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Short communication

Study on the electrical and mechanical properties of phenol formaldehyde resin/graphite composite for bipolar plate

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Abstract

With phenol formaldehyde resin (PF) powder and graphite powder as raw materials, a kind of conductive composite for bipolar plate is obtained by hot-pressure molding. The effects of PF resin content, molding temperature and time on conductivity and bending strength of the composite were investigated in this paper; and the optimum PF resin content, molding temperature and time were obtained. The results show that: the conductivity decreases and bending strength increases with the increasing of PF resin content; the conductivity varies wave-like and bending strength increases firstly and then decreases with the increasing of molding temperature; the effects of molding time on properties of the composite are similar to that of molding temperature; and the best conductivity and bending strength of the composite are 142 s cm^{-1} and 61.6 MPa, respectively, when its PF resin content is 15% molded at 240 °C for 60 min.

Keywords: PF resin; Graphite; Hot-pressure molding; Fuel cell; Bipolar plate

1. Introduction

The polymer elecetrolyte membrance fuel cell (PEMFC) is a very promising power source for residential and mobile applications [1]. In order to move towards its commercialization, fuel cell components must be cheaper and easier to produce, especially for the bipolar plate, which accounts for as much as 60% of the stack cost [2]. Resin/graphite composite bipolar plate is a promising alternative to pure graphite bipolar plate, and has the advantages of low cost, easy manufacturing and lightweight. American Ministry of Energy advanced a series of property requirements of resin/graphite composite for bipolar plate, in which the main properties, electrical conductivity and bending strength are above 100 s cm^{-1} and 50 MPa, respectively [3].

Recently, a series of researches on PF resin/graphite composite for bipolar plate were carried out in literatures [4–6], in which PF resin (liquid) was mixed with graphite powder in a mechanical mixer, and then hot-pressure molded into bipolar plate material. The research results revealed significant disadvantages such as complex technology, worse uniformity and properties. Compared with those in our research, we expect to simplify the preparing technology and improve the bipolar plate material uniformity and properties when PF resin powder (dry) is mixed with graphite powder (dry) in planetary high-energy ball miller, and then also hot-pressure molded into bipolar plate material. In the same time, we also investigated the rule of PF resin content and molding temperature and time affecting the electrical and bending strength of the composite, and wish to get the optimum PF resin content and molding condition.

2. Experiments

2.1. Materials

Graphite powder, with purity ⩾95% and granularity ⩽150 μm, was produced in Laixi, PR China; PF resin powder mixed with hexamethylene tetramine, with granularity ⩽75 μm, was produced in Laiwu, PR China.

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2.2. Sample preparation

Graphite and PF resin powders with different mixture ratios were dry-milled for 2–4 h in planetary high-energy ball miller (QIF-16) at speed of 380 rpm, and then passed through 75 μm sieve, and hot-pressure molded at different temperatures in a hot-pressure molding furnace for different times to obtain the composite samples.

2.3. Measurements of properties

The samples were cut into specimens 5 mm × 5 mm × 20 mm in size. Conductivity was measured by using four-point probe technique (apparatus model QJ44); and bending strength was measured on universal testing machine (CMT5105). The fracture surface was observed by scanning electron microscopy (JXA-840); and differential scanning calorimetry (apparatus model DSC404) was used to discern curing process of conductive composite.

3. Results and discussion

3.1. Effect of PF resin content on composite properties

3.1.1. Effect of PF resin content on conductivity

The variation of conductivity with different content of PF resin is shown in Fig. 1. It shows that the conductivity of the composite decreases with the increasing of PF resin content. The conductivity will be below 100 s cm^{-1} when the content of PF resin is above 15%.

Conductivity of graphite depends on the density of conducting current carrier (electron and cavity) in crystal lattice [7]. The moistening and interdiffusion of PF resin to graphite should increase with the increasing of PF resin content and reduce the number and magnititude of conducting graphite phase which can reduce the number of conducting current carrier and make conducting current carrier flow difficult. Therefore, conductivity should decrease with the increasing of PF resin content.

