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The effects of manufacturing processes on the physical and mechanical properties of basalt fibre reinforced polybenzoxazine

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ABSTRACT

The present work provides a comparative investigation between different methods of manufacturing basalt fibre reinforced polybenzoxazines (BFRP), including vacuum infusion, hand laminating, dynamic fluid compression moulding and autoclave curing processes. In comparison to the high pressure based autoclave-cured and compression-moulded BFRPs, vacuum-infused BFRPs showed similar or even higher mechanical properties. Despite the low pressure curing, vacuum infusion yielded BFRPs with a 10% higher tensile strength and a 24% higher strain at failure compared to its autoclave-cured counterparts. Thus, it is possible to gain BFRPs with near-zero porosity and high mechanical properties without the need of high pressure curing methods.

1. Introduction

Fibre-reinforced polymers (FRPs) possess unique mechanical properties but can present additional challenges when meeting fire safety requirements [1]. Among thermally stable polymeric matrices utilized in FRPs, polybenzoxazines exhibit high glass transition temperatures, as well as good inherent fire, smoke and toxicity properties. Additionally, benzoxazines are conducive to application in various FRP manufacturing processes as they exhibit suitable viscosities, polymerize and crosslink without the formation of by-products, and display near-zero volume shrinkage [2]. As previously reported in the literature, diverse manufacturing techniques, including vacuum infusion, hand layup, RTM, filament winding, compression moulding, and autoclave curing have been used to fabricate polybenzoxazine-based fibre reinforced polymers (FRPs) [3,4]. Nevertheless, little is known on the influence of different manufacturing processes on the properties of fibre reinforced polybenzoxazines as the studies differed in the applied types of fibres, textiles, benzoxazine monomers, and additives.

In order to better understand the effects of manufacturing and curing processes on the resulting physical and mechanical properties of basalt fibre reinforced polybenzoxazines, four different processes were applied and studied. Three out-of-autoclave processes, namely layer-by-layer powder-based hand layup with oven curing (LBL), vacuum infusion with oven curing (VI), and dynamic fluid compression moulding (DFCM), were compared to a vacuum infusion with subsequent autoclave curing (AC) process.

2. Materials & methods

2.1. Materials

Basalt fibre fabric (atlas weave, 350 g/m^2) was provided by Centexbel (Gent, Belgium), while bisphenol-F and aniline-based benzoxazine (BF-a) (Araldite MT 35700) was provided by Huntsman Advanced Materials GmbH (Basel, Switzerland).

2.2. Manufacturing

BF-a monomers were melted at 140 °C and degassed in a vacuum oven at 140 °C under reduced pressure ($p = 1$ mbar) for 15 min. 15 layers of basalt fibre atlas weave fabric were stacked in a 0° configuration. Fibre impregnation and curing were performed according to four different processes: i) a layer-by-layer powder-based prepregging followed by hand-layup and convection oven curing (LBL), ii) one-step vacuum infusion followed by curing of pre-impregnated laminates in a convection oven (VI), iii) dynamic fluid compression moulding (DFCM)

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and iv) vacuum infusion followed by curing in an autoclave (AC).

2.2.1. *Layer-by-layer (LBL) processing*

After BF-a monomers were degassed in the vacuum oven, they were processed at room temperature by ball-milling monomers into a fine powder. The surface of the fibre reinforcement was coated with BF-a monomer powder though the motor-driven lateral movements of an application sieve at a frequency of 3 cycles per second utilizing the LBL processing equipment depicted in Fig. A1. After the desired mass of powder was applied to a single layer of fibre reinforcement, the fibres and matrix were consolidated for 50 s in a hot press under moderate pressure and a temperature of 140 °C. The resulting pre-impregnated plies had the dimensions of 300 × 300 mm^2. A low fibre volume content (FVC) of 30 vol% was selected for prepreg processing to take into account resin bleeding and the resultant increase in FVC that occurs during curing. It was expected, that the increase in FVC of the FRP during curing leads to the desired FVC of 50 vol%. For laminate production, single pre-impregnated plies were stacked according to the desired layup configuration. Pre-impregnated laminates were cured in a vacuum bag in a convection oven according to a heating program of 3 h at 170 °C, 2 h at 180 °C, and 4 h at 200 °C.

