

OPTIMIZATION OF STRUCTURAL REACTION INJECTION MOLDING PROCESS (S-RIM) WITH DICYCLOPENTADIENE RESIN AS A MATRIX

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ABSTRACT

Dicyclopentadiene is a low viscosity resin which forms a poly-dicyclopentadiene (p-DCPD) rapidly through the ring opening metathesis polymerization (ROMP). This p-DCPD has outstanding resistance against low-temperature, water and impact. Molybdenum (Mo), ruthenium (Ru), tungsten (W) are commonly used catalysts for making p-DCPD through ROMP. Recently, ruthenium-based catalysts have widely been used due to their reaction stability and capability of reacting with the pure DCPD resin without any activator. To add the glass fiber reinforcement, a lab-scale structural reaction injection molding (S-RIM) equipment was designed and used to fabricate glass fiber reinforced p-DCPD composites. Differential scanning calorimetry (DSC) was used to investigate the cure behavior of the DCPD resin in order to obtain information regarding the optimal process temperature and the curing time. Viscosity changes with temperature were measured using a viscometer and modeled using an analytic function. These results were applied to the equipment design, which includes an air pump and a stirrer, to obtain high quality composites. Further, numerical analysis was performed in order to predict the processing time depending on the resin's viscosity and the fiber volume fraction. Fabrication of high glass fiber (GF) content p-DCPD composites was possible due to the low viscosity of the DCPD resin. The mechanical properties of composites were increased along with increasing the glass fiber content. For the 55 wt.% GF/p-DCPD composite material, the resulting tensile, flexural, and impact strengths increased by 101, 93, and 767%, respectively, compared with the neat p-DCPD specimen.

1 INTRODUCTION

Dicyclopentadiene (DCPD) is a colorless liquid with a low viscosity extracted from crude oil. When activated by a catalyst, the DCPD resin rapidly undergoes a ring opening metathesis polymerization (ROMP) reaction to form the network structure of polydicyclopentadiene (p-DCPD). Tungsten (W), molybdenum (Mo), ruthenium (Ru), and chromium (Cr) are commonly used catalysts for making p-DCPD through ROMP. Among these catalysts, W, Mo based catalyst are widely used because of their good mechanical properties and cheap price. However, the reaction is unstable in the atmosphere and the viscosity is relatively high according to the addition of the activator to activate the reaction. On the other hand, Ru-based catalysts have been favored recently because of their capability of carrying out the polymerization reaction in the air (1-3). When DCPD resin is activated by the Ru based Grubbs catalyst, the molecular weight increases as the double bond of the norbornene is ring-opened by the Ru catalyst. Upon the ring-opening, the double bond of cyclopentene is also ring-opened where the cross-linking begins (4, 5). The p-DCPD with network structures has good mechanical properties at a significantly low temperature, water resistance, and impact resistances. These properties are advantageous in applications to automobile bumpers, heavy machinery, and offshore structures (6, 7). The low viscosity and short reaction time of DCPD make it especially useful for reaction injection molding (RIM) (8). Among the RIM technology capable of adding reinforcements, S-RIM generally uses a fiber mesh which is firstly arranged in the mold before the polymer mixture injection takes place. These preforms are impregnated by the resin injected through

the injection nozzle of the mold. After the mold is filled, the resin is cured and the product is removed from the mold. Since the mold filling time takes few seconds to minutes, it is possible to manufacture long fiber reinforced composites. Numerous researches about the S-RIM process parameters have been performed (9, 10). However, there are less desirable attributes related to its unfavorable smell and unstable reactions, and these and other problems have stymied progress and redirected focus to DCPD composite reinforcements. Therefore it is important to indentify and optimize the process variables.

2 EXPERIMENT

2.1 Materials

The neat DCPD resin and Ru-based Grubbs 2nd catalyst were purchased from the Sigma-Aldrich Korea Corporation. A chopped strand mat intertwined with a glass fiber (50mm lengths and average diameters is 16 μm) was purchased from Owens Corning Corporation (Figure 1).



