against the temperature at the frequency 1 Hz were presented.

Material	Polymer	Filler	T_1 (°C)	T_g (°C)	T_m (°C)
PPU_1	PP	0%	406	44	164
PPU_2	PP	75 wt% Gr	468	45	160
PPU_3	PP	60 wt% Gr+10 wt% CB	450	45	159
BMA5	PVDF	~ 80 wt% Gr	453	47	171
PPS	PVDF	~ 80 wt% Gr	551	96	266
BBP4	phenolic resin	~ 80 wt% Gr	589	/	/

Table 2. Glass transition T_g , thermal degradation T_1 and melting temperature T_m of samples.

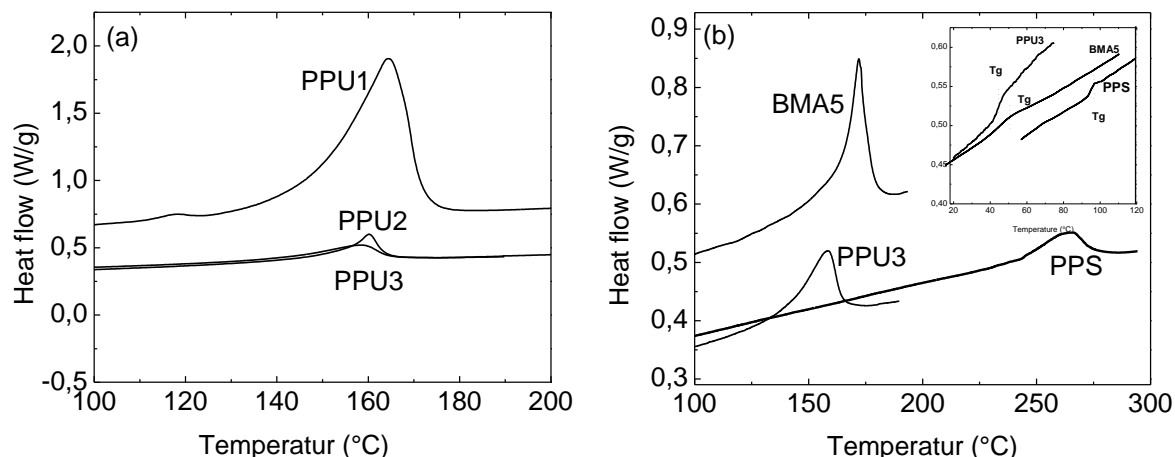


Figure 2. Temperature dependent DSC curves for PPU1, PPU2, PPU3 (a) and for PPS, PPU3, BMA5. The corresponding curves showing the glass transition temperature T_g were added (b).

3. Results and discussion

3.1 Thermal properties

The quantitative analysis of the weight loss against the temperature was characterised by TGA measurements. The temperature range used for the analysis is 22 °C -800 °C. TGA curves of pure PPU (PPU1) and PPU composites (PPU1 and PPU2) are shown in Fig. 1 (a). TGA of pure graphite (dashed line) was added to show its high stability against the temperature. The curve reveals that PPU2 and PPU3 degrade at higher temperature compared to PPU1. The values of the thermal degradation temperature T_1 are reported in Table. 2. It is seen that T_1 for PPU1 is 406 °C, while for PPU2 and PPU3 it increases to 468 °C and 450 °C respectively. These results indicate that the thermal stability of the pure PPU1 was enhanced by the incorporation of the Gr. The same behaviour has been reported for graphite/epoxy composite [5]. T_1 for PPU3 is slightly lower compared to that PPU2. This could be related to the CB filler which is less stable than Gr at high temperature. Fig 1 (b) shows the TGA curves for PPS and BMA5. The thermal degradations for PPU3 and BMA5 are almost similar ($T_1 \sim 450$ °C). The values T_1 for PPS (551 °C) and BBP4 (589 °C) are significant higher (see Table. 2). BBP4 and PPS show higher thermal stability compared to PPU3 and BMA5.

DSC curves of the samples were plotted against the temperature in Fig. 2. DSC analysis indicates that the melting temperature T_m for pure PPU slightly shifts towards lower temperature after incorporation of graphite particle (Fig 2 (a)). PPS exhibits a higher T_m ((266 °C) and higher glass transition temperature T_g ((96 °C) (Fig 2 (b)).

Material	Polymer	Filler	σ (S/cm)
PPU_2	PP	70 wt% Gr	59
PPU_3	PP	60 wt% Gr+10 wt% CB	104
PPG86	PP	~ 80 wt% Gr	46
BMA5	PVDF	~ 80 wt% Gr	87
PPS	PPS	~ 80 wt% Gr	124
BBP4	phenolic resin	~ 80 wt% Gr	130

Table 3. In plane electrical conductivity of samples.