2.2.2. *One-step vacuum infusion (VI)*

BF-a monomers were melted in a convection oven and degassed in an automated degassing system (Thinky mixer ARV-930, Laguna Hills, CA, USA). The degassing parameters included a rotational velocity of 14000 rpm, a vacuum of 0.5 kPa and a degassing time of 4 min. In the one-step vacuum infusion process, dry preforms with dimensions of 600 × 850 mm^2 were infused with degassed molten monomers and directly cured within a single vacuum bag setup. The infusion procedure for polybenzoxazine-based FRPs consisted of three steps (Fig. A2): (i) preheating of the evacuated setup at 140 °C for 1 h, (ii) infusion of dry fibres until complete wetting was obtained, and (iii) curing in the convection oven for 3 h at 170 °C, 2 h at 180 °C, and finally 4 h at 200 °C.

2.2.3. *Dynamic fluid compression moulding (DFCM)*

One promising method of rapid FRP manufacturing is dynamic fluid compression moulding (DFCM), which has been developed by Huntsman Advanced Materials and combines fibre impregnation with monomer degassing in a compression moulding process [5]. Within a preheated mould (170 °C), one side of the dry fibre reinforcement was initially coated with molten benzoxazine monomers as depicted in Fig. A3 on the left. The cavity was subsequently sealed, and vacuum was applied for 3 min to degas the molten monomers and reinforcement. After degassing, vacuum was vented and the hydrostatic pressure in the cavity was increased to 65 bar. The closed mould was adjusted to fabricate composites with a thickness of 4 mm. The impregnated basalt fibres underwent an initial curing process at 170 °C for 5 h in the pressurized DFCM-mould. The resulting FRPs had the dimensions of 550 × 550 mm^2. Afterwards, the FRPs were transferred to a convection oven and cured according to the temperature-time cycle of 3 h at 170 °C, 2 h at 180 °C, and 4 h at 200 °C. The second curing step was necessary due to current technical limitations as the maximum process temperature of the DFCM equipment was 170 °C.

2.2.4. *Autoclave curing (AC)*

Basalt fibres were first vacuum-infused according to steps (i) and (ii) of the one-step vacuum infusion process. The resulting pre-impregnated plies had the dimensions of 300 × 300 mm^2. The subsequent curing of the pre-impregnated laminates occurred in a second bag set-up (semi-permeable membrane, breather, vacuum bag) in the autoclave. The semi-permeable membrane allowed withdrawal of air and volatiles from the pre-impregnated laminates but was impermeable to molten monomers so that BFRP fibre volume contents could be controlled. The curing in the autoclave was performed at 15 bar without vacuum and with the temperature-time cycle of 3 h at 170 °C, 2 h at 180 °C, and 4 h at 200 °C.

Table 1
BFRP physical properties; data for vacuum infused BFRP was published in Ref. [4].

Process	Ply Count	Thickness (mm)	FVC (vol%)	Density (g/cm^3)
LBL	15	9.50 ± 0.89	37.2 ± 1.5	1.00 ± 0.072
VI	15	3.89 ± 0.05	56.7 ± 0.3	1.92 ± 0.004
DFCM	15	4.16 ± 0.01	50.5 ± 0.3	1.84 ± 0.007
AC	15	3.45 ± 0.01	61.6 ± 0.2	1.98 ± 0.002

