MECHANICAL AND THERMAL CHARACTERISTICS OF THE PARTICLES REINFORCED PHENOLIC FOAMS

SA. Song, HJ. Oh, SS. Kim*
Department of Organic Materials and Fiber Engineering, Chonbuk National University, Jeonju, 560-756, Republic of Korea.
* Corresponding author (sskim@jbnu.ac.kr)

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1. Introduction

Polymer foams of low density such as polyurethane and polystyrene foam are formed closed cell or open cell by using foaming agent, flame retardants, cross linking agents and surfactants. However, blowing agents have been found to cause ozone depletion in the upper atmosphere. [1]. Furthermore, the commercial polymer foams generated toxic gases during combustion so it was limited the use [1-3]. Recently, to solve the problem, the studies about thermal insulation foams using the phenolic resin are proceeded.

The phenolic foam has high strength, excellent flame resistance, and low generation of toxic gases during combustion. The phenolic foam has high self-ignition temperature of 480˚C and high thermal stability over a broad temperature range, maintaining performance and stability from -196˚C to 200˚C. So it has led to a broad range of applications as an insulating material. [4-5]. However, the phenolic foam applications are limited by their inferior mechanical strength and high thermal conductivity compared with other polymer foams. They have rarely been used as a sandwich structures because the phenolic resin make it more difficult to control the cell morphology. [5-7].

The foams were characterized to determine their densities, cell sizes, and cell shapes. So the properties of the phenolic foam are improved by controlling the cell uniformity and the cell morphology [8-11]. Many studies about polymer foam have focused on the improvement of properties. First, several studies to increase of properties have reported by increasing the cell density and decreasing the cell size. Nemoto et al. prepared the nano-micro cellular foam from a poly(propylene)/propylene-ethylene copolymer blend by controlling the viscoelasticity and CO₂ solubility [12]. Song et al. studied the effect of viscosity on aluminum structure, pore distribution and pore diameter [13]. In other study to improve the strength and stiffness of polymer foams, different kinds of organic and inorganic fillers were used [14-19]. Desai et al. have shown that mechanical properties of phenolic foam are improved by adding 1:1 ratio of glass to aramid fiber [14]. Also, carbon nanotube and graphene are widely used in polymer foams as filler due to their outstanding physical properties. Zhang et al. found that the strength of foam with multi wall carbon nanotube (MWNT) and functionalized MWNT are increased about 73%, 74%, respectively [15]. Chen et al. showed that the closed cell of PMMA foam is fabricated by adding the MWNT and their mechanical properties are increased [16]. In addition, many studies are investigated the effect of improvement of mechanical properties by preventing the crack propagation and increasing interaction between matrix and particle [17-19]. Several studies about particles reinforced polymer foams are explained the mechanical properties according to changing of cell morphology. However, the analysis about the effect of particle to cell formation is rare. Cell formation during the foaming process of the resin is influenced by cross linked of polymer, viscosity and filler. Optimal viscosity of the resin controls the expansion of the resin in foaming process. Accordingly, the cell morphology and cell uniformity are influenced by viscosity [13]. When the foam has large specific surface area, the foam has excellent performance as thermal insulation foam. And it has great thermal stability by low thermal conductivity. Total thermal conductivity in polymer foam is the sum of the conductivities of both the gas and solid [15-16]. Radiative heat transfer happens through cell walls so many small cells will transfer. The cell morphology has a larger impact to determine the mechanical and thermal properties than just changing the density.

In this work, the particle reinforced phenolic foams are prepared by microwave foaming process...
to improve the thermal performance. To solve the extremely friable properties of the phenolic foams, the effect of the particles on the cell formation was investigated. To obtain the optimal cell morphology, different shape of particle such as Multiwall carbon nanotube (MWNT) and graphene was added with the different weight fraction in phenolic resin, and cure monitoring was performed to find the proper foaming point by using a dielectric sensor. The cell morphology was estimated by foam density and porosity, and SEM topographies were investigated to confirm the cell morphology. Compressive tests and thermal conductivity tests were performed to investigate effect of cell morphology on the mechanical and thermal properties. To evaluate the thermal stability, TGA was performed to estimate the weight loss as temperature increases. Using the measured material properties, the optimal foaming condition was suggested.

