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Influence of particle size and shape on electrical and mechanical properties of graphite reinforced conductive polymer composites for the bipolar plate of PEM fuel cells

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Abstract—Graphite reinforced conductive polymer composites (CPCs) with high filler loadings were fabricated by compression molding technique. Various sizes and shapes of graphite particles were mixed with phenol resin to impart the electrical conductivity in composites. Fabricated CPCs showed good electrical conductivity (>100 S/cm) and flexural strength (>40 MPa) for the bipolar plate of polymer electrolyte membrane (PEM) fuel cells. The electrical conductivity of CPCs was affected by the formation of conductive networks among graphite particles. CPCs made of sphere-type particles (SG-CPCs) had the same physical density regardless of particle size; and they also showed the same bulk electrical conductivity. This means that there is a close correlation between the electrical conductivity and the densification level, or density, of graphite/phenol compounds. The particle shape was also a principal factor in influencing electrical conductivity. In this study, the electrical conductivity of CPCs made of flake-type graphite particles (FG-CPCs) was higher than that of SG-CPCs due to the difference of the densification characteristic. The flexural strength of SG-CPCs tended to increase with decreasing graphite particle size because the interfacial coherence between graphite particle and phenol resin increased as graphite particle size decreased. This influence of interfacial coherence was also founded in the variation of particle shape. FG-CPCs have higher flexural strength than SG-CPCs because a flake-type particle has larger specific area than a sphere-type particle.

Keywords: Conductive polymer composites (CPCs); high filler loadings; particle size; particle shape.

1. INTRODUCTION

Much intensive research has been carried out on conductive filler reinforced CPCs. It was found that electrical properties could be achieved in polymer composites

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by addition of conductive fillers. With increasing temperature, the positive and negative temperature coefficient (PTC and NTC) effects of conductivity were also observed. Because of these electrical characteristics, CPCs can be applied to sensors, electromagnetic shielding and thermistor devices. Various conductive fillers (graphite particles, carbon fiber, carbon black, carbon nanotubes, etc.) have been used to impart electrical properties to an insulating polymer resin. Generally, some researches have focused on low filler loadings: <1–5 wt% (nanoparticle) [1, 2], or 20–30 wt% (micro-particle) [3]. With increasing conductive filler loadings, a region where the electrical conductivity of CPCs increased rapidly appeared. This is called the percolation phenomenon of CPCs and the critical transient point is the percolation threshold. The percolation phenomenon results from the strong electric field influence among conductive fillers and their continuous network structure. Now, theoretical approaches on percolation are being performed too [4–6].

A number of manufacturers, including major automobile makers and various governments, have supported ongoing research into the development of PEM fuel cells for use in vehicles and other applications. Nowadays, research on PEM fuel cells is being vigorously pursued, with the aim of reducing costs for commercialization. Especially, the cost of bipolar plates accounts for a high portion of the total cost of fuel cell systems [7, 8]. So, various studies to reduce their price are being conducted globally. Unfortunately, the electrical conductivity of the existing CPCs with low filler loadings, 10^{-4} – 10^{-1} S/cm, is too low for this application, despite the percolation phenomenon. Conducting polymers such as polyaniline (PANI) are also unsatisfactory, in spite of good electrical conductivity at low conductive filler loadings, because of thermal instability [9]. To satisfy the specification of the US D.O.E. (>100 S/cm), the study of CPCs with high conductive filler loadings above 60 wt% is needed. CPCs for bipolar plates of PEM fuel cells offer the potential advantages of lower cost, lower weight and greater ease of manufacture than traditional machined graphite and metal plates [10–14]. In recent years, new manufacturing processes for mass production and research to achieve high electrical conductivity at low filler loadings have been gradually attempted [15–17].

Many studies on the influence of conductive filler particle size have shown that the percolation threshold decreases as the particle size decreases [18–20]. In several studies, it was reported that physical properties deteriorated as graphite particle size decreased because this increased the porosity in the CPCs with high filler loadings [21, 22]. Especially, Kuan *et al.* reported that the electrical conductivity and the flexural strength decreased as graphite particle size decreased. In their study, CPC density also decreased with particle size. This showed that fabrication states differed according to particle size. Also, the maximum density obtained in their study was very low compared to the theoretical density. Therefore, these results do not clearly show the effect of particle size alone.

