A PROCESS FOR CREATING HYBRID COMPOSITE STRUCTURES USING ADDITIVE MANUFACTURING WITH DUAL-CURING THERMOSETS

BY

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Abstract

As designers and engineers continue to push the boundaries of high-performance design, fiber reinforced plastics (FRP) are increasingly finding use in structural applications due to their light weight and superior mechanical properties. Many applications, especially in the aerospace and automotive industries, require geometrically complex designs with multiple components and materials assembled during manufacturing – typically using mechanical fasteners or adhesives. Adhesive bonding is the generally preferred technique when manufacturing FRP structures for a multitude of reasons: adhesive bonding does not require material removal, reducing stress concentrations and stress cracking introduced by drilling; galvanic corrosion is minimized, which can be responsible for significant maintenance costs; and the weight penalty of mechanical fasteners is avoided. Despite these benefits, adhesive joining is often avoided due to quality control concerns and the need for special fixtures and surface treatments.

In order to solve these problems, a new process has been developed for joining composite members utilizing additive manufacturing and a dual-curing resin system. The resin is first 3D printed using a UV process; resulting in a semi-rigid, but only partially cured part. This part still has chemical potential and bonding availability when it is integrated with pre-impregnated fiber reinforcement. The assembly is then heated to activate a second curing reaction that co-cures the two materials, resulting in a permanent, void-free bond. Due to the co-curing nature of this new joining process, there is no longer a need for surface treatments or additional fixtures. Furthermore, these adhesive parts can utilize the design freedom of 3D printing by including intricate internal structures or customized features to improve assembly. The combination of 3D printed joining elements and FRP enables a new family of hybrid, high-performance composite structures.

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List of Symbols

2. Characterization and Curing Kinetics

Symbol	Unit	Description
α	-	Extent of conversion
β	[K / min]	Heating rate
λ	-	Di Benedetto fitting parameter
Α	[s ⁻¹]	Pre-exponential factor
<i>C</i> ₁	-	Empirical constant of the reactant
<i>C</i> ₂	-	Empirical constant of the reactant
Ε	[J / mol]	Activation energy
Ε'	[Pa]	Storage modulus
<i>E''</i>	[Pa]	Loss modulus
k	[s ⁻¹]	Reaction rate constant
k _{Arrh}	[s ⁻¹]	Chemical reaction rate
k _{diff}	[s ⁻¹]	Diffusion-controlled reaction rate
m	-	Autocatalytic reaction order
n	-	Reaction order
R	[J K ⁻¹ mol ⁻¹]	Universal gas constant
Т	[K]	Temperature
T_g	[K]	Glass transition temperature
$T_{g,0}$	[K]	Initial glass transition temperature
$T_{g,1}$	[K]	Final glass transition temperature

3. Evaluation of Single-Lap and Block Shear Test Methods in Adhesively Bonded Composite Joints

Symbol	Unit	Description
ξς	-	Non-dimensional overlap
С	[m]	Overlap length from the centerline
D	[Pa m ³]	Flexural rigidity
Ε	[Pa]	Modulus of elasticity
E_R	-	Young's modulus ratio of the adherend and adhesive
F	[N]	Maximum tensile load
J	[m ⁴]	Polar moment of inertia
k	-	Bending-moment factor
<i>M</i> ₀	[N m / m]	Moment per unit width
Р	[N / m]	Applied tensile load per unit width
S	[Pa]	Bond test strength
<i>S</i> ₁₂	[Pa]	Shear stress
<i>S</i> ₂₂	[Pa]	Peel stress
t	[m]	Adherend thickness
t _a	[m]	Adhesive thickness
W	[m]	Lateral deflection

Symbol	Unit	Description
ΔH	[1]	Exothermic heat of reaction
ΔT	[K]	Process and glass transition temperature differential
λ	-	Di Benedetto fitting parameter
С	-	Degree of cure
Ε	[Pa]	Modulus of elasticity
E_G	[Pa]	Upper modulus plateau in glassy-region
E_R	[Pa]	Lower modulus plateau in the rubbery-region
k	-	Exponential curve fitting parameter
Т	[K]	Temperature
T_g	[K]	Glass transition temperature
$T_{g,0}$	[K]	Initial glass transition temperature
$T_{g,1}$	[K]	Final glass transition temperature

4. A Model for Modulus Development of Dual-Cure Resin Systems

5. Application: Fiber-Reinforced Composite Sandwich Structures

Symbol	Unit	Description
$ ho_l$	$[kg / m^3]$	Density of the lattice structure
$ ho_s$	$[kg / m^3]$	Density of the solid structure
b	-	Number of struts in the lattice unit cell
d _s	[m]	Strut diameter
j	-	Number of joints in the lattice unit cell
М	-	Maxwell stability criterion number

1. Introduction

1.1. Composite and Hybrid-Composite Structures

The combination of light and strong materials is desirable in a number of markets, including aerospace, automotive, infrastructure, marine, and sports and recreation. Transportation industries are particularly concerned with reducing weight and minimizing fuel consumption while simultaneously optimizing structural designs for passenger safety. Fiber reinforced plastics (FRP) are increasingly finding use in these applications due to their light weight and superior mechanical properties [1,2]. In many embodiments, continuous low density fibers (often carbon fiber) are embedded in a thermoplastic or thermoset matrix to form a highly anisotropic composite on a lamina basis which results in an excellent stiffness to weight and strength to weight ratio. Figure 1.1 shows a comparison of FRP specific material characteristics to other common engineering materials [3].



Figure 1.1: Specific material properties of common engineering materials [3].

FRPs can be manufactured using a variety of processes and materials. Thermoplastic composite structures are generally constructed using tapes consisting of a continuous fiber tows or fabric encapsulated in a matrix, however, the fibers may take the form of single filaments or fiber bundles. The reinforcement is aligned in the preferential direction for the application and compacted. Compression molding is a common technique used to process thermoplastic composites, where stacks of material are heated under pressure to consolidate the layers and are subsequently cooled to allow for solidification. [4]

Thermoset composite structures are manufactured in similar processes, with the significant difference being the use of a resin that must chemically cure, rather than a matrix that melts and solidifies. Liquid resin can be used to impregnate the dry fibers in hand-lamination using brushes or rollers, or in infusion processes using pumps or vacuum assistance. Using pre-impregnated fiber reinforcement (prepreg) is a common technique. These fibers are supplied already infused with a partially cured resin matrix. The partially cured resin is viscous enough to keep the fibers in their intended alignment within a flat sheet and contains all of the curing agents necessary to complete the curing reaction. Prepregs can easily be cut and manipulated inside of a mold. After the required number of layers are placed, the mold is heated to initiate the chemical reaction between the uncured resin. Pressure is also applied to thermoset composite structures to assist in the consolidation of the layers and to remove voids. Vacuum forces can be applied by wrapping a flexible bag to one-sided molds connected to a pump. More advanced composite parts (especially in aerospace) use autoclaves, large heated pressure vessels, to reach the required temperatures and pressures. [4]

Hybrid structures combine at least two materials of different groups or characteristics to form a compound with increased properties for certain applications. Due to the planar nature of composite manufacturing, it may be advantageous to create hybrid structures for complex geometries, where the mechanical properties are provided by the composite materials and the geometry is provided by alternative manufacturing methods. One example is sandwich structures consisting of FRP skin layers and metal or polymer cores often used in aviation, aerospace and high-end automotive applications [5,6]. The specific use of these materials makes it possible to design lightweight structures with improved material properties. Hybrid composite structures have been used since 1951, when fiberglass and balsa wood were combined to manufacture panels for the German Akaflieg Stuttgart FS-24 [7]. More recently, NASA utilized hybrid composite structures to manufacture an improved cryogenic tank by co-curing an inner tank layer of PBO (poly-p-phenylenebenzobisoxazole) fibers in a polyurethane matrix with an outer layer of carbon fiber in an epoxy matrix [8]. Another novel hybrid composite structure was recently developed by Osswald [9], combining carbon fiber reinforced plastic (CFRP) composites and thermoplastic additive manufactured parts. The selective laser sintering (SLS) process with PA12 powder was used to manufacture a cowl with integrated thermoplastic CFRP for the BMW i3.

Many of these applications, especially in the aerospace and automotive industries, require geometrical complexity, multiple components, and multiple materials. These requirements lead to a need for assembly and joining elements during manufacturing – typically mechanical fasteners or adhesives. Adhesive bonding is the generally preferred technique when manufacturing FRP structures for a multitude of reasons. Unlike mechanical fasteners, adhesive bonding does not require material removal, which reduces stress concentrations and stress cracking introduced by the drilling and installation of fasteners. Galvanic corrosion is also minimized, which can be

responsible for more than 20% of the maintenance costs in aerospace and automotive applications [10,11]. Despite these benefits, adhesive joining is often avoided due to quality control concerns. Current adhesive technology can introduce air in the bondline, decreasing the bond strength and causing unpredictable failure. Special treatments may also be required to clean and prepare the surface for bonding. Unlike mechanical fasteners, adhesives cannot be easily visually inspected and ultrasonic inspection, computed tomography, or other non-destructive methods must be used to ensure a high-quality, void-free bond.

1.2. Additive Manufacturing

Additive manufacturing, commonly referred to as 3D printing, is based on the principle of directly fabricating complex objects from 3D model data and has distinct advantages compared to formative shaping and subtractive manufacturing, as highly complex parts can be produced while simplifying product development and manufacturing [12,13]. For many years, 3D printing was predominately used for rapid prototyping applications, however, in the last decade 3D printing has gained practical adoption in multiple industries such as aerospace, automotive, consumer electronics, footwear, and dental industries. This growth is due to new 3D printing technologies enabling the production of complex architectures and geometries which are not possible with conventional manufacturing methods [14].

Vat photopolymerization techniques, in particular stereolithography (SLA), were first developed in 1984 [15], but have seen significant market penetration in just the last 10 years. This growth in utilization can be attributed to the improvement of manufacturing processes, materials, and final part quality [16]. One of these techniques to develop high quality, end-use parts is Digital Light Synthesis (DLS) developed by Carbon. DLS, depicted in Figure 1.2, differs from the

fundamentally similar digital light processing (DLP) additive manufacturing principles by its oxygen permeable window, which inhibits UV activated polymerization at the window surface to prevent the part from adhering to the window. Resin can then freely flow into this liquid "dead zone" at the window surface, enabling continuous, rather than layer-by-layer, production of the part to enable faster production times by eliminating rate-limiting separation and realignment steps in the generation of high-resolution structures [17,18]. This continuous printing process is also commonly known as Continuous Liquid Interface Production (CLIP). The DLS technology and Carbon's proprietary resins show potential to extend the utility of additive manufacturing with the breadth of available materials, mechanically isotropic parts, and improved processing speeds to lower the manufacturing costs of complex polymer-based objects [19].



Figure 1.2: Schematic of the Digital Light Synthesis printing process.

While there are some materials available that cure in a single step, many of the advanced materials are enabled by a proprietary two-stage resin reaction technology [20]. The first step is the photopolymerization occurring within the printer by the UV imaging unit. The partially cured parts are then removed from the printer build platform and the second step is a thermal cure in an

external heat source. This second step can be several hours in duration depending on the exact resin system.

1.3. Motivation and Objectives

Many composite applications, especially in the aerospace and automotive industries, require geometrical complexity, multiple components, and multiple materials, resulting in challenges and limitations in manufacturing. In order to solve these problems, a new process has been developed for joining composite members utilizing additive manufacturing and a dual-cure epoxy resin. The resin is first 3D printed using DLS - a UV curing process; resulting in a semi-rigid, but only partially cured part. This part still has chemical potential and bonding availability when it is integrated with pre-impregnated fiber reinforcement. The assembly is then heated to activate the second curing reaction and co-cure the two materials, forming a permanent, void-free bond. Furthermore, these parts can utilize the design freedom of 3D printing by including intricate internal structures (e.g., lattice, cooling channels, cable routing, etc.), textures to increase bonding surface area and joint performance, or customized features to improve assembly. The combination of 3D printed joining elements and FRP enables a new family of hybrid, high-performance composite structures. The general concept of integrating a complex 3D printed part with fiber reinforcement using vacuum consolidation is depicted in Figure 1.3.



Figure 1.3: Integration of 3D printed dual-cure resin and fiber reinforcement.

The research objectives and organization of this dissertation are as follows:

Chapter 2: Develop an understanding of the thermal curing process

- I. Study the thermal curing behavior of the material for different temperature cycles using different scanning calorimetry (DSC)
- II. Develop a thermal curing kinetics model capable of predicting the degree of cure during processing
- III. Relate the degree of cure to glass transition temperature

Chapter 3: Quantify bonding characteristics of the 3D printed hybrid composite structures

- I. Manufacture test specimen using pre-impregnated composite material systems to identify the effect of co-curing on bonding strength
- II. Conduct single-lap shear and block shear tests to compare different loading conditions
- III. Compare bonding strength to a commercially available epoxy adhesive

Chapter 4: Determine appropriate processing conditions for the 3D printed elements and composite materials

- I. Test the 3D printed elements with the different temperatures and pressure conditions that are used during the processing of the composite materials they are integrated with
- II. Develop a model for the modulus development of the dual-cure resin system to predict and avoid deformations during thermal curing

Chapter 5-7: Design and manufacture functional prototypes to demonstrate the technology at an application level

2. Characterization and Curing Kinetics

The following chapter presents an analysis of the thermal curing reaction for the dualcuring material used to create the hybrid composite structures. This material is first 3D printed and partially cured using a UV light before integration with a pre-impregnated fiber reinforcement. The partially cured 3D printed component and pre-impregnated fiber reinforcement are then thermally co-cured to bond the assembly. Each resin system used in pre-impregnated fiber reinforcement requires a different thermal curing cycle that is usually provided by the supplier. The thermal curing cycle of the 3D printed dual-cure resin must match the thermal curing cycle of the pre-impregnated fiber reinforcement in order for co-curing and bonding between the two components to occur. By studying the curing kinetics of the dual-curing material, a modified curing cycle can be created to better match the curing cycle of the selected pre-impregnated fiber reinforcement. This chapter is based on the research "Thermal curing kinetics optimization of epoxy resin in Digital Light Synthesis" published in *Additive Manufacturing*, Vol. 32, Article 101018 (2020) [21].

2.1. Introduction

Additive manufacturing has been used for several decades for rapid prototyping applications. However, in recent years there have been many new hardware and material developments leading to a new range of applications. Vat photopolymerization techniques, in particular stereolithography (SLA), were first developed in 1984 [15], but have seen significant market penetration in just the last 10 years. This growth in utilization can be attributed to the improvement of manufacturing processes, materials, and final part quality [16]. One of these

techniques to develop high quality end-use parts is Digital Light Synthesis (DLS) from Carbon, Inc. (Redwood, CA).

DLS differs from the fundamentally similar digital light processing (DLP) additive manufacturing principles by its oxygen permeable window, which inhibits UV activated polymerization at the window surface to prevent the part from adhering to the window. Resin can then freely flow into this liquid "dead zone" at the window surface, enabling continuous, rather than layer-by-layer, production of the part to enable faster production times by eliminating rate-limiting separation and realignment steps in the generation of high-resolution structures [17,18]. This continuous printing process is also commonly known as Continuous Liquid Interface Production (CLIP). The DLS technology and Carbon's proprietary resins show potential to extend the utility of additive manufacturing with the breadth of available materials, mechanically isotropic parts, and improved processing speeds to lower the manufacturing costs of complex polymer-based objects [19].

While there are some materials available that cure in a single step, many of the advanced materials utilize a two-stage resin reaction technology [20]. The first step is the photopolymerization occurring within the printer by the UV imaging unit. The partially cured parts are then removed from the printer build platform and the second step is a thermal cure in an external heat source. This second step can be several hours in duration depending on the exact resin system, presenting a challenge for the fast cycle times demanded by industrial users who are mass producing parts. The aim of this study is to optimize this second thermally activated curing step to reduce the total curing time while maintaining full mechanical properties. A schematic of the DLS process and two-stage cure is shown in Figure 2.1.



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Figure 2.1: Schematic diagram of DLS showing the UV printing process followed by second thermal cure in a convection oven and the final, fully cured part.

