

Studies of curing cycle of carbon fiber/epoxy resins (8552[®] and M21[®]) preregs based on thermal and rheological analyses

Sheila Marques Silva¹, Carolina Paiva Nascimento Silva^{2,3}, Thiago de Carvalho Silva^{2,4}, Mirabel Cerqueira Rezende², Edson Cocchieri Botelho¹, Michelle Leali Costa^{1,3+}

1. São Paulo State University, Department of Materials and Technology, Guaratinguetá, Brazil.
2. Federal University of São Paulo, Institute of Science and Technology, São José dos Campos, Brazil.
3. Lightweight Structures Laboratory, LEL/IPT, São José dos Campos, Brazil.
4. Federal Center for Technological Education Celso Suckow da Fonseca, Angra dos Reis, Brazil.

+Corresponding author: Michelle Leali Costa, **Phone:** +5511983266474, **Email address:** michelle.leali@unesp.br

ARTICLE INFO

Article history:

Received: August 23, 2021

Accepted: March 10, 2022

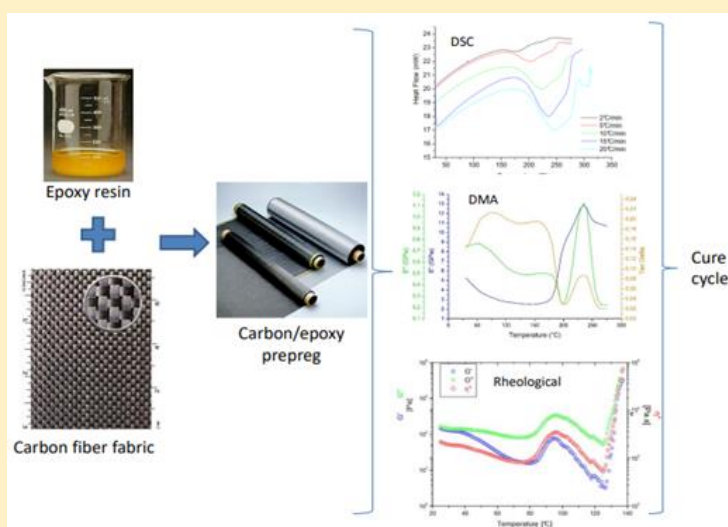
Published: August 17, 2022

Section Editor: Assis Vicente Benedetti

Keywords

1. cure kinetic
2. DSC
3. DMA
4. rheology
5. FTIR

ABSTRACT: Thermal and rheological characterizations were performed on prepreg produced with two different commercial epoxy resins - M21[®] and 8552[®] – aiming to study and optimize the curing cycle of structural components used in aerospace industry. Characterizations were performed by differential scanning calorimetry (DSC), rheology and dynamic mechanical analysis techniques were assessed and the results were correlated and supported by Fourier Transform Infrared spectroscopy. Additionally, to heating rates suggested by the material supplier, DSC analysis allowed to evaluate further heating rates: 2, 5, 10, 15 and 20 °C/min. Materials presented the n fractional order kinetic of cure and have in its formulation the presence of thermoplastics, in addition to epoxy and amine. Results confirmed that the best heating rates for processing both materials are the lower ones, as they result in a better control of the reactions between chemical compounds involved and the physical changes that are part of curing process stages. Results have analytically confirmed the suggested proposal for curing cycle from supplier is the best choice for materials involved.



1. Introduction

Polymeric composites have been widely used to produce lighter structures that have high specific strength, stiffness and good fatigue resistance (Mphahlele *et al.*, 2019). This class of materials has been used in an over an extensive range of applications such as aerospace, military, automotive, sporting and construction industries (Liu *et al.*, 2018). Polymeric composites manufacture can be processed by using thermoset resins, as epoxy, pre-impregnated in carbon fiber reinforcement. This pre-impregnated material, named also as prepreg, to be composed of a reinforcing fiber (carbon, glass, aramid, and others) that has been impregnated with a thermoset resin (epoxy, phenolic, for example) prior to the molding process. This way, parts and pieces can be produced into the desired shape and then be cured by the application of heat with the use of the prepreg. Thermoset polymers, such as epoxy resins, are the most commonly used in composites for aerospace, adhesives, hardware components, coatings and due to their good adhesion properties and thermal stability coupled with sufficient chemical resistance. However, the performance in each application is dependent on the cure process, i.e., the transformation of the resin into insoluble and infusible three-dimensional structures, by means of crosslinking reactions with curing agents and/or catalyst (Hatter *et al.*, 2020).

The polymeric matrix is an important component in a composite structure, which protects fibers or fillers against abrasion and harsh environmental conditions, and also transfer stress from the matrix to the reinforcement. In this way, the final performance of polymeric composite is strongly influenced by the interface between the matrix and the reinforcement (González-Benito, 2003; Hatter *et al.*, 2020; Liu *et al.*, 2018; Mphahlele *et al.*, 2019). Polymeric composites with similar chemical compositions may exhibit different properties, like transparency, elasticity, toughness and permeability depend on important factors such as physical dimensions and the curing cycles used (González-Benito, 2003; Hexcel Corporation, 2021a; b; Hubert *et al.*, 2019; Mesogitis *et al.*, 2019; Newcomb, 2019; Nixon-Pearson *et al.*, 2017; Ribeiro *et al.*, 2013; Wang *et al.*, 2020).

In actual use, many thermosets are cured using complex cure cycles to optimize the tradeoff between the processing time and final product's properties. This way, the low-molecular weight viscoelastic constituents of the thermoset must undergo a transformation to an amorphous high-molecular weight solid, through chemical reactions of the thermoset system, typically driven by temperature. Thus, knowing and

understanding the viscoelastic properties of the thermoset resin is essential for establishing an adequate curing cycle. Among these properties that must be monitored are minimum viscosity temperature; gel temperature; onset and peak curing temperature; minimum viscosity time; vitrification, degree of cure and glass transition temperature (Newcomb, 2019). Cure cycles used in the aircraft industry generally consist of alternating stages of heating ramps at slow rates followed by isotherms and pressure to ensure the slow, controlled, and complete cure of the thermoset resin systems used in prepregs. Heating rates must be slow to ensure that parts cured within autoclaves (which are not conventional ovens but complex pressure and temperature vessel systems) do not undergo exotherm (uncontrolled release of heat caused by the exothermic reaction of the epoxy resin cure) which could cause accidents inside the autoclaves (explosion) and generate parts with defects such as air bubbles caused by the uncontrolled release of volatiles (Agius *et al.*, 2013; Botelho *et al.*, 2001; Costa *et al.*, 2005; Hexcel Corporation, 2021a; b; Mphahlele *et al.*, 2019; Oishi *et al.*, 2013).

The quality of composites is controlled to a great extent by the cure cycle parameters such as time, temperature, pressure and their sequence of combination. Traditionally a composite manufacturer just follows the cure schedule suggested by the supplier. This cycle is usually determined in an ideal situation where the resin is still "fresh" and may not be representative to the actual curing state of the resin in a composite manufacturing facility (Liu *et al.*, 2018). The purpose of this study is to characterize thermally and rheologically the carbon fiber prepreg with commercial epoxy resins, known in the aerospace industry as M21[®] and 8552[®] systems, both produced by the Hexcel Composite, aiming to optimize de curing cycle of prepregs used in aerospace area. For this, analysis was made using differential scanning calorimetry (DSC), rheology characterization, dynamic mechanical analysis (DMA) and Fourier Transform Infrared (FTIR) spectroscopy techniques.

2. Experimental

2.1 Materials

In the present study, two different prepregs were analyzed: the first with epoxy resin type 8552[®] and the second with type M21[®], both reinforced with carbon fiber and supplied to EMBRAER by Hexcel Composites. These two systems are interesting because they are examples of two different toughening strategies. Resin 8552[®] is toughened through the introduction of a

submicron phase of a thermoplastic material that is dissolved in the uncured thermosetting epoxy resin. While the resin M21[®] is characteristic of the interlayer class of toughened thermosetting epoxy system that presents thermoplastic particles in the order of tens of microns, which are responsible for the creation of a resin-rich region between the layers (Wang *et al.*, 2020). The thermoplastic phase is introduced to address the common problem of composite brittleness as it enhances the fracture toughness and impacts laminate performance. At the same time thermoplastics affect prepreg processing characteristics. The toughening elevates the prepreg viscosity, changes inter-ply friction and morphology (Nixon-Pearson *et al.*, 2017).

2.2 Samples prepregs

The prepregs were previously conditioned in sealed plastic films, they were removed from the freezer to a controlled environment and left at room temperature for approximately 1 h. This duration time was experimentally identified for this specific sample size. After this period, the prepregs were removed from the plastic bags and cut with scissors to the appropriate sizes to be used in this study.

