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# Mechanical properties of norbornene-based silane treated glass fiber reinforced polydicyclopentadiene composites manufactured by the S-RIM process

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**Abstract:** A lab scale structural reaction injection molding (S-RIM) piece of equipment was designed and used to fabricate glass fiber reinforced polydicyclopentadiene (p-DCPD) composites for three different fiber contents. In order to obtain information regarding the optimal process temperature (>80°C) and the curing time (<30 s), differential scanning calorimetry (DSC) was used to investigate the curing behavior of DCPD resin under isothermal conditions. Further, a norbornene-based silane treatment was used to improve the interfacial adhesion between the glass fibers and DCPD as confirmed by the microdroplet pull-out test and scanning electron microscopy (SEM). Fabrication of glass fiber/p-DCPD composites with improved mechanical properties was carried out based on the optimized process conditions and surface treatment of glass fiber.

**Keywords:** dicyclopentadiene; differential scanning calorimetry; glass fiber; reaction injection molding.

## 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). Molybdenum (Mo), ruthenium (Ru), titanium (Ti) and chromium (Cr) are commonly used catalysts for making p-DCPD through ROMP. Among these catalysts, Ru-based catalysts have been favored recently because of their capability of carrying out the polymerization reaction in the air (1–4). The reaction mechanism of the DCPD resin with the Ru based Grubbs catalyst is illustrated in Figure 1. As can be seen, 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 (5–7). The p-DCPD with network structures has good mechanical properties at significantly low temperature, water resistance and impact resistances. These properties are advantageous in applications to automobile bumpers, heavy machinery and offshore structures (6, 8, 9). 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. At the same time, the low viscosity and short reaction time of DCPD make it especially useful for reaction injection molding (RIM) (9, 10). Figure 2 describes the RIM manufacturing process where the resin and catalyst are mixed in a mixing head prior to mold injection using a relatively low pressure (11). Structural reaction injection molding (S-RIM) is one of the RIM processes for better reinforcement. S-RIM generally uses fiber mesh which is first arranged in the mold before the polymer mixture injection takes place (12). 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. As the mold filling time takes a few seconds to a few minutes, it is possible to manufacture long fiber reinforced composites rapidly. Therefore, numerous researches for optimizing the process parameters have been performed (13, 14).

RIM requires the resin and the catalyst to be mixed thoroughly in order for the reaction to be correctly triggered and completed. However, it can be very difficult to obtain a high quality defect-free product since it requires not only precise mixing times and optimal curing temperature profiles but also a vacuum process for removing voids.

In this study, a lab scale S-RIM system was designed to facilitate the addition of glass fiber reinforcements along with the catalyst and resin mixing during p-DCPD composite fabrication.

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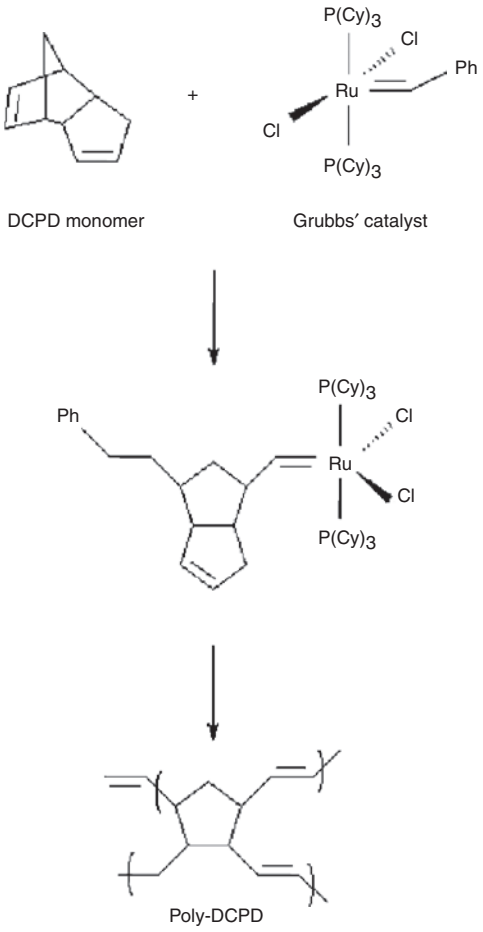


**Figure 1:** ROMP reaction mechanism.

Additionally, a surface treatment was used to increase the adhesion between the glass fibers and the DCPD. Rigorous air-free nitrogen atmospheres and ventilation systems were employed for the processing of the p-DCPD composites. Ultimately, the effect of the norbornene-treated glass fiber reinforcements was evaluated and high quality glass fiber reinforced p-DCPD composites were manufactured.