Differential scanning calorimetry (DSC) is one of the most common techniques to characterize thermosetting resins by measuring the heat flow resulting from the change in internal energy as a result of the exothermic cure [22-24]. The glass transition temperature can also be determined as a function of the degree of cure for thermosets – the higher the degree of cure, the higher the glass transition temperature. The glass transition temperature is identified by a shift of the heat capacity, resulting in an endothermal step in the DSC signal [25]. In general, to acquire detailed information about the curing behavior of thermosets with DSC, two different measurement methods can be used and are well described in previous literature. One is isothermal measurements at different temperatures, leading to a time shift of the curing reaction. The main challenge of the isothermal measurement is to capture the initial reaction that can occur during pre-heating before the target measurement temperature is reached [26,27]. The other alternative is dynamic ramp tests with different linear heating rates, which many recent studies use due to the simplified analysis of the heat flow curves and calculations of the reaction enthalpy and corresponding temperatures of the system [25,28,29]. It has been previously recommended that up to ten different heating rates should be compared to analyze the curing behavior, however, a minimum of three measurements has shown suitable results [22,30].

The dynamic DSC measurements can then be used for modelling the chemical curing behavior. The basis for all kinetic analysis is the Arrhenius equation (Equation 2.1) which describes the temperature dependence of the reaction rate. Here, k [s⁻¹] is the chemical reaction rate constant, A [s⁻¹] is a pre-exponential factor, E [J/mol] is the activation energy, R (8.314 J K⁻¹mol⁻¹) is the universal gas constant, and T [K] is the temperature [25].

$$k = k(T) = A \cdot e^{\left(-\frac{E}{R \cdot T}\right)}$$
(2.1)

The conversion rate by time for isothermal reactions, $\frac{d\alpha}{dt}$, or by temperature for dynamic heating rates, $\frac{d\alpha}{dT}$, can then be described by the following equation:

$$\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT} = k(T)f(\alpha)$$
(2.2)

where k(T) is described by Equation 2.1, β is the constant heating rate, and $f(\alpha)$ is the reaction model.

Model-free methods are useful for a first impression of the chemical reaction as they do not require the development of a new reaction model or the modification of existing models. The Friedman method is a common way to calculate the activation energy (*E*) as a function of the extent of conversion (α). With this method, the reaction is described by converting Equation 2.2 into logarithmic form and substituting *k*(*T*) from Equation 2.1:

$$\ln \frac{d\alpha}{dt} = \ln \left[\beta \frac{d\alpha}{dT}\right] = \ln[Af(\alpha)] - \frac{E}{R \cdot T}$$
(2.3)

By plotting $\ln \frac{d\alpha}{dt}$ vs. $\frac{1}{T}$ with constant α , this relationship takes the form of a straight line with a slope of $-\frac{E}{R}$. Plots at different values of *T*, for isothermal reactions, or β , for dynamic heating rates, can be created to estimate the isoconversional activation energy [31].

It is not always possible to accurately describe more complex systems with the model-free approach, such as those with multiple steps, simultaneous reactions, or diffusion influence. Diffusion control is critical in providing accuracy in models of many thermoset systems. If the glass transition temperature of the polymer increases faster than the sample temperature, the reaction is no longer controlled by the kinetics of the chemical reaction, but by diffusion processes. This can lead to vitrification, slowing the expected reaction rate, and resulting in an insufficiently crosslinked part [19,28].

NETZSCH Kinetics Neo[™] software provides the ability to combine different chemical reactions and test the accuracy of the corresponding model. Using Kinetics Neo, it is possible to calculate different reaction orders, including autocatalysis and power indices. It also provides the ability to consider diffusion-controlled processes with the inclusion of glass transition data by using the Rabinowitch equation for the total rate constant as shown in Equation 2.4 [32]:

$$\frac{1}{k} = \frac{1}{k_{Arrh}} + \frac{1}{k_{diff}}$$
(2.4)

where k_{Arrh} is the chemical reaction rate in Equation 2.1-2.2 and k_{diff} is the diffusion controlled rate. The form of k_{diff} is modified from the Willams-Landel-Ferry relationship for $T \ge T_g$ as:

$$k_{diff}(T) = k_{diff} \left(T = T_g \right) \cdot e^{\left[\frac{C_1(T - T_g)}{C_2 + T - T_g} \right]}$$
(2.5)

where C_1 and C_2 are empirical constants of the reactant under observation.

There are multiple publications which show a successful creation of a chemical reaction model with a high accuracy and a good prediction of the curing behavior [33-36]. These predictions are often used to describe the material at isothermal conditions (e.g., application temperature), describe the material behavior during the curing process, or to optimize the curing process with the aim to increase efficiency and lower cycle times. For the investigated material of this study, the material supplier recommends the curing cycle shown in Figure 2.2. The aim of this investigation is to reduce the length of the original curing cycle, with an initial duration of 750 minutes and a maximum temperature of 220 °C. During the thermal curing process, and due to the crosslinking of the material, the elastic modulus of the material increases by a factor of up to 20 in comparison to the partially cured parts immediately after printing. Parts that are sufficiently crosslinked will show a relatively constant elastic modulus through a subsequent temperature ramp, followed by a sharp decrease in mechanical properties, indicating the glass transition temperature, T_g [23,27]. In order to ensure any suggested improvements to the curing cycle result in complete crosslinking and material properties, dynamic mechanical analysis (DMA) and tensile testing can be performed on the final parts.



Figure 2.2: Manufacturer recommended thermal curing cycle for EPX 82 epoxy resin.

2.2. Materials and Methods

2.2.1. Materials

This work uses EPX 82, a dual-curing epoxy resin produced by Carbon, Inc. The first stage of the curing reaction is completed within the DLS printing process, where UV light is used to initiate photopolymerization, forming a partial acrylate network. In this state (subsequently referred to as Stage 1), parts are only fractionally cured. These parts have a defined geometry and maintain their form, but have the properties qualitatively described as a semi-rigid gel. During the second, thermal curing stage, the full material properties are developed by the cross-linking of the epoxy resin. All of the EPX 82 parts used in this study were manufactured using a Carbon M1 printer, removed from the build platform, and washed in a solvent bath. Manufacturer listed properties for the EPX 82 material in Stage 2 are shown in Table 2.1 [37].

EPX 82 Material Properties	Value	Unit
Tensile Modulus	2.8	GPa
Ultimate Tensile Strength	82	MPa
Elongation at Break	5.9	%
Glass Transition Temperature	150 - 155	°C

 Table 2.1: Manufacturer listed final material properties for EPX 82. [37]

2.2.2. Differential Scanning Calorimetry (DSC)

All calorimetric experiments are performed with a NETZSCH DSC 214 Polyma. Samples of EPX 82 are manufactured with a diameter of 2.5 mm, height of 2.0 mm, and mass of 10 mg +/- 1 mg, and stored in refrigeration until testing to prevent any second-stage curing from occurring at room temperature. Samples are placed in aluminum DSC pans with a pierced lid to allow for outgassing. Before starting the DSC tests, each sample is removed from refrigeration, shielded from UV-light, and stored in a dry environment. In order to monitor the curing reaction, Stage 1 samples are ramped from 0 °C to 330 °C at heating rates of 0.5, 1, 2, 3, 4, and 5 K/min. A linear baseline is used to calculate the total heat of reaction. The glass transition temperatures are measured at different degrees of conversion using a temperature ramp from 0 °C to 200 °C with a heating rate of 10 K/min.

2.2.3. Kinetic Analysis

The results of the DSC measurements are then implemented into the NETZSCH Kinetics Neo version 1.6.2 and the exothermal heat of reaction are calculated with a linear baseline. Modelfree Friedman analysis is used to better understand the reaction kinetics and provide insight into suitable model predictions. Different reaction models are then created within the software, and the model parameters are optimized to provide the best fit.

2.2.4. Sample Curing

The kinetic model with the highest correlation coefficient is used to generate different Stage 2 curing cycles. The goal is to optimize the total time for the curing cycle, with the limiting factors being the maximum conversion rate, the maximum heating, and maximum temperature. The maximum heating rate used in this study is 5 K/min and the maximum temperature is 220 °C due to the physical limitations of the oven. All curing cycles start at room temperature. A DKN 612C programmable convection oven from Yamato Scientific America Inc. is used to cure test samples with the newly developed temperature cycles.

2.2.5. Dynamic Mechanical Analysis (DMA)

The DMA measurements are performed on Stage 2 samples using a NETSCH GABO Eplexor with a 500 N load cell and a 20 mm three-point bending fixture. The sample dimensions are 40 mm x 12 mm x 2 mm and are manufactured with the DLS process. The resin composition and process parameters are identical during manufacturing for all of the samples. A temperature sweep is conducted from 40 °C to 200 °C with a heating rate of 2 K/min. A static strain of 0.20 % and dynamic sinusoidal strain of 0.15 % of the sample thickness is applied at a frequency of 10 Hz. In preliminary tests, this deformation was found to be within the linear viscoelastic region of the material. The glass transition temperature is indicated by the temperature at the peak loss modulus, E''.

2.2.6. Tensile Testing

Once the optimized curing cycle is identified and validated using DMA, eight Stage 2 samples cured under the new temperature cycle and original temperature cycle are tested in tensile loading. The samples are manufactured using the DLS process following geometry for Type V specimen according the ASTM D638 [38]. The tensile tests are performed on an Instron 5967

universal testing machine using a 30 kN load cell. A loading rate of 1 mm/min is used and the ultimate tensile strength is recorded. Due to the small geometry of the Type V specimen limiting the placement of an extensometer, only the cross-head displacement is recorded.

2.3. Results

2.3.1. Differential Scanning Calorimetry (DSC)

The different exothermic heat flows at the defined heating rates are displayed in Figure 2.3. At all heating rates, a complex, multi-step reaction is clearly visible from the multiple peaks in the DSC signal. From Figure 2.3 it is possible to observe that the peak reaction temperature shifts to higher temperatures for faster heating rates as described previously. A second reaction peak also becomes more clearly visible near 150 °C for the higher heating rates. The small inflection of the curve near 250 °C may possibly indicate a third reaction step. Finally, the measured correlation of the degree of cure and the glass transition temperature during the second stage thermal curing process is shown in Figure 2.4.



Figure 2.3: DSC signal at different heating rates for the UV cured EPX 82 samples.



Figure 2.4: Correlation of the degree of thermal conversion and the glass transition temperature of the UV cured EPX 82 during the second-stage curing process.

From Figure 2.4, it is apparent that the glass transition temperature increases with a higher degree of thermal stage conversion. A more exact relationship between glass transition temperature and the degree of conversion can be described with the Di Benedetto relationship [39]:

$$T_g = \frac{\lambda \cdot \alpha \cdot (T_{g,1} - T_{g,0})}{1 - (1 - \lambda) \cdot \alpha} - T_{g,0}$$

$$(2.6)$$

where λ is a fitting parameter, $T_{g,0}$ is the initial glass transition temperature of the 3D-printed (Stage 1) part, and $T_{g,1}$ the glass transition temperature of the completely cured Stage 2 part. These parameters are shown in Figure 2.4 and are used to simulate the chemical reactions with diffusion control.

2.3.2. Kinetic Analysis

NETZSCH Kinetics Neo version 1.6.2 is used to simulate the chemical reaction. From the model-free Friedman analysis described previously, Figure 2.5 shows the activation energy through the curing reaction approximated by the slope of the isoconversional lines in increments of 0.01. Only a select number of isoconversional lines in Figure 2.5(a) are shown for clarity and the error bars indicate the standard deviation of the adjacent averaging used to fit the data in Figure 2.5(b). Clearly, the activation energy varies greatly with fractional conversion. During the first portion of the reaction ($\alpha < 0.2$), the activation energy decreases to a minimum of 50 kJ mol⁻¹. This could be due to several reasons, including autocatalytic effects and the viscosity of the reaction mixture dropping dramatically due to the increase in temperature. The increased mobility of the polymer network and increasing collision of molecular reaction groups would lead to a decrease in the overall activation energy. In a second stage of the reaction ($\alpha > 0.2$), the activation energy remains constant near 60 - 70 kJ mol⁻¹ before a rapid increase towards the end of the reaction (α > 0.6). This increase may indicate that the reaction is still reaction-rate controlled and is the determining factor in the overall reaction kinetics, but now must compete with the gelation of the material, resulting in a higher overall activation energy.



Figure 2.5: Model-free analysis showing the isoconversional lines (a) and the activation energy as a function of conversion (b).

Using this information, multiple reaction model predictions are generated, including different combinations of between two to four autocatalytic and nth order reaction steps. Once these predictions are generated, the software calculates the optimal model parameters to fit the experimental data. The highest correlation factor (0.9959) is a three-step linear model. The first step is a reaction of nth order with autocatalysis by-product (C_n), and the subsequent three steps
are reactions of nth order (F_n). The log (K_{diff}), C_1 , and C_2 parameters are for the active diffusion control as described previously in Equation 2.5.

The equation of the first step $(a \rightarrow b)$ is:

$$C_n = \frac{d_{a \to b}}{d_t} = A \cdot a^n \cdot (1 + m \cdot b) \cdot e^{\left(-\frac{E}{R \cdot T}\right)}$$
(2.7)

where the reaction is of order n and autocatalysis of order m.

The equations for the subsequent steps are:

$$F_n = \frac{d_{b \to c}}{d_t} = A \cdot b^n \cdot e^{\left(-\frac{E}{R \cdot T}\right)}$$

$$F_n = \frac{d_{c \to d}}{d_t} = A \cdot c^n \cdot e^{\left(-\frac{E}{R \cdot T}\right)}$$
(2.8)
(2.9)

The full model parameters of the reaction steps are summarized in Table 2.2.

	$\mathbf{a} \rightarrow \mathbf{b}$	$\mathbf{b} \rightarrow \mathbf{c}$	$\mathbf{c} \rightarrow \mathbf{d}$
\boldsymbol{E} (kJ mol ⁻¹)	64.53	85.63	166.81
log (A) (s ⁻¹)	3.684	7.465	16.15
n	0.696	0.899	1.291
m	1.263	-	-
$\log(K_{diff})$	-5.089	-4.778	5.000
<i>C</i> ₁	11.63	7.365	91.67
<i>C</i> ₂	100.0	0.00	100.00
Contribution:	0.756	0.135	0.110

Table 2.2: Parameters of the reaction steps for the full chemical reaction model.

As predicted from the Friedman analysis, the third step of the reaction requires the highest activation energy and the first reaction step the lowest. However, the first reaction step has the highest contribution of the total chemical reaction. With this model, the predictions for heat flow at the different heating rates are conducted. The prediction curves and the fit with the measured heating rates are shown in Figure 2.6. With the correlation factor of 0.9959, the different curves shown in Figure 2.6(a) match well. Figure 2.6(b) shows the prediction deviates in the initial portion of the reaction and becomes more accurate towards the end. The higher heating rates show a better fit, which can be explained by the difficulty in measuring slow reactions with DSC due to signal loss.



Figure 2.6: Comparison between the measured and model-fit conversion at different heating rates for the entire reaction (a) and a detailed view of the first half of the same reaction (b).

The goal of this study is to develop an optimized thermal curing cycle (Stage 2) for the 3D printed EPX 82. The original thermal curing cycle is a nine-step curing cycle up to 220 °C, requiring 750 minutes to complete. With the developed chemical reaction model described in Equation 2.7 - 2.9, the maximum conversion rate of this original cycle is calculated to be 0.6 %/min. This conversion rate and a maximum heating rate of 1 K/min are the two main parameters

for the simulation. A variation in maximum conversion rates (MCR) from 0.3, 0.6, 1.2 and 2.4 %/min is done to determine the influence of conversion rate on the final processing time. The influence of the maximum heating rate (MHR) is simulated at two levels of 1 K/min and 5 K/min. The predicted temperature cycles for the different boundary conditions are shown in Figure 2.7.



Figure 2.7: Different thermal-stage curing cycles with varying maximum conversion rate (MCR) and maximum heating rate (MHR) boundary conditions.

2.3.3. Dynamic Mechanical Analysis (DMA)

The different thermal curing cycles are programmed in the convection oven and two samples for each cycle are cured for DMA tests. Figure 2.8 shows the storage modulus (E') and loss modulus (E'') of the samples cured with different curing cycles in the performed temperature sweep. To get a better resolution of the glass transition temperature (T_g) , only the temperatures from 100 °C to 200 °C are shown in the graphs.