2. Materials and experimental

2.1 Materials
Resole-type phenolic resins, OG-5000 (Kangnam Chemical Co., Korea) was mixed with acid catalyst, PTSA 65% (Kangnam Chemical Co., Korea). The multi-wall carbon nanotube (MWCNT), (5MWCNT), bon nanotubechemical Co.graphene (500m²/g, Hanwhananotech, Korea) were used for the purpose to control the cell morphology.

2.2 Cure monitoring
In our previous work, the foaming point through cure monitoring of phenolic resin was applied according to degree of cure to obtain the optimum cell morphology. From the result, the phenolic foam fabricated by applying the microwave at the cure starting point was successfully improved thermal and mechanical characteristics of the phenolic foams [20]. Based on the previous results, cure monitoring of the particles reinforced phenolic resin was performed to decide the cure starting point with respect to the particle type and weight percent (wt%) at room temperature (20°C).

MWCNT and graphene were applied to the phenolic resin at different weight fractions of 0.5, 1.0, and 2.0 wt%, respectively, and their effect on the cure reaction of the phenolic resin was monitored. Each samples were labeled with respect to the particle type and weight fraction as shown in Table 1. To estimate the degree of cure of the phenolic resins in accordance with the aging time after mixing the phenolic resins and accelerators using an impeller, a dielectric sensor (Lacomtech, Republic of Korea) and a K-type thermocouple (TT-K-30, OMEGA, USA) were used to measure the dissipation factor and the temperature, respectively. The dissipation factor D was measured in the phenolic resins using a commercial dielectric meter (ELC-133A, Escort Instruments Corp., USA) using a 1 kHz alternating current. At least three specimens were tested for each sample type to determine the repeatability of the results.

| Table 1. Sample naming of the particles reinforced phenolic resins |
|-------------------|-----------------|-----------------|
| CP 0.5            | 0.5 wt% MWNT    | GP 0.5          |
|                   | 0.5 wt% Graphene |                |
| CP 1              | 1 wt% MWNT      | GP 1            |
|                   | 1 wt% Graphene   |                 |
| CP 2              | 2 wt% MWNT      | GP 2            |
|                   | 2 wt% Graphene   |                 |

The isothermal differential scanning calorimetry (DSC), (Q20, TA Instruments, USA) experiments were carried out at room temperature (20°C) to compare with cure monitoring results by using the dielectric sensor. All the samples were ramped from 15°C to 25°C with a heating rate of 5°C/min followed by holding at 25°C for 50 min. This procedure is similar to the dielectric cure monitoring condition in the phenolic curing process.

2.3 Foaming process
The microwave foaming was performed using the following three steps: (1) mixing the resole and accelerators with or without the particles using an impeller at 500 rpm for 3 min; (2) aging the mixture under constant room temperature to control the initial degree of cure before microwave foaming; and (3) foaming by microwave using an effective intensity per unit mass of 12 kW/kg at 2.4 GHz and de-molding as shown in Fig. 1 [20]. Aging time before microwave foaming was determined by the cure monitoring results of each samples.

2.4 Characterization

2.4.1 Foam density
The foam diameter and length to measure the foam density are 75 mm and 130 mm, respectively. The specimens are dried at 80°C for 2 h to remove the internal moisture before measuring the mass.
In practice, the density (kg/m$^3$) of plastic foams is calculated as the ratio of specimen mass $m$ to geometrical volume $V$ as shown in the following equation:

$$\rho = \frac{M}{V} = \frac{kg}{\pi r^2 h} = \frac{kg}{m^3}$$  \hspace{1cm} (1)

Density of the solid specimen fabricated using phenolic resin was also measured to calculate the porosity of the phenolic foams.

2.4.2 Porosity

Porosity of the phenolic foams with respect to the test variables was calculated using the following equation:

$$P = \frac{\rho_s - \rho_f}{\rho_s} \times 100\%$$  \hspace{1cm} (2)

where $\rho_s$ and $\rho_f$ are the previously measured solid density and foam density, respectively.