2.3 Differential scanning calorimetry (DSC)

The DSC is a thermal analysis technique that measures the difference in energy provided to a sample and a reference material in function of a controlled temperature programming. The DSC technique monitors the endothermic, exothermic and specific heat variations experienced by a sample (Braga *et al.*, 2011). In this study, the DSC technique was used to determine the temperature and cure enthalpy of the prepregs and the results obtained were used to determine the curing kinetics.

The equipment used in this study is a PerkinElmer model Pyris 1 linked to a cooling system model Intracooler 2P. This arrangement is a DSC power compensated coupled with a low mass furnace (~1 g) that minimize the effect of thermal gradient. First of all, calibration was performed using indium standard as per equipment supplier instructions, ASTM E967-18 (2018) and ASTM E968-02 (2014b), which suggest calibrating temperature and enthalpy using metallic standard. The DSC equipment was calibrated for each heating rate studied in the present work (Vyazovkin *et al.*, 2011). Samples (~5 mg) were placed into hermetic aluminum pans and heated from room temperature (22 °C) to 300 °C, using different heating rates (2, 5, 10, 15, and

20 °C min⁻¹) under a constant flow of N₂ at a rate of 20 mL min⁻¹. After curing, the same sample was subjected to further heating from room temperature to 250 °C, at a heating rate of 20 °C min⁻¹ to determine the glass transition temperature (T_g) (ASTM E1356-08, 2014a; Vyazovkin *et al.*, 2011).

2.4 Rheological characterization

Classically, a thermoset resin undergoes two main phase transitions during cure, gelation and vitrification. Rheological tests were assessed aiming to determine resin changes during the cure cycle (temperature conditions only) recommended by Hexcel Composites Co. (for autoclave processing of laminates <15 mm) (Hexcel Corporation, 2021a; b). The correlation between viscosity and temperature or viscosity and time of the thermoset resin cure or the prepreg systems is very useful information for composite processing. The viscosity control during the autoclave processing allows the optimization of the resin infiltration inside the reinforcement, and, consequently, a larger densification of the composite materials in a shorter time (ASTM D4473-08, 2021; Costa *et al.*, 2006; Das and Chaudhary, 2019; Paiva *et al.*, 2006). Rheological analyses were performed on the equipment Rheometric Scientific, model SR-5 with parallel plates, a constant frequency of 0.16 Hz ($\omega = 1 \text{ rad s}^{-1}$), 500 Pa of stress, H (gap) of 0.3 mm for M21 and 0.4 mm for the sample 8552, using different heating rates (2.5; 5.0, and 10 °C min⁻¹), heating from room temperature (22 °C) to gel temperature. The method was based on the ASTM D4473-08 (2021) - Standard Test Method for Plastics: Dynamic Mechanical Properties: Cure Behavior. This way, during the cure, viscoelastic properties of the sample can be measured such as shear storage modulus (G'), shear loss modulus (G''), loss tangent or loss factor, $\tan \delta = G''/G'$ and the complex dynamic viscosity (η^*).

2.5 Dynamic Mechanical Analysis (DMA)

DMA is currently used to study viscoelastic behavior of polymer composites and its basic principle are the same of the rheology (Das and Chaudhary, 2019; Ştefanov *et al.*, 2020). In this way, depending on the testing mode, three quantities are usually monitored, i.e., the storage modulus, E' , which is a measure of the stored energy (the elastic part), the loss modulus, E'' , which is a measure of the energy lost as heat (the viscous part), and the loss tangent or loss factor, $\tan \delta = E''/E'$, which indicates how efficiently the material loses energy due to internal friction and molecular rearrangement. One of the

most important transitions in polymers is the T_g . This is the temperature region where the material changes from a glassy to a rubbery state. While materials can be used above, below, and within this region, thermosets tend to be used below T_g , because approaching T_g , stiffness decreases significantly resulting in a corresponding decrease in strength (Stefanov *et al.*, 2020).

The DMA characterization of the studied epoxy systems was assessed using the equipment TA2980 supplied by TA Instruments, with single cantilever, frequency of 1 Hz, 10 μm of amplitude, heating rates (2, 5, 10, 15, and 20 $^\circ\text{C min}^{-1}$), heating from 30-300 $^\circ\text{C}$. After curing, the same prepreg sample inside the equipment was again subjected to DMA analysis, at a heating rate of 2.0 $^\circ\text{C min}^{-1}$, frequency of 1 Hz, heating from 30-300 $^\circ\text{C}$ for the determination of T_g .

2.6 Fourier transform infrared spectroscopy (FTIR)

The FTIR is a technique that allows following the curing reactions, studying and quantifying the conversion of different representative functional groups (Sánchez-Soto *et al.*, 2007). In this study, the equipment used was a Spectrum One supplied by PerkinElmer with the Universal Attenuated Total Reflectance (UATR) accessory. This equipment works in the regions from 4000 to 400 cm^{-1} , resolution of 0.5 cm^{-1} and 20 scan were performed. The analyses of the two prepreg samples used the samples as received and also after a carefully preparation, to emphasize the main bands of the modifiers present in the epoxy resin samples. In order to separate the polymeric matrix from the fibers, a treatment with cold acetone was carried out. During the treatment with cold acetone, the sample showed a cloudy color coming from a fine light gray solid and the sample was centrifuged, treated with acetone and again centrifuged for a better elimination of interferers. Afterwards, a fraction of the sample was treated with pyridine and the soluble part evaporated. This procedure resulted in a film that was analyzed. Pyridine was used because it is a good solvent for polyethersulfones (PES), according to the literature (Silverstein *et al.*, 2000). A fraction of the sample was also pretreated with formic acid and the soluble part evaporated, as this acid is a good diluent for polyamides in general.

3. Results and discussions

3.1 DSC

The first step to calculate exothermic heat flow on DSC measurements is to determinate the appropriate heat flow 'baseline' for the instrument. Heat flow at any time can then be calculated from the difference between the established baseline and the actual measured heat flow. For dynamic scans, the baseline is calculated by measuring the heat flow at reaction start and at its completion, assuming a linear variation between the extremes. For an isothermal experiment, this baseline is constant and it can be determined from the measured flow at the completion of the reaction (Hubert *et al.*, 2019).

3.1.1 Prepreg 8552

Figure 1 shows DSC and conversion degree curves for the 8552-epoxy system. A typical dynamic DSC curve can be seen in Fig. 1a and shows the results obtained for the 8552-epoxy system in different heating rates. By assuming that the heat evolved during cure is directly related to the disappearance of the epoxy groups during the reaction, the area above the peak at the exothermic region was used to determine the epoxy resin fractional conversion.

The kinetic parameters in this work were obtained by dynamic DSC scans using the mathematical model described by Eq. 1 (Agius *et al.*, 2013; Costa *et al.*, 2005; Friedman, 1964; Paiva *et al.*, 2006; Paris *et al.*, 2010; Vyazovkin *et al.*, 2014):

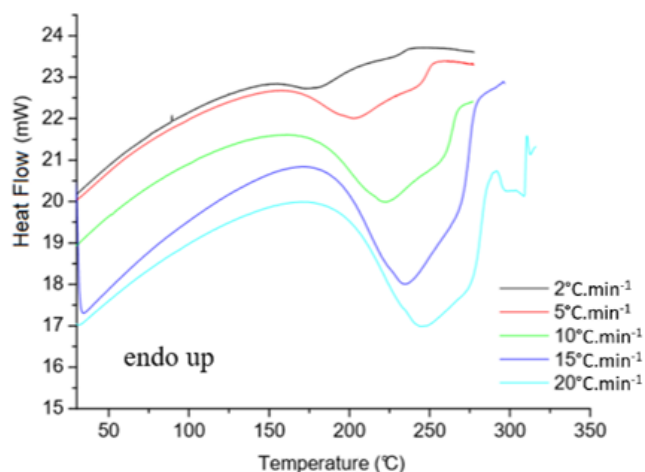
$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \quad (1)$$

where α is the degree of chemical conversion, n is the order of the reaction, k is the reaction rate constant and da/dt is the derivative α with respect to time or temperature or reaction rate (Costa *et al.*, 2005; Friedman, 1964).

