

Compression Molding Fabrication of C/C Composite Produced via Highly Processable BODA-Derived Precursor Resin System

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Bis-ortho-diynylarene (BODA) resins are an emerging class of high-char-yield (>80%) carbon matrix precursor resins that offer enhanced processability compared to industry-standard phenolics. In this study, a carbon-carbon composite was fabricated using a BODA-derived resin system (BDR) through a one-step powder-melt infusion and compression molding process. A novel high-temperature, 10-ton heated press process was developed to successfully cure BODA-derived resins, enabling the production of carbon-carbon composite coupons within two days while maintaining an 80% carbon yield. This paper examines the manufacturing challenges encountered during processing and the resulting optimizations that improved composite quality and consistency. This work demonstrates a streamlined processing route for BODA-based carbon-carbon composites, contributing to the advancement of high-char-yield precursor resin systems for aerospace and high-temperature structural applications.

I. Nomenclature

BODA = Bis-ortho-Diynylarene
BDR = BODA-Derived Resin
C/C = Carbon/Carbon
PMC = Polymer Matrix Composite

II. Introduction

CARBON/CARBON (C/C) composites, consisting of carbon fiber tows and a carbonaceous matrix, are a class of extreme materials known for their extreme strength and extremely high thermal stability under inert atmospheres. They are widely used in high temperature applications in the aerospace industry such as leading edges on hypersonic vehicles like the Space Shuttle Orbiter and X-43A[1]. Historically, this class of composites have been fabricated by thermosetting resins (usually phenolic based), mesophase pitches, and pyrolyzed hydrocarbon gases [2].

Bis-ortho-diynylarene (BODA)-derived resins stand as new and desirable precursor resin candidates for C/C composite manufacturing. Advantages of this resin class include high oxidative thermal stability, low flammability, and high char yield (>80%) after post-cure carbonization (above 1000°C) [3]. These properties theoretically allow for a one-step resin infiltration process, increasing the efficiency of decades-old carbon matrix precursor resin technology. As well as high char yielding, this resin system is melt-processable, rendering vacuum infiltration steps potentially unnecessary. Current carbon/carbon production technology requires up to 8-9 months of processing time [4]; While using BODA-derived resins (BDR), the production process can be shortened to days. The purpose of this project, therefore, is to demonstrate the high processability of BDR by creating C/C test coupons via compression molding. Compression molding being a simplified method for creating carbon/carbon composite parts, it was selected as the manufacturing method for undergraduate engineering students. Our process was designed for fabricating coupons for tensile testing via ASTM D3039.

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III. Methodology

A. Materials and Mold Specifications

Our composite features a 3K 8-Harness satin weave carbon fiber ply from Toray and BODA-derived resin sourced from Hand Technologies, LLC. Compressive molding specimens were prepared in a Grimco Press with a 1-foot x 1-foot test bed with a student-designed mold shown in Figure 1.