2.4.3 Compressive test

To evaluate the possibility of whether the prepared phenolic foams can be used for building materials, such as sandwich cores and insulating foams, a uniaxial compression test was conducted to measure the compressive strength. The cylindrical-shaped specimens of 16.0 mm in radius and 32.0 mm in width were fabricated using cylindrical acrylic mold.

The compressive strength of the each sample with respect to the test variables was measured according to ASTM C 365 using a computer-controlled material testing system (4206, INSTRON, USA). To remove the water content, the specimens were dried at 80°C for 2 h before the test. The crosshead speed of the test was 0.5 mm/min.

2.4.4 Thermal conductivity

The thermal conductivity was measured using a hot-wire method based on the DIN 51046. To measure the thermal conductivity using the hot wire parallel technique, a constant electric current was applied throughout the nichrome wire (0.6 mm in diameter). The cylindrical-shaped specimen of 75 mm in diameter and 130 mm in length was initially placed.

A constant electric current with a 0.9 V voltage was continuously applied to the specimens, and the temperature was measured using the thermocouple at time intervals ranging from 80 to 180 s. Using these data, the basic thermal conductivity was calculated with following equation [21]:

$$k = \frac{q'}{4\pi} \times \frac{ln(t_2/t_1)}{T_2 - T_1}$$  \hspace{1cm} (3)

2.4.5 Thermal stability

Volutility measurements were carried out by thermo-gravimetric analysis (TGA), (Q600, TA instruments, USA). During the TGA experiments, the 4.0g sample test specimens were heated between temperature ranging from 40°C to 600°C at 20°C/min under a oxygen environment.

3. Result and discussion

Fig. 1 illustrates the dissipation factor and temperature of the phenolic resin during the cure.
reaction at room temperature with respect to the particle type and weight fraction, and each graph shows the results of the representative specimen whose cure starting point is the closest to the average value of the three specimen in each test variable shown in Table 2. The cure starting point presented in each graph was determined as the inflection point at which the second derivative of the dissipation factor was zero \( (d^2D/dt^2=0) \) [22].

### Table 2. Cure starting point of neat phenolic resin and the particles reinforced phenolic resin.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cure starting point (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NP</td>
<td>11.58</td>
</tr>
<tr>
<td>CP 0.5</td>
<td>21.53</td>
</tr>
<tr>
<td>CP 1</td>
<td>15.96</td>
</tr>
<tr>
<td>CP 2</td>
<td>18.31</td>
</tr>
<tr>
<td>GP 0.5</td>
<td>19.54</td>
</tr>
<tr>
<td>GP 1</td>
<td>19.23</td>
</tr>
<tr>
<td>GP 2</td>
<td>19.33</td>
</tr>
</tbody>
</table>

Phenolic resin reinforced with the particles showed low dissipation factor compared to the neat phenolic resin because the dipole and ion mobilities were restricted due to relatively high viscosity of the particle reinforced phenolic resin [23]. Also the temperature at the cure starting point and the peak temperature of the particles reinforced phenolic resins were lower than those of the neat phenolic resin. This means the cure reaction of the particles reinforced phenolic resins progressed under lower temperature compared to the neat phenolic resin.

Graphene reinforced phenolic resin showed similar cure starting point regardless of the particle fraction as shown in Table 2, but MWNT reinforced phenolic resin showed a little different cure starting point with respect to the particle weight fraction. The CP0.5 showed the latest cure starting point, while the CP1 showed the fastest cure starting point. In case of the CP0.5, dispersaibility is relatively higher than the other MWNT reinforced phenolic resins due to the small particle contents so that the cure retardation effect of the MWNT on the cure reaction was more remarkable than the other samples. Cure reaction was delayed again at the CP2.0 sample, and this means that the effect of the increasing viscosity by high particle contents on the dipole and ion mobilities comes to be dominant rather than the effect of the dispersaibility.