There have been almost no schematic comparisons of different particle shapes in the case of CPCs with high filler loadings. Celzard *et al.* found correlations between

the electrical properties and the morphology of graphite particles [23]. However, there are some restrictions in the application of the results of this study because many assumptions were made and the effect of particle size was not considered. Therefore, experimental verification was necessary.

In this study, a systematic approach to various kinds of the graphite particles used in CPCs with high filler loadings was performed. The electrical and mechanical properties were measured and the correlation between graphite morphology and properties was analyzed.

2. EXPERIMENTAL

2.1. Materials and fabrication

The thermosetting 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 particles were selected because they have high electrical conductivity, high mechanical strength and immunity to corrosion [11]. Figures 1a and 1b represent the shape of elongated sphere-type and irregular flake-type graphite particles, respectively. These graphite particles were supplied by Carbonix, Korea. The diameters of sphere-type graphite particles were 7, 15 and 25 μm , as shown in Fig. 2, while the mean diameter of flake-type graphite particle was 25 μm only and their thickness was several microns. 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 85 : 15 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 \times 80 \times 2.4 mm³.

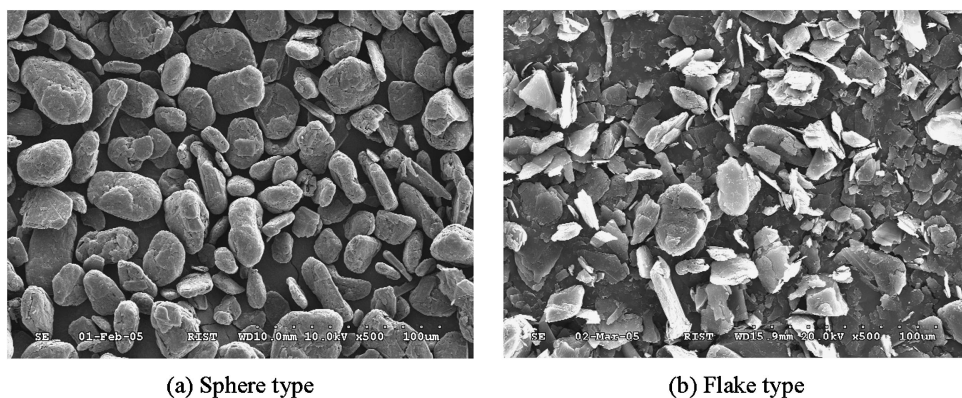


Figure 1. Shape of graphite particles (average particle size: 25 μm).

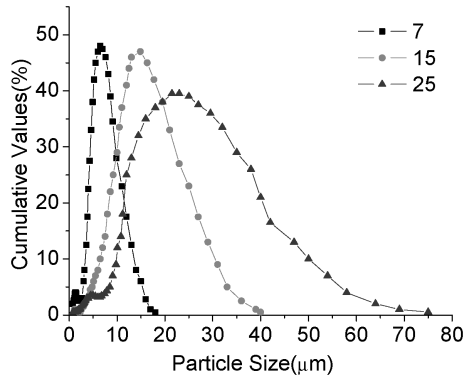


Figure 2. Size distribution of sphere type graphite particles.

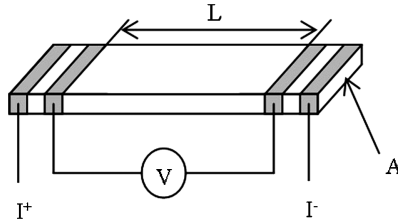


Figure 3. Measuring electrical conductivity.

2.2. Measurements

The density of fabricated CPCs were measured based on Archimedes's principle (ASTM D792-00) and microstructures of the CPCs was observed using a Philips XL 30S Scanning Electron Microscope.

The electrical conductivity was measured by a well-known four-point probe technique, shown in Fig. 3. Fabricated CPCs were cut to a size of $60 \times 12.7 \times 2.4 \text{ mm}^3$ 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:

$$\sigma = \frac{I}{V} \cdot \frac{L}{A}, \quad (1)$$

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.

