Study of heating system on the battery module for PHEV

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Abstract
Polyamide 6 (PA6) was compounded with boron nitride (BN) and nickel-coated carbon fiber (NiCF) to fabricate thermal conductive polymer composites. After printing the silver (Ag) ink on the polymer-based substrate, heat generation and dissipation behaviour has been examined under constant electric voltage. Thermal conductivity of pure PA6 (λ = 0.25 W/mK) has been improved about 4 and 2 times upon addition of BN and NiCF. At the same PA6/BN composition, higher thermal conductivity was achieved with the larger fillers. Heat generation was highly sensitive to the pattern formation, conductive line width and length, and electric voltage. The substrate printed with wider and shorter silver lines was the most effective in heat generation. Temperature rise was more evident when applied the high voltage.

Keywords: thermally conductive composites, heat generation, boron nitride, nickel-coated carbon fiber, silver paste.

1 Introduction
Lithium (Li) ion battery is commonly encountered in our daily life. The consumption of Li battery may grow rapidly once the electric vehicle (EV) market is open. In order to commercialize the EV earlier, the capacity and lifetime of Li battery system should be further improved. Li battery is known to be effective when operated within a certain temperature range. Suppose temperature is too high or low, the life span and efficiency of Li battery drop quickly due to declination of battery capacity, pulse performance, and irreversible reaction. Therefore, effective heat manipulation is a prerequisite to maximize the performances. For instance, the heat generated during the charging and discharging process should be removed quickly, while sometimes additional heat should be provided when the battery is operated at the cold place. In this regard, effective heat management is of paramount importance in EV industry.
In terms of thermal conductive materials, metals are idealistic to dissipate the heat, but they are intrinsically heavy and difficult to process. Much attention has been paid to develop the thermally conductive polymer composites [1–5]. Although the conventional thermoplastics are not thermally conductive, the conductivity can be imparted by adding the appropriate inorganic fillers. In order to generate heat, electric field is useful. Electrical current passes through the substrate which serves as an electrical resistance where heat is generated. Heating rate is proportional to electric field strength and electrical conductivity of the media. Considering that electrical conductivity increases with increasing temperature, the heat generation effect is expected to be more apparent at an elevated temperature. The degree of heat generated is mainly affected by the materials used. Electrical heterogeneity, heat channelling, and shape and distribution may be varied depending on the conductive materials. Although various metallic and non-metallic materials are utilized as heating elements, several hurdles to overcome such as thermal stability, complicated manufacturing steps, and durability still remain [6–10]. Recently, silver (Ag) particles are widely used due to their intrinsic high conductivity and thermal stability [11,12].
In present work, thermally conductive composites have been prepared by simply mixing polyamide 6 (PA6) with boron nitride (BN) and nickel-coated carbon fiber (NiCF), respectively. PA 6 was selected because of high thermal stability, high mechanical properties, and superior barrier properties for oxygen transport. Heat generation behaviour under the voltage ‘on’ state has been monitored by directly printing the silver (Ag) paste on the thermally conductive composites. The effect of thermal conductivity of the substrate, printing design, and electric voltage on heat generation and dissipation has been thoroughly investigated.

2 Experimental

2.1 Materials and Preparations

Polyamide 6 (PA6) was purchased from LG Chem. Ltd. Boron nitride (BN) having average particles size of 5 μm (BN5) and 20 μm (BN20) were supplied from Denka and Changsung Corporation, respectively. Nickel-coated (NiCF) carbon fibers with about 7 μm in diameter were provided by Bullsone Material Ltd. Prior to mixing, the polymer and fillers were dried in a convection oven overnight at 70 °C to remove the absorbed moisture. Well-dispersed silver (Ag) paste ink with 65 wt% Ag content was kindly contributed by Paru Co. Ltd. The average size of Ag particle is approximately 5 μm.

Incorporation of conductive fillers into a polymer matrix was carried out using twin screw extruder (BA-19, Bautek) equipped with main hopper and side feeder. The extrusion was conducted in a temperature range of 210 ~ 240 °C. The extrudate was air-dried and then pelletized. The specimens for thermal conductivity and heat generation measurement were prepared using injection molding machine (PRO-800, DongShin Hydraulics Co. Ltd).

The conductive lines composed of Ag particles were directly printed on the composite plate having dimensions of 100 × 100 mm² using a screen printer (HC-CA400, Hyochang Machinery Corporation). Silver ink was poured on the woven meshes and then squeezed into an open space by moving the bar at a constant speed. Continuous and smooth lines were formed. Wetting problem was not detected during printing process. The specimen was then dried in an oven at 150 °C for 60 min to remove the solvent and solidify tightly on the substrate. The thickness of the printed layer was in the range of 100–120 μm. Figure 1 showed three different patterns tested in our experiment and morphology of Ag particles obtained after finishing the printing process. The line width of the printed specimen in Figure 1(a) and (b) was varied from 1mm to 3mm, while the line width of the pattern in Figure 1(c) was fixed at 3 mm. Electric voltage in the range of DC 3 ~ 9 V was applied to the electrodes at both ends of the plate.