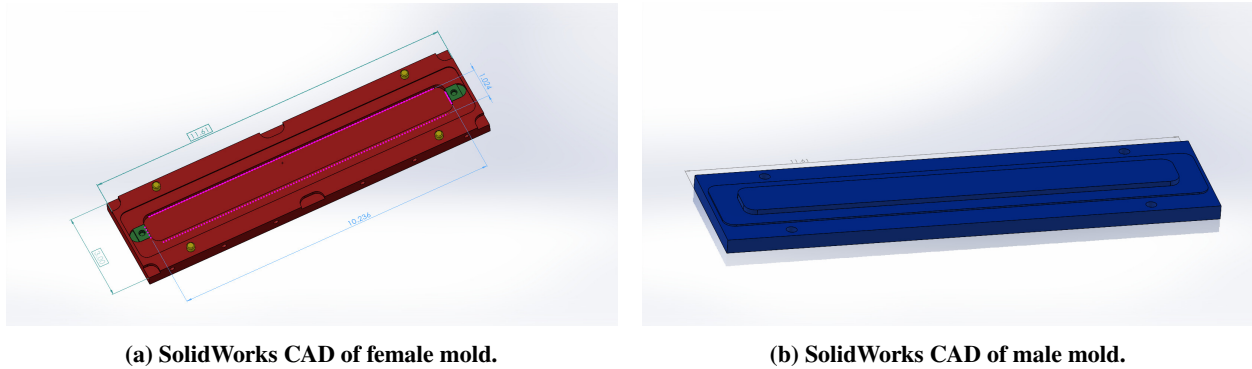


Figure 1. Solidworks CAD of Mold

The mold was fabricated from Aluminum 6061-T6 in a Haas UMC-750SS 5-axis CNC Mill. The mold consists of male and female constituents. The female constituent features a 3° bed draft angle to facilitate in de-molding. Two ejection access plugs were drafted on the female constituent seen in figure 2b. A thermocouple porthole was drilled into the lengthwise side of the female mold to facilitate accurate test bed temperature readings. Pry points were machined along the corner and midpoints of the mold for de-molding with lever tools such as a flat-head screwdriver.

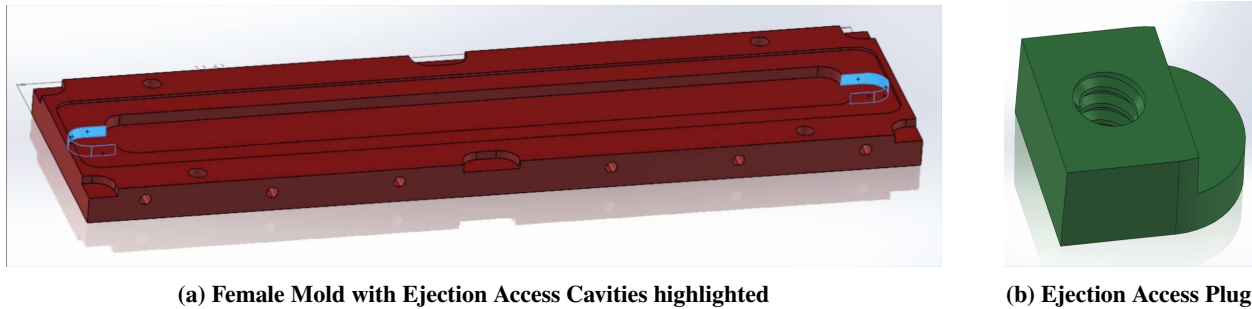


Figure 2. Mold with Features Highlighted

Figure 1 depicts the mold and its male and female constituents, which when interlinked, form a rectangular prism with dimensions 295 mm x 76.2 mm x 21.4 mm when interlinked. The mold is designed to create rectangular test specimens with dimensions 260 mm x 26 mm x 1 mm per ASTM D3039 [5], a test specification for composite tensile testing. Standard methods for coupon construction usually begin with a fabrication of a larger parent composite then cut the test specimens from this parent composite. Our design was constrained by a limited resin budget which required us to minimize waste in the event of a failed fabrication. By selecting a smaller size of coupon mold, we were able to make more coupons and more easily optimize our process via an Edisonian approach. This small mold methodology did lend to some manufacturing trade-offs further discussed in the results section of this article. Post-polymerized composite test articles were cut to dimensions 260 mm x 13 mm x 1 mm using a water-lubricated saw.

B. Mold Use Procedures

The subsequent method was followed when utilizing our molding tool.

- 1) First, try to separate the male and female molds by hand. If this works, skip to step 3; if not, continue to step 2.

- 2) If you cannot separate the molds by hand, pry them apart using a flathead screwdriver or similar lever arm, utilizing the Pry Points located on corners and midpoints.
- 3) After the male and female molds are separated, position the female mold closely over a surface, and slowly turn it upside down.
- 4) If the coupon does not fall out, place the female mold face down on a surface and hit the back of the mold with your hand or a rubber mallet.
- 5) If the coupon still does not fall out, remove the Ejection Access Plugs using needle nose pliers. If additional grip is needed, ¼ - 28 bolts can be installed in the Ejection Access Plugs.
- 6) With the bottom edge of the coupon now exposed, use a small flathead screwdriver, shim, or similar tool to release the bottom surface of the coupon from the mold.
- 7) Repeat steps 3 and 4 to remove the coupon or lift the coupon from the mold with a finger on each end via the Ejection Access Cavities.