# 2 Experimental

## 2.1 Materials

The DCPD resin and Ru-based Grubbs 2nd catalyst were purchased from the Sigma-Aldrich Corporation (Korea). A chopped strand mat intertwined with a glass fiber with average diameters of 16 μm and lengths of 50 mm was purchased from the Owens Corning Corporation. Norborene-based silane for surface treatment was provided from the Gelest Corporation (Figure 3).

## 2.2 Characterization of the DCPD resin

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

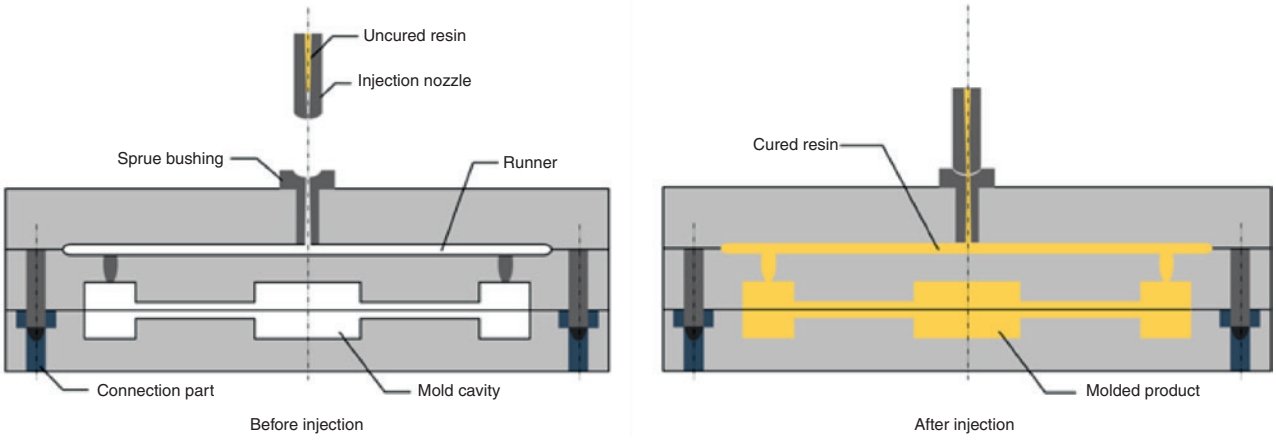


**Figure 2:** Reaction injection molding process.

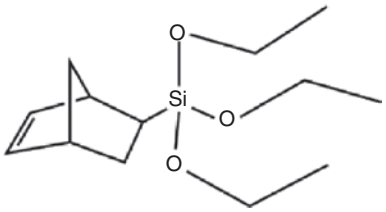


**Figure 3:** Norbornene-based silane.

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

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

Furthermore, 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, Bognor Regis, UK).

## 2.3 Norbornene based silane treatment of glass fiber

In order to increase the interfacial adhesion between the DCPD resin and the glass fiber, the surface of the glass fibers were treated with norbornene based silanes (8, 15). The silane treatment was performed after drying the glass fiber at 200°C for 24 h to remove moisture and impurities from the surface. The specific surface treatment solution was a mixture of silane, ehanol and acetic acid mixed in a 5:4:1 mass ratio. The treatment solution was added to the glass fibers in a 100:1 mass ratio. The treated glass fibers were used after further drying for 4 h at 140°C (16).

Surface treatment verification was carried out using the Fourier transform infrared spectroscopy (FT-IR, Thermo Scientific, Nicolet 6700, waltham, USA) under the 4000–650 $cm^{-1}$ wavenumber range.