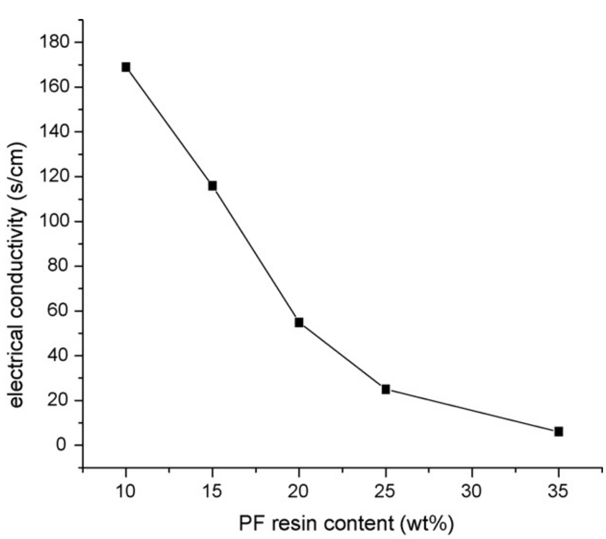


Fig. 1. Effect of PF resin content on conductivity.

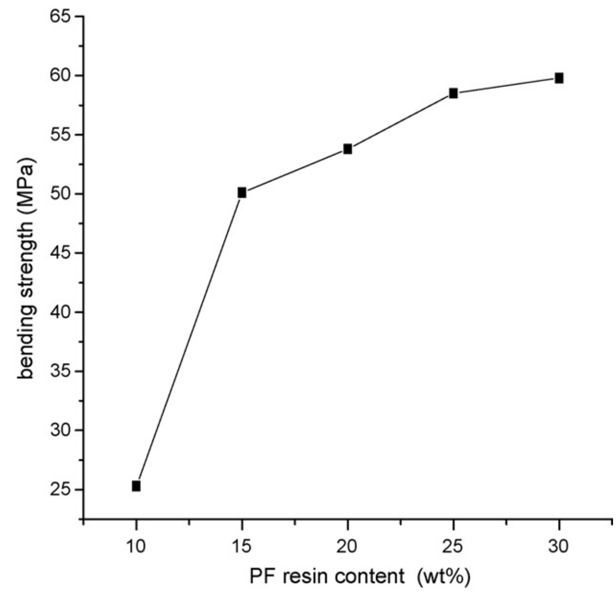


Fig. 2. Effect of PF resin on bending strength.

3.1.2. Effect of PF resin content on bending strength

The bending strength curve of different PF resin content is shown in Fig. 2. It indicates that the bending strength of the composite increases with the increasing of PF resin content. The bending strength of the composite is below 50 MPa when the content of PF resin is lower than 15%.

Graphite is an inorganic matter bonding by covalent bond between intraformational particles and van der Waals force between interlaminar particles. PF resin is an organic matter bonding by covalent bond. Organic matter can coat the surface of graphite particles as a flexible disperse phase at utmost. PF resin cannot coat surface of graphite particles completely if its content is too low, then van der Waals force still is the major bonding mode between interformational particles, and the bonding force between graphite particles is also low. PF resin would coat the surface of graphite particles better as its content increases, which can reduce the porosity of composite, and then bond the interface by contacting with organic matter bonding by covalent bond [8]. Furthermore, the cross linking reaction will occur between resin and some active groups (such as hydroxy) on the surface of graphite particles. Otherwise, the PF resin tends to form a three-dimensional network skeleton structure as its content increases [9], which can raise the bonding force between graphite particles. Therefore, bending strength of the conductive composite would increase with the increasing of PF resin content.

Considering the requirement of the American Ministry of Energy, the optimum PF resin content of this composite is about 15%.

3.2. Effect of molding temperature on the composite properties

Keeping the content of PF resin and the molding pressure constant, the composites were prepared by hot-pressure molding with different molding temperature for 60 min, and the properties of the composites were measured.