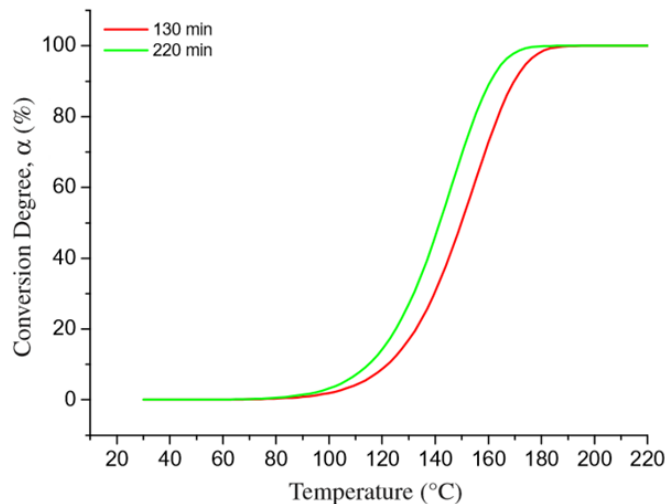
The reaction rate is generally assumed to have a temperature dependence characterized by the Arrhenius relationship (Eq. 2):

$$k = Ae^{\frac{-E_a}{RT}} \quad (2)$$

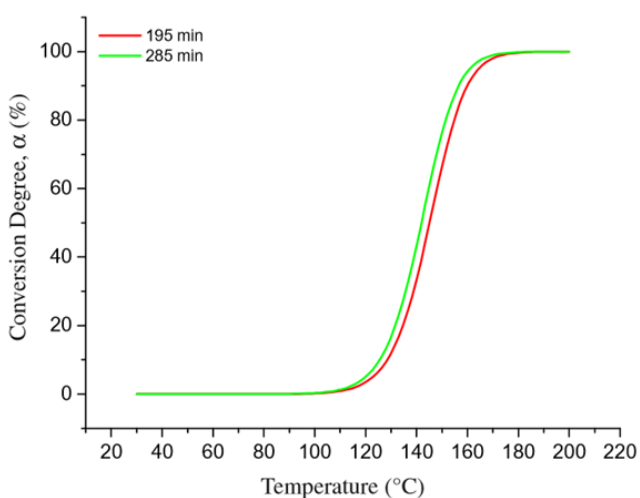
where A is the pre-exponential constant, E_a is the activation energy for the reaction, R is the universal gas constant, and T is the absolute temperature in degrees Kelvin.



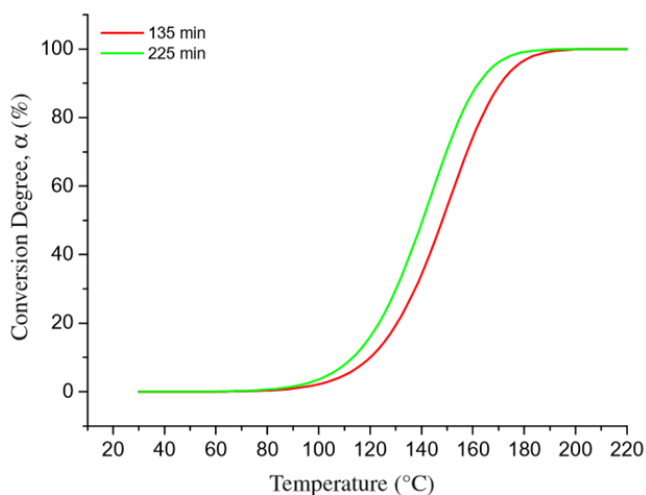
(a)



(d)



(b)



(c)

Figure 1. DSC and conversion degree curves for the Carbon/8552 epoxy prepreg. (a) Dynamic DSC curve. (b) Degree of conversion, α , at 2 °C min⁻¹, (c) 10 °C min⁻¹, and (d) 15 °C min⁻¹ considering isotherms of 120 and 210 min (b).

When Eqs. 1 and 2 are combined, they produce Eq. 3:

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E_a}{RT}\right) (1 - \alpha)^n \quad (3)$$

which yields one independent variable (t), two dependent variables (α and T), three unknown constants (A , E_a , and n), and the universal gas constant (R). Equation 4 has three degrees of freedom, or three variables. In order to have a definite solution, one variable may either be held as a constant during the reaction process or it may be related to another variable; therefore, the reaction process can be defined.

In the DSC, the temperature varies linearly with the time, following the relation (Eq. 4):

$$T - T(0) = \beta t \quad (4)$$

and

$$\beta = \frac{dT}{dt} \quad (5)$$

where T is the current temperature, $T(0)$ is the initial temperature, t is the time, and β is the heating rate.

Furthermore, the $\frac{d\alpha}{dt}$ can be described by the following equation:

$$\frac{d\alpha}{dt} = \frac{dT}{dt} \frac{d\alpha}{dT} = A \exp\left(\frac{-E_a}{RT}\right) (1 - \alpha)^n \quad (6)$$

Combining Eqs. 5 and 6 with Eq. 3, which will give:

$$\beta \frac{d\alpha}{dT} = A \exp\left(\frac{-E_a}{RT}\right) (1 - \alpha)^n \quad (7)$$

The Eq. 7 represents the theoretical shape of DSC curve that is determined in this work. The value of degree of chemical conversion, α , is obtained by dividing the $\Delta H_{\text{partial}}$ by total the heat ΔH generated during the whole reaction, as shown in Eq. 8.

$$\alpha = \frac{\Delta H_{\text{partial}}}{\Delta H} \quad (8)$$

In the present work, the values for $\Delta H_{\text{partial}}$ and ΔH are evaluated from the area above the DSC curve. Equation 9 can be obtained to a linear form by taking the natural logarithm of both sides of Eq. 7 and can be solved by a multilinear regression $\ln\left(\beta \frac{d\alpha}{dT}\right)$ with $-\frac{1}{RT}$ and $\ln(1 - \alpha)$ as variables, which have been evaluated from DSC data and solving for A , E_a and n .

$$\ln\left(\beta \frac{d\alpha}{dT}\right) = \ln A - \frac{E_a}{RT} + n \ln(1 - \alpha) \quad (9)$$

So, it was possible to determine the kinetic parameters of both systems and compare the results using the equations described above and with the results of the dynamic scanning of the M21 and 8552 epoxy prepreg systems at different heating rates.

Table 1 shows all kinetic parameters obtained by dynamic method for the five heating rates: 2, 5, 10, 15, and 20 °C min⁻¹ for carbon/8552 epoxy resin prepreg. T_{initial} and T_{final} describe the temperature rate in that the prepreg cure kinetic was studied. The T_{peak} and T_{final} of the cure shows an increase with the increment of the heating rate used, showing a displacement of the beginning and final of the cure. This fact shows that despite the reduction in the curing time of the material, it does not represent an advantage for the selection of curing cycle. Higher temperature in the autoclave would be required to reduce the curing cycle leading to a much higher cost of the process than curing at lower rates. The T_g values reduce with increasing heating rate, due to the decrease in the formation of cross-links. It is known that greater density of crosslinks system contributes to increase the T_g (Agius *et al.*, 2013; Costa *et al.*, 2005; Paris *et al.*, 2010).

Table 1. DSC results and kinetic parameters obtained for the 8552 prepreg at different heating rates.

Heating Rate (°C min ⁻¹)	T _{initial} (°C)	T _{onset} (°C)	T _{peak} (°C)	T _{final} (°C)	-ΔH (J g ⁻¹)	n	lnA (s ⁻¹)	E _a (kJ mol ⁻¹)	T _g (°C)
2	145	171	181	220	106	1.5±0.1	39.4	170 ± 4	215
5	158	176	204	256	142	1.4±0.1	18.9	98 ± 9	211
10	161	185	224	273	171	1.2±0.1	18.0	96 ± 7	210
15	172	190	236	281	201	1.1±0.1	17.5	94 ± 6	205
20	172	197	248	291	203	1.0±0.1	16.6	91 ± 5	197

As the DSC equipment was calibrated for each heating rate studied, it can be stated that T_{onset} , T_{peak} , T_{final} and the enthalpy value increase with increasing the heating rate. This indicates that slower heating rates, such as 2 °C min⁻¹, favor higher collision between the molecules, allowing a greater interaction between the components (epoxy and curing agent) even promoting a more controlled curing of the material with less exotherm (high energy release during the cure) and at lower temperatures. Therefore, a recommended heating rate to be used for curing this prepreg in an autoclave is 2 °C min⁻¹.

The heats of reaction, ΔH , are over the range 106-203 J g⁻¹ and the order of reaction found is between 1.5 and 1.0. This evidence demonstrates that there is a consistent dependence among the kinetic parameters and the heating rate using in the curing process.

The fractional cure reaction order ($n \sim 1.5$ to 1.0) found implies in complex reaction mechanisms. The

appearance of the fractional reaction order suggests the existence of a reaction mechanism via formation of free radicals. The beginning of the curing reaction of the epoxy resin requires the opening of the epoxy groups through the amine catalyzed by the temperature. The curing reaction of epoxy resin with amine hardeners leads to formation of two main reactions: secondary amine and tertiary amine formation. The groups hydroxyls generated during the reaction or from the addition of solvents or others catalysts, or by the presence of impurities and even moisture, accelerate significantly the reaction between the glycidyl ether and the amine. However, in all cases, the hydroxyl groups behave only as reaction catalysts and not as consumers of epoxy groups in competition with the amine group (Agius *et al.*, 2013; Costa *et al.*, 2005; 2006; Paiva *et al.*, 2006; Paris *et al.*, 2010; Sánchez-Soto *et al.*, 2007). Thus, complex reaction mechanisms characterize the cure of epoxy resin with amine hardeners.