The interfacial shear strengths between a glass fiber (treated and untreated) and the DCPD resin were measured through the micro-droplet pull-out test (17). Micro-droplets of the DCPD resin were formed on each fiber strand using a pin-tip. After curing the resin droplet, the interfacial shear strength was calculated according to the following expression:

$$\tau = \frac{F}{\pi D_f L} \quad [2]$$

where $F$ is the measured pull-out force, $D_f$ is the diameter, and $L$ is the length of fiber embedded in the resin, respectively. Pull-out force was measured with a UTM (LLOYD Instrument, LR50K, Bognor Regis, UK) at a test speed of 1 mm/min. The critical length of the glass fiber was also calculated with the measured shear strength in the following equation:

$$l_c = \frac{\sigma_f}{2\tau} D_f \quad [3]$$

where $\sigma_f$ is the tensile strength of fiber, $\tau$ is the shear strength of the interface, and $l_c$ and $D_f$ represent the critical length and the diameter of glass fiber, respectively. The test was performed for three times.

## 2.4 Processing of GF/DCPD composites

The mold was designed to manufacture the GF/DCPD composite specimens with dimensions of $150 \times 120 \times 3$ $mm^3$. The customized 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. Three different fiber content specimens were manufactured containing three, five and seven sheets of glass fiber mat. The resin vessel was wrapped with heating tape to maintain a temperature of 40°C as 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. 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

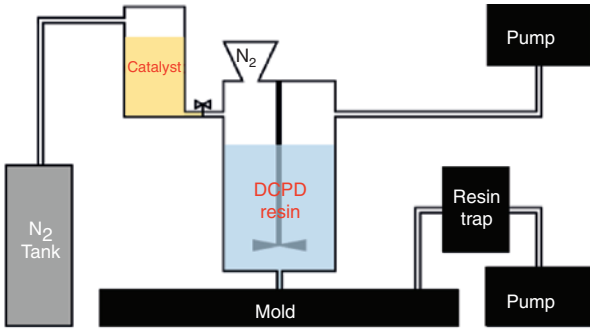


**Figure 4:** Schematic diagram of equipment.

strength, and D256 for the impact strength. Five specimens were tested at each test.

# 3 Results and discussion

## 3.1 DSC and mechanical testing results

DSC scans were performed for the DCPD resin in order to accurately establish the composite molding temperature and the mixing time (Figure 5). Initially, the endothermic peak was observed when the frozen DCPD and catalyst mixture melted. Separately, the exothermic peak was observed when the polymerization began. The polymerization was complete within 2 min. Higher reaction temperatures resulted in shorter polymerization times and narrower peaks. The total heat of reaction was obtained by measuring peak areas for each temperature (Figure 6). When the polymerization occurred at higher