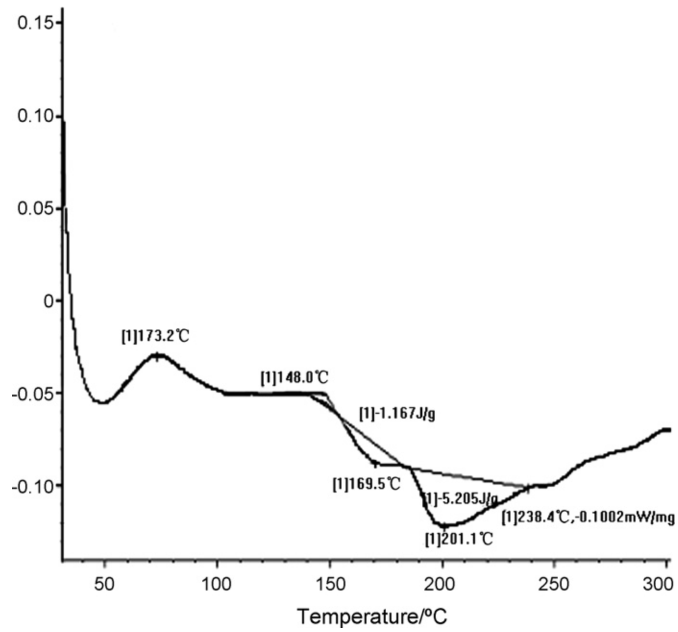
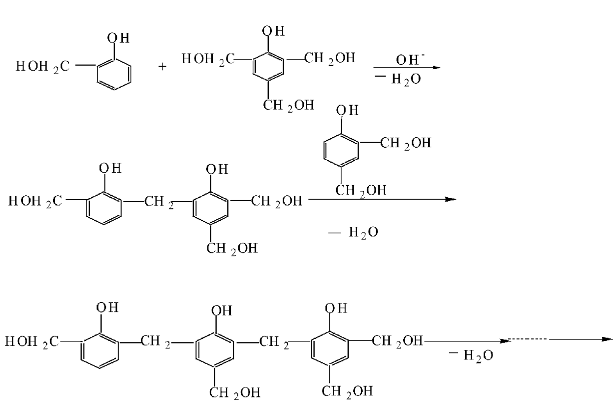


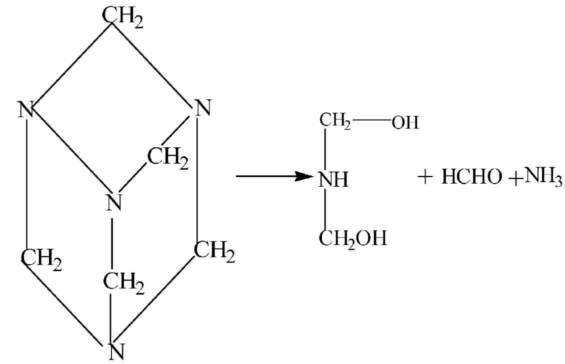
Fig. 3. DSC curve of composite (whose PF resin content is 15%).

3.2.1. DSC analysis

The DSC curve of the composite with 15% PF resin is shown in Fig. 3. As shown in Fig. 3, endothermic peak ended at about 148.0 °C might be the evaporation of water. After that, two exothermic peaks appear continuously at 169.5 and 201.1 °C. The first exothermic peak is transition of PF resin from soluble A to B stage. Polyreaction is the major reaction, and dehydrated condensation of hydroxymethyl occur in this stage, which express long-chain molecular in the macroscopic view (Eq. (1)) [10,11]. The second exothermic peak is the transition of PF resin from B stage to insoluble and infusible stage (C stage), which ended at 238.4 °C. Methylene bridge is provided to junction of benzene ring in the molecular chain of linear PF resin (Eq. (2)), and the hydrogen nitride with water produced in fasculation reaction can be as basic catalyst to accelerate cross linking reaction in this stage [12,13], which express three-dimensional network skeleton structure in the macroscopic view.



Polyreaction of PF (1)



Decomposition of hexamethylene tetramine (2)

3.2.2. Effect of molding temperature on conductivity

The conductivity curve of different molding temperatures is shown in Fig. 4. It shows that conductivity varies wave-like with the increasing of molding temperature. It can reach maximum value (142 s cm^{-1}) at 240 °C.