The activation energy, E_a , was determined using the variation of the maximum temperature of the exothermic peak with the heating rate based on the Ozawa and Arrhenius method (Costa *et al.*, 2006; Paiva *et al.*, 2006). The E_a and reaction order (n) decrease with increasing heating rate, showing that the higher the temperature, lower the dependence on reaction with the formation of products and less is the amount of energy needed to overcome the activation barrier. Increased heating rate increase the speed of transfer of thermal energy, which consequently decrease the curing reaction time. On the other hand, enthalpy increases with the increment in the heating rate, suggesting that higher heating rates favor the release of energy by the system. This fact must be studied carefully, if high heating rates used in the autoclave to cure large parts, there is a risk of high energy release (phenomenon called exotherm), which may compromise the quality of the part or even damage the autoclave.

The use of two-stage cure cycles is known to develop stronger laminates in the aerospace industry and the cycle suggest by the 8552 prepreg supplier is: heating from 30 to 180 °C at 0.6-2.8 °C min⁻¹ and holding at 180 °C for 120 to 210 min. Based on this information, mathematical simulations of the degree of conversion of 8552 epoxy resin was carried out. Figure 1b presents the simulation of the prepreg system conversion degree as function of temperature for 195 and 285 min. This is the time necessary to elevate the temperature from 30 to 180 °C, using the heating rates of 2 °C min⁻¹ and holding at 180 °C by 120 min (total cycle of 195 min) and 210 min (total cycle of 285 min). This curve was obtained based on Eq. 10 (Costa *et al.*, 2006), using a predetermined time and temperature range.

$$\alpha = 1 - [1 - (1 - n) \cdot A \cdot t \cdot \exp\left(-\frac{E_a}{RT}\right)]^{\frac{1}{1-n}} \quad (10)$$

For the heating rate of 2 °C min⁻¹ in Fig. 1b, the conversion degree of a temperature below 120 °C is less than 5% and that after 120 °C the cure actually begins. When the temperature of 180 °C is reached, practically 100% of the conversion has been completed, for both the 120- and 210-min isotherms. However, the degree of conversion at the other heating rates (Fig. 1c and d) is observed that at a temperature of 120 °C the degree of conversion is high (> 5%), showing that the rise in temperature stimulates the start of curing in a disordered way. But the temperature of 180 °C is not sufficient to ensure a complete cure of the prepreps at these higher rates (considering the isotherm of 120 min).

3.1.2 Prepreg M21

Figure 2 shows DSC and conversion degree curves for the Carbon/M21 epoxy. Figure 2a shows the dynamic DSC curve with the presence of an endothermic peak in the region of 190-200 °C more accentuated at the rates of 2 and 5 °C min⁻¹. This behavior can be directly related to the formulation of prepreg M21, because, according to the literature, it has polyamide and poly(ether sulfone) thermoplastics in its composition (Mesogitis *et al.*, 2018; Paris *et al.*, 2012).

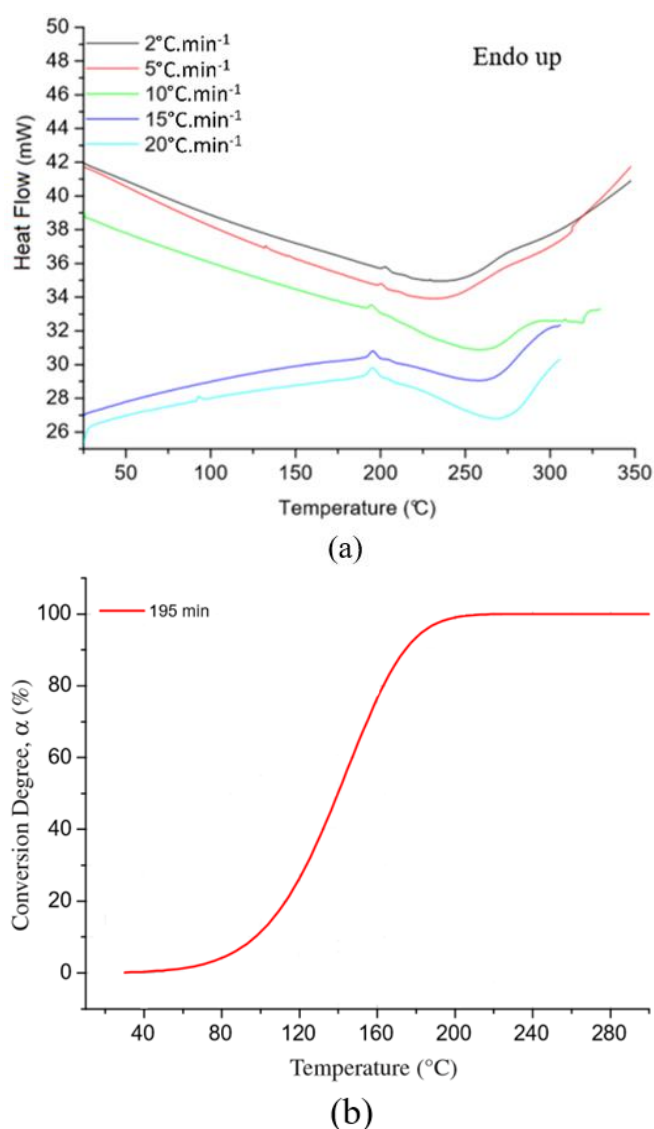


Figure 2. DSC and conversion degree curves for the Carbon/M21 epoxy prepreg. (a) Dynamic DSC curve at different heating rates. (b) Degree of conversion, α , at 2 °C min⁻¹, considering an isotherm of 120 min.

According to Paris *et al.* (2012), prepreg M21 is a thermoset resin loaded with thermoplastic particles, which limit the propagation of cracks. Thermoplastics, which represent around 30% by weight of the resin, consist of polyamide 6; polyamide 6/12 copolymers introduced as nodules after mixture of the reagent system and the melted poly(ether sulfone) (PES). Although the composition of the epoxy/amine system is a classic composition, the presence of polyamides suggests that after the melting of the particles (the melting of the polyamide occurs at temperatures greater than 190 °C-PA 6/12), they can react with the epoxy resin, modifying the curing kinetics of the conventional epoxy/amine system. This reaction can either improve the functional characteristics of the system, but it can also cause a rupture in the property of resistance to crack propagation.

Due to the possible complex chemical formulation of M21 (Paris *et al.*, 2010; 2012), it can be understood that the physical-chemical study itself is not trivial, both for the characterization of its chemical components and for the kinetic study, since, as previously noted, kinetics involves so much the available reagents as to the stoichiometric proportion present in the resin.

Thus, identifying trends in Tab. 2 becomes a difficult task. The initial temperature of cure was identified as occurring immediately after the endothermic peak. It can

be observed that the cure of M21 in the DSC starts at practically all heating rates studied around 202 °C and finished around 303 °C.

According to Tab. 2, the reaction order (n), the activation energy (E_a) and the pre-exponential factor ($\ln A$) increase with the reduction of the heating rate. The order of reaction and the enthalpy are related to the area of the curve obtained in the DSC graph, which is straightly involved with the disappearance of epoxy groups during curing. As also found for prepreg 8552, the cure reaction order is fractional ($n \sim 1.8$ to 0.6), implying complex reaction mechanisms.

The enthalpy value decreases with increasing heating rate. It was expected that the greater the enthalpy, the greater the formation of cross-links, that is, the greater the crosslinking and, consequently, the greater the value of the T_g found. However, the highest T_g value found was for the heating rate of 5 °C min⁻¹, suggesting that for this system the enthalpy value, that is, the heat of reaction generated during curing should not be considered as an indication of the T_g reached. For all these reasons, it is observed that an interpretation of the data in Tab. 2 is very difficult, a fact that can be attributed to the formulation of M21, as shown in the literature (Costa *et al.*, 2005; Paris *et al.*, 2010; 2012).

Table 2. DSC results and kinetic parameters obtained for the M21 prepreg at different heating rates.