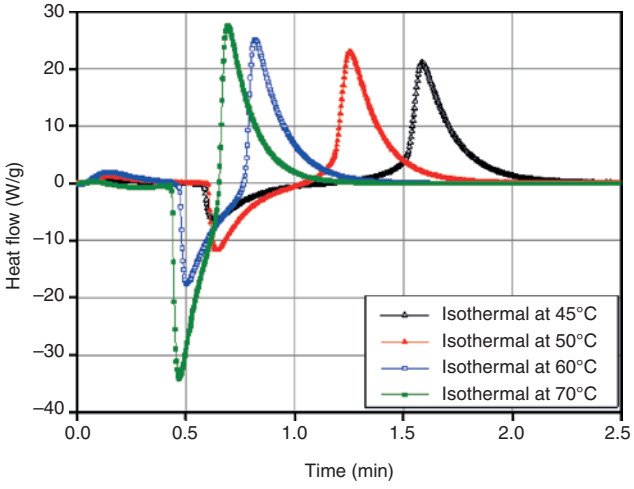


**Figure 5:** DSC isothermal graphs.

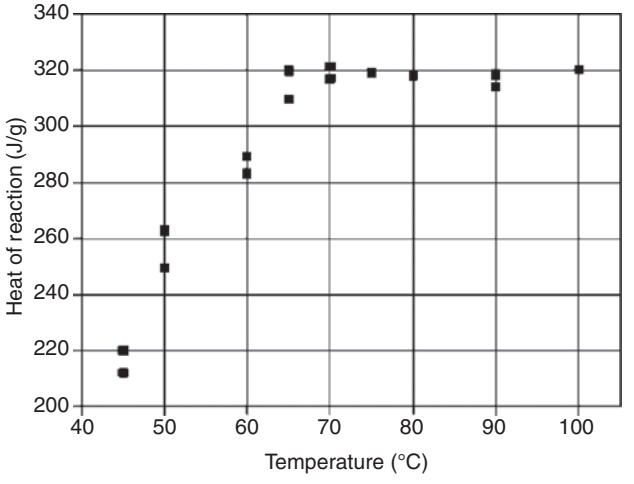


**Figure 6:** Total heat of reaction.

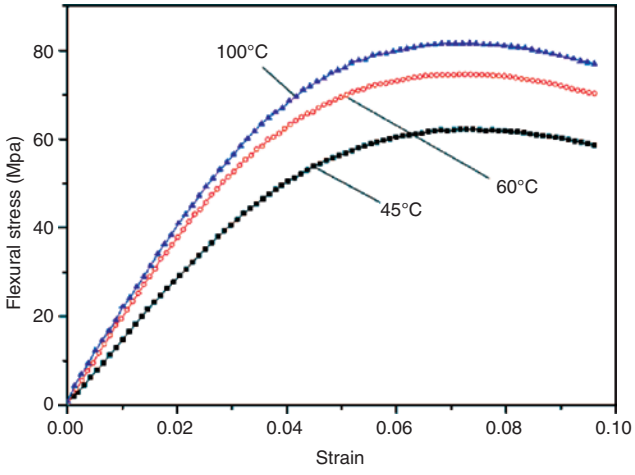


**Figure 7:** UTM results.

**Table 1:** Three-point bending results of p-DCPD by curing temperature.

| Sample | Temperature (°C) | $\sigma_f$ (MPa) | $E_B$ (GPa) |
|---|---|---|---|
| Poly-DCPD | 45 | 63 ± 1.8 | 1.5 ± 0.04 |
| | 60 | 75 ± 0.6 | 1.8 ± 0.03 |
| | 100 | 79 ± 1.7 | 1.9 ± 0.07 |