The results in Figure 2.8 show that the mechanical properties over the tested range are influenced by the different curing cycles. These differences can be seen in the T_g indicated by both the E' onset temperature, where the storage modulus first begins to decline, and in the peak of the loss modulus E'' [40].



Figure 2.8: E' and E'' of EPX 82 samples cured with different maximum conversion rate (MCR) and maximum heating rate (MHR) boundary conditions.

The samples cured with the highest maximum conversion rate and highest maximum heating rate (MCR 2.4 / MHR 5.0) are characterized by the lowest T_g at 146 °C. All remaining samples were closely grouped, with the highest T_g of 158 °C appearing in the curing cycle with the lowest maximum conversion rate and lowest maximum heating rate (MCR 0.3 / MHR 1.0). In comparison to the original cycle, which has a maximum conversion rate of 0.6 %/min and a maximum heating of 1 K/min, two significantly shorter cycles, MCR 0.6 / MHR 5.0 and MCR 1.2 / MHR 1.0, result in the same T_g at 154 °C. The fastest of these cycles is the MCR 0.6 / MHR 5.0 with a total curing time of 202 minutes.

2.3.4. Tensile Testing

The results of the tensile tests are shown in Figure 2.9 for the original curing cycle and the best cycle as determined by the glass transition temperature analysis – MCR 0.6 / MHR 5.0. The ultimate tensile strength is nearly identical for tensile samples cured using both the original and optimized cycles, with an average of 81.33 MPa and 81.51 MPa, respectively. These averages are within the reported value for EPX 82 when considering the standard deviation (Table 2.3). Samples cured with the original cycle may show a slightly higher extension at break, however, this deviation is small (< 1 mm) and could partially be due to slippage in the loading train since only the cross-head displacement could be measured with the Type V geometry.



Figure 2.9: The results of the tension tests showing the tensile stress as a function of cross-head extension for the original curing cycle (a) and the optimized curing cycle (b).

Table 2.3: Final properties of the original and optimized second-stage curing cycle for EPX 82.

Temperature Cycle	<i>T</i> _g (°C)	Ultimate Tensile Strength (MPa)
Original	154	Mean: 81.33 SD: 0.91
MCR 0.6 / MHR 5.0	154	Mean: 81.51 SD: 0.41

2.4. Conclusions

It is possible to measure the thermal curing reaction of the epoxy-based EPX 82 resin in the DLS process using DSC. The DSC curves of the EPX 82 resin during the thermal DLS process show a complex, multi-step reaction. A three-step reaction model was developed with a correlation coefficient is 0.9959. Diffusion control was considered in reaction model by including the Rabinowitch equation to calculate the reaction rate and the Di Benedetto relationship to represent the glass transition temperature as a function of conversion.

NETZSCH Kinetics Neo enabled a simple and fast development and control of chemical reaction models. It was possible to predict curing under different isothermal or non-isothermal conditions with defined boundary conditions (maximum conversion rate and maximum heating rate). Thermal curing cycles with these different boundary conditions were developed and used to manufacture DMA and tensile test specimen. These studies show that it is possible to reduce the second-stage curing time by more than 9 hours, or 73 % (Figure 2.10), with a maximum conversion rate of 0.6 %/min and a maximum heating rate of 5 K/min without a significant decrease in the mechanical properties or the glass transition temperature. This curing cycle was determined to be the optimal balance between processing time and material properties for EPX 82.



Figure 2.10: A 73% time reduction between the original and the optimized second-stage cure.

3. Evaluation of Single-Lap and Block Shear Test Methods in Adhesively Bonded Composite Joints

Measuring the bonding strength is essential to evaluating the process of co-curing 3D printed dual-cure materials with pre-impregnated fiber reinforcement. The interfaces of the integrated assembly must have sufficient mechanical properties to withstand the loading conditions experienced in structural applications. One of the most common techniques for evaluating bond strength is the lap shear test, however, standard single-lap shear geometries introduce complex stresses in the test specimen. Adhesive bonds are expected to perform in a state of primarily shear stress, but single-lap shear joints give rise to significant peeling stresses which, under significant loads, can cause the bonded fiber reinforcement layers to delaminate. The results of these tests and their failure modes must be carefully considered. The following chapter discusses the methods used to evaluate bonds in composite structures, compares the proposed process using a 3D printed adhesive to more traditional bonds, and suggests an alternative test method for more reliable results. The chapter is based on the research "Evaluation of single-lap and block shear test methods in adhesively bonded composite joints" published in *Journal of Composites Science*, Vol. 5, Issue 27 (2021) [41].

3.1. Introduction

As designers and engineers continue to push the boundaries of high-performance design, fiber reinforced plastics (FRP) are increasingly finding use in structural applications due to their light weight and superior mechanical properties. Many of these applications, especially in the aerospace and automotive industries, require geometrical complexity, multiple components, and multiple materials. These requirements lead to a need for assembly and joining elements during manufacturing – typically mechanical fasteners or adhesives. Adhesive bonding is the generally preferred technique when manufacturing FRP structures for a multitude of reasons. Unlike mechanical fasteners, adhesive bonding does not require material removal, which reduces stress concentrations and stress cracking introduced by the drilling and installation of fasteners. The installation of mechanical fasteners may lead to additional problems of uneven load distribution and stress concentrations at the threads [42], and slight pitch differences must be incorporated to improve fatigue strength and prevent loosening of the fastener [43]. Adhesive bonding also avoids a weight penalty that is incurred by mechanical fasteners, better supporting the goal of a lightweight design, and galvanic corrosion is minimized, which can be responsible for more than 20% of the maintenance costs in aerospace and automotive applications [3,10,11].

Adhesive bonds are designed to perform primarily in a state of shear, where the forces act parallel to the cross-section of the adhesive in opposite directions of its plane [44]. Shear testing is used to determine the maximum loads that a bonded component can resist when designed accordingly. In these tests, shear forces are applied through torsion, tension, or compression. Tension shear testing is among the most commonly used due to the simple test geometry, unlike torsion shear testing, which requires more complex sample geometry and manufacturing processes. Tensile single-lap shear joints are a widely used and cited test in literature for comparing adhesion properties. One challenge presented with this test is the complex loading conditions experienced at the adhesive-adherend interface, which has been well-reported to have a significant impact on the results, potentially leading to incorrect conclusions regarding the strength of the studied bond [45,46].

Contributing to this challenge with FRP single-lap shear tests is the uneven deformation and shear stress in the adhesive. The tensile stress in the adherend decreases along the overlap from a maximum at the start of the overlap nearest the edge where the load is applied, to zero stress at the far edge. Thus, the tensile strain at the adhesive-adherend interface must also decrease progressively along the joint length, leading to the distorted deformation as seen in Figure 3.1. This effect is known as differential shear and causes the shear stress in the adhesive to concentrate at the overlap edges under high loads [47].



Figure 3.1: Schematic lap shear specimen at low loads and no adhesive elongation (top), intermediate loads with even adhesive elongation and shear stress (center), and at high loads with uneven adhesive elongation and shear stress (bottom).

Another complication with single-lap shear joints is the eccentricity in the load path, which causes bending and normal forces in the adhesive zone, referred to as peeling forces (Figure 3.2). In the case of a joint with metal adherends, these forces would result in adhesive peeling. However, with FRP adherends the inter-laminar tensile strength is significantly lower than the peel strength of structural adhesives, and these peel forces often lead to failure caused by the delamination of the composite fiber layers [48]. As an approach to overcome the drawbacks of single-lap shear testing, double-lap shear joints have been used. Although the bending moment is minimized, it has been found that adherends still experience internal bending [49,50]. Because of these effects, the

failure observed in FRP lap shear testing is rarely associated with the failure of the adhesive in shear.



Figure 3.2: Representation of lap shear bending due to eccentricity in the load path.

Block shear testing is an alternative to single-lap shear testing, which essentially removes the eccentricity and subsequent bending moment. The specimen geometry for block shear is similar to single-lap shear, differing only in the shorter length and increased thickness of the adherends. In contrast to the single-lap shear tests, the shear forces are applied through compression using a specialized fixture. The standard ASTM geometry and test configuration for block shear tests and single-lap shear tests are compared in Figure 3.3 [51,52].

The aim of this study is to evaluate the differences in stress state by modifying existing models for single-lap shear tests to the block shear test. Two beam model solutions for adhesively bonded single-lap joints, one proposed by Goland and Reissner [53], and a modification by Hart-Smith [54] are introduced. These models are used as an analytical comparison for the block shear test geometry and boundary conditions. Finite element models are also used to provide a numerical comparison for the two test conditions. Finally, FRP samples are manufactured and tested in single-lap shear and block shear for an experimental comparison using three different joining materials.



Figure 3.3: Dimensions and test configuration for (**a**) a single-lap shear specimen according to ASTM D5868 and (**b**) a block shear specimen according the ASTM D4501.

3.2. Analytical Models for Adhesively Bonded Joints

When the lap shear geometry is subjected to tension, the bending moment provides the most significant contribution to the stress magnitude. In order to accurately predict the adhesive stresses in the overlap edge region, the edge moment must be determined. The following analyses of bonded joints are based on Kirchhoff-Love plate theory for thin plates in cylindrical bending [55], with the governing equation:

$$\frac{d^2w}{dx^2} = -\frac{M}{E*I} = -\frac{M}{D}$$
(3.1)

where *w* is the lateral deflection and *D* defines the flexural rigidity with the modulus, *E* and polar moment of inertia, *J*. The moment per unit width at the ends of the adherend overlap, M_0 , in this beam model is defined as:

$$M_0 = \left(\frac{Pt}{2}\right)k\tag{3.2}$$

where P is the applied tensile load per unit width, t is the adherend thickness, and k is a bendingmoment factor. The bending moment factor, k, is used to represent the edge-bending moment and provide a simplified insight into the stress state at the edge.

Goland and Reissner (GR) were the first to analyze a single-lap joint considering the rotation of the adherends and brought attention to the impact these bending deflections have on the peel and shear stresses in the adhesive layer [53]. Their original analysis modelled the lap joint as a single, homogeneous beam as shown in the schematic model in Figure 3.4 with key terms and coordinate systems defined. Their original analysis neglected adhesive thickness ($t_a = 0$) and boundary conditions used to solve the second order differential equation for deflection (Equation 3.1) are as follows:

I.
$$w_1(x_1 = 0) = 0$$

II.
$$w_1(x_1 = l) = w_2(x_2 = -c)$$

III.
$$\frac{dw_1(x_1=l)}{dx_1} = \frac{dw_2(x_2=-c)}{dx_2}$$

IV.
$$w_2(x_2 = 0) = 0$$

giving the solution:

$$M_0 = \left(\frac{Pt}{2}\right) \frac{1}{1 + 2\sqrt{2} \tanh\left(\frac{\xi c}{2\sqrt{2}}\right)}$$
(3.3)

where *c* is the overlap length from the centerline of the joint, $\xi^2 = \frac{P}{D}$, and D is the unit-width adherend bending stiffness:

$$D = \left(\frac{E}{1 - \nu^2}\right) \frac{t^3}{12}$$
(3.4)

This solution takes the form of Equation 3.2, where the bending-moment factor is defined by Goland and Reissner (k_{GR}):

$$k_{GR} = \frac{1}{1 + 2\sqrt{2} \tanh\left(\frac{\xi c}{2\sqrt{2}}\right)}$$
(3.5)



Figure 3.4: The reference system and critical terms used to model the lap shear joint. Origin for the coordinate system (1) is located at the center of the upper adherend and origin for coordinate system (2) is located at the centroid of the joint.

Goland and Reissner's derivation assumes that the overlap region is deformed as a single block with a uniform stiffness. Hart-Smith (HS) suggested an improvement by considering adhesive plasticity and including the effect of adherend thickness, t_a [54]. The boundary conditions used in the Hart-Smith analysis considered joint deflection only in the unbonded section of the adherend:

I.
$$w_1(x_1 = l) = w_2(x_2 = -c)$$

II. $\frac{dw_1(x_1=l)}{dx_1} = \frac{dw_2(x_2=-c)}{dx_2}$
III. $\frac{d^2w_1(x_1=l)}{dx_1^2} = \frac{d^2w_2(x_2=-c)}{dx_2^2}$
IV. $\frac{d^4w_1(x_1=l)}{dx_1^4} = \frac{d^4w_2(x_2=-c)}{dx_2^4} = \frac{t+t_a}{2D}\frac{d\tau(x_2=-c)}{dx_2}$

which, when reducing non-significant terms, gives the full expression for edge moment, M_0 :

$$M_{0} = P\left(\frac{t+t_{a}}{2}\right) \frac{1 + \frac{t_{a}}{t}}{1 + \frac{\xi c}{\tanh(\xi l)} + \frac{\xi^{2}c^{2}}{6}}$$
(3.6)

where the edge bending-moment factor is defined by Hart-Smith (k_{HS}) as:

$$k_{HS} = \frac{1 + \frac{t_a}{t}}{1 + \frac{\xi c}{\tanh(\xi l)} + \frac{\xi^2 c^2}{6}}$$
(3.7)

For large ξl , this expression can be simplified by $tanh(\xi l) \approx 1$, and Equation 3.7 becomes:

$$k_{HS} = \frac{1 + \frac{t_a}{t}}{1 + \xi c + \frac{\xi^2 c^2}{6}}$$
(3.8)

Considering next the block shear specimen, the conditions of the experimental set-up constrict the faces of the adherends with the compression fixture. This essentially eliminates any of the out-of-plane bending and reduces the eccentricity to zero. The two analytical models for single-lap shear are compared to block shear in Figure 3.5. The eccentricity decreases for both the GR and HS models with an increase in the non-dimensional overlap term ξc , though only the HS model reduces to zero, and is more accurate when observing eccentricity in bonded materials where the adherend has a much higher stiffness than the adhesive.

It is important to note that several corrections have been developed for the GR and HS models, including those by Oplinger [56], and more recently by Li and Lee-Sullivan [57]. While the variations of these models provide improved solutions, the original GR and HS models continue to be frequently cited in literature and provide a satisfactory representation of the edge bending-moment for the purposes of this study.



Figure 3.5: Edge bending-moment factor k for single-lap shear geometry as determined by Goland and Reissner and Hart-Smith compared to block shear.

3.3. Finite Element Model

A finite element analysis is performed using the commercial software package ABAQUS to study the shear and peel stresses at the bondline in both single-lap shear and block shear tests. To simplify the analysis, a 2D model is determined to be sufficient to predict the shear and peeling stresses along the length of the bondline.

3.3.1. Single-Lap Shear

The model is generated with dimensions as per ASTM D5868 [51]. Second order plane strain elements (CPE8R) are used to mesh the adherends and the adhesive material with four elements in the through-thickness direction to achieve convergence. This results in an element edge length of 0.25 mm. The bonding between the adhesive and adherends is assumed to be perfect, and a tie-constraint is imposed between the two as shown in Figure 3.6.



Figure 3.6: Single-lap shear modeled using plane strain elements in ABAQUS. A tie-constraint simulates a perfect bond between the adherend and adhesive.

A parametric study is performed to understand the effect of moduli of the adherend and adhesive on the peel and shear stresses at the bondline. The ratio between the Young's modulus of the adherend and the adhesive, or E_R is used as a metric to study this. The adhesive is assigned a typical Young's modulus of 3.0 GPa [44] and the adherends are assigned Young's modulus values of 32.8 GPa [58] for a representative glass fiber composite and 145 GPa and 230 GPa for a lowmodulus and high-modulus carbon fiber composite, respectively [59]. The resulting modulus ratio values were approximated as $E_R = \{10, 50, 80\}$. The ends of both adherends are fixed in the 2direction, with one adherend fixed in the 1- direction and the other adherend having a force of P = 1000 N applied to the end face. Tab geometries are added to the ends of the adherends to replicate the ASTM test procedure and maintain in-line displacement. A local coordinate system is generated to follow the nodal displacements where the origin is centered in the adhesive and the 1- direction was along the bondline, instead of the global 1- or loading direction. This allows for the generation of shear (S₁₂) and peel (S₂₂) stresses along the bondline.

3.3.2. Block Shear

Block shear analysis is set up similar to the single-lap shear analysis as described above. The geometry is modelled based on the suggestions from ASTM D4501 [52]. Additionally, steel blocks to apply the shear force are added as shown in Figure 3.7 and a contact condition is established between the steel plates and the adherends. It is important to note that the same force P = 1000 N is applied for block shear while the overlap area is half that compared to single-lap shear test.