C. Layup Procedures

Within the mold, three layers of carbon fiber weaves and three layers of resin were applied. This configuration was chosen based on the thickness of the carbon fiber ply and our design target of 1 mm cross-sectional thickness. These composites were targeted to have a 60:40 fiber volume to resin volume ratio to normalize fiber-dominant properties. The density of the carbon fiber weave used is 1.76 g cm^{-3} and the density of the resin is around 1.12 g cm^{-3} when cured. The volume of the mold cavity was calculated to 6.76 cm^3 ; therefore, $60\% \times 6.76 \text{ cm}^3 \times 1.76 \text{ g cm}^{-3} = 7.14 \text{ g}$ of fiber weight, and $40\% \times 6.76 \text{ cm}^3 \times 1.12 \text{ g cm}^{-3} = 3.03 \text{ g}$ of matrix weight. The BDR has a char yield of roughly 80% per the manufacturer's instruction. Therefore, to make a C/C composite with 40% carbonaceous matrix, an amount of 3.79 g BDR will result in 3.03 g of post-carbonized matrix weight. The weighing procedures are similar to the methods found by Borrego et. al in [3]. Once weights were found, fiber was cut from a preform using a Gerber machine to fill the mold's female bed to initial molding.

D. Compression Molding Method

To create test coupons, the procedure for compression molding is as follows: first, heat the mold to 190°C and hold for 15 minutes to melt the resin and allow for infusion into the fibers. As temperature increases, the resin is partially crosslinking, or b-staging, and this causes the viscosity of the resin to increase. After 15 minutes of melting and partial polymerization, the compression is activated to "wet out" the remaining fibers, and a force of 10 tons is applied. The temperature is brought up to 250°C so that the coupon may fully cure and harden. The mold is left under isothermal compression for three hours. After this step, the process is completed, and the mold can be taken out to cool and the coupon retrieved. The mold setup in the Grimco Press is seen in Figure 3 as well as the BDR resin powder melting. A diagram of the ply layup and cure schedule can be viewed in Figure 4. After compression molding, parts were de-molded and evaluated for delamination. If delamination did not occur, then post-polymerized parts were cut to dimensions $260 \text{ mm} \times 13 \text{ mm} \times 1 \text{ mm}$ using a water-lubricated saw. Parts were then shipped to be carbonized to 1000°C at $10^\circ\text{C}/\text{min}$ under 50 mL min^{-1} Ar flow in a CM Furnaces Inc. 1730-HT tube furnace.