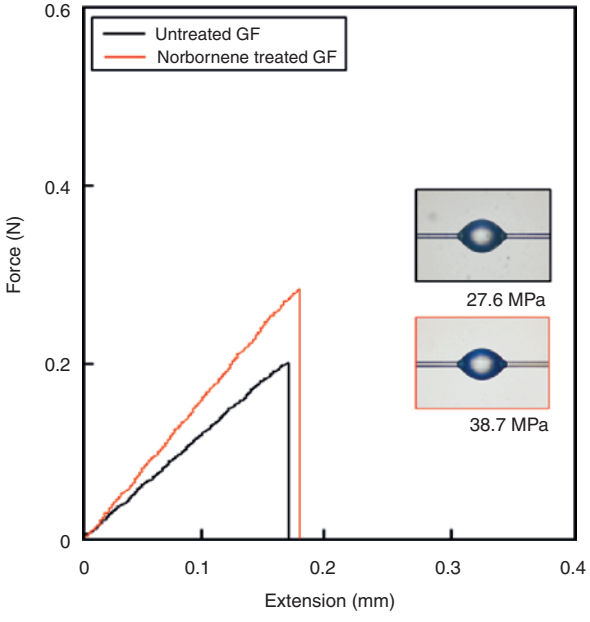


**Figure 8:** Microdroplet pull-out test.

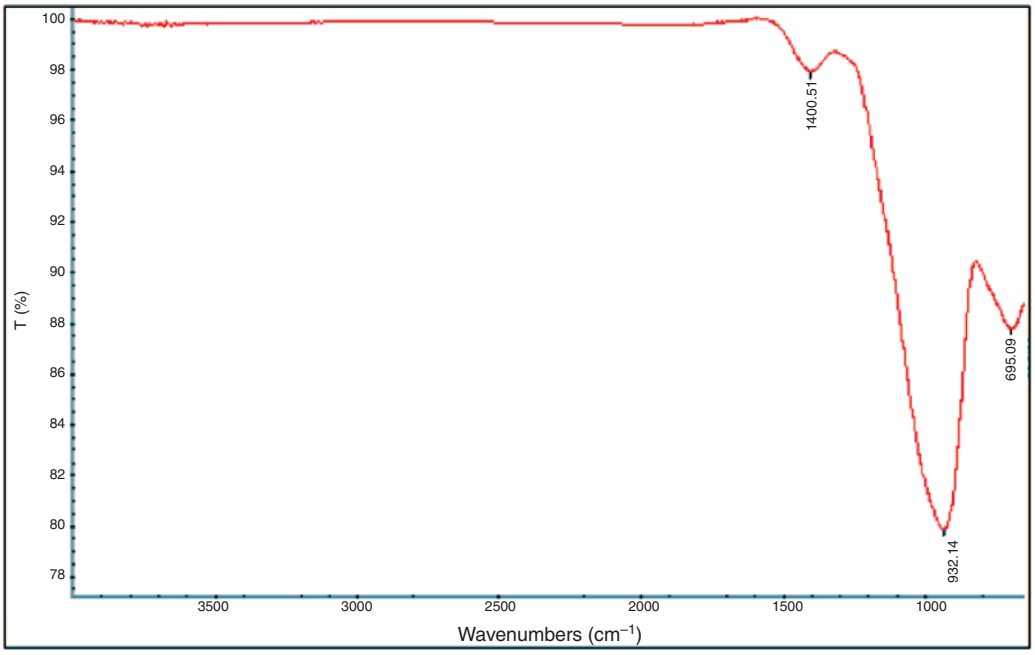


**Figure 9:** Results of FT-IR spectroscopy.

temperature, it showed that the total heat of reaction was also high. For temperatures above 80°C, the total heat of reaction converged to 330 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.

Figure 7 and Table 1 show 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.

## 3.2 Norbornene based silane treatment effect

Figure 8 displays data from the pull-out tests from glass fibers embedded in DCPD resin and cured with and without the norbornene-based silane treatment. The surface treated specimen showed shear strength of 38.7 MPa, which was 40% greater than that of the untreated specimen. This increased shear strength is due to the interaction between the silane and the surface of the glass fiber. After surface treatment, norbornene group was formed at the surface of the glass fiber. When the DCPD resin was polymerized by a catalyst, the reaction at the surface occurs with the norbornene moiety. As a result, the interfacial adhesion between the fiber and the resin was significantly improved. Using the shear strength value, the tensile strength of a glass fiber strand (1664 MPa) and the fiber diameter of 16 μm, the critical length of the fiber in the surface treated specimen was calculated to be 0.344 mm. To further increase the shear