The three-point bending test was performed to measure the 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. RESULTS AND DISCUSSION

3.1. Density

The optimum conditions for curing were determined by our previous research [14]. In the case of the sphere-type graphite particle, the level of densification increased with increasing molding pressure from 0.69 to 6.89 MPa, but scarcely changed from 6.89 MPa to 13.78 MPa. This tendency was also verified by the optical microscope images. The electrical conductivity and flexural strength of CPCs rapidly increased till 6.89 MPa and then the rate of increase reduced gradually. Therefore, the optimum molding pressure for electrical conductivity and flexural strength was determined to be 10.34 MPa. Figure 4 shows that SG-CPCs had nearly the same density, irrespective of graphite particle size in the 7–25 μm range. This means that the level of the densification is uniform regardless of graphite particle size in this range. Some other research on particle size reported that densities of fabricated CPCs were different from each other [22]. Generally, it is difficult to fabricate specimens with high density as the particle size decreases because voids are generated inside the CPCs. It was possible, however, to obtain uniform density regardless of graphite particle size in this range. The uniformity of density is necessary to exactly evaluate characteristics of samples according to the particle size.

The density according to the molding pressure was measured to verify the densification behavior according to the particle shape. Figure 5 represents the density of CPCs according to the particle shape. With increasing molding pressure at curing, the density increased, though there was very little change above the

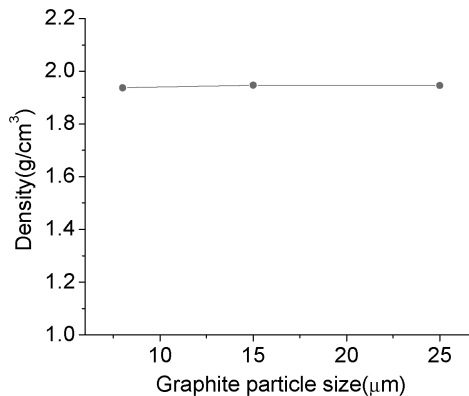


Figure 4. Density of CPCs according to particle size (sphere type, molding pressure: 10.34 MPa).

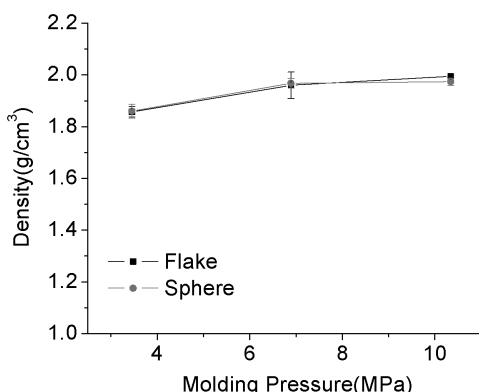


Figure 5. Density of CPCs according to particle shape.

molding pressure of 6.89 MPa. The optimum molding pressure of FG-CPCs was also 10.34 MPa, just like SG-CPCs. In addition, Fig. 5 shows that density remained the same between SG- and FG-CPCs in spite of their morphological differences. Graphite particle shape did not affect the density of CPCs.

3.2. Electrical conductivity

3.2.1. Influence of particle size (sphere-type). The density of CPCs is one of the most important factors affecting the electrical conductivity. In the case of sphere-type graphite particles, the same density of CPC samples induces the same conductive networks among graphite particles. The electrical conductivity of CPCs is a function of the number of conductive networks among conductive fillers, namely graphite particles. Therefore, CPCs which have the same density showed the same electrical conductivity in the 7–25 μm range as shown in Fig. 6.

The electrical conductivity of CPCs can be explained by two mechanisms: inter-particle conductivity and intra-particle conductivity. The inter-particle conductivity is related to the connectivity by direct contact among graphite particles. The intra-particle conductivity is proportional to the conductive path length of the inside of a unit particle, or to particle size. Figure 7 shows simplified 2-dimensional schematic diagrams of conductive networks in a specific area. In Fig. 7a, small graphite particles with diameter D already form conductive networks, while large graphite particles with diameter $3D$ are isolated. It was widely known that the percolation threshold decreases with decreasing particle size [18–20]. In the case of nano-particles (carbon nanotube, carbon black, etc.), the percolation threshold is only around 1 wt% [1, 5]. At low filler loadings, the more the graphite particle size decreases, the more efficiently conductive networks form because inter-particle conductivity is predominant.