2.3. *Material characterization*

Densities and fibre volume contents (FVC) of BFRPs were determined according to EN ISO 1183–1 and ASTM D3171-15, respectively. Furthermore, optical microscopy images were taken with a Keyence VHX-1000 microscope (Neu-Isenburg, Germany). Tensile testing (DIN EN ISO 527–4, specimen type 3, testing speed of 2 mm/min, and specimen dimensions of d × 250 × 25 mm^3 in which d represents thickness in mm), flexural testing (DIN EN ISO 14125, specimen type 3, dimensions of d × 30d × 15 mm^3, testing speed of 2.5 mm/min, and a distance between supports of 20d in mm), and interlaminar shear strength testing (DIN EN ISO 14130, testing speed of 1 mm/min, specimen dimensions of d × 10d × 5d mm^3, and a span of 5d mm) were performed with a RetroLine 100 kN from ZwickRoell (Ulm, Germany). Fivefold repetitions were performed except for LBL manufactured BFRPS, which were tested in threefold repetitions.

3. Results & discussion

3.1. *Impact of manufacturing processes on BFRP physical properties*

The impact of the manufacturing processes on the resulting physical properties of basalt fibre reinforced polybenzoxazine (BFRP) was investigated. Table 1 summarizes the BFRP's compositions as well as thicknesses, fibre volume contents (FVC), and densities, while cross-sectional microscopy images are depicted in Fig. 1.

BFRPs fabricated by VI, DFCM and AC displayed homogeneous morphologies with near-zero porosities (magnification of 50×) and well-penetrated fibres (magnification of 200×). The autoclave-cured BFRPs showed the overall highest FVC, highest density, and smallest thickness. The high pressures consolidate and compress the pre-impregnated laminates so that melted monomers flow into dry areas, entrapped volatiles or gas bubbles collapse, and cure-generated volatiles are supressed. Hence, the applied pressure yields composites with high fibre volume contents and low porosity as well as high dimensional reproducibility.

The vacuum-infused BFRPs showed lower FVCs and densities as well as greater thicknesses compared to autoclave cured BFRPs primarily due to the lower pressure. The unique cavity geometry of DFCM generated BFRPs with lower FVCs compared to autoclave-cured BFRPs despite a fourfold increase in applied pressure. This was primarily due to the closed tooling utilized in DFCM which prevented resin bleeding and therefore maintained both, the desired FRP thickness of 4 mm as well as FVC of 50 vol%.

LBL-processed BFRPs displayed high porosity contents and inhomogeneous morphologies in the through-thickness direction, as observed in Fig. 1 (left). Oven curing methods have been shown in the literature to often produce FRPs with high void contents due to low compaction pressures and the expansion of entrapped gases with applied vacuum [6]. Therefore, the entrapment of air that occurred during ply stacking and subsequent vacuum-bag curing in LBL manufacturing was thought to explain the high porosity contents of LBL samples. The high porosities of LBL-manufactured BFRPs resulted in thicker composites with the lowest average FVC and density. Furthermore, the desired FVC of 50 vol% in the final FRP was not obtained.