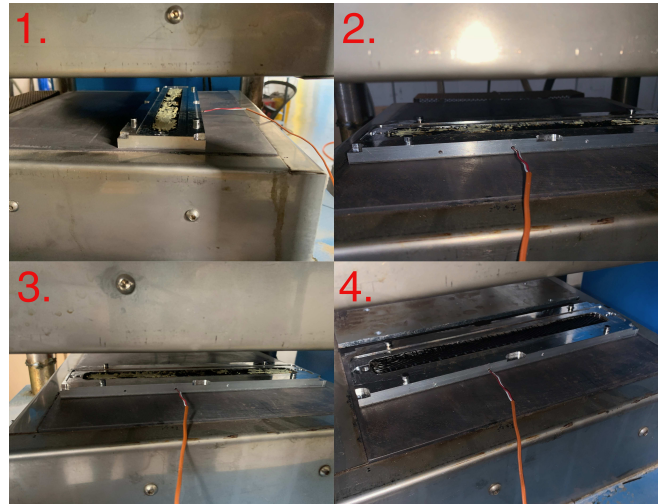


Figure 3. BDR melting into fibers

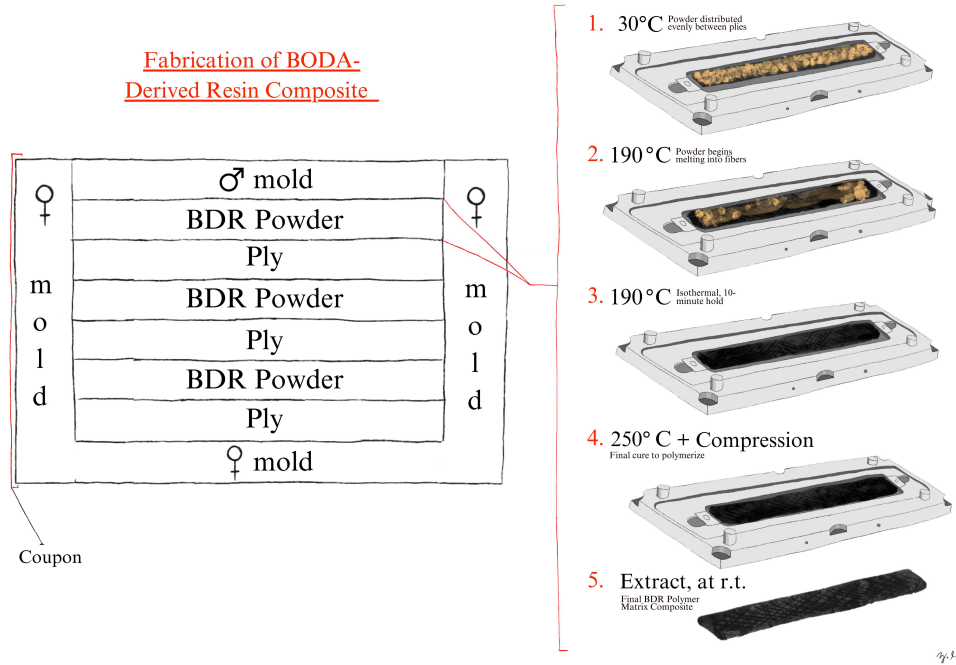


Figure 4. Lay-up Diagram and Cure Method

IV. Results and Discussion

A. Coupon Manufacturing

Our molding dates operated in two phases: Phase I and Phase II. Phase I was a preliminary prototyping phase and lasted from the fall to winter. During this phase, parts were experimented with by altering how the carbon fiber plies were cut out and resin distribution. We had multiple problems that had to be solved over this phase. For example, resin powder was originally clumped together on the axial line of each ply (Fig. 5a) and resulted in uneven resin distribution which led to delamination. This was resolved with the use of spreading apparatus, usually a scoopula. The first trials were crude and served mainly as a proof of concept; however, they usually ended in delamination due to a miscalculation in resin content and failed operation of equipment (For example, the heat press could heat past designated temperatures unexpectedly).

Trial	Problem Encountered
1	Resin starved, 1 ply saturated with resin
2	Resin starved, 2 plies saturated with resin
3	Partial resin starvation, successfully carbonized, upon handling total delamination
4	No resin starvation, delamination upon carbonization
5	No resin starvation, carbonized

Table 1. Summary of trials and problems encountered in Phase I.

Through trial and error, our methodologies changed to combat the resin starvation that plagued our first trial experiments in compression molding. Our original methodology consisted of heating the open mold at 200 °C for 30 minutes, ramping to 230 °C for 30 minutes or until viscous, and then closing the mold while ramping to 250 °C and applying pressure. This would be held for three hours. The purpose of this methodology was to melt the resin into the plies, partially polymerize to increase viscosity (to prevent flashing of the resin when pressure was applied), and then to fully polymerize or cure into a hardened resin-fiber coupon. Both the initial mass calculations and the compression



(a) First trial setup w/hand-cut fiber plies and under-spread BDR



(b) Fully delaminated polymer matrix composite produced during first trial

Figure 5. First trial setup and polymerized mold specimens from initial process

mold schedule resulted in a failure. The carbon fiber plies were dry and loose, and appeared as if they had seen no resin at all (See Figure 5b). For the second trial, we increased the amount of resin per layer by 25%, but this trial still resulted in resin starvation.

For the third trial, the mass calculations were revisited. Once again, mass for resin and plies were calculated via the inner mold volume and a 60% mass of fiber to 40% mass of resin ratio. These masses were representative of the “ideal” conditions. To validate our calculations, the individual carbon fiber plies (cut to dimension) were individually weighed out and individual ply mass was averaged. From these new values, the third trial resulted in only small amounts of visible resin starvation. By increasing the amount of resin per layer by .2 grams and then .3 grams, the fourth and fifth trial had no visible signs of resin starvation. These last three trials were then successfully carbonized, losing expected amounts of mass in the process. For the third coupon, after carbonization, delamination was observed upon processing to the dimensions required by the testing standards. For the fourth coupon delamination was observed after carbonization. Table 1 shows a consolidated view of manufacturing results from the Phase I.

