DEGRADATION OF GRAPHITE REINFORCED POLYMER COMPOSITES FOR PEMFC BIPOLAR PLATE AFTER HYGROTHERMAL AGEING

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Abstract

Effect of moisture absorption in graphite reinforced polymer composites was studied experimentally. Two different types of graphite reinforced polymer composites were exposed to hygrothermal environment for about 3000 hours. During the ageing, the behavior of moisture absorption was monitored by gravimetric test method. As a result, large size of graphite flake reinforced composites absorbed moisture more actively than small one. This is attributed to the difference of free volume generated by imperfectly bonded graphite flake and polymer resins according to the size difference of graphite flake. It was also resulted that larger amount of moisture absorbed at higher temperature. This can be explained as diffusion theory that diffusivity of polymer composite has lager value at higher temperature. After hygrothermal ageing, flexural strength and electric conductivity of composites were decreased with increasing amount of absorbed moisture. This shows that absorbed moisture in composites makes small cracks in polymer resin or debonding between graphite flake and polymer resin and results in degradation of material properties.

1 Introduction

Nowadays, the research of fuel cell is being performed widely. A number of manufacturers including major automobile makers and various governments have supported ongoing research into the development of fuel cell for use in vehicles and other applications. There are various types of fuel cells, which as a rule can be classified according to the kind of electrolytes used. Polymer electrolyte membrain fuel cells (PEMFCs) are under widespread development to produce electrical power for a variety of stationary and transportation applications. To date, the bipolar plate remains the most problematic and costly component of PEMFCs [1,2].

The bipolar plates have to achieve many functions in the fuel cell stack. Main functions are: (1) distribution of fuel and oxidant within cell, (2) facilitation of water management within cell, (3) separation of the individual cells in the stack, and (4) conduction of current from cell to cell [3].

Graphite reinforce polymer composites showed good electrical conductivity (>100 S/cm) and flexural strength (>40 MPa) for the bipolar plate of polymer electrolyte membrane (PEM) fuel cells. And also offer the potential advantages of lower cost, lower weight and greater ease of manufacture than traditional machined graphite and metal plates[4].

Bipolar plates in PEMFC are exposed to moisture at high temperature over 70^{o}C during the operation because of water used to cooling the cell and generated by chemical reactions. For the polymer matrix composites exposed to hygrothermal environment, it is believed that moisture absorption occurring and results in degradation of material properties [5-10].

Moisture absorption in polymeric composites has shown to be governed by several different mechanisms [11] and [12]. The first involves of diffusion of water molecules inside the micro gaps between polymer chains. The second involves capillary transport into the gaps and flaws at the interfaces between fibre and the matrix. This is a result of poor wetting and impregnation during the initial manufacturing stage. Generally, based on these mechanisms, diffusion behavior of polymeric composites can further be classified according to the relative mobility of the penetrant and of the polymer segments, which is related to either Fickian, non-Fickian or anomalous, and an intermediate behaviour between Fickian and non-Fickian [13] and [14]. In general moisture diffusion in a composite depends on factors such as volume fraction of fibre, voids, viscosity of matrix, humidity and temperature [15].

The polymer matrix and the fiber/matrix interface can be degraded by a hydrolysis reaction of unsaturated groups within the resin [16-19]. Debonding may occur at fibre/matrix interface [20]. A concern with using graphite reinforce polymer composites in PEMFC is lack of understanding and small database of information of their long term durability in hygrothermal environment. This hygrothermal ageing can be expected to degradate the functional properties of bipolar plates.

The aims of the present work are to find the mechanism of hygrothermal ageing occurring to graphite reinforced polymer composites for various parameters. This will tell us how to increase the hygrothermal durability of bipolar plates in PEMFC.

2 Theoretical approach

Hygrothermal ageing of bipolar plates in PEMFC results in moisture absorption. It is believed that moisture absorption behavior occurring to the classical diffusion theory which is well known as Fick's laws.