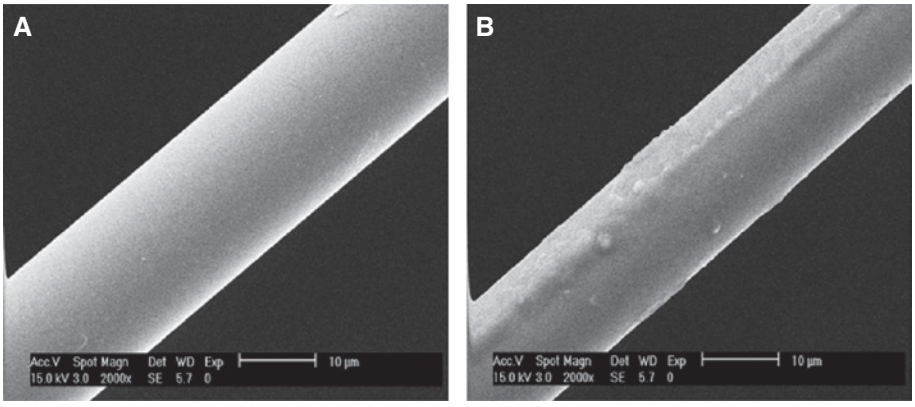


**Figure 10:** Glass fiber strand of (A) neat and (B) surface treated.

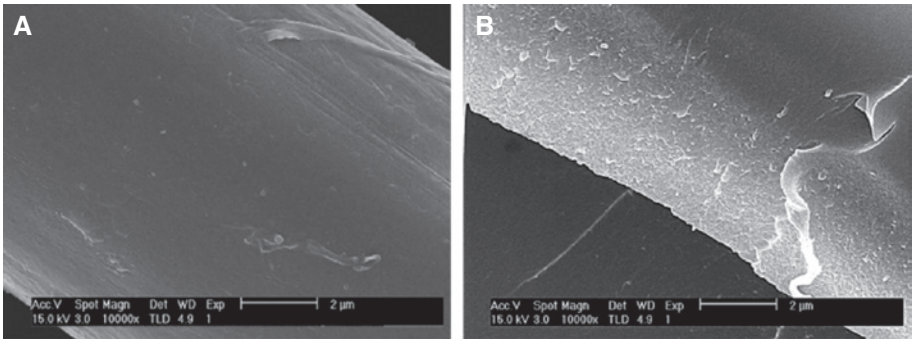


**Figure 11:** Pull-out test results of (A) neat and (B) surface treated GF/DCPD.

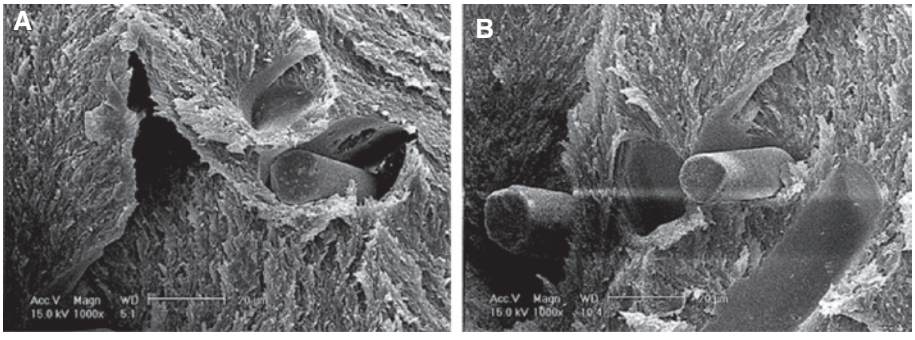


**Figure 12:** Tensile test results of (A) neat and (B) surface treated GF/DCPD.

strength and mechanical properties of the manufactured composite specimen, 50 mm chopped glass fibers (above 100× the critical length) were dried and treated with the norbornene-based silane. FT-IR spectroscopy was performed on part of the chopped fiber in order to verify the quality of the surface treatment. The results of the FT-IR spectroscopy for the neat and the treated glass fibers are shown in Figure 9. Unlike the results from the neat fibers, peaks for the treated fibers are shown at 1010, 715, 3400, 3056, and 2964 $cm^{-1}$ where these values correspond to C-O, Si-C, -OH, -CH2-, and =CH- functional groups, respectively. The presence of these modes indicates sufficient surface functionalization using the surface treatment.

## 3.3 Microstructure observation results

Figure 10 shows an SEM image of a glass fiber with and without the surface treatment. Figure 11 provides micrographs of glass fibers with and without surface treatment following the micro droplet pull-out test. Cohesive failure was frequently observed for surface treated fibers whereas untreated samples possessed a smooth surface. The micrographs in Figure 12 show the fractured interface between a glass fiber and the DCPD resin after the tensile test. The results suggest a higher interfacial affinity between the surface-treated GF/DCPD interfaces.

## 3.4 Mechanical properties

Figures 13–15 and Table 2 show the mechanical properties of the composites depending on the glass fiber content.