It is obtained from the analysis of DSC that linear PF resin can form a three-dimensional network skeleton structure by cross linkage from 160 to 220 °C. The flow of conducting current carrier is baffled by the formation of the structure, which reduce the conductivity of the composite. Curing process is over at about 240 °C, and the complete three-dimensional network structure is formed. But simultaneously, the cavity is formed due to evaporation of NH_3 (produced by decomposition of hexamethylene tetramine) and H_2O (produced by condensation reaction), which can raise the number of conducting current carrier, then improve the conductivity of the composite. Decomposition rate of hexamethylene tetramine is accelerated due to rising molding temperature, which produces excess methylene bonding with active site of benzene ring [8], then baffle the transition from the linear structure to the three-dimensional network structure. Although it is beneficial to the flow of conducting current carrier, the evaporation of excess NH_3 and sublimation of hexamethylene tetramine can raise porosity of composite, then

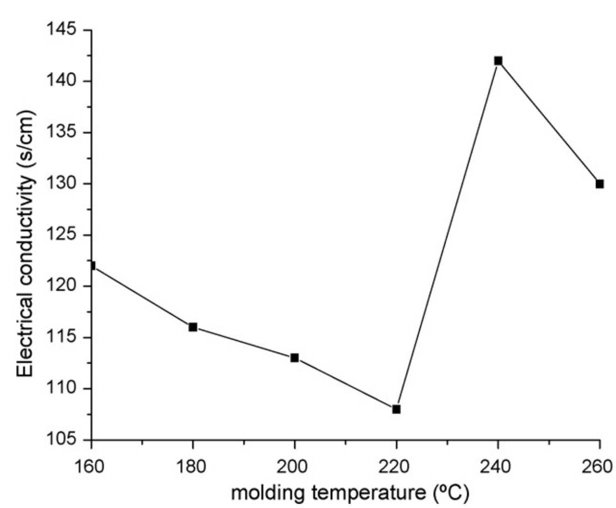


Fig. 4. Effect of molding temperature on electrical conductivity.

reduce density of conducting current carrier per unit volume, and reduce conductivity of composite.

3.2.3. Effect of molding temperature on bending strength

The bending strength curve of different molding temperature is shown in Fig. 5. It shows that bending strength increases firstly and then decrease with the increasing of molding temperature, and it can reach maximum value (61.6 MPa) at 240 °C.

It can be known from the DSC analysis that the linear PF resin can form a three-dimensional network structure as temperature increases, and the formation is over at 238.4 °C. Consequently, the bending strength of the composite will increase with the increasing of the molding temperature from 160 to 240 °C. Especially, the slope coefficient of the curve from 180 to 200 °C is larger due to the transition of PF resin from polyreaction to cross linking reaction. Subsequently, the effect of cross linking reaction is in evidence on the bending strength of the composite. Decomposition rate of hexamethylene tetramine is accelerated due to rising molding temperature, which produces excess methylene bonding with active site of benzene ring, then baffles the transformation from the linear structure to the three-dimensional network structure. In the meantime, the excess NH_3 is also produced, which can raise porosity of the composite, so the bending strength of composite decreases.

3.3. Effect of molding time on properties of the composite

The effect of different molding time on composite properties is studied when PF resin content and molding temperature are 15% and 240 °C.

Figs. 6 and 7 show the effect of molding time on electrical conductivity and bending strength. The effects of molding time on properties of composite are similar to that of molding temperature. Conductivity and bending strength can reach maximum value (142 s cm^{-1}, 61.6 MPa) when molding time is 60 min.