Fick first put diffusion on a quantitative basis by adopting the mathematical quation of heat conduction after realing the analogy between the heat conduction and the diffusion process

$$F = -D\frac{\partial C}{\partial x} \qquad (1)$$

where F is the rate of transfer per unit area of section, D is the diffusion coefficient, C is the concentration of diffusion substance and x is the space coordinate measured normal to the section. This equation is referred to as Fick's first law. Now let's assume that the diffusion coefficient is constant, and diffusion is one-dimensional so that means the concentration gradient is only along the x-axis, and diffusion occurs in an isotropic medium, with a rectangular whose sides are parallel to the axes of coordinates. Then the fundamental differential equation is derived by considering as follows:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \qquad (2)$$

Eq. (2) is referred to as Fick's second law.

For the case of thin plane with uniform initial distribution and equal initial surface concentrations under non-steady-state, a solution can be expressed by

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty}\frac{8}{(2n+1)^2\pi^2}\exp[(-D(2n+1)^2\pi^{2t}/(4l^2))] \qquad (3)$$

where M_t denotes the total amount of diffusion substance entering the sheet at time t, M_∞ denotes the corresponding quantity after infinite time, and l denotes the half thickness of sheet.

At initial absorption stage, moisture absorption (M_t) shows linear increase with $\sqrt{t}$; that leads to Eq. (4) be simplified to the following equation:

$$M_t = \frac{2M_\infty\sqrt{D}}{\sqrt{\pi}}\frac{\sqrt{t}}{l} \qquad (4)$$

From the above result, the average diffusion coefficient can be represented as follows:

$$D = \frac{\pi}{4}M_\infty^{-2}l^2\theta^2 \qquad (5)$$

where θ is the slope of M_t versus $\sqrt{t}$ plot.

We should remind that for the case of composites, in many cases anisotropy of composites results in different behavior of moisture absorption with Fick's law[21]. But we can use the classical diffusion theory to explain the behavior of moisture absorption for graphite reinforced polymer composites approximately.

3 Experiments

3.1 Preparation of composites

Graphite reinforced polymer composite specimens were made as shown in figure 1. The polymer resin used in this study was novolak type phenol resin (Kolon Chemical, Korea) which has low shrinkage rate and good chemical stability, thermal resistance, and mechanical strength. Graphite flake were selected because they have high electrical conductivity, high mechanical strength and immunity to corrosion [1]. Figures 2a and 2b represent the different size of flake-type graphite particles-that is 20 μm and 200 μm, respectively. These graphite flake particles were supplied by Carbonix, Korea. The analysis of particle size distribution was carried out using a Laser Particle Size Analyzer (CILAS 920 Liquid, CILAS, France).

Graphite and phenol powders were mixed at a initial mixing ratio of 80 : 20 wt% and were shaken for approximately 1 hour to obtain a uniform mixture of graphite powder and phenol compound, which was then poured in a steel mold. The mold was placed into a hot press (Tetrahedron, US) and heated to 150◦C for 10 min. The dimension of cured specimens was 80 × 80 × 1.2 mm^3.

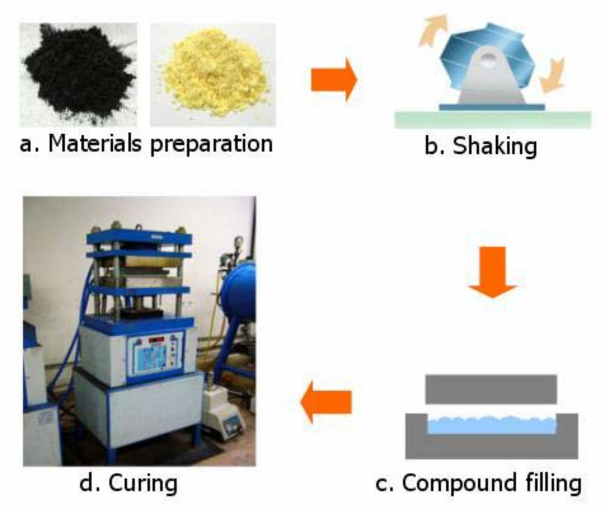
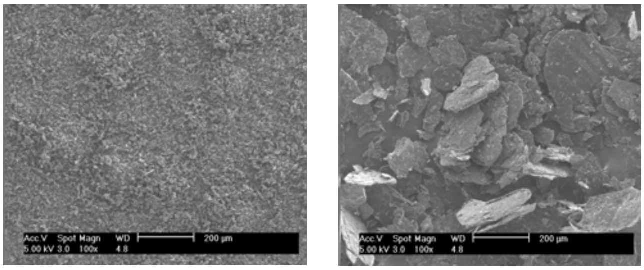