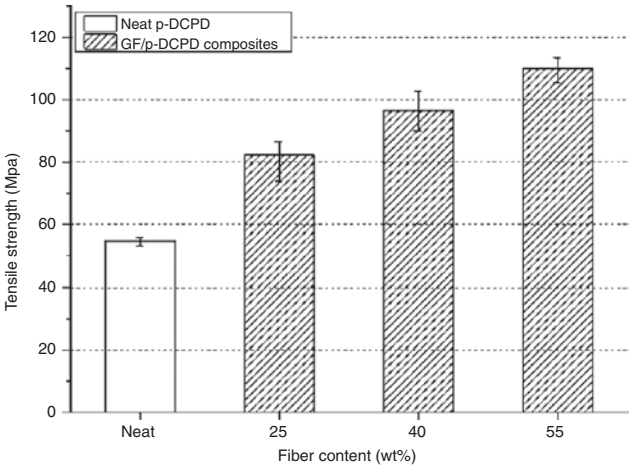


**Figure 13:** Tensile strength of GF/p-DCPD composites.

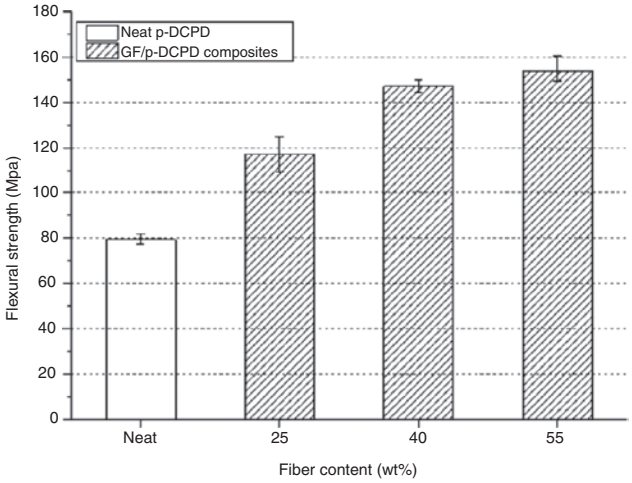


**Figure 14:** Flexural strength of GF/p-DCPD composites.

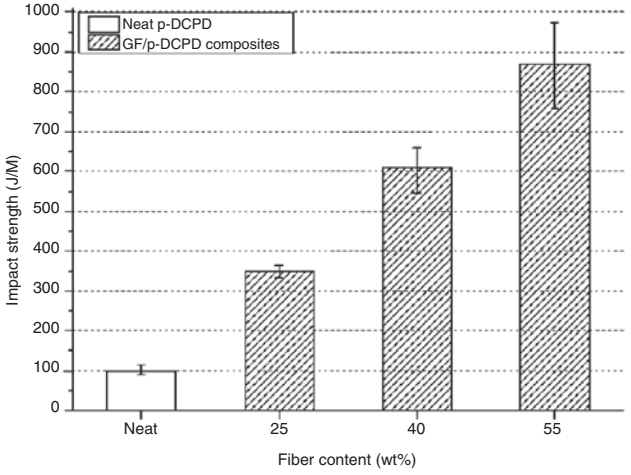


**Figure 15:** Impact strength of GF/p-DCPD composites.

Higher quantities of glass fibers resulted in increased tensile, flexural, and impact strengths. With glass fiber contents of 25, 40, 55 wt.%, tensile strength increased by 50, 76, 101%, flexural strength by 51, 85, 93%, and impact strength by 248, 508, 767%, respectively, compared with the neat p-DCPD. Enhanced mechanical properties of GF/p-DCPD can be explained by achieving sufficient impregnation despite the short processing time even at the highest loading levels. The theoretical tensile strength when the fibers are in a random orientation can be calculated using the equation below (18).

$$\sigma_c = 0.2\sigma_f\left(1-\frac{l_c}{2l}\right)V_f + \sigma_m V_m \qquad \text{if } l \geq l_c \qquad [4]$$

where $\sigma_c$, $\sigma_f$, $\sigma_m$ are the strength of composite, fiber, matrix, $V_f$, $V_m$ are the volume fraction of fiber, matrix, $l_c$ is

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

| Sample | Fiber content (wt.%) | Tensile strength (MPa) | Flexural strength (MPa) | Impact strength (J/M) |
|---|---|---|---|---|
| Poly-DCPD | Neat | 55 ± 1.1 | 79 ± 1.7 | 100 ± 10 |
| GF/p-DCPD composites | 25 | 82 ± 5.8 | 120 ± 12.1 | 349 ± 11 |
| | 40 | 97 ± 4.7 | 147 ± 2.1 | 609 ± 56 |
| | 55 | 110 ± 3.7 | 153 ± 4.5 | 869 ± 94 |

the critical length of composites and $l$ is the length of the fiber. The theoretical values with the fiber contents of 25, 40, 55 wt.% were 87 MPa, 113 MPa and 144 MPa, respectively, which were higher than the experimental results of 82 MPa, 97 MPa and 110 MPa. This was mainly due to imperfect bonding between the resin and the fiber. Differences between the theoretical and the experimental increased when the fiber volume contents was higher.