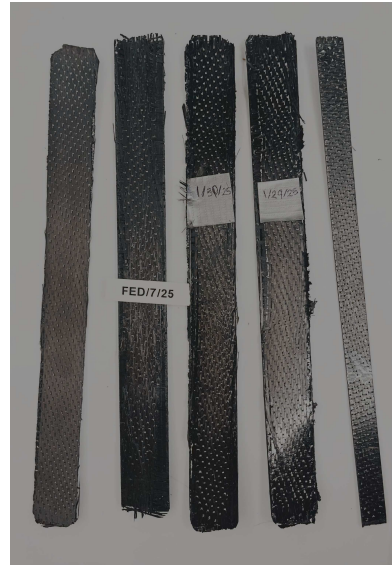
B. Phase II

The first experiment performed in the fall semester resulted in the male mold being warped, as it was not correctly aligned with the pins when pressure was added, causing the aluminum to shift. In consecutive experiments, it could be visually seen that the male mold was not flush with the female mold at the ends. After the successful coupon manufacture on January 22, the male mold’s pin slots were realigned such that it exactly fit the female mold’s pins. However, after this calibration the next four experiments experienced wrinkling and were failures. Over the next four experiments on January 29, 30, 31 and February 7, the mold was allowed to cool overnight and was opened and found to that the entire coupon was delaminated sinusoidally.

This was attributed to a mismatch of coefficients of thermal expansion (CTE) and was unaccounted for the day of fabrication. When allowed to cool, the aluminum mold would shrink and compress the coupon, causing it to buckle and fail. This was fixed on February 11 and 13 when the mold was taken off the press, not allowed to cool, and the coupon was extracted while the mold was still relatively hot. Unfortunately, February 18’s experiment resulted in failure due to human error in the layup of the carbon fiber: layers were not aligned properly inside the mold before compression, and the misalignment caused delamination upon removal.



(a) Improved trial setup w/machine-cut fiber plies and evenly spread BDR



(b) Polymer Matrix Composites before carbonization. Furthest right sample cut to final dimension.

Figure 6. First trial setup and polymerized mold specimens from optimized process



Figure 7. Composite compromised by CTE mismatch.

Trial	Result
January 22	Success
January 29	Failure due to wrinkling from compression
January 30	Failure due to wrinkling from compression
January 31	Failure due to wrinkling from compression
February 7	Failure due to wrinkling from compression
February 11	Success
February 13	Success
February 18	Delaminated while removed from mold

Table 2. Summary of trials and problems encountered in Phase II.

V. Conclusions/Future Work

A novel method for creating carbon/carbon composites derived from bis-*ortho*-diynylarene -derived resins (BDR) utilizing compression molding was developed. A student-designed mold was utilized to fabricate 13 Polymer Matrix Composites (PMC) with a one-step powder-melt-infiltration, and composites were subsequently evaluated for conformance to ASTM D3039 geometries. Once conformed to design specifications, these coupons were subjected to carbonization at a rate of 1000 °C/min and created Carbon/Carbon (C/C) test species under 3 days significantly shortening production times compared to phenolic-derived thermosetting resins' 7-9 month production time.

Several parts of this process can be optimized and improved. Future optimizations could include larger mold sizes to make a bulk amount of coupons rather than fabricating individual small coupons at a time. With a larger mold, BDR can be used to create large plates of PMC, where solid and strong coupons may then be cut out from a single compression molding. Furthermore, an improved mold design would include a releasing bottom bed, allowing the female mold to also be pulled off from the coupon. This would allow the part to cool down and minimize damage if prying the part with force is needed. Further characterization of these composites is desirable. Tensile testing as well as Mercury Intrusion Porosimetry and Scanning Electron Microscopy have been examined as possible options for future work regarding these preliminary composites.

VI. Acknowledgments

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