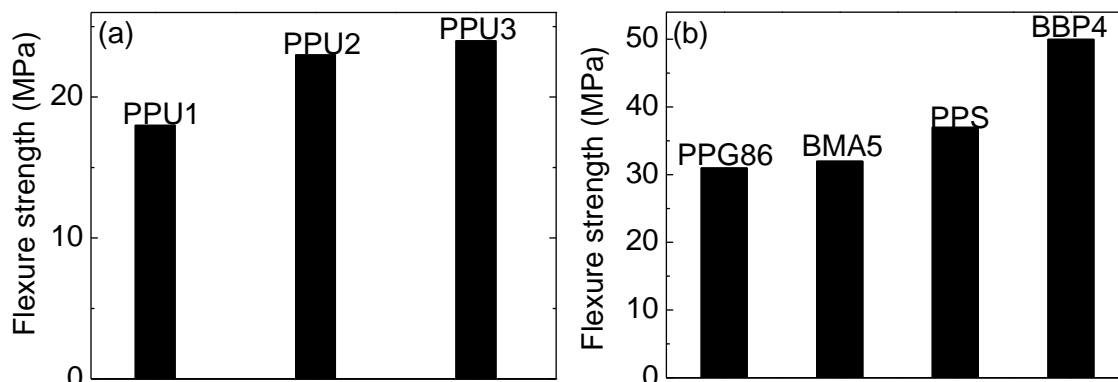


Figure 3. Flexure strength for PPU1, PPU2 PPU3 (a) and for PPG86, BMA5, PPS and BBP4 (b).

2 Electrical properties

The in-plane electrical conductivity of samples was determined at room temperature through the conventional four-point-probe method. The electrical conductivity is strongly influenced by the total content of filler and also by the filler and polymer type [7]. The results of the in-plane electrical conductivity of all samples are summarised in Table 3. High values of conductivity were shown for BBP4, PPS and PPU3. These values exceed the limit value of conductivity (100 S/cm) defined by US Department of Energy (DOE). The conductivity of PPU3 is 3 times higher than that of PPU2, although the total filler content is similar for both materials. The measured conductivity is caused by the macroscopic resistance of the polymer composite which depends not only on the graphite aggregates resistance but also on the resistance of inter-aggregates space. The incorporation of 10 wt% CB with 60 wt% Gr to polypropylene matrix for PPU3 probably created additional connection between Gr-aggregates because CB aggregates were located between graphite layers leading to an increase of the conductivity of the material.

The thermoplastic composite materials PPG86, BMA5, and PPS show different values of the conductivity (59, 87, 123 S/cm, respectively) although they were prepared with the same content of graphite. This could be referred to the viscosity during the processing of the material. The PPS composite, which has a high value of electrical conductivity, has probably lower viscosity compared to that of PPG86 and BMA5. This leads to a better mixing with graphite in the kneader. Furthermore the phenolic resin BBP4 shows the highest electrical conductivity (130 S/cm).

2 Mechanical properties

Bipolar plates support the membrane electrode assembly and undergo the constant effect of the compressive load of the PEMFC. For this reason the determination of good or adequate mechanical properties is important. The three-point bending flexural technique was performed at room temperature on the samples in order to obtain the flexure strength parameter. The flexure strength for PPU2 and PPU3 are nearly similar (~ 24 MPa) (Fig. 3(a)). This value is very close the value defined by US DOE (25 MPa, (Table. 1)). The reinforced composites PPU2 and PPU3 show lower flexure strength than that of PPU1 [7]. Furthermore the flexure strength of the BBP4 (49 MPa) is higher compared to those obtained for thermoplastic composites (PPG86 (31 MPa), BMA5 (32 MPa) and (37 MPa)) (Fig. 3(b)).

Dynamic mechanical analyzer (DMA) was carried out to get more information of mechanical properties of samples at operating temperature (80 °C- 120 °C) of PEMFC. The storage modulus E' parameter was measured and plotted into a temperature range from 20 °C 120 °C

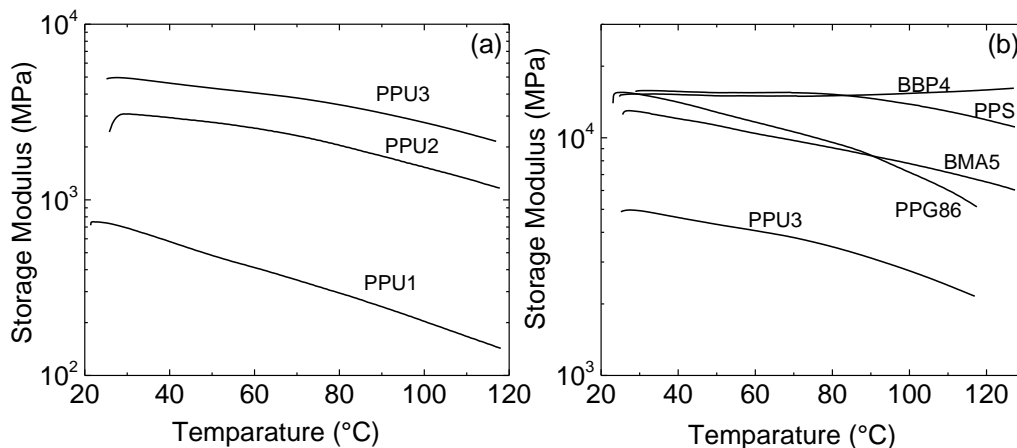


Figure 4. Storage modulus E' against the temperature for both PPU1, PPU2, PPU3 (a) and for BBP4, PPS, BMA5 and PPG86. E' for PPU3 was added in order to show the difference with the storage modulus of the rest of samples (b).