Fig. 1. Fabrication process of graphite reinforced polymer composites



(a) (b)

Fig. 2. SEM pictures of graphite flake used in composites (a) size of 20 ㎛ , (b) size of 200 ㎛

3.2 Moisture absorption tests

To find the hygrothermal ageing occurring to composites, the amount of moisture absorption was measured according to ASTM D5229. Two types of different composites were embedded in distilled water. 80 × 80 × 1.2 mm^3 of composites were edge-sealed with Teflon-tape to reduce edge side moisture absorption so to simulate 1-D diffusion situation. To find the relation of moisture absorption behavior with temperature, composites were exposed to room temerature and 85 ^{o}C of steady state environments. And the changes in mass of composite specimens were measured by weighing machine accuracy of 0.001g for every day. Moisture content of a specimen was computed as follows:

$$M_t = \frac{W_t - W_o}{W_o} \times 100\% \tag{6}$$

where W_o and W_t denote the dry weight of the specimen and the weight at any specific time t, respectively. This test was executed until 3000 hours for each cases. At least 5 of specimens were measured to reduce the error of the results. The average amount of absorbed moisture in a specimen is taken as the ratio of initial mass and expressed as a percentage.

3.3 Mechanical testing

Bipolar plate in PEMFC should endure pressure of gases passed through the plates, and it should protect cell from external impacts. So it should maintain high mechanical strength while used in the cell. So the flexural of graphite reinforced composites were measured during hygrothermal ageing. Three-point bending test was performed to measure the flexural strength.

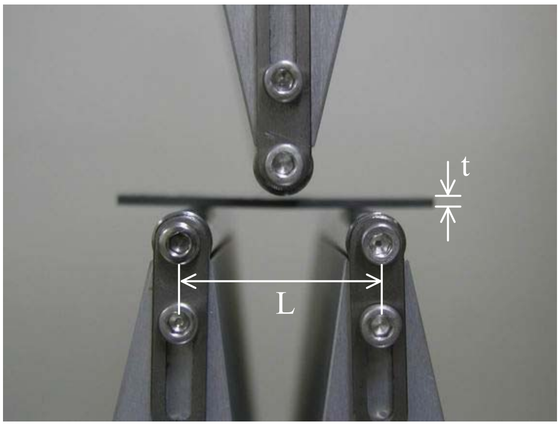


Fig. 3. Three point bending test for measuring flexural strength

In accordance with ASTM D790-02, at least five tests were carried out using a universal testing machine (Shimadzu, 5 ton) for each case. Specimens used to measure the electrical conductivity were reused for the consistency of experiments. The support span was 38 mm, and the cross-head speed was 1 mm/min, which corresponds to a strain rate of 0.01 mm/mm/min.

3.4 Electrical testing

Bipolar plate in PEMFC should be the passage of electric current generated in Fuel cells. So it should maintain high electrical conductivity while used in the cell. So the electrical conductivity of graphite reinforced composites were measured according to exposed time in hygrothermal environments. The electrical conductivity was measured by a well-known four-point technique, shown in Fig. 4. Fabricated CPCs were cut to a size of 60 × 12.7 × 1.2 mm^3 using a bandsaw and painted with conductive silver paste on the four regions to be contacted with probes. Specimens were then heat-treated at 50◦C for 2 h. A current between −80 and 80 mA was applied stepwise through the two outermost probes by a 220 Programmable Current Source (Keithley) and the resultant voltage across the two inner probes was measured by a 196 System digital multimeter (Keithley). The electrical conductivity was calculated according to the following equation:

$$\sigma = \frac{I}{V} \cdot \frac{L}{A} \tag{7}$$

where I is the applied current, V is the resultant voltage potential, A is the cross sectional area of the specimen and L is the distance between the inner probes.