## 4 Concluding remarks

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 plateauing at 80°C. Further, lower maximum strength and modulus values were measured with the three point bending tests for specimens prepared at lower curing temperatures. Hence, the experimental apparatus was designed to operate for curing temperatures above 80°C with stirring times of less than 30 s. Also a vacuum process was adopted in order to remove any unwanted voids within the mold.

It was found that the shear strength of the glass fiber was 40% higher for specimens treated with a norbornene-based silane compared with the untreated sample. FT-IR spectroscopy analysis further confirmed the quality of the surface treatment. Use of optimized S-RIM process enabled the fabrication of surface treated chopped glass fiber reinforced composite specimens with up to 55 wt.% fiber content. The corresponding test results revealed increases in tensile, flexural, and impact strengths depending on the increase in the fiber content. Due to the low viscosity of DCPD, glass fibers could be sufficiently impregnated with the resin well despite the large fiber mass fraction. These data imply that this new GF/DCPD composite manufacturing approach as a promising route to stronger, lighter, and more efficient structures.

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## References

1. Schwab P, Grubbs RH, Ziller JW. Synthesis and applications of RuCl2(CHR')(PR3)2: the influence of the alkylidene moiety on metathesis activity. J Am Chem Soc. 1996;118(1):100–10.
2. Kessler MR, White SR. Cure kinetics of the ring-opening metathesis polymerization of dicyclopentadiene. J Polym Sci A1. 2002;40(14):2373–83.
3. Li H, Wang Z, He B. Ring-opening metathesis polymerization of dicyclopentadiene by tungsten catalysts supported on polystyrene. J Mol Catal A Chem. 1999;147(1):83–8.
4. Brown EN, White SR, Sottos NR. Microcapsule induced toughening in a self-healing polymer composite. J Mater Sci. 2004;39(5):1703–10.
5. Davidson T, Wagener K. The polymerization of dicyclopentadiene: an investigation of mechanism. J Mol Catal A-Chem. 1998;133(1):67–74.
6. Yang Y-S, Lafontaine E, Mortaigne B. Curing study of dicyclopentadiene resin and effect of elastomer on its polymer network. Polymer. 1997;38(5):1121–30.
7. Sheng X, Lee JK, Kessler MR. Influence of cross-link density on the properties of ROMP thermosets. Polymer. 2009;50(5):1264–9.
8. Jeong W, Kessler MR. Toughness enhancement in ROMP functionalized carbon nanotube/polydicyclopentadiene composites. Chem Mater. 2008;20(22):7060–8.
9. Macosko CW. RIM fundamentals of reaction injection molding. Munich, Germany: Hanser Publisher; 1989.
10. Lee LJ, Ottino JM, Ranz WE, Macosko CW. Impingement mixing in reaction injection molding. Polym Eng Sci. 1980;20(13):868–74.
11. Kim DH, Kim SC. Vitrification effect during the reaction injection molding (RIM) process of epoxy resin. Polym Eng Sci. 1989;29(7):456–62.
12. Ashida K. Polyurethane and related foams: chemistry and technology. Florida, USA: CRC press; 2006.
13. Chang W, Kikuchi N. Analysis of non-isothermal mold filling process in resin transfer molding (RTM) and structural reaction injection molding (SRIM). Comput Mech. 1995;16(1):22–35.
14. González-Romero V, Macosko C. Process parameters estimation for structural reaction injection molding and resin transfer molding. Polym Eng Sci. 1990;30(3):142–6.
15. Yang G, Lee SC, Lee JK. Reinforcement of norbornene-based nanocomposites with norbornene functionalized multi-walled carbon nanotubes. Chem Eng J. 2016;288:9–18.
16. Sage Jr DB. Polyolefin fiber-reinforced composites using a fiber coating composition compatible with romp catalysts. Google Patents; 2002.
17. Park J-M, Wang Z-J, Kwon D-J, Gu G-Y, Lee W-I, Park J-K, Lawrence DeVries K. Optimum dispersion conditions and interfacial modification of carbon fiber and CNT-phenolic composites by atmospheric pressure plasma treatment. Compos Part B-Eng. 2012;43(5):2272–8.
18. Moon CK. Polymer matrix composites. Seoul, Republic of Korea: Sigma Press; 2006.