DSC results were checked to confirm the cure behaviors of the particle reinforced phenolic foams derived from the dissipation factor. Fig. 2 shows the curing of the neat phenolic and the particles reinforced phenolic resins. The thermograms demonstrated typical isothermal behaviors in the cure of thermoset polymers. It was found that the particles reinforced phenolic resins with high weight fraction are slightly slower in reaching the exothermic peak than the neat phenolic and the particle reinforced phenolic resin with low weight fraction. To take a better look at the initial curing, the thermograms during the first 10 min are presented in Fig. 2(b) and indicated that the neat phenolic resin exhibited a higher exothermic curing peak than the particles reinforced phenolic resin, which is consistent with the result from dissipation factor and temperature measurement results. The two kinds of particles investigated here showed a difference in the initial curing stage as evidenced by the initial curing slopes and exothermic peak heights.

### Table 3. Total heat reaction (\( \Delta H_f \)) for isothermal scanning at room temperature (25°C)

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \Delta H_f ) (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NP</td>
<td>3.361</td>
</tr>
<tr>
<td>CP 0.5</td>
<td>2.997</td>
</tr>
<tr>
<td>CP 1</td>
<td>2.528</td>
</tr>
<tr>
<td>CP 2</td>
<td>3.098</td>
</tr>
<tr>
<td>GP 0.5</td>
<td>3.105</td>
</tr>
<tr>
<td>GP 1</td>
<td>2.961</td>
</tr>
<tr>
<td>GP 2</td>
<td>2.894</td>
</tr>
</tbody>
</table>

Table 3 shows total heat reaction (\( \Delta H_f \)) for isothermal scanning at room temperature (25°C). The enthalpy data confirmed that the addition of the particles in the phenolic resin hindered the cure to a certain degree.

Fig. 3 shows the density and porosity of the phenolic foams fabricated by microwave at the cure starting point shown in Table 2. Densities of the particles reinforced phenolic foams were lower than that of the neat phenolic foam as shown in Fig. 3(a). In case of the solid phenolic, density was decreased by addition of particles due to the internal void generation induced by the particle aggregation. Porosity of the phenolic foams calculated from measured solid and foam densities shows similar tendency with the foam density. CP1 shows the highest porosity in the MWNT reinforced phenolic foams, but it is slightly lower than GP2. Fig. 4 shows SEM topographies of the phenolic foams with respect to the particle type and weight fraction. Generally, polymer foams without any
CP1 and GP1 which have high porosity and uniform cell morphology showed the highest specific compressive strength, and this means the strength of the phenolic foam and cell density are closely related each other. Specific compressive strength of the CP1 and GP2 increased by 6.1% and 7.6%, respectively, compared to the neat phenolic foam.

Fig. 2 Isothermal DSC curve of the neat phenolic and particle reinforced phenolic resins: (a) isothermal scanning at 20°C for 50 min, (b) initial curing from 0 to 10 min.

pressure during the foaming process show the anisotropic cell structures because the resin with foaming gases move to the top surface along the molding wall as the foaming process proceeds. The particles reinforced phenolic foams, however, show the entirely round cell structures and smaller cell size compared to the neat phenolic foam as shown in Fig. 4 (b)-(g). CP1 and GP1 show thinner cell wall and small and uniform cell structures compared to the other particles reinforced foams. Thick cell walls are observed in the CP2 and GP2 although their porosities are relatively high. GP2, which has outstanding porosity, partially shows very large cavities as shown in Fig. 4. Particles in the phenolic resin filled with high weight fraction of particles can be easily aggregated each other and the air at the tiny gaps between the aggregated particles expands dramatically as the microwave heating proceeds. This large bobbles are merged each other and then they make large cavities demonstrated in Fig. 5.

Fig. 3 Cell properties of the neat phenolic foam and particle reinforced phenolic foams: (a) density of the foams and solid, (b) porosity of the foams.