Heating Flow (°C/min)	T _{initial} (°C)	T _{onset} (°C)	T _{peak} (°C)	T _{final} (°C)	-ΔH (J g ⁻¹)	n	lnA (s ⁻¹)	E _a (kJ mol ⁻¹)	T _g (°C)
2	206	213	242	310	194	1.8 ± 0.1	20.3	112 ± 9	178
5	200	206	239	303	158	1.2 ± 0.1	18.3	101 ± 3	183
10	201	207	258	304	153	0.8 ± 0.1	11.9	75 ± 2	176
15	204	206	268	304	125	0.7 ± 0.1	10.1	67 ± 1	168
20	203	207	270	306	137	0.7 ± 0.1	11.3	71.6 ± 0.4	170

An important factor to remember is that the cure cycle suggested by the manufacturer (Hexcel Corporation, 2021a), shows that M21 must be cured at a maximum temperature of 180 °C. This may be an indication of confirmation of the presence of polyamide 6/12 in the formulation, as this curing temperature prevents the polyamide from melting (melting of polyamide 6/12 occurs at 190 °C (Paris *et al.*, 2010; 2012) and begins to react with the epoxy resin during its cure with the amine (Paris *et al.*, 2012). Ersoy and Tugutlu (2010) state that there are thermal events occurring in the M21 formulation below 150 °C, however, such events are of low intensity and therefore are not registered by the DSC equipment. This explains why although the DSC does not record cure before 200 °C, it is occurring at 180 °C,

as suggested by the prepreg supplier's cure cycle (Hexcel Corporation, 2021b). To try to confirm this information, rheological studies were carried out in order to find the system's gelling temperature, thus indicating the actual beginning of M21 cure. This subject is covered in the topic Rheological Characterization.

The cure cycle suggested by the prepreg supplier is constituted by two steps: heating from 30 °C to 180 °C at 2.0 °C min⁻¹ and holding at 180 °C for 120 min. Thus, Fig. 2b represents the mathematical simulations of the degree of conversion of the M21-epoxy resin obtained from the time and temperature values suggested by the cure cycle provided by the supplier.

In Fig. 2b, it is possible to identify an important data for the heating rate of 2 °C min⁻¹ (heating rate suggested

by the prepreg supplier), with the gradual increase in temperature at this rate, a degree of conversion close to 10% of the total cure at 100 °C. Another important point is that when the temperature of 180 °C is reached, the degree of conversion is already greater than 90% for this heating rate.

3.2 DMA

3.2.1 Prepreg 8552

Pre-impregnated epoxy resin 8552 was cured at the different heating rates studied (2, 5, 10, 15, and 20 °C min⁻¹) inside the DMA equipment. Then, after dynamic curing of the material, the same sample was heated again at a rate of 2 °C min⁻¹, according to the [ASTM D7028-07 \(2015\)](#) standard, to obtain the T_g . This study was carried out with the objective of evaluating the influence of the heating rate used on the curing of the material and on the T_g .

Figure 3 shows the DMA, storage modulus (E'), loss modulus (E'') and tan delta curves as a function of the temperature of the 8552-epoxy resin prepreg samples cured at 2 °C min⁻¹ and **Tab. 3** summarizes the values found for T_g . At the start of heating at 2 °C min⁻¹ the storage modulus (E') is 5.1 GPa, after the temperature of 160 °C the (E') begins to increase again until reaching its maximum value of 12.9 GPa at around 240 °C. This probably occurs due to the reduction of the viscosity of the resin with the increase of the temperature, consequently reducing the rigidity of the material (E') and, after reaching the gelation point, the curing process of the prepreg begins, until its consolidation, where the (E') presents its maximum value.

The same behavior is observed for all heating rates studied (although the E' values are lower) with the exception of the rate of 20 °C min⁻¹, which does not appear to allow an adequate cure of the prepreg. The heat transfer carried out inside the DMA furnace occurs through radiation and convection, therefore, heat transfer processes are not as efficient as in a DSC, where the heat transfer occurs by conduction (thermal contact). Therefore, high heating rates in DMA are not widely used due to the inefficiency in controlling the sample temperature, which is much higher than that used in a DSC. Thus, these factors can damage the cure of the prepreg inside the DMA.

Another interesting fact observed in **Fig. 3a** is that the tan delta presents several peaks during the heating of the material, suggesting that different thermal events are happening during/final cure. This event illustrates that the formulation of epoxy resin 8552 does not consist only

of epoxy resin and amine, but of other components such as thermoplastics. This fact is investigated with FTIR technique.

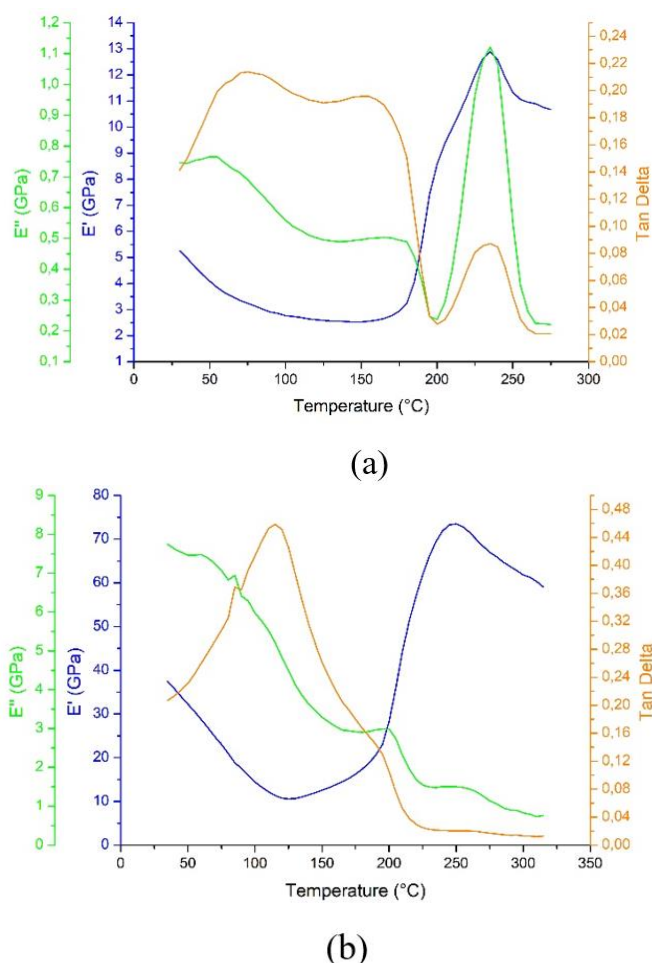


Figure 3. DMA curve of curing of prepreg systems at a heating rate of 2 °C min⁻¹. **(a)** Carbon/8552 prepreg and **(b)** Carbon/M21 prepreg.

For amorphous polymers, as in the case of epoxy resin prepreps, the dynamic-mechanical behavior in the glass transition region can change from a typical behavior of rigid materials to that of an elastomeric material and its modulus, on average, from 10³ to 10⁴ Pa. Therefore, it is possible to observe in this region a reduction in the storage module (E') and increments in both the loss module (E'') and the mechanical damping or internal friction in a viscoelastic system tan delta ([Wetton et al., 1991](#)).

The value obtained from T_g by E' onset (215 °C) for the prepreg cured at 2 °C min⁻¹ is greater than the value reported by the prepreg supplier (195 °C) ([Hexcel Corporation, 2021a](#)). Although the T_g measurement technique is the same in both cases (E' onset), the curing cycle, the size of the specimen and the apparatus used in

the prepreg processing were different. In the case of the prepreg supplier, it was used an autoclave to cure a laminate with defined thickness and with a curing cycle with dynamic temperature variations and isotherms. In the present study, only a dynamic cure of one pre-impregnated ply at a constant heating rate. Thus, different types of processing generate materials with different thermal and mechanical properties.

Table 3. Glass transition temperature obtained DMA by different methods: Onset E'; Peak E'', and tan delta for the 8552-prepreg cured at different heating rates.

Heating Rate (°C min ⁻¹)	T _g (onset of E')	T _g (peak of E'')	T _g (peak tan delta)
2	215	232	236
5	211	229	231
10	210	227	230
15	205	224	227
20	197	223	230

3.2.2 Prepreg M21

M21 prepreg was also cured at the different heating rates studied (2, 5, 10, 15, and 20 °C min⁻¹) inside DMA equipment. Then, after dynamic curing of the material, the same sample was also heated again at a rate of 2 °C min⁻¹, according to the [ASTM D7028-07 \(2015\)](#) standard, to obtain the glass transition temperature.

Figure 4 shows the DMA for M21 prepreg samples cured at 2 °C min⁻¹. It is observed that E' starts on heating with a value of approximately 40 GPa at 30 °C (2 °C min⁻¹) and decreases with the temperature increasing. From the heating temperature of 120 °C, the E' starts to rise again until it reaches its maximum value of 73 GPa around 250 °C. This probably occurs due to the reduction of the resin viscosity with increasing temperature, consequently reducing E' and, after reaching the gelation point, the prepreg curing process begins, until its solidification, where E' presents its maximum. The same behavior is observed for all rates studied (not showed in the presented work) with the exception of the rate 20 °C min⁻¹, similar to the process in prepreg 8552.