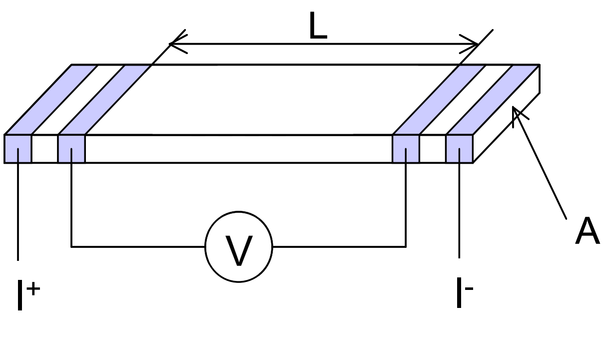


Fig. 4. Measuring Electric conductivity

4 Results and discussions

4.1 Moisture absorption behavior

4.1.1 Effect of graphite flake size

Fig 6 shows the result of moisture absorbing behavior of two types of graphite reinforced polymer composites at 85°C. Two remarkable phenomena are shown in this result. First, 20 ㎛ size of graphite flake used composites absorbed twice amount of moisture comparing to 200 ㎛ size of graphite flake used composites after reaching steady state. Second, 20 ㎛ size of graphite flake used composites reached to steady state very quickly with comparing to 199 ㎛ size of graphite flake used composites. These two phenomena can be explained as difference of micro-structure of composites due to the size of graphite flake reinforced in composites. Fig 5 shows schematic diagram of micro-structure of graphite reinforced composites. Small size of graphite flake has large surface area. This means that small size of graphite flake used composites should have much larger interface area between graphite flake and polymer resins comparing to large size of graphite flake used composites. It is believed that for the case of moisture absorption of composite materials,

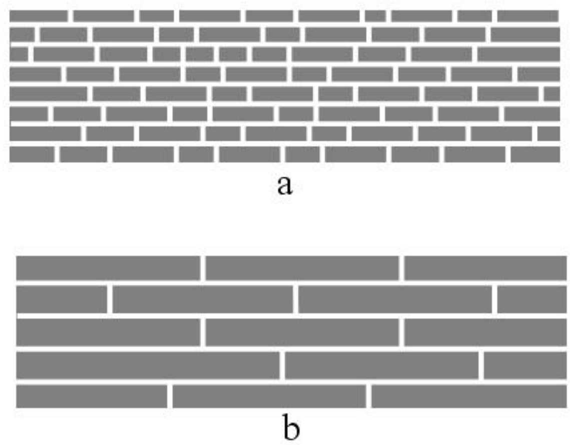


Fig. 5. Schematic micro-structure of composites: (a) 20 ㎛ graphite flake; (b) 200 ㎛ graphite flake

defects and voids presented by imperfect bonding between fiber and polymer matrix are the dominant spaces of moisture absorbing. For the same way in this research, small size of graphite flakes producing a lot of void and defects in composites between the graphite flake and polymer resin, and large amount of moisture absorbing. Second phenomena can be explained in similar way. Void and defect produced in composite construct network as shown in fig 7. Diffusion of moisture can be explained as capillary action that water moving through the narrow channel between graphite flake and polymer resin. Small size of graphite flake used composites should have various path and so many connect between the channel, so capillary action can be occurring more actively and rapidly. So small size of graphite reinforced composites show remarkably rapid absorbing behavior comparing to large one.