However, the importance of intra-particle conductivity gradually increases as graphite loading ratio increases. After graphite particles are fully compacted, as illustrated in Fig. 7b, the advantage of inter-particle conductivity among small

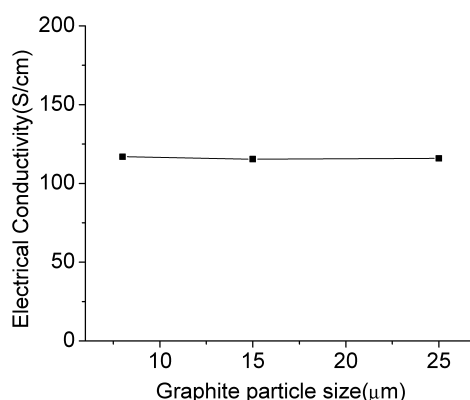


Figure 6. Electrical conductivity of CPCs according to particle size (sphere type, molding pressure: 10.34 MPa).

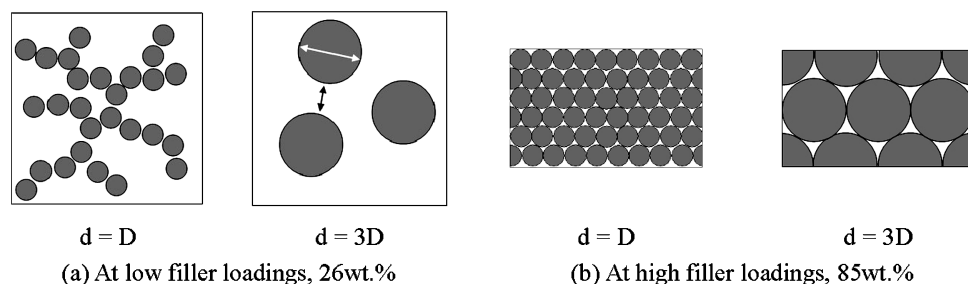


Figure 7. Simplified schematic diagrams of conductive networks in the specific area (Black arrow: inter-particle conductivity, white arrow: intra-particle conductivity).

graphite particles that was observed at low filler loadings is offset by the intra-particle conductivity of large graphite particles. In this state, the electrical conductivity of fabricated CPCs was uniform regardless of graphite particle size. These results can change according to the thickness ratio, D/t (particle diameter/specimen thickness), because of edge influence [23]. The thickness ratio used in this study was limited to 0.003–0.01, and research on the very large or small thickness ratio was not considered. This matter is subject to further investigation.

3.2.2. Influence of particle shape. The electrical conductivity slightly increased as the molding pressure increased from 3.45 to 10.34 MPa, as shown in Fig. 8. This can be backed by Fig. 5 because the variation of the density is directly linked with electrical networks.

Figure 5 also shows that there is no difference of the density between SG- and FG-CPCs as above mentioned. It means CPCs have similar densification states regardless of graphite particle types at these molding pressures. Nevertheless, the electrical conductivity was greatly influenced by the shape of graphite particles. Figure 8 shows that the electrical conductivity of FG-CPCs was about 2.4 times

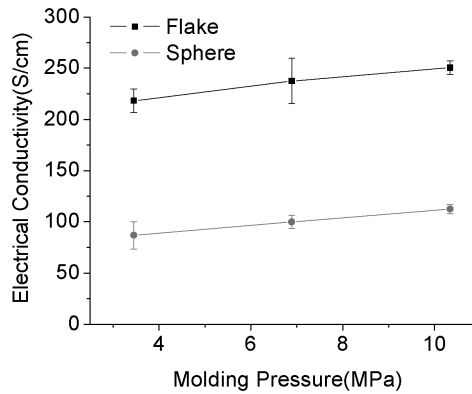


Figure 8. Electrical conductivity of CPCs according to particle shape.

higher than SG-CPCs at the same molding pressures. Besides, the FG-CPCs at 3.45 MPa have much higher electrical conductivity than SG-CPCs at 10.34 MPa, even though the density of the former is smaller than that of the latter.