![Figure 1](image-url) Figure 1. (a-c) Three different pattern formations tested, (d) SEM picture of Ag particles coated on the substrate, and (e) micrograph showing cross-section between substrate and printed layer.

2.2 Computational Simulation

Heat dissipation behaviour in a battery package has been predicted using COMSOL Multiphysics. For numerical modelling, a rectangular-shaped package having dimension of 310 mm in length, 175 mm in width, 60 mm in height was used, which is similar to the size of real Li battery package used for PHEV (Figure 2a). Heat is assumed to generate constantly from the top and bottom plate, while air temperature is maintained at -10 °C. The geometry and free tetrahedral mesh composed of 225,083 elements are shown in Figure 2(b). Aluminium is selected as a housing material to clarify the heat transfer. The thermal behaviour is described using a combined Navier-Stokes (N-S) and heat transfer equation.
2.3 Characterizations

Thermal conductivity of the composite was measured using Unitherm™ machine (Model 2022, Anter Corporation). Experiment was performed following ASTM E1530 procedure using guarded heat flow meter. Disc-shaped samples with diameter of 50 mm and thickness of 3 mm were prepared. The measurement was conducted at ambient temperature under an applied load of 30 psi. Heat generation was evaluated by applying electric voltage on the Ag-printed compounds using Potentiostat (IVIUMSTAT, IVIUM Tech). At constant voltage, the current flowing through the specimen having 30 mm in length and about 2 mm in thickness was measured. To obtain temperature profiles over the entire specimen, the infrared thermal camera (FLIR E60, FLIR Systems) with thermal sensitivity < 0.05 °C and accuracy of ± 2 °C was used. The homogeneity and spatial distribution of heat were monitored as a function of time and voltage.

3 Results and Discussion

3.1 Thermal Conductivity and Mechanical Properties of PA6 Compounds

Table 1 shows the thermal conductivity of the PA6/BN compounds having particle size of 5 μm and 20 μm. The compounds contain 60 wt% of BN. By addition of BN fillers, the thermal conductivity value of PA6 increases from 0.26 W/mK to 0.75 W/mK for BN5 and 0.74 W/mK for BN20. It is realized that the composites show the similar conductivity regardless of particle size and temperature. At 100 °C, thermal conductivity of the compounds is still 0.75 W/mK. The thermal conductivity of the PA6/NiCF composite is found to be 0.29 W/mK at 5 wt% and 0.48 W/mK at 40 wt% NiCF. Thermal conductivity also remains unchanged upon increasing temperature. In contrast to boron nitride (BN), nickel-coated carbon fibers are electrically conductive due to presence of nickel layer and thus the compounds are expected to be thermally and electrically conductive.

<table>
<thead>
<tr>
<th>Components</th>
<th>Temperature (°C)</th>
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<tr>
<td></td>
<td>30</td>
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<tr>
<td>40/60 PA6/BN5</td>
<td>0.75</td>
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<tr>
<td>40/60 PA6/BN20</td>
<td>0.74</td>
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<tr>
<td>95/5 PA6/NiCF</td>
<td>0.29</td>
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<tr>
<td>60/40 PA6/NiCF</td>
<td>0.48</td>
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Figure 3 shows the comparison of mechanical properties of the PA6 composites prepared by adding nickel coated carbon fiber and boron nitride. It is apparent that the tensile strength (TS) and flexural strength of the PA6/NiCF are much higher than those of PA6/BN in spite of low filler loading, i.e., 5, 40 wt% for NiCF, 60 wt% for BN. The tensile and flexural strength at 60/40 PA6/NiCF composition are about 218 MPa and 267 MPa, respectively. It indicates that the impregnation of carbon fibers is more effective than the BN particles to achieve high mechanical properties. No virtual change is observed for the PA6/BN compounds compared to those of pure PA6 (TS ~ 66 MPa, FS ~ 93 MPa) possibly due to the poor compatibility within the compounds.

Specific gravity of PA6 compounds increases as filler content increases, revealing the highest value of 1.58 at 60/40 PA6/BN composition (Figure 3b). It is associated with relatively high density of BN (SG~2.1) compared to that of pure PA6 (1.13-1.15). The compounds containing 40 wt % of NiCF exhibit specific gravity of 1.43 due to introduction of metal-coated layer on carbon fibers. Considering the high specific gravity of metallic materials such as 2.7 for aluminium and 8.9 for copper, it is realized that the weight can be reduced more than 40-50% by simply replacing the materials.
3.2 Heat Generation and Dissipation Behaviour of Ag-Printed Polymer Composites