Figure 3.7: Block shear test modeled using plane strain elements in ABAQUS. Contact condition is applied between the adherend and the rigid steel loading plates.

3.4. Experimental Methods

3.4.1. Materials

The FRP material used in this study is a woven 7781 E-glass fiber reinforced preimpregnated material, NB-EP4030 D, produced by Mitsubishi. This is a low-temperature curing epoxy resin which is processed at 135 ± 15 °C. The shear test specimens were manufactured with two different epoxy-based resins used for the adhesives: Scotch-Weld DP190 (3M) and EPX 82 (Carbon). The NB-EP4030 D reinforcement material used for the adherends is also used as a control in the same test geometry. The properties for these materials are listed in Table 3.1.

Material Properties	Value	Unit
NB4030-D [58]		
Tensile Modulus	32.8	GPa
Tensile Strength	2370	MPa
Elongation at break	-	%
Glass Transition Temperature	130	°C
Fiber Volume Content	60	%
DP190 [60]		
Tensile Modulus	-	GPa
Tensile Strength	24.13	MPa
Elongation at Break	30	%
Glass Transition Temperature	20	°C
EPX 82 [37]		
Tensile Modulus	2.8	GPa
Tensile Strength	82	MPa
Elongation at break	5.9	%
Glass Transition Temperature	150 - 155	°C

Table 3.1: Properties for materials used in this study.

3.4.2. Manufacturing

Both single-lap shear and block shear test samples are manufactured using the same process for each of the adhesive materials. For samples using the DP190 epoxy, the adhesive is applied in a secondary bonding process. First, the NB-EP4030 D laminate stack is first cured using a 2 $^{\circ}C$ / minute heating ramp to 135 $^{\circ}C$, followed by a 60 min. hold under vacuum pressure (100 kPa). A 600-grit sandpaper is used to prepare the composite adherend surface for bonding, and is followed

by a solvent wipe using isopropyl alcohol. An adhesive layer thickness of 0.76 mm is fixed using spacers and uniform pressure of 200 kPa is applied for 24 hours.

EPX 82 is used to co-cure the composite adherends in a single thermal curing stage. This material is a dual-curing, additive manufactured epoxy-acrylate. The EPX 82 joints are first additively manufactured to the correct thickness of 0.76 mm using ultraviolet light. These bonding elements are then placed between the pre-impregnated laminate stack in a mold and cured under vacuum pressure using the EP4030 cycle. The samples with the EP4030 composite material as the adhesive layer are manufactured in the same way.

For single-lap shear testing, the specimen geometry are used as specified in ASTM D5868 [51] and depicted in Figure 3.9 (a). NEMA Grade G-10 glass epoxy laminate alignment tabs are bonded onto the specimens to ensure the centering of the specimens between the tensile testing grips. An Instron testing machine with a 30 kN load cell is used to apply a loading rate of 13 mm/minute. Eight specimens are tested for each bonding material used and the test strength, *S*, is calculated from the measured maximum tensile load *F* by:

$$S = \frac{F}{w \, l} \tag{3.9}$$

where w and l are the bond width and length, respectively.

The block shear test specimens are cut to dimensions as specified by ASTM D4501 [52]. An Instron testing machine is also used to characterize the strength of the bonded samples with a 30 kN load cell. Block shear testing requires a special fixture to clamp the sample in place, reducing the peeling effects which occur during single-lap shear tests. The block shear sample is placed in one half of the fixture, referred to as the adapter plate. A toggle clamp is then used to apply compression to the sample and prevent slipping during testing. Tension is applied to one side of the test fixture (shearing tool), while the other side remains static. Eight samples using each material for the adhesive are sheared apart until failure using a testing speed of 1.26 mm/minute. The failure modes are recorded and the test strength is calculated using Equation 3.9. The final manufactured samples are shown in Figure 3.8, and the test setup is shown in Figure 3.9.



Figure 3.8: Manufactured (a) FRP single-lap shear specimen and (b) block shear specimen.



Figure 3.9: Tensile test setup for (a) single-lap shear specimen and (b) a block shear specimen.

3.5. Results

3.5.1. Stress Analysis

The results of the finite element analysis confirm what was predicted with the discussion of analytical models in Section 3.2. Shear and peel stresses for the single-lap shear geometry are shown in Figure 3.10 comparing different adherend-adhesive modulus ratios (E_R). Shear stresses at the bondline edge are higher than at the center due to the differential shear as discussed previously. The peel stresses are also significantly higher at the bondline edge than in the center of the bond. This effect is what is responsible for the delamination in FRP adherends, and demonstrates the difficulty with making conclusions about bond quality in such joints using this geometry. Trends are also visible with increasing E_R . A higher adherend modulus reduces edgebending and produces a more consistent shear stress along the bondline and reduces the peel stress at the edges.



Figure 3.10: Shear stress and peel stress distributions along the bondline in a single-lap shear geometry for different modulus ratios, E_R .

An identical analysis for the block shear geometry is shown in Figure 3.11. In block shear, the shear stress is still higher on the bondline edge for the lowest modulus ratio, but because the overlap length recommended by the ASTM standard for block shear is half that for the single-lap shear geometry, this effect is significantly reduced and a more consistent stress state is observed over the length of the bondline. As shown in Figure 3.11 (right), a shorter overlap length can be used because the peel stress does not play a role in block shear tests. Throughout the entire bondline length, the peel stresses are negative due to the compression of the block shear test fixture. This should prevent any premature delamination in the FRP adherend and give more reliable test values that can be used for design purposes. Figure 3.12 provides a comparison of the difference in these test geometries, showing the ratio of peel stress to shear stress. The peel stress at the bondline edge in single-lap shear is clearly more influential on the measured joint strength than in block shear.



Figure 3.11: Shear stress and peel stress distributions along the bondline in a block shear geometry for different modulus ratios, E_R .



Figure 3.12: Comparison of the ratio of peel stress to shear stress for single-lap shear (SLS) and block shear (BS) geometries along the bondline.

3.5.2. Shear Testing

The results of the shear tests are shown in Figure 3.13 with error bars indicating the standard deviation over eight samples. For these, the NB-EP4030 material from Mitsubishi is used for the adherend. The DP190 adhesive has the highest average single-lap shear strength, but also the highest standard deviation. This indicates issues with consistent application of adhesives in secondary bonding applications. EPX 82, the 3D printed adhesive, demonstrates a failure strength within one standard deviation of the commercial adhesive comparison. Both adhesive materials outperform the standard single-lap shear joint with the NB-EP4030 bonded directly to itself. This is due to the nature of the single-lap shear testing and the peeling stresses inherent in the test geometry. While combined loading conditions with normal stresses are useful and common in real applications, these results do not clearly indicate shear strength.

Block shear testing is subsequently conducted to evaluate a primarily shear loading situation. The same adhesive materials are used for comparison in this test. The block shear tests show that the EPX 82 performs well in comparison with the commercial DP190 adhesive and is within one standard deviation of the bonding strength of the adherends themselves. Results for all

combinations are at least a factor of two higher than the measured single-lap shear strengths, indicating that the test configuration plays a significant role in the calculated bonding strength using Equation 3.9.



Figure 3.13: Comparison between single-lap shear (SLS) and block shear (BS) test results for the three different bonding materials.

The results indicate a clear difference in the measured single-lap shear and block shear strength. While the results of single-lap shear tests suggest the commercial adhesive (DP190) provides the best bond quality, the results of block shear tests contradict these findings with the highest average strength demonstrated by direct prepreg-prepreg bonding. The differences between the two loading conditions explained in Chapter 3.2.1 and demonstrated in Chapter 3.5.1 provide insight into these results. Differences between the two test configurations are further illustrated by evaluating the failure modes (Figure 3.14). All single-lap shear specimens failed due to delamination of the composite adherend regardless of adhesive material. In contrast, all block shear specimens failed in a cohesive mode, better indicating the true adhesive strength.



Figure 3.14: Demonstration of (**a**) a typical delamination failure in single-lap shear samples and (**b**) a cohesive failure in block shear samples.

3.6. Conclusions

The single-lap shear test is a widely used method to measure the performance of adhesives and surface treatments. A significant challenge with this method is acquiring consistent and reliable engineering data due to complex stress states caused by the sample geometry and loading condition. Analytical models, such as those proposed by Goland and Reissner or Hart-Smith, demonstrate the effect of the edge-bending moment for single-lap shear in tension. The same analysis shows how the block shear test configuration effectively eliminates bending in the overlap and provide a better method for measuring shear strength.

Finite element analysis confirms the analytical models, showing the peel stresses are nearly equivalent in magnitude to the shear stresses at the bondline edge in the single-lap shear configuration. In contrast, the shear stresses are dominant in block shear and peel stresses are all in compression due to the nature of the test fixture. The higher peel stresses in single-lap shear samples result in a much lower testing strength due to premature failure caused by delamination of the composite adherend. Block shear samples failed at test strengths over 100% higher than the single-lap shear samples, indicating the challenges of using single-lap shear geometry for acquiring reliable engineering data for pure-shear strength.

The analytical models suggest that the eccentricity, and therefore the peeling stress, can be reduced in lap shear testing by increasing the relative overlap length, and the practical improvements of modifying the current test standards for longer overlaps could be a compelling future study. However, if peeling stresses and adherend delamination are of interest, single-lap shear provides a valid test for comparing the strength of the adhesive to the interlaminar strength of the composite. While both test configurations may have their own merits in evaluating adhesive bonds in composite structures, which one to use will depend on which stresses will be most significant in the final application.

4. A Model for Modulus Development of Dual-Cure Resin Systems

Dual-curing thermoset systems with a thermally activated reaction in the second stage experience temperatures exceeding the glass transition temperature of the intermediate product during processing. This leads to a non-linear development of the elastic modulus, with an observable softening effect. Prior chapters discuss how an external force is used to consolidate the 3D printed component with the pre-impregnated fiber reinforcement. These forces can result in large structural deformations during curing due to the softening of the intermediate 3D printed component. Understanding how the mechanical properties of the 3D printed component develop during the thermal cure is essential to creating a robust manufacturing process for the hybrid composite structures. The following chapter describes a new phenomenological model for the cure-dependent modulus for materials undergoing a two-stage curing reaction. Additional applications and a processing guideline are also discussed. This chapter is based on the research "A model for modulus development of dual-cure resin systems" published in *Polymer Engineering and Science*, Vol. 61, Issue 3 (2020) [61].

4.1. Introduction

Dual-curing resin systems use a combination of two different polymerization processes, either in simultaneous or sequential order. These polymerization processes can be activated by similar or dissimilar stimuli, such as a combination of UV and temperature (thermal energy) or the combination of two different temperatures [62]. Dual-curing resin systems combining an ultraviolet curing composition with a thermal curing composition have been widely developed and commercialized over the last two decades. Common applications include adhesives for optical component bonding and display panel assembly [63,64], transparent coatings [65,66], and as dental resin cements and restoratives [67,68]. These applications benefit from the rapid UV cure, reducing initial processing times to a few seconds or less, while the thermal curing systems provide the required final mechanical properties. A more recent application has been found in additive manufacturing, where ultraviolet light in a vat photopolymerization process such as stereolithography (SLA), digital light processing (DLP), or digital light synthesis (DLS) is used to form the initial geometry. These parts are then removed from the build platform and placed in an oven to initiate thermal curing, allowing high performance materials to be used in these processes [20,69-71].

The UV composition of these resin systems generally contains an acrylate monomer, acrylate oligomer and photoinitiator, while the thermal curing composition is a resin with desirable final properties, such as epoxy or polyurethane and a suitable curing agent. During the initial UV curing, an interpenetrating polymer network (IPN) is rapidly formed and a weak intermediate structure is formed [72,73]. This intermediate structure is then fully cured in a second, thermally activated stage, producing the final monolithic properties required for the end application. While many researchers have evaluated and characterized the reaction kinetics for dual-curing reactions [70,71,74-78] and measured modulus changes between the discrete reaction steps [79], the development of the modulus and mechanical properties during processing is not well understood.

The two separate curing reactions result in different glass transition temperatures (T_g) before and after the thermal curing process. This leads to unique behavior in dual-cure resins, where the temperatures used for the thermal curing process exceed the glass transition temperature of the IPN, leading to a decrease in the modulus and an observable softening. This differs from

traditional thermosetting resins which are processed in a single thermal stage to the final mechanical properties. As a simplification, traditional thermosetting resins can be described as a viscous liquid using chemorheological models until an approximate degree of cure of 5% is reached [80,81]. The modulus then increases linearly until some point around 80% cure where it becomes a rigid solid [82-84]. A general comparison of the modulus development during processing of dual-curing and traditional thermoset materials is demonstrated in Figure 4.1.



Figure 4.1: Simplified representations of modulus development during curing for traditional thermosetting material (left) and dual-cure resin system with UV and thermal activated stages (right).

Due to dramatic decreases in modulus during the thermal curing stage, dual-cure resin systems can experience critical deformations, such as a reduction in bondline thickness during adhesive application or overhang deflections and collapsing structures in additive manufactured parts. The modulus is a factor of the degree of cure of the material and the temperature that the material is being processed at. Because both the degree of cure and the processing temperature are changing simultaneously during the thermal curing stage, predicting the modulus decrease and resulting part failure is difficult. A new method to track and predict modulus development during thermal cure is proposed. By measuring the T_g at different stages of cure, the effect can be reduced to a single variable ΔT .

The proposed model for the modulus as a function of the difference between glass transition temperature and operating temperature is defined as:

$$E = \frac{E_G - E_R}{1 + e^{k\Delta T}} + E_R$$
(4.1)

where E_G is the upper modulus plateau in the glassy-region, E_R is the lower modulus plateau in the rubbery-region, k is the gain parameter to control the shape of the exponential curve, and ΔT is a variable of temperature defined as:

$$\Delta T = (T - T_g) \tag{4.2}$$

where T is the processing temperature during the thermal curing stage and T_g is the glass transition temperature at a specified stage in the thermal curing process.

Equation 4.1 can be modified to relate the modulus as a function of degree of cure (*c*) using the empirical relationship defined by DiBenedetto [85], which provides a simple relationship between T_g and *c*. A form of the DiBenedetto equation introduced by Pascault and Williams [86] derived the relationship:

$$T_g = \frac{\lambda \cdot c \cdot (T_{g1} - T_{g0})}{1 - (1 - \lambda) \cdot c} + T_{g0}$$
(4.3)

where λ is a structure dependent parameter related to the ratio of isobaric heat capacities of the fully reacted and initial system ($\lambda \le 1$), and T_{g1} and T_{g0} are the glass transition temperatures of

the completely reacted system and the initial system, respectively. Combining Equations 4.1-4.3 gives the fully defined relationship of modulus during thermal curing:

$$E = \frac{E_G - E_R}{1 + e^{k \left[T - \left(\frac{\lambda \cdot c \cdot (T_{g_1} - T_{g_0})}{1 - (1 - \lambda) \cdot c} + T_{g_0}\right)\right]}} + E_R$$
(4.4)

4.2. Experimental Methods

4.2.1. Materials

This work uses EPX 82, a dual-curing system containing epoxy and urethane acrylate used for additive manufacturing and produced by Carbon, Inc. (Redwood, CA). The two-part resin, with the A and B components shown in Table 4.1, is combined using a 1:1 static mixing nozzle. The ure than a acrylate network is first formed by UV irradiation during the digital light synthesis (DLS) additive manufacturing process [17]. A thermal reaction is used to complete the cure of the epoxy resin (Bisphenol A-epichlorohydrin polymer), and a small fraction of epoxy acrylate oligomer (Bisphenol A-epichlorohydrin acrylate) with both epoxy and acrylate functionality on the same backbone chemically connects the two networks, reducing cracking and phase separation. A nonionic acrylic monomer (N,N-dimethylacrylamide) is a reactive diluent used to reduce viscosity and improve printing performance. The curing agents used in combination with the epoxy resin 3,3'-diaminodiphenyl sulfone and 4,4'-diaminodiphenyl sulfone. and 2,4,6are trimethylbenzoylphenyl phosphinate is the photoinitator. [87-89]

Part A [88]	Part B [89]		
Component	% wt	Component	% wt
Bisphenol A-epichlorohydrin polymer	25-75	Urethane acrylate	25-40
Bisphenol A-epichlorohydrin acrylate	10-30	N,N-Dimethylacrylamide	30-50
N,N-Dimethylacrylamide	5-15	3,3'-Diaminodiphenyl sulfone	5-15
2,4,6-Trimethylbenzoylphenyl phosphinate	< 2	4,4'-Diaminodiphenyl sulfone	5-15

 Table 4.1: Composition of EPX 82 resin.