Moreover, a comparison of fibre waviness among manufactured

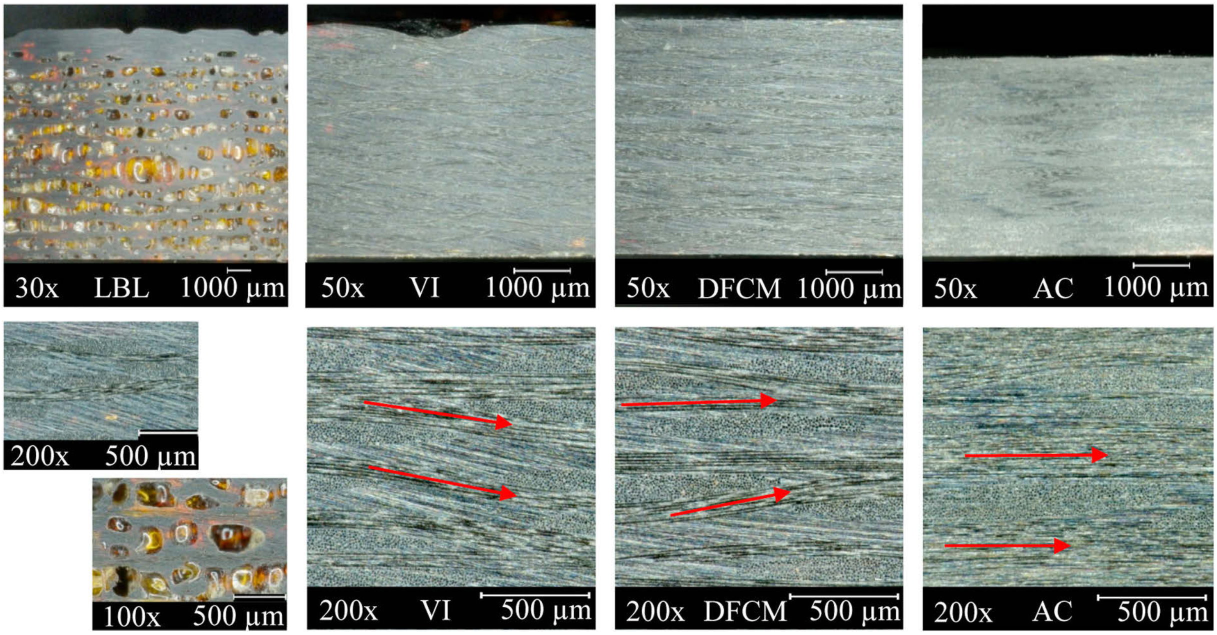
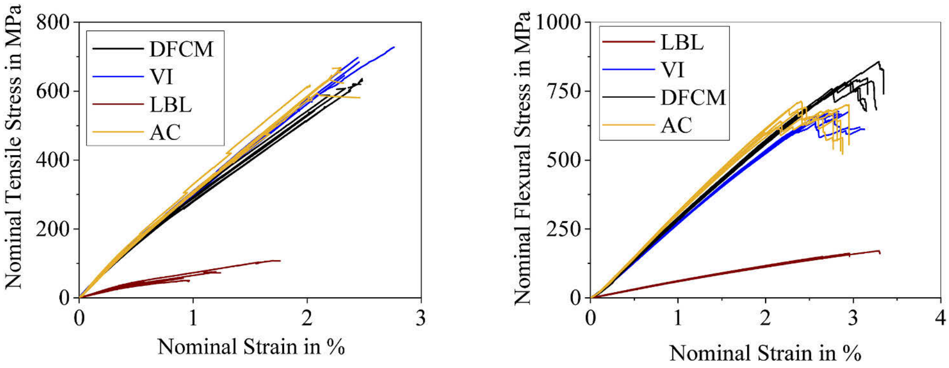


Fig. 1. Microscopy images of BFRP specimens produced with LBL, VI, DFCM and AC processes.



a) b)

Fig. 2. Nominal stress - strain curves of quasi-static a) tensile testing and b) flexural testing; data for vacuum infused BFRP was published in Ref. [4].

composite samples showed that autoclave curing most greatly reduced out-of-plane waviness, as indicated with red arrows in the cross-sectional images (Fig. 1, bottom). The high pressures during autoclave curing consolidate and compress the pre-impregnated laminates so that the out-of-plane waviness is reduced. Fibre waviness is important as it can introduce complexity into the load transfer abilities of the laminate, which often negatively affects mechanical properties [7].

3.2. BFRPs mechanical performance

The influence of the manufacturing process on the mechanical properties of BFRPs was assessed by quasi-static tensile, flexural, and interlaminar shear strength (ILSS) testing. The measured mechanical properties of BFRPs are summarized in Table A1. The stress-strain curves of tensile testing and flexural testing of BFRPs are depicted in Fig. 2.

BFRPs manufactured with LBL processing showed significantly lower Young's moduli and strengths coupled with lower strains at failure. Additionally, the LBL-fabricated specimens displayed a comparatively low average ILSS value of 10.3 ± 0.2 MPa. These results were attributed to high porosity contents and microstructural defects, which induce inhomogeneous stress concentrations and can initiate cracking. Pores also prevent effective transfer of shear stresses by reducing fibre-matrix interfacial bonding and causing delamination of plies during loading.