This result is due to different conductive networking mechanisms according to particle types. In Fig. 9a, every sphere-type graphite particle (gray) is connected with neighboring graphite particles and generally forms point-to-point contacts rather than surface-to-surface contacts. Phenol resin, an insulating material, is placed in the gaps among graphite particles and some gaps remain pores. These non-conducting regions, namely phenol resin regions (white) and pore regions (dark gray), were observed among sphere-type particles. Non-conducting regions block the connection of electrical conductive paths.

In the case of the flake-type particles, phenol resin rich regions were not observed, as shown in Fig. 9b, because flake-type particles were stacked neatly and compactly. Therefore, surface-to-surface contacts among flake-type particles were much more dominant than among sphere-type particles. Scattered small pores (several or sub-

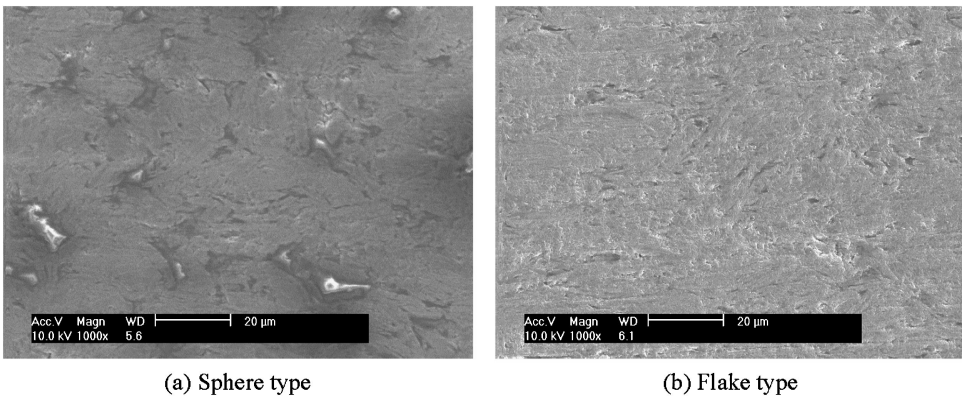


Figure 9. Microstructure of the polished surface (average particle size: 25 μm , molding pressure: 10.34 MPa).

microns) scarcely influenced the electrical conductivity, compared with the non-conducting regions of SG-CPCs.

3.3. Flexural strength

3.3.1. Influence of particle size (sphere-type). The flexural strength of CPCs increased with decreasing graphite particle size from 25 μm to 7 μm as shown in Fig. 10. Figure 12a shows the microstructure of the fractured surface after the 3-point bending test. The shape of graphite particles can be observed plainly. It means the fracture of the specimen occurred at the interface between the graphite particle and phenol resin. Therefore, the interface adhesion between the graphite particle and phenol resin is an important factor in mechanical behaviors, like the flexural strength. If the amounts of phenol resin were sufficient, total interface adhesion would be proportional to the interface area. Consequently, the flexural strength increases as the graphite particle size decreases because the specific surface area of the graphite particle, or the interface area, increases.

3.3.2. Influence of particle shape. Figure 11 shows that flexural strength increased somewhat with increasing molding pressure from 3.45 to 10.34 MPa for both particle types, because the increase of molding pressure improves the adhesion between graphite particle and phenol resin by reducing the distance between graphite particles.

The flexural strength was also affected by particle shape. In Fig. 11, the flexural strength of FG-CPCs is about 8–27% higher than SG-CPCs at the same molding pressures. Especially, FG-CPCs showed good flexural strength, above 50 MPa, at low molding pressure, 3.45 MPa, because flake-type graphite/phenol compound is easy to be compressed.

There are two feasible reasons: one is the difference of the interface area between the graphite particle and phenol resin, and the other is the stacking structure of graphite particles. A flake-type particle has a larger specific surface area than a

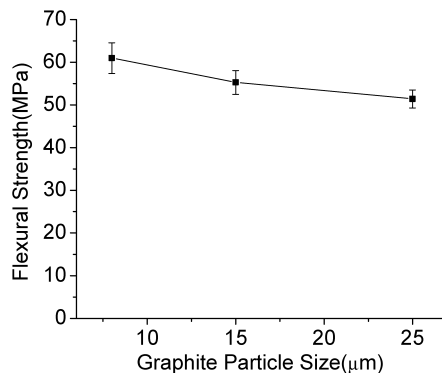


Figure 10. Flexural strength of CPCs according to particle size (sphere type, molding pressure: 10.34 MPa).