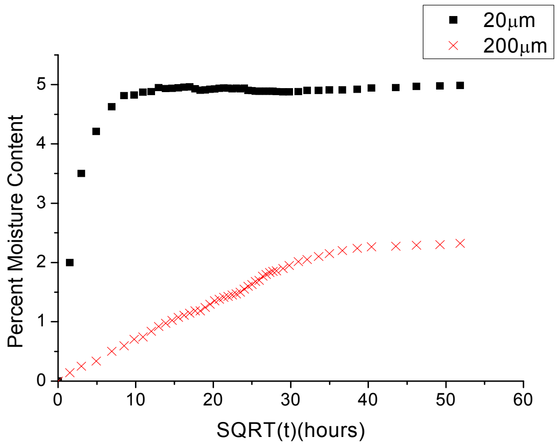
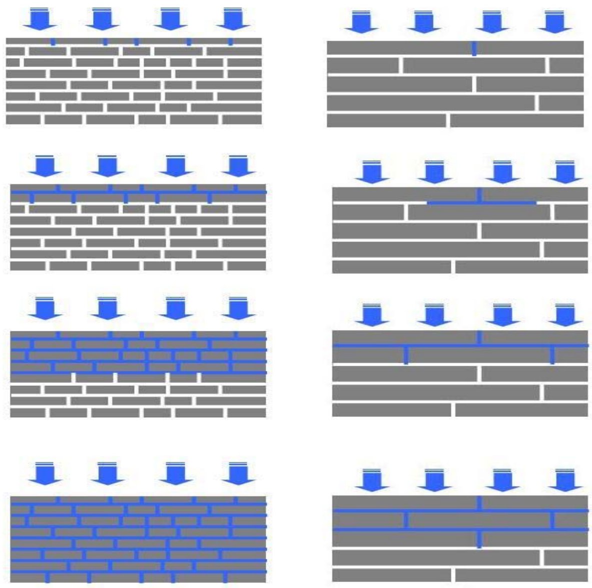


Fig. 6. Moisture contents of two types of graphite reinforced composites at 85°C



(a) (b)

Fig. 7. Moisture absorption behavior of composites: (a) 20 μm graphite flake; (b) 200 μm graphite flake

4.1.2 Effect of temperature

Fig 8,9 show the results of moisture absorption behaviors according to the different temperatures. Both of different kinds of composites show the similar phenomena that for the higher temperature, moisture absorbed more rapidly and reached high moisture contents in equilibrium condition. By the assumption that behavior of moisture absorption in composites obeying the diffusion theory, we can use the following equation to define diffusivity D:

$$D = D_0 \exp\left(-\frac{E_a}{RT}\right) \qquad (8)$$

where T is temperature and D is diffusivity. So the diffusivity has higher value at high temperature and results in more active absorption behavior.

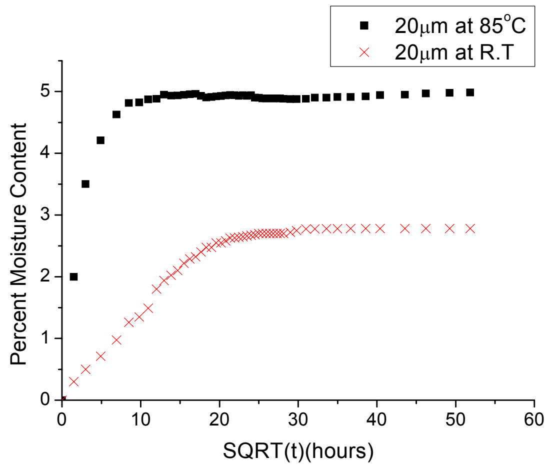


Fig. 8. Moisture contents of 20 μm graphite reinforced composites at different temperatures

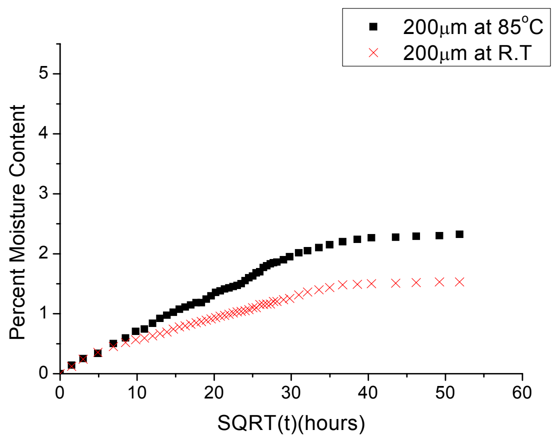


Fig. 9. Moisture contents of 200 μm graphite reinforced composites at different temperatures

For the each cases, the diffusivity can be calculated by eq(5). Table 1 shows this result. From the result, with higher temperature, diffusivity of composites increases. Particularly, diffusivity of small size of graphite flake reinforced composites shows greatly increasing but large one is not. We concluded that the lack of network in large one does not being actively enough to accelerate diffusion process.