Fig. 4 SEM topographies of the phenolic foams with respect to the particle type and weight fraction.
However the deviation of the compressive strength of the particles reinforced phenolic foams was much larger than that of the neat phenolic foam because of the partially large void induced by particle aggregation and stress shielding by thick cell wall [20]. The specific compressive strengths of the graphene reinforced phenolic foams were slightly higher than those of the MWNT reinforced phenolic foams, and this might be caused by a difference of aggregated shape of the particles. From these results, it was found the mechanical properties could be enhanced more if the dispersion state of the particles in the resin is improved.

MWNT and graphene reinforced phenolic foams showed lower thermal conductivity compared to the neat phenolic foams although the particles have remarkable high thermal conductivities. Although the conductivity through gases is usually the predominant component of the total transferred heat due to the huge volume of the gaseous phase in foams, the main quantity of heat transferred of foams is the factor by conduction through the solid polymer [7,24]. This means the thermal conductivity is directly affected by the foam density as shown in Fig 7. Accordingly, phenolic foams with low density (CP1 and GP1) showed the low thermal conductivities compared to the other foams. In case of the GP1, which has the highest cell density and cell uniformity, thermal conductivity decreased by 36.3% compared to that of neat phenolic foams. However, CP2 and GP2, which has partially thick cell walls due to the high viscosity before microwave foaming, the thermal conductivities increased dramatically.

TGA was used to quantify the decomposition of the phenolic foams at elevated temperatures and to investigate the volatility of the phenolic foams. In this work, the volatility of the phenolic foams was measured using the weight loss of the phenolic foams over the temperature range of 200°C to 500°C, as shown in Fig. 8. The particle reinforced phenolic foams showed the high thermal stability compared to the neat phenolic foam at 200–300°C as shown in Fig 8(a). Low thermal conductivity of the particle reinforced phenolic foams, which makes it possible to retard heat transfer from outside into the foams, reduced the volatility of the phenolic foams.
Accordingly, GP1 which has the lowest thermal conductivity showed the lowest weight loss. All specimens presented the rapid weight loss around 450°C related to self-ignition temperature of the phenolic materials as shown in Fig. 8(b). The average volatility of the particles reinforced phenolic foams was a little bit higher than that of the neat phenolic foam at 400–500°C. The high specific area of the particles reinforced phenolic foams has effective interfacial area with high temperature air and high thermal conductivity of the MWNT and graphene enhances the heat transfer rate of the phenolic foams. Accordingly, the volatility of the particles reinforced phenolic foams increased more sharply compared to that of the neat phenolic foam. The volatilities of all the specimens were less than 40% at 500°C, which was much lower than those values reported for commercial urethane foam and polystyrene foam at the same temperature [3].

![Graph showing weight loss vs. temperature](image)

**Fig. 8 TGA analysis of the foams: (a) weight loss from 200°C to 300°C, (b) weight loss from 450°C to 500°C.**

**4 Conclusions**

In this work, the particles reinforced phenolic foams were fabricated using microwave to improve the thermal and mechanical performance. The effect of the particle type and weight fraction on the cell morphology was investigated. From the experiments, the following results were obtained:

1. Phenolic resin reinforced with the particles showed low dissipation factor compared to the neat phenolic resin because the dipole and ion mobilities were restricted due to relatively high viscosity of the particles reinforced phenolic resin.
2. Density and porosity of the particles reinforced phenolic foams were lower than that of the neat phenolic foam due to the high cell density.
3. CP1 and GP1 show thinner cell wall and small and uniform cell structures compared to the other particles reinforced foams.
4. Specific compressive strength of the CP1 and GP2 increased by 6.1% and 7.6%, respectively, compared to the neat phenolic foam.
5. GP1, which has the highest cell density and cell uniformity, has the lowest thermal conductivity in the phenolic foams and it decreased by 36.3% compared to that of neat phenolic foams.
6. GP1 showed the highest thermal stability from 200-300°C due to its low thermal conductivity, however, its volatility sharply increased above 450°C.

Our findings suggest that the graphene reinforced phenolic foams with 1wt%, fabricated using the proper foaming conditions, are promising materials for insulating foams due to their low thermal conductivity, low density, and reliable compressive strength.

**5 Reference**