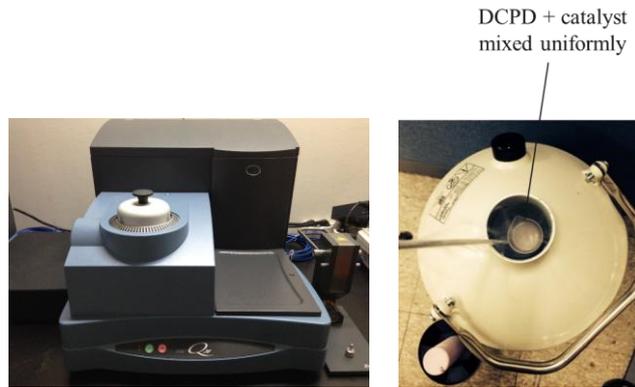
. Figure 1: A chopped strand mat.

2.2 Curing behavior of the DCPD resin

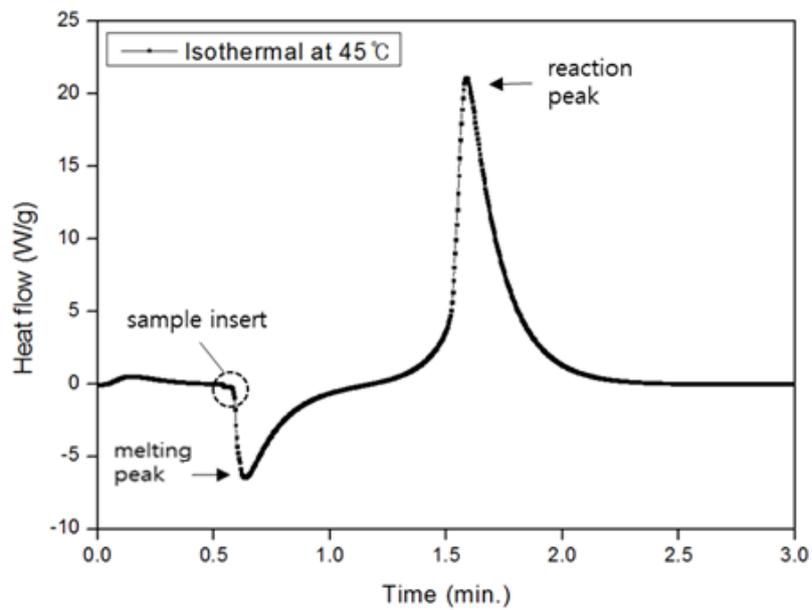
The curing behavior of DCPD was investigated with DSC (TA instrument, Q20). DSC recorded the heat flow in accordance with the time under the isothermal conditions ranging from 45 to 100 $^{\circ}\text{C}$. When the measurement of the DCPD resin is undertaken at isothermal conditions, it is difficult to obtain the reaction peaks since the curing reaction advances rapidly during the time for the DSC pan to reach the desired temperature (1). In order to avoid the problem, the part of the pre-mixed catalyst and the DCPD solution (2wt.%) cooled in a liquid nitrogen was used for DSC measurements in order to delay the DCPD reaction (Figure 2,3). The total heat of reaction of the ROMP process was estimated from the DSC reaction peak plots using the following equation :

$$\text{Total heat of reaction, } H_{total} = \int_0^{t_f} \frac{dq}{dt} dt \quad (1)$$

Where q is the heat flow, t_f is the end point of reaction.



. Figure 2: DSC (Q20, TA Instrument) and liquid nitrogen



. Figure 3: DSC result of DCPD resin

Additionally, in order to confirm the fact that the DCPD resin possessed a lower degree of cure at a lower temperature, the p-DCPD specimen was made under different mold temperatures. According to ASTM D790, three point bending tests were conducted with a universal testing machine (UTM, LLOYD instrument, LR50K, UK).