Table. 1 Diffusivity of graphite reinforced composites

	θ (%/s^0.5^)	M∞ (%)	D(cm²/s X 10⁻⁹)
20 ㎛, 85◦C	0.0143	4.980	93.206
20 ㎛, R.T	0.002383	2.781	8.300
200 ㎛, 85◦C	0.001224	2.302	3.198
200 ㎛, R.T	0.000666	1.526	2.143

4.2 Effect of moisture absorption in material properties

Fig. 10 and 11 show the result of flexural strength and electrical conductivity tests after hygrothermal aged composites versus time. For both type of composites, flexural strength reduced as aging time increased. And for 20 ㎛ size of graphite flake used composite shows remarkable degradation comparing to 199 ㎛ size of graphite flake used composite. We can easily find that degradation of strength is a function of the amount of absorbed moisture in composites. Moisture absorbed in composites invade to the interface between graphite flake and polymer resin and result to weak the bonding between them. This makes strength of composites decreases as hygrothermal ageing goes on. Moisture absorbed in composites also makes void in composites. This results in decreasing of compactness of graphite reinforced composites, and passage of electron is lost. So the electric conductivity decreased by moisture absorption.

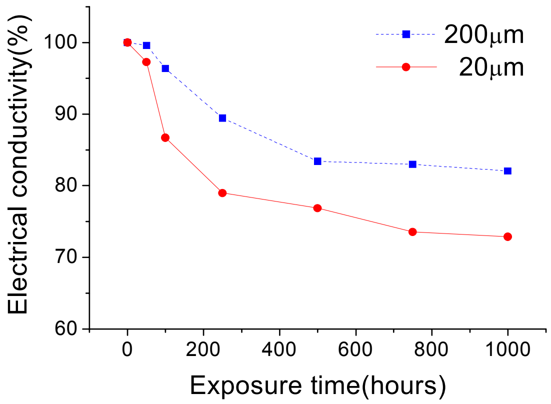


Fig. 10. Degradation of electrical conductivity of composites after hygrothermal ageing

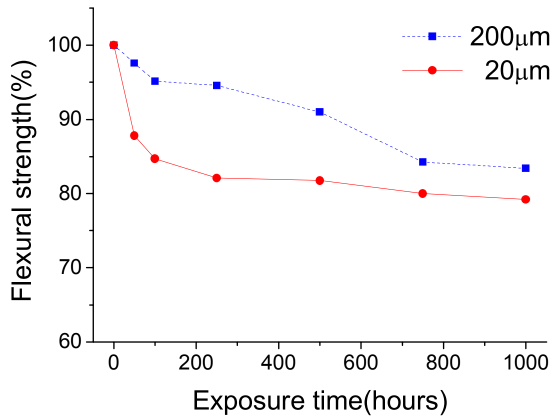


Fig. 11. Degradation of flexural strength of composites after hygrothermal ageing

5 Conclusions

In this study, behavior of graphite reinforced polymer composites after hygrothermal ageing was studied experimentally. During hygrothermal ageing, moisture absorption occurred in composites and degrade mechanical strength and electric conductivity. Larger amount of moisture absorbed in composites results in greater decreasing in material properties. Composite reinforced with larger size of graphite flake constraints the amount moisture absorption initial absorbing speed. This can be explained as difference between large size of graphite flake reinforced to composites and small one makes different interfacial area between graphite flake and polymer resin. For the lower temperature, diffusion process restrained and less moisture absorbed. These results can be a good application to PEMFC bipolar plate with good durability in hygrothermal environment.

6 Acknowledgements

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