In contrast to LBL-manufactured BFRPs, AC-, VI-, and DFCM-manufactured specimens showed nearly linear stress-strain relationships until final failure in quasi-static tensile and flexural testing. The tensile and flexural properties, such as modulus, strength and strain at failure, were in the same range for all three specimens (Table A1). Autoclave-cured BFRPs showed the highest tensile and flexural moduli as well as the lowest strain at failure. This was attributed to high FVCs and low out-of-plane fibre waviness, which leads to stiffer composites.

Despite the lower pressure during oven curing in VI-processing, vacuum infused BFRPs possessed higher tensile strength and strain at failure compared to autoclave cured or DFCM-manufactured BFRPs. Furthermore, it was shown that DFCM-manufactured BFRPs exhibited highest flexural strength and strain at failure despite its higher thickness and lower FVC.

ILSS testing was performed to assess the influence of the manufacturing methods on fibre-matrix interactions (Fig. A4). BFRPs manufactured by VI and DFCM yielded interlaminar shear strengths of 66.8 ± 3.5 MPa [4] and 73.7 ± 2.0 MPa, respectively, and thus outperformed autoclave-cured BFRPs with an average ILSS value of 64.0 ±

6.6 MPa.

4. Conclusion

This work provides a comprehensive study demonstrating the mutual interdependence between manufacturing processes and final composite part quality. Results from quasi-static mechanical testing were correlated to FRP morphologies, with the absence of voids and defects in VI-, DFCM-, and AC-produced BFRPs corresponding to higher mechanical properties. Similar morphologies and mechanical properties were obtained through vacuum infusion with oven curing in comparison to AC and DFCM, demonstrating that benzoxazines do not necessarily require high pressure curing. Thus, VI is promising manufacturing method due low investment costs and the ease of processing.

CRediT authorship contribution statement

Nick Wolter: Technical and scientific challenge, planning and performing of experiments, FRP manufacturing, evaluation of test results, Conceptualization, Methodology, Validation, Investigation, Writing - original draft, Writing - review & editing, Visualization, Investigation. **Vinicius Carrillo Beber:** Evaluation of mechanical experiments and reviewing, Writing - review & editing. **Catherine Mae Yokan:** FRP manufacturing with LBL process supervised by N. Wolter, Investigation. **Christof Storz:** FRP manufacturing with DFCM process using process parameters selected by . **Bernd Mayer:** Scientific discussion, Supervision, Writing - review & editing, Supervision. **Katharina Koschek:** Scientific challenge and scientific evaluation, project supervision and management, reviewing, Supervision, Project administration, Funding acquisition, Validation, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendices.

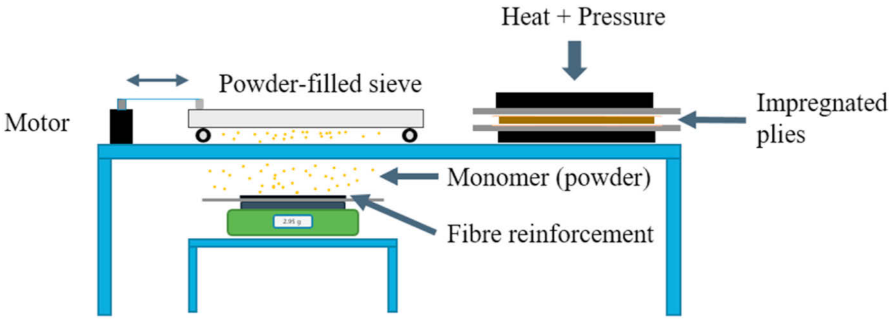


Fig. A1. Schematic model of equipment for LBL processing.