2.3 Processing of glass fiber reinforced composites

The S-RIM equipment was designed to manufacture the glass fiber reinforced DCPD composite specimens with dimensions of 150 x 120 x 3 mm³. The S-RIM equipment shown in Figure 4 was specifically designed to minimize voids by pulling vacuum. The equipment facilitated mixing of the DCPD resin and the catalyst prior to injection into the mold with a preformed chopped glass strand mat. The resin vessel was wrapped with heating tape to maintain a temperature of 40°C since the melting point of the DCPD resin is 33°C. The mold itself was also maintained at 40°C with a temperature controller. A vacuum pump was connected to the resin vessel to remove the void within the vessel. After removing the void, the catalyst was injected into the resin vessel from the top and stirred solution was injected into the mold (11).

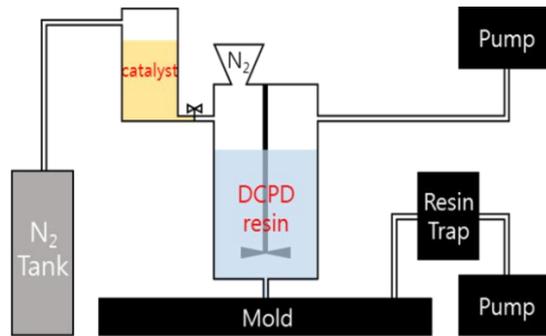


Figure 4: Schematic diagram of S-RIM process

The composite specimens were made with a mold temperature which was increased up to 100°C. The manufactured specimens were cut and tested according to the ASTM standards of D638-10 for the tensile strength, D790-10 for the flexural strength, and D256 for the impact strength.

2.4 Results and discussion

DSC scans were performed for the DCPD resin in order to accurately establish the composite molding temperature and the mixing time. Initially, the endothermic peak was observed when the frozen DCPD and catalyst solution melted. Separately, the exothermic peak was observed when the polymerization began. The polymerization was complete within 2 min. The total heat of reaction was obtained by measuring peak areas for each temperature (Table 1). When the polymerization occurred at higher temperature, it showed that the total heat of reaction was also high. For temperatures above 80°C, the total heat of reaction converged to about 320 J/g. This is thought to be due to insufficient cross linking of DCPD under 80°C. Additional DCPD specimens were prepared at 45, 60, and 100°C and subjected to bending tests in order to verify if insufficient polymerization had occurred at lower temperatures.

Temperature (°C)	45	50	60	70	80	90	100
Total heat of reaction (J/g)	212±2	256±3	286±5	320±4	319±3	318±7	320±5

Table 1: Total heat of reaction of DCPD at different temperatures

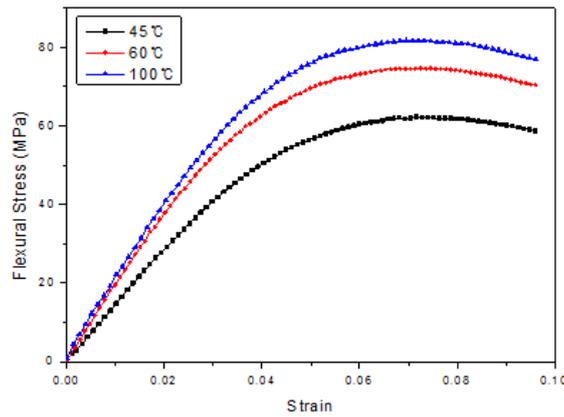


Figure 5: Result of three-point bending test

Figure 5 shows that the specimens have different mechanical properties depending on the molding temperature. Further, p-DCPD specimens prepared at lower temperatures had low maximum bending stress and modulus values. These data support the notion that the polymerization did not fully occur at temperatures below 80°C. As such, the minimum experimental temperature for DCPD resin was determined to be 80°C.