The existence of more than one thermal event is also confirmed by the loss modulus and tan delta curves in the M21 prepreg sample, with increasing temperature, since more than two peaks are generated in (E'') and tan delta.

These events, as shown by DSC, must be related to the complex cure of M21, associated with its formulation, which has other constituents besides epoxy resin and amine.

Figure 4 and **Tab. 4** shows that the M21 glass transition temperature measured by E' onset was between 168 to 184 °C. It is not possible to establish a relationship between the heating rate used in curing the material and the T_g obtained. The E'' and tan delta curves (**Fig. 4**) show graphs with more than one peak, suggesting that the material may not have homogeneously cured. For this reason, different types of cures obtain different values of T_g, a fact that suggests a material consisting of several components or some other thermal event, such as melting.

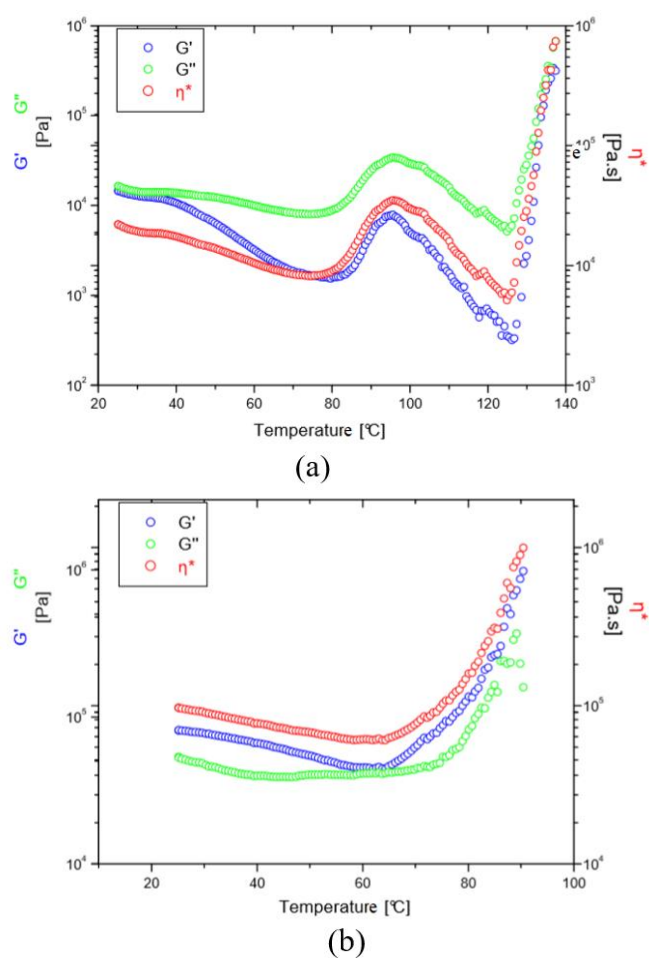


Figure 4. Rheological curves obtained for prepreg systems at 2.5 °C min⁻¹. (a) 8552 and (b) M21.

Table 4. Glass transition temperature obtained by DMA by different methods: Onset E'; Peak E'' and tan delta for prepregs M21 cured at different heating rates.

Heating Rate (°C min ⁻¹)	T _g onset of E' (°C)	T _g peak ₁ of E'' (°C)	T _g peak ₂ of E'' (°C)	T _g peak ₁ tan delta (°C)	T _g peak ₂ tan delta (°C)
2	178	207	248	205	253
5	184	-	214	-	257
10	177	-	218	-	222
15	168	-	221	-	223
20	170	-	221	-	223

The variation of T_g that occurs in the material can be studied through the tan delta (relation between the values of elasticity moduli (E''/E')) that has influence of the internal and/or external characteristics of the phase. The presence of a more rigid phase in the material can move the T_g to higher values. This increase can be caused by the polymeric chain (inclusion of rigid groups, bulky side groups, low symmetry of the molecule, increased molar mass or through secondary forces). On the other hand, the plasticization of a phase by external agents or low molar mass fractions increases the mobility of polymer chains within this phase, reducing the T_g measured by tan delta (Menard, 1999; Urban *et al.*, 2007).

The M21 epoxy resin system showed an endothermic event in the DSC experiments, recognized by Paris *et al.* (2010; 2012) as the melting of polyamide 6/12, and it is important to note that the T_g of the material is very close to the temperature of melting, which can cause interference when assessing M21 by DMA and DSC techniques.

For more detailed studies of the factors, which can influence the curing kinetics and the T_g of the material, it is important to use techniques that can identify and also quantify the components present in the M21 resin system.

3.3 Rheological characterization

As previously described, a parallel plate rheometer was used to measure the gelation temperature of the prepreg studied. The gel temperature (T_g) of a thermoset system is specific to each system, depending on the purity, shelf life, chemical nature, and degree of cure of resin. In T_g , there is an infinite three-dimensional network coexisting with countless free chains. When the system reaches the gel time, the polymer network becomes denser, with the consequent branching and increase of the molecular chains and, due to this behavior, the flexibility and mobility of the material decreases (Costa *et al.*, 2006).

3.3.1 Prepreg 8552

Figure 4a and Tab. 5 show the rheological parameters for epoxy resin type 8552 analyzed at various heating rates. It was found that the region of minimum viscosity occurred at higher temperatures with the increase in the heating rate, probably due to slower curing kinetics, caused by the faster heating of the analyzed sample. However, the minimum viscosity value decreased significantly with the increase in the heating rate, due to the higher temperatures favoring the breaking of secondary bonds existing in the polymer matrix structure and also the increase in free volume (Menard, 1999).

During the rheological analysis, a significant evolution of the complex viscosity was verified after passing through the region of minimum viscosity, characterizing a continuous increase of the elastic component, due to a network formed by particles or aggregates interconnected by elastic interactions, characterizing the phase from a Newtonian system to a viscoelastic system. During polymerization, as the reaction occurs, the polymer chains grow, and then branch and, depending on the density of cross-links, their flexibility and mobility decrease (Menard, 1999).

The gradual increase in viscosity after the minimum point is due to a slow restructuring of the system. Thus, simply by observing the evolution of the complex viscosity allowed determining the gel time or temperature. The gel temperature increased with increasing heating rate ranging between 130 and 177 °C.

Rheological curves obtained in this work (not showed in this article) showed initially $G'' > G'$ (i.e., viscous behavior dominates elastic behavior: liquid behavior). This behavior was followed by the gel state with $G' > G''$ (gel or solid-like behavior). When the curves of G' and G'' intersect ($G' = G''$ or $\tan \delta = G''/G' = 1$) the sol-gel transition point or the gelation point was achieved. At this point the epoxy resin is in the liquid state and the curves of G' , G'' , and η^* show minimum values. This decrease in the η^* value is attributed to the gradual destruction of existing interaction forces, i.e., gradual destruction of van der Waals forces. The observed viscosity behavior shows that the heating rate increasing

shifts the minimum viscosity temperature to higher value (T_{η} minimum) (Tab. 5). Subsequently, over time, the curves of G' , G'' , and η^* increase due to the curing reaction and the formation of a three-dimensional network of crosslinked molecules. After the gel time, the

network of polymeric chains densifies and the molecular chains growth, with a decrease in the flexibility and mobility of the polymer (Costa *et al.*, 2006; Mphahlele *et al.*, 2019).

Table 5. Prepreg rheological parameters for M21 and 8552 epoxy systems at different heating rates.

	Heating Rate (°C min ⁻¹)	η^*_{minimum} (Pa.s)	$T_{\eta^*_{\text{minimum}}}$ (°C)	T_{gel} (°C)	T_{gel} (°C) $G'=G''$
Prepreg M21	2.5	60406	64	67	-
	5.0	419	64	96	106
	10.0	2014	75	96	108
Prepreg 8552	2.5	5133	125	130	137
	5.0	340	156	163	169
	10.0	6.77	158	177	189

Table 5 shows for prepreg 8552 that the increase of the heating rate reflected in the reduction complex viscosity (η^*) associate with the increase of the temperature of minimum viscosity. This decrease in viscosity occurs due to the increase in free volume and the gradual destruction of interaction forces (van der Waals interactions). After this point the curing process of the prepreg begins, with the formation of a three-dimensional network.

3.3.2 Prepreg M21

Figure 4b and Tab. 5 present the rheological parameters determined for the resin M21 analyzed at different heating rates. It was found, again, that the region of minimum viscosity occurred at higher temperatures, with the increase in the heating rate. However, the value of the minimum viscosity decreased significantly with the heating rate increase, mainly for the rate of 5 °C min⁻¹, not showing a linear behavior when compared to the heating rate of 10 °C min⁻¹, also observed by Paris *et al.* (2010; 2012). They have used on their research with M21 resin, six heating rates (1, 3, 5, 10, 20, and 50 °C min⁻¹) and observed that the complex viscosity decreases with the increase of heating rate, however when comparing the heating rate of 5 °C min⁻¹ and 10 °C min⁻¹, the rate of 5 °C min⁻¹ has a lower viscosity than 10 °C min⁻¹.