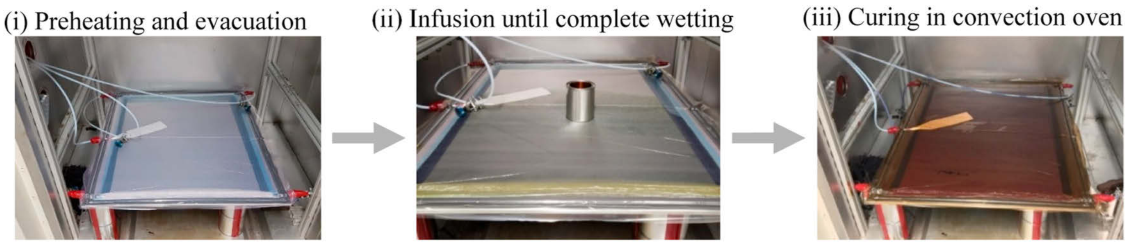
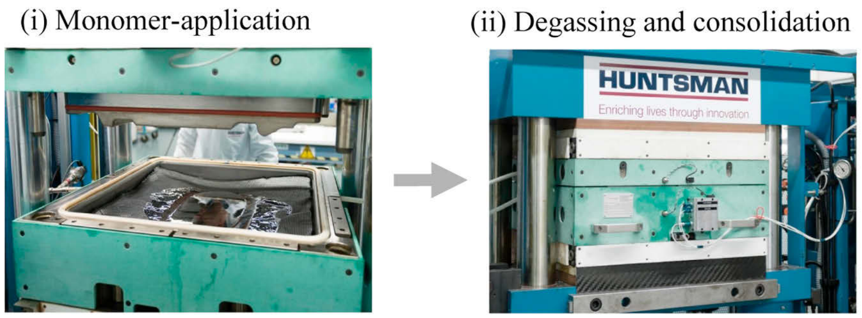

(i) Preheating and evacuation
(ii) Infusion until complete wetting
(iii) Curing in convection oven

Fig. A2. Process steps of one-step vacuum infusion with immediate curing in convection oven.



(i) Monomer-application

(ii) Degassing and consolidation

Fig. A3. Hot press and process steps for DFCM with subsequent curing in convection oven.

Table A1
Tensile, flexural and interlaminar properties of BFRPs; data for vacuum infused BFRP was published in Ref. [4].

Process	Young's Modulus (GPa)	Tensile Strength (MPa)	Strain at failure (%)	Flexural Modulus (GPa)	Flexural Strength (MPa)	Strain at failure (%)	ILSS (MPa)
LBL	7.6 ± 0.8	63 ± 22	1.0 ± 0.4	6.0 ± 0.1	160 ± 11	3.0 ± 0.3	10.3 ± 0.2
VI	31.6 ± 0.7	685 ± 28	2.6 ± 0.2	26.3 ± 1.2	666 ± 12	2.8 ± 0.1	66.8 ± 3.5
DFCM	31.2 ± 0.8	600 ± 46	2.2 ± 0.2	29.2 ± 0.4	787 ± 41	3.1 ± 0.1	73.7 ± 2.0
AC	35.1 ± 1.3	624 ± 29	2.1 ± 0.1	32.2 ± 0.7	682 ± 25	2.5 ± 0.2	64.0 ± 6.6

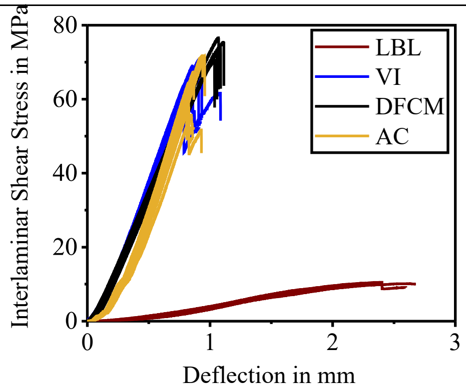


Fig. A4. Interlaminar shear stress – deflection curves of apparent interlaminar shear strength testing; data for vacuum infused BFRP was published in Ref. [4].

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