Table 2 describes the mechanical properties of the composites depending on the quantity of the glass fiber. Higher quantities of glass fiber resulted in increased tensile, flexural, and impact strengths. With glass fiber content 25, 40, 55wt.%, tensile strength increased by 50, 76, 101%, flexural strength 51, 85, 93%, impact strength 248, 508, 767% compared with the neat p-DCPD. Although increasing the glass fiber content can reduce the impact strength, continuously increasing impact strengths were achieved with long (50 mm) glass fibers. Since the mechanical properties continued to increase with increasing glass fiber content, the fiber was considered fully impregnated, even at the highest loading levels.

Sample	Fiber content (wt.%)	Tensile strength (MPa)	Flexural strength (MPa)	Impact strength (J/M)
P-DCPD	Neat	55±1	79±2	100±10
GF/p-DPCD composites	25	82±6	120±12	349±10
	40	97±5	147±2	609±60
	55	110±4	153±5	869±90

Table 2: Mechanical properties of GF/p-DCPD composites

3 NUMERICAL ANALYSIS OF S-RIM PROCESS

3.1 Modeling and conditions

The S-RIM process modeling was performed. The curing kinetics and viscosity variation of the resin with temperature was analyzed and flow simulation was carried out using these analyzed results. Before resin was cured, the viscosity change of resin with temperature was expressed using the exponential viscosity model (Figure 6). The domain of the porous media made of a glass fiber preform

was designed similarly to a real glass fiber media (Figure 7). The porosity was determined using the volume fraction and the reference values of the permeability of the air and the resin were used (12).

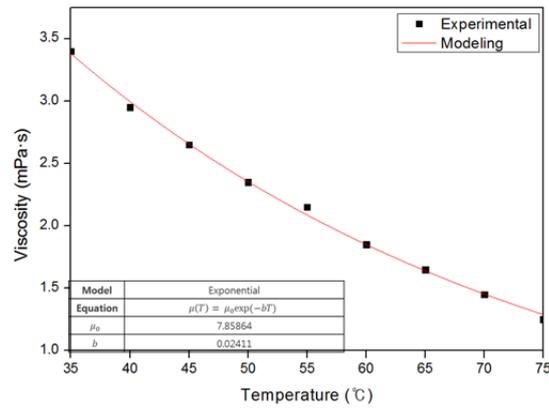


Figure 6: Viscosity change with temperature using exponential viscosity model

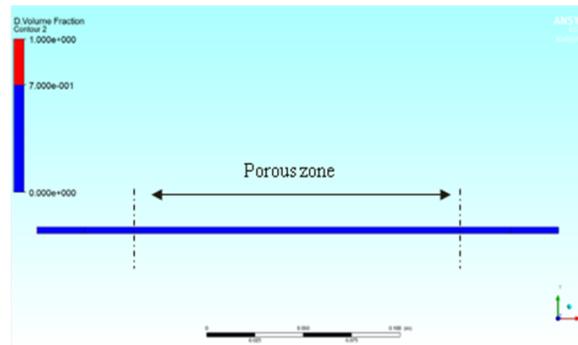


Figure 7: Geometry about numerical simulation of DCPD resin with porous zone

3.2 Results of numerical simulation

The flow analysis was carried out with mold temperature using the calculated exponential viscosity model. As it can be seen from the Figure 8, the higher the mold temperature, the shorter the process time. However, when the mold is filled, the resin have a higher temperature distribution as the mold temperature rises (Figure 9). When the mold temperature is too high, the quality of the product is poor because the resin is cured rapidly at a temperature above 80 °C.