(Fig. 4). It can be seen that the storage modulus of all samples decreases with increasing temperature (Fig. 4). The value of E' for PPU3 is approximately one order of magnitude higher compared to the E' value of pure PPU1 (Fig. 4 (a)). In addition it can be observed for both figures that the highest value of E' corresponds to the lowest slope of E' curve in Fig. 4 (a) and (b). The E' curve for BBP4 is nearly flat, a slight change against the temperature is observed. It is worth noticing that the mechanical properties (for example for the flexure strength) for thermoplastic composite could be decreased by increasing the temperature.

3.4 Thermal conductivity

Thermal conductivity λ was determined for the examined samples in the temperature range from 20 °C to 120 °C. The graphite material is characterised with a high value of thermal conductivity (~ 160 W/m K). The thermal conductivity of the graphite/ polymer composite is widely influenced by the thermal conductivity of the polymer, which is very low compared to that of graphite.

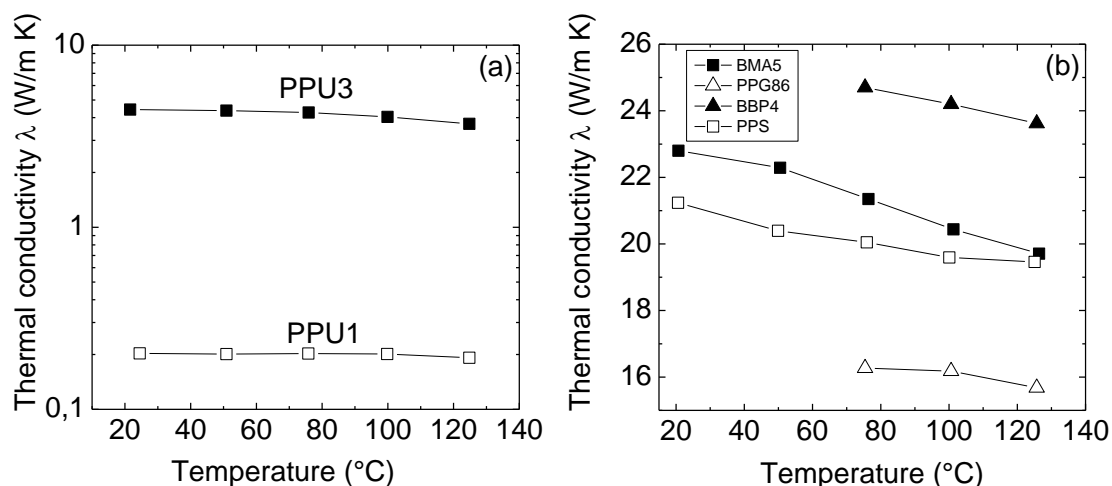


Figure 5. Temperature dependence of the thermal conductivity λ of both PPU1 (open symbol) and PPU3 (full symbol) (a) and of PPG86 (open triangle symbol), PPS (open square symbol), BMA5 (full square symbol) and BBP4 (full triangle symbol) (b).

The parameter λ is plotted as function of the temperature for PPU1 and PPU2. A semi-logarithmic scale was chosen to show the difference between both graphs. It can be seen, in Fig. 5 (a), that the parameter λ of PPU3 is one order of magnitude higher than λ of PPU1. It is to notice that the value of the parameter λ defined in requirements of DOE (10 W/ m K) was not reached for PPU3 ($\lambda \sim 3$ W/ m K). The figure 5 (b) displays the λ parameter for BMA5, PPS, PPG86 and BBP4. A drop of λ parameter against the temperature can be observed for all samples. This drop is more pronounced for BMA5 and PPS samples. The thermal temperature λ for BBP4 reaches the value ~ 25 W/m K.

By considering the results in the previous sections, BBP4 shows the best mechanical, thermal and electrical properties. The requirements are widely reached for this composite on the electrical, thermal conductivity properties and on the mechanical properties.

4. Conclusion

Highly graphite polymer composites have been investigated to be used as bipolar plates. The data of Graphite-filled phenolic resin composites BBP4 on in-plane electrical conductivity, thermal conductivity and mechanical properties meet widely the requirements defined by US department of energy. It has been shown that BBP4 composite is suitable material to be used as bipolar plates for PEMFC. In addition the previous properties have been determined for different graphite polymer composites which differ in polymer matrix.

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