Figure 2 shows the spatial temperature distribution of Ag-printed PA6 depending on the line width and length. When the conductive line is long enough, no noticeable occurrence in heat generation is observed (Figure 4a). The weak bright spot at the center may be originated from the reflected heat from the thermal camera. When the line width increases from 1 mm to 3 mm, heat is generated (Figure 4b and 4c). Especially, the red spot area representing high temperature is relatively broader with short path length (Figure 2c). In Figure 4(b), temperature distribution is not uniform presumably due to the agglomerates of the Ag particles. As displayed in Figure 4(d), the current flowing through the specimen is reduced as the Ag line becomes longer and narrower. As the Ag pattern having 17 lines along with 1 mm in width is not conductive, heat evolution is no longer detectable. At the same path length, the current increases about 3 times when the line width increase from 1 mm (about 170 mA) to 3 mm (about 500 mA). It implies that the current value is almost proportional to the line width.

In Figure 5, thermal images taken at 10 min after applying electric voltage are shown. With pure PA6 substrate, the heated region is strongly localized around the conductive lines due to accumulation, revealing maximum temperature around 41.5 °C (Figure 5a). When the thermally conductive substrate is used, temperature distribution becomes more uniform over the entire area (Figure 5b, c). The temperature rise is suppressed to 37.9 °C for 5 wt% and 36.1 °C for 40 wt% NiCF. However, heat is still accumulated in the vicinity of the electrodes. Similar behaviour is also observable for the PA6/BN compounds. It should be noted that the heat generation of the PA6/NiCF compounds are more significant over compared to that of the pure PA6 substrate. Since the PA6/NiCF substrate alone is electrically conductive by incorporation of nickel-coated carbon fibers, heat may be easily generated and dissipated.
Figure 5. Thermal images of Ag-printed substrates under the constant voltage of 3V; (a) pure PA6, (b) 95/5 PA6/NiCF, (c) 60/40 PA6/NiCF substrate. The images were taken at 10 min after applying electric voltage of 3V.

Figure 6 displays the time-dependent current and temperature curve of the PA6/BN5 compounds measured at 3V, 6V, and 9V, respectively. Electrical conductivity increases when a higher voltage is applied (Figure 4a). Current value at 3V, 6V, 9V is about 300 mA, 600 mA, and 900 mA. At 9V, it is realized that current decreases steadily with time. The steady decrease may be attributable to an increase in the surface resistance of the substrate with time. In the case of temperature profile with time, heat generation is easy by employing a high DC voltage, as shown in Figure 6(b). Maximum temperature after 600s reaches at around 70 °C for 9V, 40 °C for 6V, and 30 °C for 3V, respectively. Sharp increase in temperature of the printed specimen is observed in first 300s with the applied voltage, which is then stabilized with an almost plateau region. During the initial stage, the electrical energy exceeds the thermal energy losses and therefore temperature increases. Upon continued heating, the heat losses increase to be balanced with the heat generated, resulting in suppression of the temperature rise.

Figure 7(a) compares the current values passing through the Ag-printed PA6, PA6/BN5, and PA6/NiCF substrates under the constant electric voltage of 3V. The same pattern design having 5 lines along with 3 mm in width is used. The PA6/NiCF compounds show relatively high current value at around 600 mA in spite of lower filler loading of 40 wt%. The PA6/BN and PA6 substrate, on the other hand, show the current value of about 540 mA and 500 mA, respectively. It is observed that the 60/40 PA6/NiCF compounds reveals about 2 mA of current prior to performing silver printing, while the pure PA6 and PA6/BN substrates themselves are not conductive. Therefore, it is inferred that the conductive NiCF fillers may induce the synergetic effect on increasing current.
3.3 Heat Flow Behaviour in a Li Battery Package

Effect of heat generation on the temperature profiles of the battery package has been investigated by monitoring the heat distribution of the cross-sectional and side area. Heat generated during a course of charging and discharging process from the cells is ignored in our system. Temperature gradient along the vertical direction is apparent at 0s, as presented in Figure 8(a). After 30s elapsed, heat generated from the top and bottom plate is readily dissipated to the centered area maintained at -10 °C, showing gradual reduction in temperature (please see Figure 8b). Figure 8c clearly indicates that the whole area becomes warmer even after 30s, revealing around -2 °C at the center. It is anticipated that temperature rise becomes more apparent with time.

Figure 8. Comparison of temperature distribution in a battery package after 30s of heat generation; (a) cross-sectional view at 0s, (b) cross-sectional view at 30s, and (c) side view at 30s.

4 Conclusion

The addition of BN and NiCF fillers affected the mechanical properties and thermal conductivity of pure PA6 remarkably. The electrical energy supplied to the silver-printed specimen was effectively converted into thermal energy, showing temperature rise more than 40 °C at 9V. From the thermos-mechanical behaviour and heat generation performance, it is realized that the processing strategy is a critical factor to determine the temperature and thus final performance of Li
battery. The formation of effective conductive path at lower filler loading is under investigation to further increase electric conductivity and heat generation performance.

5 References


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