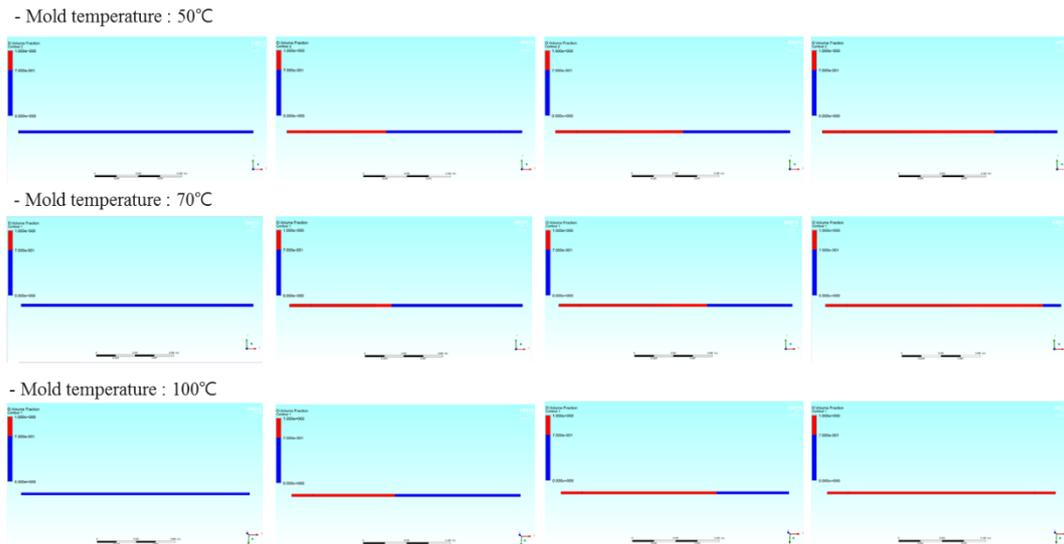


Figure 8: Numerical simulation of DCPD resin flow for different mold temperature

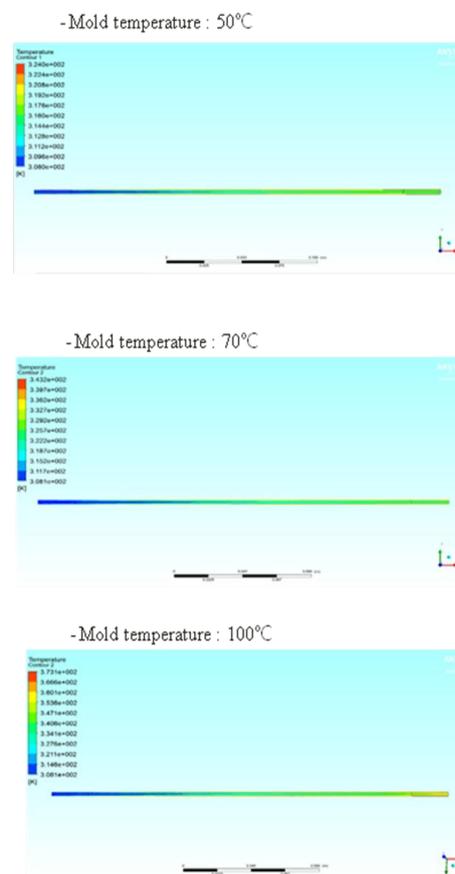


Figure 9: Temperature distribution of resin with mold temperature

4 CONCLUSION

The total heat of reaction and the curing time were obtained through the DSC analysis of the DCPD resin. The total heat of reaction increased with increasing temperature before converging at 80°C.

Further, the three point bending tests data for specimens prepared at lower curing temperatures mean the notion that the curing did not fully at temperature below 80 °C. Hence, the experimental condition was set to operate for curing temperatures above 80 °C with stirring times of less than 30 s. With calculated exponential viscosity model, the resin flow simulation of S-RIM process was carried out. Although the process takes a short time under the high mold temperature, above 80 °C, the quality of DCPD specimen was expected to be bad because of rapid curing reaction. Use of flow simulation and optimized condition of S-RIM process enabled the fabrication long fiber reinforced composite specimens. The corresponding test results revealed increases in tensile, flexural, and impact strengths depending on the increase in the fiber content. Fibers could be sufficiently impregnated with the resin well despite the large fiber volume fraction. These results imply that the DCPD composite manufacturing approach as a promising route to stronger, lighter, and more efficient structures.

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