In viscoelastic monitoring, the gel time/temperature can still be obtained by two other methods: by crossing

G' (storage module) with G'' (loss module) or by varying the $\tan \delta$ (damping), in which the curing temperature starts to occur for values of $\tan \delta$ equal to 1 ($\tan \delta = G''/G'$).

The gel temperature (T_{gel}) observed from η^* curves vary between 67 and 96 °C, depending on the heating rate used. The gel point obtained from the crossing of G' with G'' is not observed for 2.5 °C min⁻¹, but it is verified in the other heating rates studied, and varied between 106 and 108 °C. The difference between the T_{gel} values obtained by method of in η^* analysis and by the crossing of G' with G'' was 10% on average.

3.4 FTIR

3.4.1 Prepreg 8552

The UATR accessory was used to evaluate the studied samples. Figure 5 line A (spectrum A) shows the spectrum obtained for the prepreg 8552 without any treatment and shows the presence of epoxy resin, and some absorption of an amino component, probably due to the curing agent. The presence of absorption in the carbonyl region was observed and it can come from a modified epoxy resin or reaction product with the curing agent used. Table 6 presents the main bands of the components that are probably part of the composition of the 8552 and M21 epoxy resin systems studied.

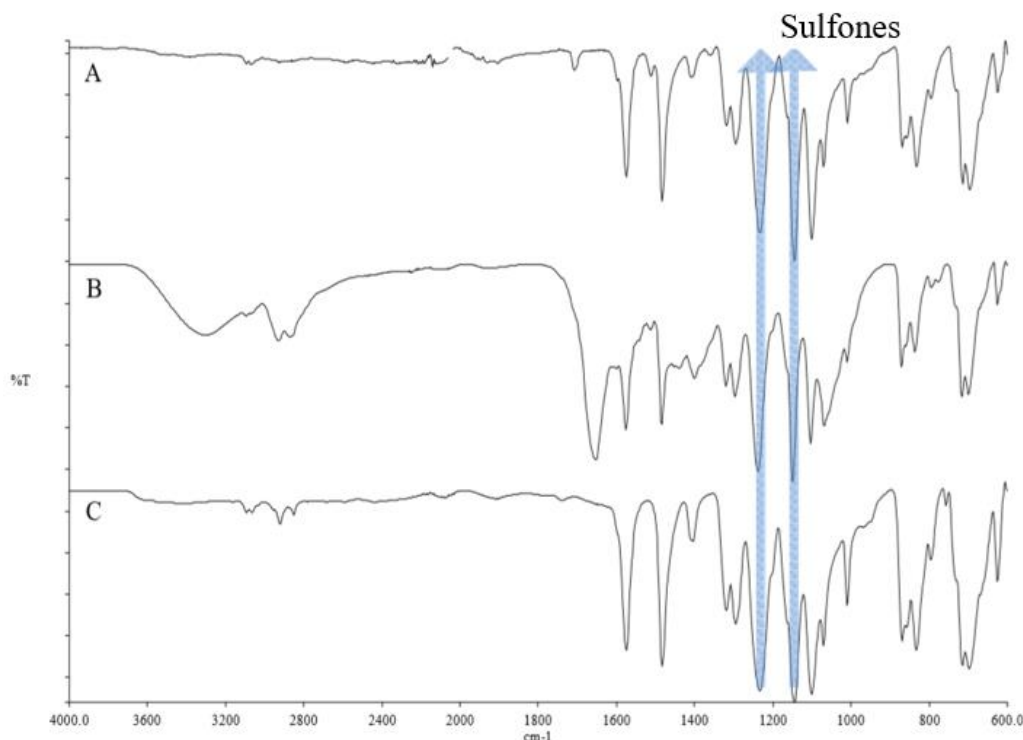


Figure 5. Infrared spectra obtained for the Carbon/8552 prepreg system. Spectrum (A) Surface of the prepreg sample 8552 using the UATR technique, (B) Part soluble in hot pyridine, (C) pure PES obtained using the UATR technique.

Table 6. Main FTIR bands of prepreg 8552 and M21 (Silverstein, *et al.*, 2006).

Component	Technical features	
	8552	M21
Amines	Average ~3400	Average ~3400
	Strong ~1510	Strong ~1510
Epoxy	Average ~2990 – 3050	Average ~2990 – 3050
	Average ~815 – 950	Average ~815 – 950
Sulfones	Strong ~1290 – 1340	Strong ~1290 – 1340
	Strong ~1120 – 1165	Strong ~1120 – 1165
Amides	-	Strong ~3300
	-	Strong ~1550

Figure 5 shows the spectrum of 8552 sample using the UATR (A), and also from the film obtained after treatment with acetone and dilution with pyridine (B), and the spectrum of pure PES (C). The similarity between the spectra showed that the PES polymer is part of the composition of this epoxy resin system.

Although the infrared spectroscopy technique is not a separation technique, the treatments with solvents allowed identify, even at low levels, the presence of thermoplastics. So, based on the analysis performed by infrared spectroscopy of the prepreg sample 8552, it is possible to observe the presence of epoxy resin, probably bisphenol-A diglycidyl ether (DGEBA), amine curing agent and PES.

3.4.2 Prepreg M21

The UATR was also used to evaluate the prepreg M21. Figure 6a shows the spectrum obtained from the surface of M21 prepreg (A) and the spectrum of pure PES (B). The spectrum A shows the presence of typical contributions of epoxy resin, and some absorptions of amine component. It is also observed the presence of absorption in the carbonyl region and its presence may come from a modified epoxy resin or reaction product. This spectrum when analyzed by means of polymer libraries for commercial use (HR Hummel Polymer and Additives) brought a good correlation to the product called poly(1,4-phenyleneethersulfone), commercially known as PES. Table 6 presents the main contributions present in the M21 epoxy system. The similarity between

the spectra A and B in Fig. 6a and the correlation provided by the commercial polymer library shows that the PES polymer is part of the composition of the M21 epoxy resin system.

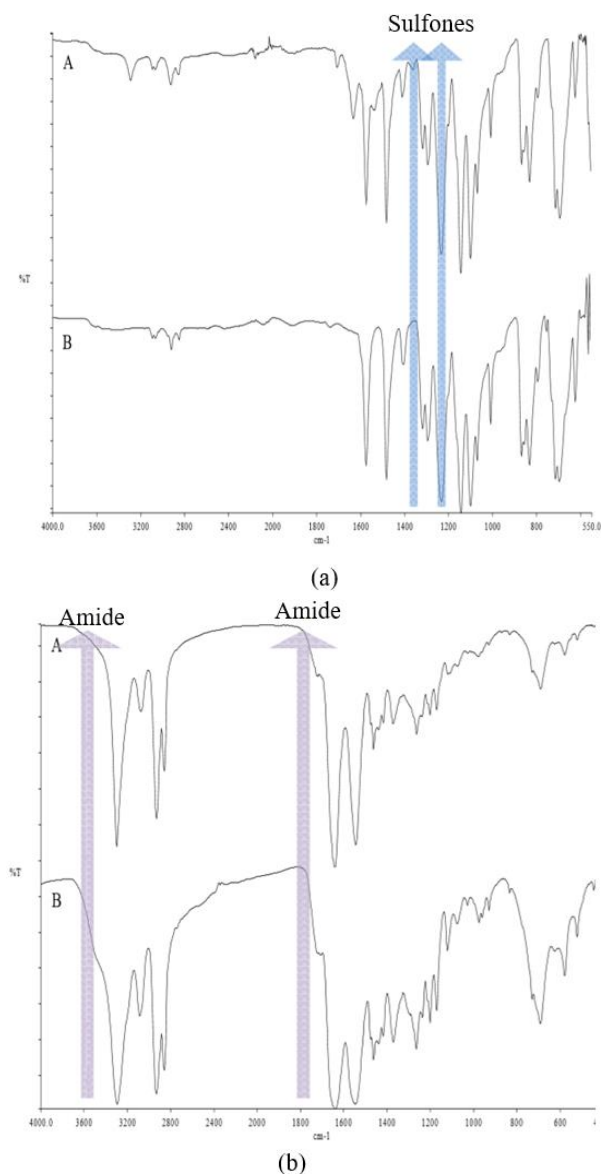


Figure 6. Infrared spectra obtained for the Carbon/M21 prepreg system. (a) Spectrum (A) surface of the prepreg sample M21 and (B) pure PES, both obtained using the UATR technique. (b) Spectrum (A) part soluble in hot formic acid of the M21 sample using the cast film technique and (B) pure polyamide.