4.2.2. Preparation of Samples

All of the parts produced with EPX 82 are manufactured using DLS with the machine default settings and a layer height of 100 μ m. The parts are subsequently removed from the build platform and cleaned to remove excess resin. The recommend cleaning processes involves using 99% dipropylene glycol methyl ether (DPM) as a solvent for removing the excess resin from the printed parts, limiting the solvent exposure to a maximum of four minutes. The parts are then rinsed with isopropyl alcohol (IPA) before the thermal curing process.

4.2.3. Thermal Analysis

The thermal curing reaction of the EPX 82 is measured using differential scanning calorimetry (DSC). The measurements are performed with a heat flux DSC 214 Polyma (NETZSCH, Germany) using nitrogen as a purge gas. Cylindrical EPX 82 samples are printed with a diameter of 2.5 mm, height of 2 mm, and a mass of 10 ± 1 mg. The UV-cured samples are refrigerated in sealed containers and shielded from UV-exposure until testing. Dynamic DSC measurements using multiple heating rates between 1-5 K/min were used to characterize the material in this study. A starting temperature of 0 °C is held for 10 minutes to ensure an equal

temperature of the sample. The chamber heats up to 330 °C with the chosen heating rate, and holds the maximum temperature before rapidly cooling. The heat of the exothermic reaction was calculated with a linear baseline, and the degree of thermal curing ($C_{Thermal}$) was determined by:

$$C_{Thermal} = \frac{\Delta H}{\Delta H_{Total}} \tag{4.5}$$

where ΔH is the exothermic energy released at any time during the thermal curing process, and ΔH_{Total} is the total thermal reaction enthalpy.

The glass transition temperature of the EPX 82 was then measured using dynamic DSC measurements with a heating rate of 10 K/min. A starting temperature of -20 °C was held for 30 minutes before heating to a maximum temperature of 200 °C. Measurements were conducted at various degrees of thermal conversion based on the full results from the previous kinetics study using the same material system in Chapter 2.

4.2.4. Mechanical Analysis

Cylindrical samples were additively manufactured with a diameter of 5.0 mm and height of 5.0 mm. The samples were thermally cured to four different levels (0%, 30%, 60%, and 100%) in order to achieve a range of values for ΔT as described in Equation 4.2. A GABO EPLEXOR dynamic mechanical analysis unit (NETZSCH, Germany) was used to measure the samples in compression using a transient test configuration. The samples were placed in a parallel plate compression fixture and heated to the desired testing temperature at a rate of 1 K/min. Samples tested at low temperatures were cooled to the target temperature and soaked for one minute for each degree below room temperature. A preload of 5 ± 0.1 N was applied to ensure full contact with the sample before the test began. The load was applied at a rate of 1 mm/min and measured

with a 500 N load cell. Strain is calculated as a percentage of sample height using the vertical displacement measured directly by the mechanical testing unit. Modulus values are then calculated from the load and strain data to a maximum of 0.25 % strain in order to minimize changes in the cross-sectional area and gage length.

4.3. Results

The glass transition temperature (T_g) as a function of the extent of thermal conversion is shown in Figure 4.2. A linear relationship is observed throughout the thermal conversion process and is described by the DiBenedetto parameters shown in Table 4.2. With the values of T_g , it is possible to fit the measured modulus values with the model described in Equations 4.1-4.4.



Figure 4.2: The glass transition temperature of the EPX 82 material as a function of thermal conversion.
Parameters	Value	Unit
T_{g0}	16.8	°C
T_{g1}	144.1	°C
λ	1.0	-

 Table 4.2:
 Calculated DiBenedetto parameters.

Based on the values of T_g at different stages of the thermal curing process, the ΔT value is calculated at each test temperature for the experimental modulus measurements. The experimental measurements for modulus at various processing temperatures and degrees of thermal conversion are shown in Figure 4.3. As expected, a decrease in the modulus for each set is observed, with the transition point occurring at increasing temperatures for more highly cured samples. Table 4.3 shows a summary of the test conditions, including the processing temperature (*T*) ranges for each set by thermal conversion ($C_{Thermal}$).

Set	C _{Thermal} (%)	T_g (°C)	<i>T</i> (°C)
1	100	144	50 - 230
2	60	94	5-170
3	30	55	-20 - 140
4	0	17	-20 - 110

 Table 4.3: Test conditions for modulus measurements.



Figure 4.3: The experimental data of measured modulus as a function of processing temperature *T* for different degrees of thermal conversion.

By plotting the results from Figure 4.3, but instead using the ΔT term from Equation 4.2 on the x-axis, the data sets shift and form a single overlapping curve as shown in Figure 4.4. A sigmoidal relationship is clearly visible with an inflection point near $\Delta T = 0$. This behavior is independent of degree of thermal conversion as demonstrated by the overlapping trend from the different data sets. For low values of ΔT , the modulus remains linear at a glassy plateau. As the test temperature approaches values near T_g , the modulus remains constant, followed by a sharp transition to the rubbery plateau region. The same experimental data is plotted with a model fit from Equation 4.1 in Figure 4.5. The parameters for the model are listed in Table 4.4.



Figure 4.4: The experimental data of measured modulus as a function of ΔT for different degrees of thermal conversion.



Figure 4.5: The experimental data of measured modulus as a function of ΔT with the proposed model fit.

Parameters	Value	Unit
k	0.545	-
E_{G}	1.48 x 10 ⁹	Pa
E_R	1.03 x 10 ⁷	Pa
R^2	0.9913	-

Table 4.4: Model fitting parameters for EPX 82.

Using this model, the decrease in modulus during initial temperature ramps can be predicted and tracked, providing valuable processing guidelines. An example of one potential processing guide is shown in Figure 4.6, which shows the calculated strain as a function of ΔT at constant uniaxial stress (or pressure) defined by the modulus model for the material used in this study. Each strain curve in Figure 6 is calculated by assuming a simplified Hookean relationship - σ/E , where σ is an applied uniaxial stress and *E* is the ΔT dependent modulus model described in Equation 4.1. With this graph, failure can be predicted in unsupported structures by defining a critical strain value, or an appropriate pressure can be determined for adhesive applications in order to achieve the specified final adhesive layer thickness.



Figure 4.6: A processing diagram showing strain as a function of ΔT at constant stress or pressure.

4.4. Conclusions

A phenomenological model is developed for describing the cure-dependent modulus for materials undergoing a two-stage curing reaction. The proposed model for tracking the modulus of dual-curing resin systems during the thermal curing stage is demonstrated for an epoxy-urethane acrylate resin system. It is shown that the model fits well with experimental data and the modulus can be described with a single variable, ΔT . This model allows for processing guidelines to assist in predicting deformation of these materials during the thermal curing process.

5. Application: Fiber-Reinforced Composite Sandwich Structures

A first application for the new process of manufacturing hybrid-composite structures is the creation of sandwich structures consisting of a 3D printed lattice structure integrated between fiber-reinforced facesheets. Multiple variations of lattice structures are designed and 3D printed using the DLS process and dual-curing resin. The lattice structures are only partially cured after the printing process and subsequently co-cured with pre-impregnated fiber reinforcement. The prior work to understand how the 3D printed structures soften and deform during the thermal curing stage is used to understand what external pressures can be applied for manufacturing without causing the lattice structures to collapse. After manufacturing, mechanical properties are evaluated through both compressive and flexural testing. The mechanical behavior indicates the viability of these hybrid lattice structures for high-stiffness panels in lightweight applications. Furthermore, the strength of the co-cured bond interface is shown to exceed the strength of the lattice core in bending and validates prior lap-shear testing. This chapter is based on the research "Fiber-reinforced composite sandwich structures by co-curing with additive manufactured epoxy lattices" published in *Journal of Composites Science*, Vol. 3, Issue 2, 53 (2019) [90].

5.1. Introduction

An enduring challenge in modern mechanical engineering is the design of lightweight components which are strong and highly integrated, meaning they fulfill several tasks. While currently most prevalent within the aerospace industry, more fields are now demanding materials and processes capable of fulfilling these requirements [91]. Particularly within the automotive industry, lightweight design is a key technology to meet stricter emission regulations, and to balance the shortcomings of today's alternative drive systems [92,93].

One common approach to these challenges is the use of composite sandwich structures. Such structures are made up of a low-density core and facesheets manufactured from high specific strength fiber-reinforced polymers (FRP). Foam cores, honeycombs, or folded cores are the most commonly used [94]. The elements of sandwich structures fulfill specific roles in typical bending applications. The facesheets can be subjected to either compression or tension loads, depending on which surface of the load they are located [95]. The core fulfills two primary roles. One, it spaces out the facesheets, thus increasing the second moment of area, which leads to increasing rigidity [96]. Due to the low density of the core material, this is accompanied by only a slight increase in mass. The core's second role is to carry the shear loads occurring under bending [96]. Overall, sandwich structures combine light weight and high mechanical properties. However, the design freedom of sandwich structures is limited, and manufacturing can be cumbersome. Furthermore, the integration of additional features, as well as the joining and assembly of sandwich structures, are significant constraints in traditional methods [96,97].

Emerging additive manufacturing (AM) technology allows for a potential solution, with nearly unrestricted design freedom and customization [15,98]. As such, geometries which were formerly impossible to manufacture are now moving into the focus of research [99,100]. One example of a geometrically complex design are lattice structures. These combine highly customizable geometry and low overall weight [101-103]. Thus, the utilization of additive manufactured lattice structures as core materials for sandwich structures can serve as an alternative for more traditional lightweight design strategies [99,104-106].

Lattice structures are an arrayed network of struts, which are connected at nodal points, and are made up of basic geometrical structures. These so-called "unit cells" are periodically or stochastically repeated in the desired directions of space. Frequently used types of unit cells are geometric primitives, as shown in Figure 1a, or surface-based geometries, as shown in Figure 5.1b. Figure 5.1c shows a lattice structure built up by a repetition of geometric primitives. In the examples shown, a simple geometry is chosen. However, arbitrarily complex geometries can be filled using unit cell-based lattice structures, enabling a multitude of design applications [100,102,103].



Figure 5.1: (a) Geometric primitives and (b) surface-based unit cells used in the generation of (c) lattice structures.

The properties of lattice structures are determined by three main factors: material, geometry, and relative density. While the material defines the basic properties, topology and geometric design influence the behavioral characteristic of the lattice. The relative density is the ratio of the density of the lattice structure, ρ_1 , compared to the density of the solid, ρ_s . It corresponds the properties of the lattice to the amount of void volume and thus characterizes the weight savings [100,102,103].

An important distinction for lattice structures is the differentiation in bending or stretch-dominated mechanical behavior. Bending-dominated lattices show comparatively high compliance and energy absorption, albeit at the cost of lower overall strength [103]. In contrast, stretch-dominated lattice structures are exceptionally strong and stiff. This behavior is reflected in the compressive stress-strain diagram shown in Figure 5.2 [103].

The stress-stain curves of a typical lattice structure can be divided into three segments. At low strains, linear elastic compression (I) occurs. After the elastic limit is reached, a plateau of constant stress is observed (II). In this domain, plastic deformation, buckling, and fracture of the lattice struts occurs. Finally, it comes to densification of the collapsed lattice structure (III). This is characterized by a sharp rise in stress, as formerly opposing unit cell walls come into contact.

Bending-dominated lattice structures show a transition between Segment I and II and a distinct plateau of almost constant stress in Segment II (Figure 5.2a). This behavior makes them favorable in applications in which high energy absorption is required. In contrast, stretch-dominated structures show a pronounced peak in Segment I followed by post-yield softening in Segment II (Figure 5.2b). This indicates a high yield strength, with a high apparent stiffness. Due to these properties, such structures can be used for the lightweight design, including load bearing components or sandwich cores. Preceding work shows that the properties of sandwich structures can be greatly influenced based on the design of the lattice core and its properties [99,100,102,103,107].



Figure 5.2: Compression behavior of bending-dominated (a) and stretch-dominated (b) lattice structures.

In order to evaluate whether a lattice structure is bending dominated or stretch dominated, the Maxwell Stability Criterion and the associated Maxwell Number, M, are used. The Maxwell Number takes into consideration the connectivity and degrees of freedom of a lattice system. Equation 5.1 gives the formula for M for the three-dimensional case. In the formula, b is the number of struts and j the number of joints of the lattice unit cell. For M < 0, the lattice system is bend dominated, also referred to as under-stiff. In contrast, lattice structures are stretch dominated, or over-stiff, for M \geq 0 [103,107].

$$M = b - 3j + 6$$
(5.1)

This study proposes the adhesive-free combination of carbon fiber (CF)-reinforced prepregs and additive manufactured lattice structures. For this purpose, a novel joining process is utilized. The bonding process is based on the co-curing of chemically similar resin systems. The lattice structures are manufactured using Digital Light Synthesis (DLS), an AM technique able to produce parts with nearly isotropic properties [108]. DLS utilizes a dual-cure epoxy-based resin

system. The resin is 3D printed in the first stage using a UV-induced curing process [17,109]. As such, a geometrically stable, but only partially cured part is produced. In the second stage, the partially cured 3D-printed part is combined with CF epoxy prepreg and thermally co-cured using the chemical potential of both joining partners to form a cohesive bond. The result is a new type of hybrid lattice-core composite structure.

In this study, the potential of hybrid lattice sandwich structures is investigated in two steps. First, the mechanical properties of DLS-printed lattice structures are evaluated by compression tests. Second, the properties of hybrid lattice sandwich structures are determined with flexural beam tests.

5.2. Experimental Methods

5.2.1. Materials

All lattice structures are 3D printed using the epoxy-based photopolymer resin EPX 81, supplied by Carbon, Inc (Redwood, CA, USA). EPX 81 is a dual-curing resin, and as such, the curing from an initially liquid resin into a solid part is subdivided into two distinct and separate reactions. The first curing step is a photo-polymerization reaction, initiated by UV radiation. This stage is used to solidify the resin during printing, forming the solid structure part. The second stage of curing is thermally initiated, and with the completion of this step, a full cure is reached. The strength and stiffness properties of fully cured EPX 81 are shown in Table 5.1. All parts are manufactured using a Carbon M1 printer [110-112].

For the reinforcement material, EP4030-pre-impregnated carbon fiber, supplied by Mitsubishi Chemical Carbon Fiber and Composites, Inc. (Irvine, CA, USA), is used. The prepreg is composed of woven 34-700 carbon fibers embedded in an epoxy resin system. Table 5.1 shows the mechanical properties of the cured EP4030 [58].

 Material Property
 EPX 81
 EP4030

 Tensile Strength (MPa)
 88 ± 3 2370

 Tensile Modulus (GPa)
 3140 ± 105 146

 Flexural Strength (MPa)
 119 ± 21 1720

 Flexural Modulus (MPa)
 3250 ± 45 140

Table 5.1: Material properties of EPX81 and EP4030; mechanical properties are given in fiber direction [58,111].

5.2.2. Lattice Structure Design

A lattice structure is designed to be used as sandwich cores. For simplicity, only unit cell-based lattice structures are considered. The lattice configurations are further reduced by only taking into consideration equilateral, geometric primitive unit cells. Unit cell geometries meeting these criteria are shown in Figure 5.3. Figures 5.3a–c show the base configuration of Body-Centered Cubic (BCC), Face-Centered Cubic (FCC) and Cubic-Primitive (CP) unit cells, respectively. The unit cells shown in Figures 5.3d,e are combinations of these base configurations.



Figure 5.3: Unit cell types considered for the lattice generation with the respective Maxwell Number. (**a**) Body-Centered Cubic (BCC); (**b**) Face-Centered Cubic (FCC); (**c**) Cubic-Primitive (CP); (**d**) Body-Centered Cubic combined with Cubic-Primitive (BCC+CP); (**e**) Face-Centered Cubic combined with Cubic-Primitive (FCC+CP); (**f**) Body-Centered Cubic combined with Face-Centered Cubic (BCC+FCC).