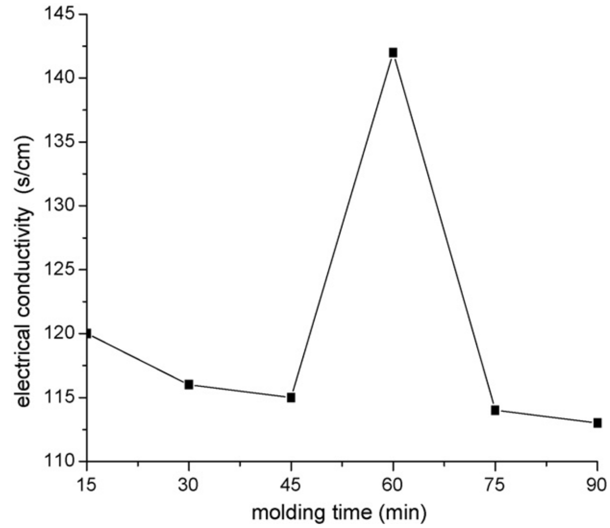


Fig. 6. Effect of molding time on electrical conductivity.

As molding time below 60 min, conductivity of the composite decreases firstly and then increases, but bending strength increases with the increasing of curing time. The three-dimensional network structure transformed from linear structure increases as molding time increases. The conductivity might be decreased due to the existence of three-dimensional network structure, which can baffle conducting current carrier flow. Simultaneously, the bending strength is raised due to the structure, which can bond aggregates particles better. Furthermore, the bending strength can reach its peak as curing reaction has already completed in 60 min. And the existence of more cavities due to decomposition of curing agents and evaporation of small molecule (such as H_2O) produced by polyreaction, can raise the number of conducting current carrier and be beneficial to its flow. Therefore, conductivity can be improved when

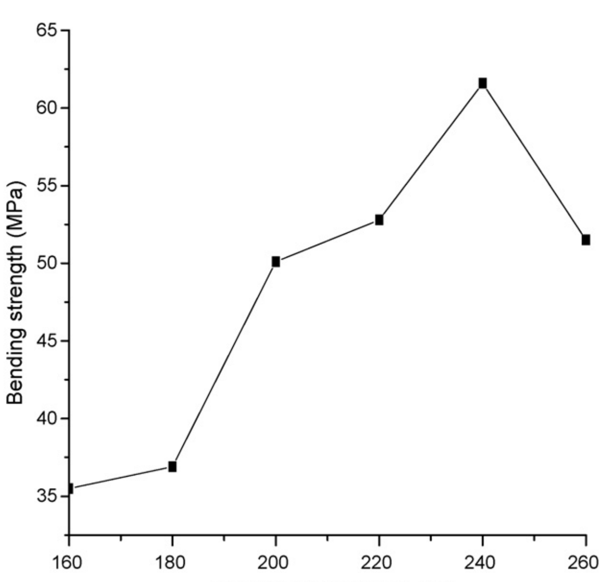


Fig. 5. Effect of molding temperature on bending strength.

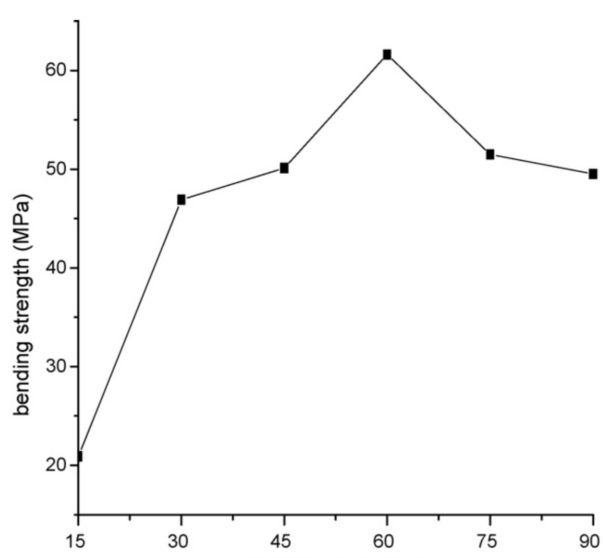


Fig. 7. Effect of molding time on bending strength.