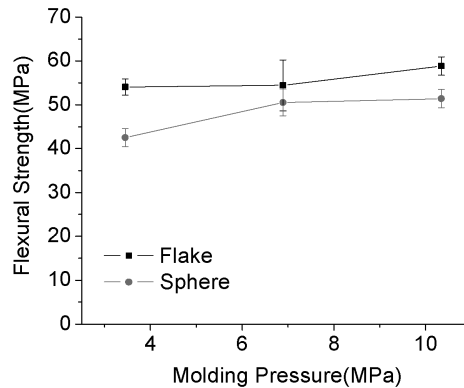


Figure 11. Flexural strength of CPCs according to particle shape.

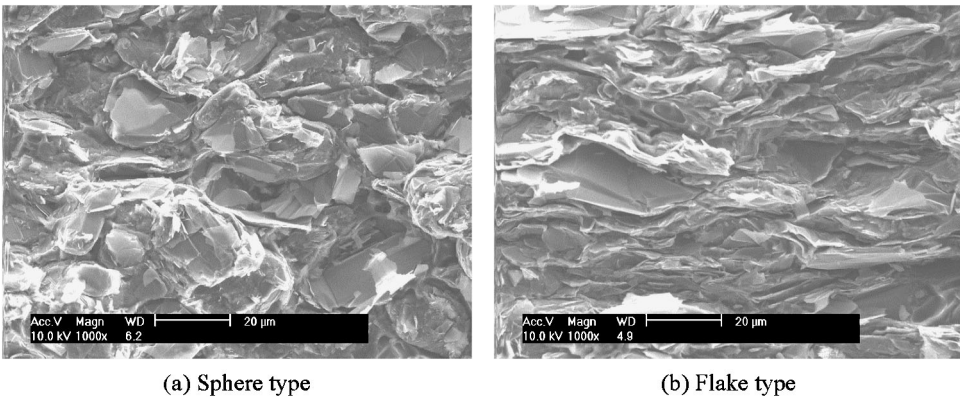


Figure 12. Microstructure of the fractured surface (average particle size: 25 μm , molding pressure: 10.34 MPa).

sphere-type when both particles have same diameter. As previously mentioned, the larger the interface area, the stronger the interface adhesion. Therefore, FG-CPCs, with the large interface area, have higher flexural strength than SG-CPCs. From another point of view, the flexural strength is closely related to the stacking structure according to the particle type. As shown in Fig. 12b, flake-type graphite particles were layered perpendicularly to the compression direction, or thickness, and formed a layered structure. So, the resisting force of FG-CPCs against the applied flexural load was higher than that of SG-CPCs.

Synthetically, these results can be briefly explained by the absolute quantity of phenol resin participating in adhesion when the ratio of the graphite particle to phenol resin is fixed. The absolute quantity of phenol resin participating in adhesion becomes large as the specific surface area of the graphite particle increases. Consequently, the total adhesion force increases. The above two cases, namely, (1) decreasing the particle size and (2) changing the particle shape from the sphere-

type to the flake-type, show that larger specific surface area of the graphite particle results in higher flexural strength.

4. CONCLUSIONS

CPCs (conductive polymer composites) with high filler loadings were fabricated by using various kinds of the graphite particle and characterized by electrical and mechanical tests. The electrical conductivity related to the level of the conductive networks in the CPCs. When CPCs were fabricated uniformly using the sphere-type graphite particles, the electrical conductivity was constant regardless of the particle size in the 7–25 μm range. However, variation in particle shape had significant effects on the electrical conductivity. While having the same density, FG-CPCs were more than twice as conductive as SG-CPCs. This is because the flake-type graphite particle is superior in the electrical network formation to the sphere-type. The flexural strength was affected by the specific surface area of the graphite particle. With increasing specific surface area, or decreasing the particle size and changing the particle shape from the sphere-type to the flake-type, flexural strength increased. Thus, CPCs containing particles with higher specific surface areas have superior mechanical properties when the density is uniform. Graphite reinforced CPCs with high filler loadings are promising materials for PEM fuel cell bipolar plates. Although every possible kind of graphite particle was not studied, these results are expected to be applied to development of CPCs with high filler loadings.

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