Sandwich structures with highly rigid mechanical properties are desired. Thus, in order to complement the mechanical properties of the sandwich structures, a stretch-dominated, stiff lattice behavior is required. Consequently, only unit cells with a Maxwell Number $M \ge 0$ are suitable. The basic unit cell structures, shown in Figure 5.3a–c exhibit under-stiff behavior and are excluded. Similarly, the BCC+CP and BCC+FCC unit cells depicted in Figure 5.3d,f are excluded. Only the FCC+CP unit cell satisfied the above stated condition, as shown in Figure 5.3e. An FCC+CP unit cell structure is chosen for all subsequent experimental investigations. With the lattice design determined, two types of tests are performed: First, compressive testing of 3D-

printed lattice structures without the fiber reinforcement, and second flexural testing of fully 3Dprinted lattice sandwich structures and CFRP hybrid lattice sandwich structures.

5.2.3. Compression Testing

Compression testing is conducted to determine the mechanical behavior and characteristics of the 3D-printed lattice structure manufactured using DLS. Both of the investigated parameters, unit cell size and strut diameter, impact the geometry and change the relative density, and thus specific lattice characteristics.

Two cell edge lengths of 5 and 7.5 mm are used for the unit cell size in order to fit the specimen dimension with a whole-numbered amount. The second parameter, strut diameter, uses three parameter levels as shown in Table 5.2. The strut diameter for each unit cell size is selected based on the ratio of these parameters. Similar ratios result in similar relative densities. The respective values and specimen designations are shown in Table 5.2. The lattice structures are designed so that the ratios of diameter and unit cell size match for both unit cell sizes, as to guarantee comparability. The ratios used provide a balance between low relative density and supposed structural integrity. An intentional deviation from this pattern is specimen designation 5-0.5. With a strut–unit cell ratio of 0.1, the parameter set is used to estimate whether very low relative density lattice structures are possible.

Specimen Designation	Unit Cell Size (mm)	Strut Diameter (ds) (mm)	Ratio of Strut Diameter and Unit Cell Size
5-0.5		0.500	0.10
5-1.0	5	1.000	0.20
5-1.5		1.500	0.30
7.5-1.5		1.500	0.20
7.5-1.875	7.5	1.875	0.25
7.5-2.25		2.250	0.30

Table 5.2: Specimen designation based on unit cell size and strut diameter as well as ratio of strut diameter and unit cell size.

The mechanical properties of the lattice structures are determined by conducting uniaxial compression tests in accordance to ASTM D1621 [113]. The specimen design stated in the standard is adapted to match the unit cell-based lattice structure. Based on square specimens with a cubic geometry, a design for each unit cell size is derived as depicted in Figure 5.4. For the 5-mm unit cell-based lattices, a specimen with a cubic side length of 25 mm is used (Figure 5.4a). In the case of a unit cell size of 7.5 mm, the specimen results in a side length of 22.5 mm, shown in Figure 5.4b. These lengths refer to the strut middle axis. Furthermore, the respective testing speeds are shown in Figure 5.4 [113]. As specified by ASTM D1621, the testing speed is equal to 10% of the specimen length. Before testing, a preload of 10 N is applied. Testing is performed using an Instron universal testing system 5930 series with a 30-kN 2580 series static load cell. For each parameter set, five specimens are tested.



Figure 5.4: Schematic depiction of the (a) 5-mm unit cell, and (b) 7.5-mm unit cell compression test specimen and the respective loading speeds. The strut diameter is designated as d_s .

5.2.4. Flexural Beam Testing

An adapted three-point bending method based on ASTM D7249 is used. ASTM D7249 suggests a rectangular specimen with a width of 75 mm and a length of 600 mm. These dimensions are not compatible with the maximum build volume of the M1 printer ($141 \times 79 \times 326$ mm), so the specimen is scaled down [114,115]. A depiction of a hybrid lattice sandwich specimen, its measurements, and the testing set up are shown in Figure 5.5. The figure shows values referring to the strut middle axis. The respective strut diameter has to be added to these fixed values in order to reach the true measurements. Five layers of the CF prepreg reinforcement were used on the top and bottom surfaces to form the facesheets.

Flexural testing is conducted to measure the mechanical properties of hybrid lattice sandwich structures. Furthermore, the bonding quality between the 3D-printed lattice structure and CF prepreg is assessed to determine whether or not it poses a structural weakness. For this, hybrid bending specimens with different strut diameters are manufactured and tested under flexural bending following ASTM D7249.

Using results from the compression experiments, only the strut diameter of the lattice structures is varied. A 7.5-mm unit cell was chosen with strut diameters of 1.5, 1.875, and 2.25 mm. The unit cell size guaranteed a whole-numbered amount of unit cells in the specimen. As a benchmark for the hybrid lattice sandwich structures, the same flexural bending specimen geometry is tested without the CF reinforcement. The resulting design of experiments is shown in Table 5.3.

Specimen Designation	Face Sheet Material	Strut Diameter (ds) (mm)	Ratio of Strut Diameter and Unit Cell Size
Hybrid 1.5		1.500	0.20
Hybrid 1.875	5 layers	1.875	0.25
Hybrid 2.25	er prepreg	2.250	0.30
DLS 1.5		1.500	0.20
DLS 1.875	EXP 81	1.875	0.25
DLS 2.25		2.250	0.30

Table 5.3: Specimen designation based on unit cell size and strut diameter as well as ratio of strut diameter and unit cell size.



Figure 5.5: Set up of three-point bending and measurements of test specimen in accordance to ASTM D7249. The strut diameter is designated as d_s .

In order to improve the bonding between the 3D-printed part and CF prepreg, a surface is added to the top and bottom of the beam's lattice core. The surface has a thickness of 0.2 mm to minimize its impact on the mechanical properties of the lattice while offering more surface area for bonding. The specimen is loaded with a constant testing speed of 1 mm/min. The same universal testing machine is used as for the compression tests. For each CF-reinforced parameter set, three specimens are tested, whereas four specimens are tested for each non-reinforced parameter set.

5.2.5. Manufacturing

The first step in the manufacturing process is the DLS printing process. For this, the manufacturer's recommended EPX 81 profile is used, with a sliced layer thickness of 100 μ m. Compressive specimens are oriented so that the bottom side is attached to the printers build stage. Flexural specimens are oriented lengthwise with the long side edge being attached to the build stage. Finished parts are removed from the build stage using a razor. Post processing of the printed parts consists of resin removal through iterative part spinning in an immersion of cleaning solution.

The manufacturing of flexural specimen consists of the thermal co-curing of EPX 81 and the CF-Prepreg after the UV printing process. First, five uncured CF prepreg layers are stacked on the top and bottom surface of the DLS-printed lattice core. Next, the finished layup is packed in a vacuum bag and co-cured using the supplier recommended curing temperature profile for the EPX 81 as shown in Figure 5.6 [112]. After the completion of the curing cycle, the specimen is slowly cooled, demolded, and manually cleaned. An overview of finished flexural beam specimens is given in Figure 5.7.



Figure 5.6: EPX 81 curing temperature cycle [112].



Figure 5.7: Finished flexural beam specimens for (**a**) hybrid specimens and (**b**) Digital Light Synthesis (DLS)-printed specimen.

5.3. Results

5.3.1. Mechanical Characterization of DLS Lattice Structures

The average maximum compressive stress of the DLS lattice structures reached before failure and the average specific strength are shown in Figure 5.8a,b. The results are compared to the respective parameter set. In order to compute the stress from the recorded compressive test data, the minimal area of the specimen cross-section is used. The specific strength is the ratio of maximum strength and lattice density and is used to normalize the strength in regard to the specimen mass. Error bars indicate one standard deviation. No results for parameter set 5-0.5 can be presented, as the specimen are severely damaged due to build plate adhesion forces when removing them from the build plate after printing as shown in Figure 5.9.

Figure 5.8a shows that the highest compressive strength of 131 MPa is reached by parameter set 5.0-1.5. The second strongest parameter set, 7.5-2.25, reaches a compressive stress of 106 MPa. As such, smaller unit cell sizes yield higher maximum stresses compared to larger unit cells at the same relative density. This conclusion is further reinforced by the same trend when comparing parameter set 5.0-1.0 and 7.5-1.5.

This behavior can be explained by the higher number of unit cells the specimen consists of due to the smaller unit cell sizes. This in turn leads to higher stress allocation, as more overall struts are available. Furthermore, an increase in strut diameter is followed by an increase in maximum compressive strength. The progression appears to be linear, with an average increase in compressive strength by 17% based on a strut diameter increase of 0.5 mm. Finally, the low standard deviation for each parameter set with regards to the maximum stress indicates high consistency of the mechanical properties of DLS-printed lattice structures.

The specific strength of each parameter set is calculated, and the results are shown in Figure 5.8b. The highest relative strength is reached by parameter set 5.0-1.0 with a value of 236 kNm/kg. The second highest specific strength is observed for specimen with a unit cell size of 7.5 mm and a strut diameter of 1.5 mm at 194 kNm/kg. We conclude that lattice structures with the lowest strut diameter to unit cell size ratio, and thus lowest relative density, show the highest specific strength. The findings confirm the lightweight potential of these DLS-printed lattice structures.



Figure 5.8: Maximum compressive stress (a) and specific strength (b) of tested parameter sets.



Figure 5.9: Example of damaged lattice in 5-0.5 DLS specimen.

5.3.2. Flexural Testing of Hybrid Lattice Structures

Figure 5.10a shows the average maximum load at failure for each parameter set for both the DLS lattice structures and hybrid lattice structures, with error bars indicating one standard deviation. The hybrid lattices with the CF reinforcement and the DLS lattice structures without the CF reinforcement fail at approximately the same maximum load. The highest loads are reached by hybrid parts with a strut diameter of 2.25 mm, which fail at 7.2 kN. The DLS parts with a strut diameter of 2.25 mm fail at a load of 6.9 kN, which is a difference within the range of one standard deviation. The failures occur in the epoxy lattice structure, which implies that the strength of both specimen types is dictated by the maximum strength of the epoxy lattice core.

A second observation is the linear relationship between strut diameter, and thus relative density, and maximum load. This applies for both variations of the sandwich structures. The results follow the observations made for the compression tests. Furthermore, both the hybrid lattices and standard DLS lattice structures show brittle behavior and fail instantly upon reaching the maximum load. This behavior confirms that stretch-dominated lattice structures are suitable for use in sandwich structures where stiff and strong material behavior is required.

The results of the flexural beam tests are normalized by dividing them by the respective specimen weight, shown in Figure 5.10b. Regarding the normalized loads, the values for the standard DLS lattice structures are generally higher compared to the hybrid lattice structures with the CF reinforcement. The highest normalized load is reached by the DLS specimen with a strut diameter of 2.25 mm at a value of 101 kN/kg. This is followed by the hybrid specimen with a strut diameter of 2.25 mm at 97 kN/kg. While these two values do not significantly differ, a higher divergence is observed for lower strut diameters. An explanation for this result is a comparatively higher mass of hybrid specimens due to the higher density of the CF facesheet layers.



Figure 5.10: Maximum load (a) and mass-normalized load (b) before failure during flexural beam test.

The mode of failure for the DLS lattice structures and the hybrid lattice sandwich structures is shown in Figure 5.11a,b, respectively. For the standard lattices, a change in the angle of the failure can be observed. While the angle of fracture of a strut diameter of 1.5 mm is approximately 30° , at 1.875 mm, the angle is 50° and 90° for 2.25 mm. This indicates a shift in failure mode from shear to flexural tensile failure with an increase in strut diameter. For all hybrid lattice sandwich structures, failure occurs at an angle of 45° in the core region. This indicates core shear failure, as shown in Figure 5.11b. The observation further reinforces the assessment of the lattice strength being the limiting factor for the maximum load of hybrid lattice sandwich structures. In turn, the results confirm good bonding strength between the DLS epoxy lattice core and CF reinforcement.



Figure 5.11: Mode of failure for the DLS lattice structures (a) and hybrid sandwich structure (b).

The flexural stiffness determined by three-point bending is shown in Figure 5.12. It is evident that the stiffness of hybrid structures is considerably higher than the stiffness of the standard DLS parts. The maximum stiffness is reached by hybrid parts with a strut diameter of 2.25 mm at 4200 kN/m. The same lattice configuration for the DLS specimen only yields about half the stiffness at 2300 kN/m. The high stiffness further confirms the high potential for structural lightweight parts of hybrid 3D-printed epoxy lattice core and CF-reinforced sandwich structures.



Figure 5.12: Flexural stiffness of the DLS and hybrid lattice structures with CF reinforcement.

5.4. Conclusions

An FCC+CP unit cell topology was designed based on the requirements identified for sandwich structures. Facilitating this lattice structure, compression specimens were designed and tested. The topology proves to be stretch dominated and shows mechanical strength and stiffness sufficiently high to be used as sandwich core structures at low relative densities. Higher strut diameters yield better absolute mechanical properties at the cost of a higher relative density and total mass, as reflected by a decrease in specific strength. Moreover, smaller unit cell sizes result in better mechanical properties compared to larger unit cells. However, very low relative density lattice structures could not be removed from the build plate without damage to the struts. Thus, such structures are not consistently manufacturable. In conclusion, the lattice structures used in this study show a high structural efficiency and can be applied to hybrid lattice sandwich structures.

Hybrid lattice sandwich structures are successfully manufactured using an adapted manufacturing process. The mechanical behavior of these structures is evaluated and compared to the corresponding geometries of the DLS-printed parts without CF reinforcement. It is shown that high strength and stiffnesses can be reached by hybrid lattice sandwich structures, while maintaining low weight. This makes such structures suitable for the application as lightweight structural components. The bonding strength between the DLS lattice core and CF prepregs is suitable to sustain high loads in bending. The overall strength of the hybrid parts is limited by the strength of the DLS epoxy lattice structure, demonstrated by the similar load at failure of the hybrid part and the DLS part. An optimization of the lattice topology could further improve the strength of these structures.

The overall conclusion of these experiments is that the co-curing of the 3D-printed epoxy parts using DLS and CF prepreg reinforcement is possible. Furthermore, the manufacturing of hybrid lattice sandwich structures is demonstrated. The resulting sandwich structures yield high mechanical properties and light weight. Future research can be conducted on improving the properties of the lattice sandwich core. One approach could be the optimization of the sandwich lattice core by using proposed lattice designs found to yield good mechanical properties, for example octet-truss lattices [116-118]. Another approach is the optimization of lattice topology based on a given load case. The implementation of additional functions into the lattice core is also possible. Based on the high degree of freedom given by additive manufacturing, this could include fluid channels, cable routing or foam pockets for insulation.

6. Application: Hybrid Composite T-Joints

There are many instances when angled or perpendicular joints are required in composite structures. However, due to the limitations in how much fiber reinforcement can be bent, a gap is formed in the structure. In perpendicular joints, this gap is known as the "deltoid" and must be filled in some way to properly transmit the experienced loads. The spar-wingskin structure in a wing is one example of an aerospace structure with these perpendicular joints (T-joints). There are different ways of filling the deltoid region, but by using the newly developed manufacturing process, the geometry can be 3D printed to the exact shape required. Changing geometry to account for a different radius or angle is as simple as changing the design file and printing a new part. The 3D printed joining element can then be integrated into the composite structure using the previously discussed co-curing method, providing the necessary load transfer capability. The technology provides the ability to manufacture complex composite structure using fewer fixtures while decreasing manufacturing time and preventing geometric defects. This chapter is based on the research "Fabrication of hybrid composite T-joints by co-curing with 3D printed dual cure epoxy" published in *Composites Part B*, Vol. 183, Issue 15, 107728 (2020) [119].

6.1. Introduction

Fiber reinforced plastics (FRPs) have excellent mechanical properties; however, their design freedom is often limited due to tooling and process conditions. Despite these challenges, the demand for hybrid design with high complexity and a flexible product spectrum for the manufacturing industry is increasing [120]. The application of composite structures is expanding from classical load bearing structures to complex, multifunctional components with tailored integrated functionality, such as flow channels or lattice structures [121-123]. In order to create

such structures, it is necessary to join several smaller components by either mechanical fasteners or adhesive bonding [124]. Both bonding techniques are schematically depicted in Figure 6.1 for a FRP single-lap joint (SLJ).



Figure 6.1: Schematic cross section of single-lap joint with mechanical fastening (top) and adhesive bonding (bottom) in FRP.