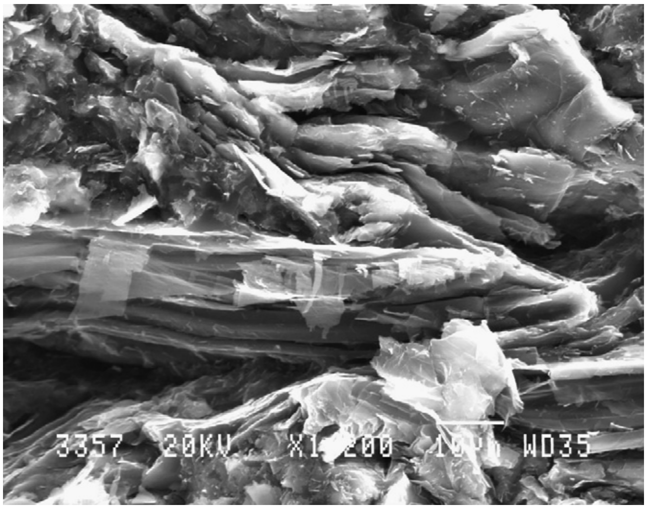


Fig. 8. SEM pattern of composite whose PF resin content is 15%.

molding time varies from 45 to 60 min. Especially, the slope of the curves (rising or falling) as the molding time varies from 15 to 30 min is larger due to transition between the chain structure and three-dimensional network.

The conductivity and bending strength of the composite would decrease when molding time is above 60 min. The porosity of the composite is raised due to excess decomposition of hexamethylene tetramine and evaporation of small molecule, which can reduce the properties of the composite. Simultaneously, generation of inner stress (even internal crack) between graphite and PF resin particles, produced due to pressure, may rusult in the decrease of the properties.

3.4. SEM analysis

Figs. 8 and 9 show SEM photographs of the composite with PF resin content 15 and 30%. The fracture surface has apparent lamellar when PF resin content is 15%, which has better directivity. Lamellar structure (Fig. 8) makes graphite flow along lamellar direction preferentially [14], which allocates PF resin uneven. PF resin spreads on surface parallel to lamellar. The structure keeps pattern of conducting aggregate and channel of graphite basically, and makes composite have better conductivity. But the structure may conduce to the stress concentration, which can reduce the bending strength. Structure of fracture surface (Fig. 9) is beneficial for PF resin to flow to every direction, and graphite can be bonded in every direction, which can form firm and uniform three-dimensional network, and obtain better bending strength. The existence of three-dimensional network baffles the flow of conducting current carrier and then reduce conductivity of the composite.

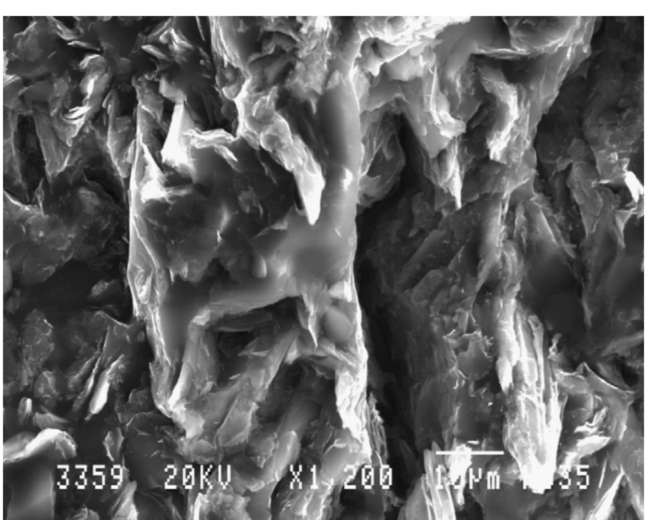


Fig. 9. SEM pattern of composite whose PF resin content is 30%.

4. Conclusions

(1) With PF resin powder as the adhesive and graphite powder as the conductive filler, PF resin/graphite composite for bipolar plates were prepared by hot-pressure molding, which can simplify technology, improve uniformity and performance.
(2) Conductivity of the composite decreases with increasing of PF resin content, but its bending strength changes inversely. Conductivity of the composite varies wave-like with increasing of molding temperature and time, and bending strength will increase firstly and then decrease.
(3) The optimum content of PF resin, molding temperature and time of composite are 15%, 240 °C and 60 min, respectively, in which the conductivity and bending strength of the composite are 142 s cm^{-1} and 61.6 MPa, respectively, which can meet the requirement of conductivity and bending strength of bipolar plate in PEMFC.

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