In general, joining FRP structures with conventional mechanical fasteners is avoided when possible, as they increase the weight and sever the reinforcing fibers, which evokes stress concentrations and decreases the load transfer capabilities [50,125,126]. Furthermore, mechanical fasteners add significant weight compared to a lightweight adhesive polymer. An adhesive joint in lightweight FRP structures is generally preferred, as it better transfers load in tension and shear across the entire joint, resulting in improved stress distribution and overall joint performance [127].

Figure 6.2 depicts three common manufacturing processes for joining composite components with different combinations of cured and uncured adherends. The secondary bonding procedure bonds two fully cured adherends and is usually applied for accessible structures with simple geometries. In the co bonding process, a cured adherend is combined with an initially uncured adherend, which is further co-cured with the adhesive during processing. This method is commonly applied for multi-material structures - for instance when a FRP is bonded with a metal

[128]. Finally, co curing allows the two un cured adherends to cure simultaneously in a single cycle [129].



Figure 6.2: Schematic drawing of common manufacturing processes to join composite components with an adhesive bond.

Adhesive bonds are particularly important for the aerospace industry, which is constantly being challenged to enhance airframe structures, as they amount to a large fraction of the total weight and cost of an airplane [130]. The structural adhesive most commonly used for airframe structures is epoxy resin due to its durability, wide temperature ranges, and ability to adhere to most surfaces, including aluminum and composites. Other types of adhesives used include silicones or urethanes [131].

One structural aerospace application, the T-joint, is extensively used for spar-wingskin joints in aircraft wings, which transfers out of plane loads for applications with integrated stiffeners [126,132,133]. An example of this is shown in Figure 6.3. Within the T-joint structure there are several components. The first component, the primary horizontal structure, is referred to as the platform. The vertical internal structure, or web, consists of two bent components to provide an interface which is over laminated onto the platform. Last, the so called "deltoid" is the area between the platform and the bent part of the web components. When the deltoid is filled with a suitable material, it primarily supports the overlaminate, ensuring continuity in the load transfer

between the perpendicular components. As the deltoid stabilizes the primary load bearing plies, the overall strength of the joint is increased [132,134]. Previous literature has shown the strength of specimens with structural deltoid filling was 20% higher compared to the specimens without deltoid filling [135].



Figure 6.3: Schematic cross-section of a T-joint (left) and schematic 3D drawing of a sparwingskin joint (right).

In standard T-joint manufacturing processes, commercial adhesives or rolled up preimpregnated reinforcement material are applied in the deltoid area [130,132,136,137]. However, due to the geometry of the deltoid, combined with the manual application and the time sensitivity of the adhesive, it is difficult to ensure uniform surface wetting and geometrical accuracy [130,135]. The insert may need to be formed using custom molds and fixtures before application, which results in a multi-step process. As there are varying deltoid sizes and geometries (e.g., triangular, circular, elliptical), that are commonly applied, this impacts the reproducibility and precision of the bondline, and process times and manufacturing costs are increased [130,132]. In order to solve this problem, there is a need for geometrically tailored bonding materials that improve manufacturing speed, joint reproducibility, and joint strength. Additive manufacturing (AM), often referred to as 3D printing (3DP), is well suited to produce parts with complex shapes and geometries [138]. When creating hybrid composite structures with 3DP parts, a structure with geometric complexity and specific properties can be achieved. In order to fully utilize a 3DP part as a bonding element in load-bearing structures, it needs to fulfill two requirements: isotropic mechanical properties and chemical potential after the 3DP process. The chemical potential is particularly important to ensure a uniform adhesive bond with the FRP. However, 3DP parts are usually fully cured after their manufacturing [139].

Digital Light Synthesis (DLS) is an AM technology driven by the Continuous Liquid Interface Production (CLIP) process developed by Carbon, Inc. (Redwood, CA). DLS uses an ultraviolet light source directed through an oxygen-permeable window to continuously and additively generate layers, leading to a part with excellent surface properties and nearly isotropic mechanical behavior [15,108]. The UV curing of DLS creates a rigid part with stable dimensions. However, when a Carbon dual-cure resin such as the EPX epoxy-based resin is used, the printed parts are only partially cured. This first stage of the dual-cure epoxy system has chemical potential to form an adhesive bond. In the secondary, thermally activated stage, the parts are fully cured [15,58].

Utilizing the DLS process and a dual-cure epoxy provides the opportunity to adhesively bond AM parts with FRP structures. The printed parts in their first curing stage can easily be integrated with pre-impregnated fiber reinforcement and the hybrid structure can be cocured together during the thermal cycle. The work presented here investigates the suitability of dual-cure epoxy manufactured by DLS as bonding material for composite structures. The joints co-cured with the dual-cure epoxy are compared to joints manufactured with conventional bonding materials. T-joints are assessed in terms of manufacturability and joint strength, which is determined by visual bondline inspection and tensile testing, respectively.

6.2. Experimental Methods

6.2.1. Materials

The tested adherends are manufactured with woven epoxy resin prepreg NB4030-D, by Mitsubishi Chemical Carbon Fiber and Composites, Inc. (Irvine, CA). The layer wise material properties are listed in Table 6.1 [58]. The specimens are manufactured with three different adhesive materials: the 3D printed dual-cure epoxy, a standard epoxy adhesive, and prepreg. These three materials are tested to enable a comparison of the dual-cure epoxy with the conventional deltoid materials.

Material Properties	Value	Unit
NB4030-D		
Nominal Ply Thickness	0.3	mm
Tensile Strength	2370	MPa
Glass Transition Temperature	130	°C
Gel Time (at 135 °C)	5-8	min

Table 6.1: Material data of NB4030-D pre-impregnated reinforcement [58].

First, the epoxy-based photopolymer resin EPX 81 from Carbon is manufactured with DLS, completing the first stage of curing reaction during the UV printing process. The printed parts are then removed from the build plate, washed per Carbon's recommended solvent wash process, and stored in a dry container free from external heat or light before being fully co-cured

with the prepreg materials. Second, a two component commercially available epoxy, 3M Scotch Weld DP190, is applied to a separate set of test samples using the manufacturer recommended dispenser and static mixing nozzle. The material properties of EPX 81 and DP190 are listed in Table 6.2 [60,111]. Third, the NB4030-D reinforcement material used for the adherends is also used as a control in the same test geometry. The material properties of NB4030-D are listed in Table 6.1.

Material Properties	Value	Unit
EPX 81		
Density	1.12	g/cm ³
Tensile Strength	88 ± 3	MPa
Elongation at Break	5.2 ± 0.7	%
Heat Deflection Temperature (at 1.82 MPa)	131	°C
DP190		
Density	1.32	g/cm ³
Tensile Strength	24.13	N/mm ²
Glass Transition Temperature	20	°C
Elongation at Break	30	%
Fixture Time	90	min
Full Cure Time	7	days

Table 6.2: Material data of adhesive materials [60,111].

6.2.2. Manufacturing of T-Joint Specimens

Currently, there are no well-documented standards for the mechanical testing of T-joint specimens. In the following, the manufacturing procedure as well as the tensile testing set-up are adapted from Trask et al. [132] and Hélénon et al. [136]. The T-joint specimens are manufactured by co-curing the prepreg material with the varied bonding materials in three steps.

The first step of the manufacturing process is the lay-up, which can be subdivided into four steps as shown in Figure 6.4. For each half of the web section, six plies of prepreg material are aligned on two molds, which provide a basis for the geometry of the web sections (1). Next, the two molds with the laid-up prepregs are aligned against each other (2) and clamped. Subsequently, the specified deltoid insert is placed in the deltoid area (3). When applying the deltoid material, the application varies for the three different materials. First, when applying dual-cure epoxy as deltoid material, the part is simply placed in the deltoid area, as it is manufactured to fit the exact deltoid specifications. When applying the prepreg, the material is cut into long strips, manually rolled into a cylindrical shape, and pressed into a mold to form the deltoid. If the epoxy adhesive is used as deltoid material, it is applied to the deltoid area by means of a static mixing nozzle. Finally, six plies of prepreg are placed for the platform section (4).



Figure 6.4: Schematic lay-up process for T-joints.

In order to cure the parts, the lay-up is turned over, placed on an aluminum plate and sealed with a vacuum bag, as depicted in Figure 6.5. The materials are co-cured according to the temperature cycle for the EPX 81 [111] and are cut to fit the requirements of the tensile testing procedure. To ensure accurate geometry and an even surface, the specimens are finished by light sanding. The final dimensions of the T-joint specimens are depicted in Figure 6.6. A finished T-joint specimen is shown in Figure 6.7.



Figure 6.5: Arrangement of T-joints for co-curing under vacuum.



Figure 6.6: Dimensions of T-joint test specimen.



Figure 6.7: Final manufactured T-joint test specimen.

6.2.3. Tensile Testing of T-Joint Specimens

As previously mentioned, there are no official standards for the mechanical testing of Tjoint specimens. The tensile testing set-up and procedure, adapted from Trask et al. [132] and Hélénon et al. [136] are adjusted to fit the requirements and boundary conditions for the experiments of this investigation. Analyzing the out of plane behavior, a tensile pull-out load is applied to the web-section while the platform-section was braced by pins at both ends. For this experimental set up, the perpendicular section is clamped with the standard tensile testing fixture. In order to support the horizontal web section, a customized test fixture was fabricated. The fixture
was designed with the purpose to symmetrically support the horizontal section of the T-joint at the designated points. The base of the T-joint is not fixed to the bottom plate to generate a more realistic load case, allowing the horizontal components to bend down [121]. The experimental set up is shown in Figure 6.8. For each bonding material, five specimens are evaluated.



Figure 6.8: Schematic drawing of experimental set-up with relevant dimensions.

The individual T-joint specimens are tested with a 30 kN load cell on an Instron 5967 universal testing machine from Illinois Tool Works Inc. (Norwood, MA). A tension load is applied to the vertical section at a loading rate of 2 mm/min until joint failure. An initial preload of 5 N is applied to ensure initial contact.

6.3. Results

Before the T-joint tensile testing was performed, the specimens are visually inspected to evaluate the bondline quality. Figure 6.9 shows the deltoid areas filled with the three materials. The specimens manufactured with the EPX 81 show an exact geometry and a good material distribution along the bondline without voids or discontinuities. The specimens manufactured with the commercial epoxy adhesive, however, show that the material can easily be distributed unevenly within the deltoid area due to insufficient filling during the manual application and/or shrinkage during curing. The T-joint specimens with the prepreg insert generally show a filled deltoid area and a void-free bondline. However, some specimens show a small defect in the middle of the deltoid, which is possibly induced during manufacturing of the insert where the prepreg is rolled, formed, and placed in the deltoid area manually. None of the defective parts are considered for the subsequent mechanical tests.



Figure 6.9: Close-up of deltoid areas filled with the different deltoid materials.

Figure 6.10 shows the average load at break and standard deviations for the T-joints with the various deltoid materials. The highest average pull-out joint strength of 418 N is reached by the T-joints with the NB4030-D prepreg as the deltoid inserts. The T-joints that are co-cured with the printed EPX 81 inserts performed nearly the same, with only a 3% reduction in average joint strength of 381 N. The higher standard deviation of the T-joints with the prepreg deltoid inserts may indicate that the quality is susceptible to manufacturing variability. The specimens with the standard DP190 epoxy adhesive show a significantly lower pull-out joint strength at 284 N.



Figure 6.10: Average load at break for T-joints by deltoid material.

From the experimental data it can be concluded that not only the bonding quality has an impact on the results of the mechanical testing, but also the different material properties of the varied bonding/deltoid materials (Table 6.1 and Table 6.2). In terms of material properties, the results of the mechanical testing of the T-joints correlate with the data from the shear joints reported in Chapter 3. For example, the commercially available epoxy adhesive, DP 190, shows the highest single-lap shear strength, likely due to a high elongation at break. However, the prepreg material EP4030-D performs best in T-joint pull-out testing, likely due to a higher modulus. Thus, it can be concluded that the EPX 81 is well suited for out-of-plane loading conditions due to bondline quality in addition to its material properties.

The failure modes for the different deltoid materials are depicted in Figure 6.11. The EPX 81 specimens primarily broke by interlaminar failure in the vertical section of the web component. This interlaminar failure propagated to the deltoid section, causing it to crack. In some cases, a bondline failure occurred from the tip of the deltoid along one side. Eventually the bondline failure shifts to a cracking of the deltoid part. The specimens bonded with the commercial DP190 epoxy adhesive experience interlaminar and bondline failure. The interlaminar failures accumulates around the deltoid region. For the T-joints with NB4030-D prepreg as deltoid material, a bondline

failure is observed. This behavior can possibly be traced back to the manufacturing procedure, as the rolled-up deltoid may not accurately fit the deltoid area. As a result, the bondline proves to be a weak point in the joint structure.



Figure 6.11: Failure modes of T-joint specimens with varied deltoid material.

6.4. Conclusions

This study systematically analyzed the application of Digital Light Synthesis and the dualcure EPX 81 material for manufacturing hybrid composite T-joint structures. In the investigation of different deltoid materials for T-joints, the 3D printed EPX 81 and NB4030-D prepreg material show the best results as deltoid materials. The DP190 commercial epoxy adhesive had a significantly lower pull-out strength, even though it showed the highest mechanical properties in lap shear testing. Thus, it can be concluded that the different bonding materials are suited for different load cases due to differences in application and material properties.

Furthermore, the specimen manufactured with the EPX 81 showed more exact deltoid geometries as well as improved material distribution along the bondline. Due to precise manufacturing, the reproducibility of the T-joints was highest when using the EPX 81 for the deltoid insert. The results demonstrate a new technique for manufacturing T-joint structures as well as the potential for manufacturing and hybridization of FRP structures with parts 3D printed by the DLS technology utilizing the advantages of co curing.

7. Application: Economic Mass Production of Composite Truss Structures

7.1. Introduction

Hollow profiles made of fiber-reinforced composites are ideally suited for the production of highly rigid, lightweight truss structures. Due to their excellent mechanical properties and ability to be economically mass produced, these structures follow the current trend towards resourceefficient construction. Compared to the flat structures typical when manufacturing composites, there are still major challenges in the joining process of these three-dimensional profiles. Today, these challenges are often circumvented by the use of additional metallic node elements and mechanical fasteners [140,141]. The requirement for drilling and material removal when using mechanical fasteners results in damage to the fiber composite structure, which can lead to premature stress cracking as well as galvanic corrosion at the interface. In order to solve these problems, a novel joining method was developed at the wbk Institute of Production Science of the Karlsruhe Institute of Technology (KIT) capable of producing such truss structures with a high load-bearing capacity. With the use of a vertical articulated robot and a connected kinematic system consisting of a stator and an internal rotor, individual rovings and pre-impregnated thermoset tapes can be autonomously applied to the joining zone of adjacent profiles in a load-fair and non-destructive manner, resulting in both a load-bearing form and adhesive bond [142].

The developed joining process has both a high productivity through automation and high flexibility through adjustable windings. This is also the only known winding device currently capable of autonomously winding closed-frame structures, such as those required for bicycle frames made of carbon fiber-reinforced plastic. Joints can be produced that allow the replacement of metallic profile structures in automotive industry with weight-saving fiber composite structures. The invented procedure is based on Bamboo lashing formerly used in Asia for scaffolding (Figure 7.1). Here, profiles have already been wrapped with a fiber in such a way that a load-bearing knot structure was created [143].



Figure 7.1: General principle of filament winding technique for joining lightweight profiles.

The starting point for the winding is an open, c-shaped stator base structure in which a cshaped rotor rotates (Figure 7.2 left). This rotor is driven by electric motors and carries a fiber coil from which rovings are directed to the components to be wrapped. In addition to the rotary movement, a translational guidance of the stator is necessary to allow for a more flexible joining process. This is achieved with the aid of a vertical articulated robot. The open shape of the components allows collision-free connection of closed truss structures, which is not possible with any other autonomous winding process. An integrated tensioning unit in the rotor guarantees a permanent roving pre-tension and thus an even unwinding. Integrated sensors detect the position of the rotor relative to the stator and intelligently control the entire process. With the help of this winding device, dry rovings, which are impregnated inline, as well as towpregs, which already contain the necessary resin, can be used for the connection [144].

The use of the vertical articulated robot in combination with the winding ring also enables the production of joints with different winding patterns. At first, a variation of the basic pattern or global wrap pattern is possible. This results in an optimization of the joint with regard to the present load case. In the second step, the global winding pattern can be varied locally. This is particularly important to prevent the windings from slipping during the process, which is dependent on the fiber friction and the winding surface. In addition, the overall winding pattern must be changed when varying the joining angle between two profiles [144].

The number of windings can also be varied, which leads to a load case optimized joint. The tensile or longitudinal profile of the structure requires a flange surface for wrapping (Figure 7.2 right), so that a form-fit is created by the windings in addition to the pure material closure by the resin.



Figure 7.2: Filament winding ring (left) and profiles with flange (right).

While the robotic winding system provides the flexibility to join arbitrary configurations of profiles, the current technology is severely limited by the separate flange section that provides the required area for the windings to generate the high-strength form-fit. Due to the high temperatures required to cure the wound rovings or towpregs, the flange must be manufactured from a stable thermoset material, limiting the options for manufacturing. Specifically, the flange part of the transverse profile has several disadvantages considering the manufacturing and the joining process:

- Costly manufacturing of profile flange: When using profiles with a thermoset matrix, it is not possible to soften and form the profile to the required geometry. Because of this, the flange end must be produced directly during profile production. This can be done with thermoset profiles using the resin transfer molding (RTM) process. However, RTM requires complex tools consisting of a positive core and a multi-part negative outer mold (Figure 7.3 left). Instead of being able to use simple, pultruded profiles, an elaborate manufacturing process of the profiles is required, which increases the process times and costs as well as reduces the overall efficiency of the process.
- Non-customizable molds: Due to the necessity of solid molds when using thermoset profiles, the design freedom of the joint is significantly restricted. Completely new molds are required for each individual diameter, profile length, joining angle (Figure 7.3 left). Accordingly, the flexible joining process is already significantly restricted by the manufacturing process of the necessary flange.
- Surface texture of flange part is not individually adjustable: The use of molds also makes it impossible to individualize the surface finish and surface roughness without additional steps. Different surface structures can improve the bonding of the winding fibers and minimize the slipping tendency (λ) when depositing. In RTM production, however, the surface depends directly on that of the mold.
- Small winding area on flange: In order to manufacture the profile in a mold, a pre-forming step of the dry fibers is necessary before infiltration. Forming the flange with fibers requires semi-finished products made of fabrics or braided hoses and is limited by the interweaving tension of the individual rovings. Because it is difficult to shape the fibers into the necessary

dimension, a relatively small flange surface is produced. The possible area for winding when joining with the longitudinal profile is correspondingly small.

- Small enclosure of longitudinal profile through the flange: Parallel to the small winding area, the enclosure of the longitudinal profile with the flange is also limited by the restrictions of the fabrics and braids (Figure 7.3 right).
- Sharp transition between flange part and longitudinal profile: Due to the fiber reinforcement and the manufacturing process, the cross section with the flange has a constant wall thickness. This results in a sharp transition between the cross section and the longitudinal profile when it is placed on the longitudinal profile (Figure 7.3 right). This transition, in the form of a discrete step, increases the stress on the connection when it is wound with fibers. In addition, the fibers in this transition do not adhere to the longitudinal profile, which minimizes the mechanical load-bearing capacity of the coupling.



Figure 7.3: Example of an RTM-mold (left) and representation of the sharp transition between the two profiles.

All of the stated problems can be alleviated by using the 3D printed dual-cure elements, where a compatible epoxy system is first 3D printed into the specified geometry for the profile sections, but is only partially cured with the UV printing process. The 3D printed section still maintains its chemical potential and bonding availability when it is integrated with the profile

sections to be joined and wound with pre-impregnated rovings or towpreg. The assembly can then be heated to activate the second curing reaction and co-cure the two materials, forming a permanent bond.

Combining these technologies, multiple flange sections can be 3D printed in a matter of minutes to hours, depending on the specific geometry, with fully customizable dimensions (Figure 7.4). The surfaces can be textured on the flange with no added time or cost to optimize the calculated degree of friction as required for the winding process. This enables the manufacturing of completely new types of closed loop structures with low-cost, pultruded profiles. By extending the existing process chain for joining profiles, the strength of the joint is significantly increased by the synergy of adhesion and mechanical reinforcement (Figure 7.5). Lightweight structures produced with the new technologies can be used in new applications and reduce the overall mass of already existing technical solutions.



Figure 7.4: Combination of 3D-printed element and filament winding.



Figure 7.5: Extended joining process with increased strength.

7.2. Experimental Methods

This study investigates the material characteristics of hybrid composite structures with the use of a dual-curing epoxy resin, EPX 82. The material, produced by Carbon Inc., is manufactured with an M1 printer using the Digital Light Synthesis (DLS) process. A partially cured part is manufactured with the DLS process in the first stage, using UV-light to form an acrylate network. This intermediate part is dimensionally stable, but shows weak mechanical properties. A second stage consists of a thermal curing cycle to fully crosslink the material.

The material is stored in cartridges containing part A and B in separate chambers to inhibit a reaction. A static mixer with a 1:1 ratio is used to fill the resin tank for printing. Samples for this study are printed with default settings and a layer height of 100 µm. Partially cured parts have to be removed from the build platform and cleaned to remove excess resin. The recommend cleaning processes involves using 99% dipropylene glycol methyl ether (DPM) as a solvent for removing the excess resin from the printed parts, limiting the solvent exposure to a maximum of four minutes. The parts are then rinsed with isopropyl alcohol (IPA) and placed on a tray in a Yamato DKN 602C programmable convection oven to complete the second, thermal curing stage.

Pultruded carbon fiber profiles provided by vDijk Pultrusion Products (DPP) are used in the joining process. These profiles are 40 mm in diameter and are pultruded with a bisphenol A epoxy resin using unidirectional Toray T700 carbon fiber. For the winding material, a preimpregnated tape (towpreg) from Vitow Composites is used. This tape uses Teijin UTS50-F24 carbon fibers, a 24K tow size slit to a width of 6.3 mm. The assembly is wound with an articulated 6-axis robotic arm from KUKA mounted with the rotor-stator winding device as previously described. The tape tension is controlled by an automatic tensioning device and can be adjusted for different profile geometries and surface friction to avoid slipping.

7.3. Results

The joining element is designed to optimize manufacturing while meeting the load transfer requirements between the profiles. A stackable flange design is used, allowing multiple joining elements to be manufactured simultaneously (Figure 7.6). In a standard M1 or M2 model DLS printer, this design would allow between six to nine parts to be manufactured in approximately four hours. The large-area format printer would allow in the range of 20 parts to be produced in the same timeframe. Figure 7.7 shows an example of the stacking arrangement and build platform capacity.



Figure 7.6: Design of joining element for composite truss structures.



Figure 7.7: Stacking arrangement for joining elements on a M1 model DLS printing device.

The printed joining element after support removal and cleaning is shown in Figure 7.8 (left). The final mass for the printed joining element is measured as 9.5 grams, significantly less than alternative joining methods, such as the CARBONNect[™] Fixed Connector, a steel connector assembly from Rockwest Composites, which is measured to weigh 210 grams for the same profile diameter (Figure 7.8 right) [145]. The printed joining element provided a suitable connection for the winding process and was not distorted by the tension of the pre-impregnated tape or forces applied by the articulated robotic arm. A final truss structure including the carbon fiber profiles, the printed joining element, and wound pre-impregnated tape after thermal curing is shown in Figure 7.9.



Figure 7.8: The EPX joining element (left) and the fixed connector from Rockwest Composites (right).



Figure 7.9: The wound composite truss section.

7.4. Conclusions

Combining the two technologies of additive manufacturing and robotic winding enables the economic mass production of light-weight composite truss structures, aiding in increased resource efficiency in corresponding fields of application, such as the construction or transportation industries. Initial studies demonstrate the feasibility of such a process and indicate that scale-up and serial production are possible. Mass implementation of these composite truss structures can contribute to decreased CO₂ emissions, directly supporting important worldwide climate change minimization strategies. However, several fundamental questions must still be answered for mass implementation, and are discussed in the following chapter.

8. Summary

8.1. Contributions

This dissertation presented a new approach to manufacturing hybrid composite structures utilizing additive manufacturing and dual-cure resin system. The work focused on four key tasks: I. Developing an understanding of the thermal curing process, II. Quantify the bonding characteristics of the 3D printed hybrid composite structures, III. Determine appropriate conditions for the simultaneous processing of the 3D printed elements and composite material, IV. Design and manufacture functional prototypes of these hybrid composite structures to demonstrate the technology at an application level.

Chapter 2 studied the thermal curing behavior of the EPX 82 material used to manufacture the 3D printed elements. A kinetic model was created that is capable of predicting the degree of cure using different temperature profiles. Multiple temperature profiles were evaluated to better align the processing times and temperatures to those used for the pre-impregnated fiber reinforcement. Thermal-mechanical testing was conducted to validate the optimized temperature cycles, leading to a 9-hour (73%) reduction in thermal processing time compared to the manufacturer recommendation.

Chapter 3 outlined the manufacturing and testing of lap shear specimen used for evaluating the bonding quality of the 3D printed element to the composite reinforcement. Single-lap shear tests demonstrated the successful co-curing of the two components and the potential for the newly described hybrid composite technology to be used in structural applications. An alternative test, the block shear method, was suggested to better compare the bond strength results in fiber reinforced adherends by reducing peeling stresses and preventing failure by delamination. The results both tests showed that the dual-curing epoxy co-cured with pre-impregnated composite reinforcement had a similar bonding strength compared to a commercial adhesive and a standard composite overlap joint.

Chapter 4 introduced a model for the development of mechanical properties in the dualcure resin system during processing. The external forces required to consolidate the 3D printed and fiber reinforcement components (vacuum pressure, tension, etc.) can result in large structural deformations during curing due to the softening of the intermediate 3D printed part. This model uses information from the curing kinetics study conducted in Chapter 2 to relate the elastic modulus to the glass transition temperature, degree of cure, and processing temperatures. The understanding of how the mechanical properties of the 3D printed component develop during the thermal cure is essential to creating a robust manufacturing process for the hybrid composite structures. Processing guidelines were subsequently developed to assist in selecting appropriate external pressures based on allowable deformations.

Chapters 5-7 demonstrated multiple applications for this new technology. Chapter 5 focused on 3D printed lattices integrated and co-cured with fiber-reinforced facesheets, allowing for the fabrication of lightweight composite sandwich structures. Chapter 6 demonstrated an aerospace application, where the 3D printed elements were used in the fabrication of the common T-joint found in spar-wingskin structures, providing benefits in manufacturability and load transfer. Chapter 7 introduced a preliminary study on using the 3D printed joining elements in a novel robotic winding process, allowing the mass-production of composite truss structures for applications in transportation and construction. The 3D printed joining element solves many of the major challenges currently faced with the process and provides significant weight savings compared to alternative metal fastener solutions.

8.2. Recommendations for Future Work

The core focus of this dissertation was to develop the concept of using a 3D printed dualcuring resin for bonding composite structures, and to better understand the relationship between material properties, processing conditions, and final applications. The general concept was proven to be feasible, and preliminary applications show considerable promise. However, over the course of this dissertation, several new fundamental research questions were presented and should be studied to better understand and advance the technology.

A primary question is the nature of the co-curing reaction and bond. The lap shear testing conducted in Chapter 3 was an engineering solution to demonstrate and compare the bond while neglecting the exact theory of adhesion contributing to the bond strength. Optical studies were conducted to investigate the interface of the 3D printed element and the composite reinforcement and showed, within the scale of 10-100 micrometers, there is near-perfect contact with observable mechanical interlocking between the surfaces. Whether there is any interfacial diffusion or chemical cross-linking between the materials during the thermal processing is unknown. Fluorescence microscopy was attempted to identify interfacial diffusion; however, the resin of the 3D printed element and the pre-impregnated fiber reinforcement are too similar to be easily distinguished. A more comprehensive study would be beneficial for future modelling and simulation efforts.

A challenge for light-based additive manufacturing techniques in general is the nonuniformities in a printed voxel. Understanding the printing process and induced defects is significant for developing a robust method to produce the hybrid structures described in this dissertation. The non-uniform light intensity with depth through the resin layer due to Beer-Lambert absorption, reactive species diffusion at the same time and spatial scales as the polymerization reaction, and non-linear and light-intensity dependent polymerization all contribute to the varying material properties throughout a given layer and throughout the 3D printed part. The chemical and mechanical heterogeneity of printed parts complicates the prediction of structural behavior in the hybrid composites.

The model for modulus development of dual-curing resins presented in Chapter 4 solved an important issue with the softening and deformation of structures during thermal curing. Thermal residual stresses were not considered and are critical to preventing manufacturing induced defects. Especially in connector application demonstrated in Chapter 7, the joining element has a significant thickness component (1-5 mm) depending on the exact geometrical requirements, and will experience temperature and curing gradients. Thermal stresses can cause deformation, warpage, and cracking, and should be an area of study in future models.

Structural applications and their mechanical behavior are the primary focus of this research. The complications already noted in predicting mechanical behavior (e.g., through-thickness material variation, processing and manufacturing induced defects, and thermal residual stresses) require a complex multiaxial test program to properly evaluate mechanical strength. Specifically, for the profile connector application in Chapter 7, a prototype structure needs to be defined so that a failure surface and stress interactions may be developed.

8.3. Publications

The following lists detail the research products related to this dissertation:

Patents

- Rudolph, N.M., Redmann, A. (2020). U.S. Patent No. 10,751,932

Refereed Journal Publications

- Austermann, J., Redmann, A., Dahmen, V., Quintanilla, A., Mecham, S., and Osswald, T.A., 2019, "Fiber-Reinforced Composite Sandwich Structures by Co-Curing with Additive Manufactured Epoxy Lattices," *J. Compos. Sci.*, 3, 53.
- Dahmen, V., Redmann, A., Austermann, J., Quintanilla, A., Mecham, S.J., and Osswald, T.A., 2020, "Fabrication of Hybrid Composite T-joints by Co-Curing with 3D Printed Dual Cure Epoxy," *Composites Part B*, 183(15), 107728.
- Redmann, A., Oehlmann, P., Scheffler, T., Kagermeier, L., and Osswald, T.A., 2020, "Thermal Curing Kinetics Optimization of Epoxy Resin in Digital Light Synthesis," *Additive Manufacturing*, 32, 101018.
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- Redmann, A., and Osswald, T.A., 2020, "A Model for Modulus Development of Dual-Cure Resin Systems," *Poly. Eng. & Sci.*, 61(3), pp. 830-835.

Conference Proceedings

- Redmann, A., and Osswald, T.A., 2018, "3D Printed B-Stage Epoxy for Composite Joining and Feature Integration," SPE Automotive Composites Conference and Expo, Society of Plastic Engineers, Detroit, MI. (Best Paper Award)
- Redmann, A., Austermann, J., Dahmen, V., Setter, R., Quintanilla, A., Mecham, S., and Osswald, T.A., 2018, "Additive Manufactured B-Stage Epoxy for Adhesive Bonding in Composite Structures," *The Composites and Advanced Materials Expo*, Dallas, TX.
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- Redmann, A., Oehlmann, P., Kagermeier, L., and Osswald, T.A., 2019, "Kinetic Study of a Dual Curing Epoxy Resin for Additive Manufacturing Applications," *K Trade Fair* (NETZSCH), Düsseldorf, Germany.
- Chen, H., Redmann, A., Zhang, R., Mecham, S., and Osswald, T.A., "3D Printed Hybrid Composite Structures – Design and Optimization of a Bike Saddle," *SPE Annual Technical Conference*, Society of Plastic Engineers, Virtual Edition. (Best Paper Award)
- Redmann, A., Oehlmann, P.V., Zhang, R., Mecham, S.J., and Osswald, T.A., 2020, "3D Printed Dual-Cure Epoxy: Enabling High-Peformance Hybrid Composite Structures," *The Composites and Advanced Materials Expo*, Virtual Edition.

Academic Theses

- Setter, R., 2018, "Characterization of a B-Stage Resin for Additively Manufactured Adhesive Joints in Composite Structures," Semester Thesis, Technical University Munich, Munich, Germany.
- Dahmen, V., 2018, "Investigation into Co-Curing Hybrid Composite T-Joints with Additively Manufactured B-Stage Epoxy," Master Thesis, University of Wisconsin-Madison, Madison, WI.
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