In addition, there is a small band in the region of 3295 cm^{-1} , region of the NH groups and also in the regions of 1634 and 1543 cm^{-1} (Fig. 6b) which, as described by Silverstein *et al.* (2000), are regions of the polyamides. This sample was treated with hot formic acid in order to dissolve the PES and/or the separation of

a possible polyamide present in M21 prepreg. Figure 6b shows the spectrum generated in line A and also the spectrum of a pure polyamide Line B. In the spectrum obtained, it is not possible to classify polyamide 6, 6/6 or even 6/12, it is possible to conclude only the presence of polyamide in the composition of prepreg M21. This result was also found by Paris *et al.* (2010; 2012) and Ueda *et al.* (1994), which suggest a peak melting of the polyamide during curing of the material in the DSC.

Based on the analysis carried out by infrared spectroscopy of the prepreg sample M21, it is possible to observe the presence of epoxy resin, probably DGEBA, based on bisphenol A, amine curing agent of the type diaminodimethylsulfone (DDS), polyethersulfone (PES), and polyamide, probably 6/12.

4. Conclusions

In the present study, the cure kinetics for M21 and 8552 prepregs, used in the aeronautical industry, was evaluated by DSC, DMA, rheometry, and FTIR spectroscopy. DSC results demonstrated that the heating rate of 2.0 °C min^{-1} prepregs is more adequate to manufacture the polymeric composite and that the kinetic of cure occurs according to order n. M21 prepreg showed that thermoplastic components are present in its formulation due to an endothermic peak. DMA analysis confirmed that the more adequate heating rate is 2.0 °C min^{-1} for both prepregs. The 8552 and M21 resins prepregs showed in their DMA curves, other thermal transitions, which show other components in their formulations, not only epoxy resin and amine. The glass transition temperature obtained for the 8552-resin cured at a dynamic rate of 2 °C min^{-1} is 215 °C and for the M21 is 178 °C . The rheological results are consistent with DMA and with the results predicted in the literature for epoxy resins toughened with unknown agents, having contributed to confirm the presence of thermoplastic in the formulation of the studied resins. In addition, the rheological analysis confirms the use of rates lower than 2 °C min^{-1} for curing these materials, as well as the need for curing ramps. The results obtained by FTIR show that in prepreg 8552 the resin contains epoxy, probably DGEBA based on bisphenol A, amine curing agent and polyethersulfone (PES). For M21 resin, it includes epoxy resin type DGEBA, curing agent type DDS, polyamide and PES. DSC, DMA and rheological analyses have proven to be adequate techniques to establish proper curing cycles for M21 and 8552. This study contributes to the processing of structural composite materials for aerospace use, supporting to establish adequate curing cycles that prevent material losses.

Authors' contribution

Conceptualization: Rezende, M. C.; Botelho, E. C.; Costa, M. L.

Data curation: Silva, S. M.; Silva, C. P. N.; Silva, T. C.

Formal Analysis: Rezende, M. C.; Botelho, E. C.; Costa, M. L.

Funding acquisition: Not applicable.

Investigation: Silva, S. M.

Methodology: Silva, S. M.; Rezende, M. C.; Costa, M. L.

Project administration: Not applicable

Resources: Not applicable.

Software: Not applicable.

Supervision: Rezende, M. C.; Costa, M. L.

Validation: Rezende, M. C.; Botelho, E. C.; Costa, M. L.

Visualization: Silva, C. P. N.; Silva, T. C.

Writing – original draft: Silva, S. M.; Silva, C. P. N.; Silva, T. C.

Writing – review & editing: Rezende, M. C.; Botelho, E. C.; Costa, M. L.

Data availability statement

All dataset were generated or analyzed in the current study.

Funding

Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP). Grant No: 2017/16970-0.

Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq). Grant No: 306576/2020-1; 304876/2020-8.

Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES). Finance Code 001.

Acknowledgments

The authors would like to thank Milton Faria Diniz from the Chemistry Division/IAE/DCTA for his assistance in the FTIR analysis.

References

Agius, S. L.; Magniez, K. J. C.; Fox, B. L. Cure behaviour and void development within rapidly cured out-of-autoclave composites. *Compos. B. Eng.* **2013**, *47*, 230–237. <https://doi.org/10.1016/j.compositesb.2012.11.020>

ASTM E1356-08. Standard Test Method for Assignment of the Glass Transition Temperatures by Differential Scanning Calorimetry. ASTM International, 2014a. <https://doi.org/10.1520/E1356-08R14>

ASTM E968-02. Standard Practice for Heat Flow Calibration of Differential Scanning Calorimeters. ASTM International, 2014b. <https://doi.org/10.1520/E0968-02R14>

ASTM D7028-07e1. Standard Test Method for Glass Transition Temperature (DMA T_g) of Polymer Matrix Composites by Dynamic Mechanical Analysis (DMA). ASTM International, 2015. <https://doi.org/10.1520/D7028-07E01>

ASTM E967-18. Standard Test Method for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers. ASTM International, 2018. <https://doi.org/10.1520/E0967-18>

ASTM D4473-08. Standard Test Method for Plastics: Dynamic Mechanical Properties: Cure Behavior. ASTM International, 2021. <https://doi.org/10.1520/D4473-08R21>

Botelho, E. C.; Scherbakoff, N.; Rezende, M. C. Porosity control in glassy carbon by rheological study of the furfuryl resin. *Carbon*. **2001**, *39* (1), 45–52. [https://doi.org/10.1016/S0008-6223\(00\)00080-4](https://doi.org/10.1016/S0008-6223(00)00080-4)

Braga, C. I.; Rezende, M. C.; Costa, M. L. Methodology for DSC calibration in high heating rates. *J. Aerosp. Technol. Manag.* **2011**, *3* (2), 179–192. <https://doi.org/10.5028/jatm.2011.03021911>

Costa, M. L.; Botelho, E. C.; Paiva, J. M. F. D.; Rezende, M. C. Characterization of cure of carbon/epoxy prepreg used in aerospace field. *Mater. Res.* **2005**, *8* (3), 317–322. <https://doi.org/10.1590/S1516-14392005000300016>

Costa, M. L.; Rezende, M. C.; Paiva, J. M. F.; Botelho, E. C. Structural carbon/epoxy prepregs properties comparison by thermal and rheological analyses. *Polym. Plast. Technol. Eng.* **2006**, *45* (10), 1143–1153. <https://doi.org/10.1080/03602550600887251>

Das, P. P.; Chaudhary, V. Tribological and dynamic mechanical analysis of bio-composites: A review. *Mater. Today: Proc.* **2019**, *25* (4), 729–734. <https://doi.org/10.1016/j.matpr.2019.08.233>

Ersoy, N.; Tugutlu, M. Cure kinetics modeling and cure shrinkage behavior of a thermosetting composite. Istanbul: Bogazici University. *Polym. Eng. Sci.* **2010**, *50* (2), 84–92. <https://doi.org/10.1002/pen.21514>

Friedman, H. L. Kinetics of thermal degradation of char-forming plastics from thermogravimetry. Application to a phenolic plastic. *J. Polym. Sci., polym. Symp.* **1964**, *6* (1), 183–195. <https://doi.org/10.1002/polc.5070060121>

- González-Benito, J. The nature of the structural gradient in epoxy curing at a glass fiber/epoxy matrix interface using FTIR imaging. *J. Colloid Interface Sci.* **2003**, 267 (2), 326–332. [https://doi.org/10.1016/S0021-9797\(03\)00550-2](https://doi.org/10.1016/S0021-9797(03)00550-2)
- Hatter, C. B.; Shah, J.; Anasori, B.; Gogotsi, Y. Micromechanical response of two-dimensional transition metal carbonitride (MXene) reinforced epoxy composites. *Compos. B. Eng.* **2020**, 182, 107603. <https://doi.org/10.1016/j.compositesb.2019.107603>
- Hexcel Corporation. *HexPly® 8552 Epoxy matrix (180°C/356°F curing matrix)*. 2021a. https://www.hexcel.com/user_area/content_media/raw/HexPly_8552_us_DataSheet.pdf (accessed 2021-08-11).
- Hexcel Corporation. *HexPly® M21 Epoxy matrix (180°C/350°F curing matrix)*. 2021b. https://www.hexcel.com/user_area/content_media/raw/HexPly_M21_global_DataSheet.pdf (accessed 2021-08-11).
- Hubert, P.; Johnston, A.; Poursartip, A.; Nelson, K. Cure kinetics and viscosity models for Hexcel 8552 epoxy resin. In *International SAMPE symposium and exhibition*. SAMPE. 2019.
- Liu, H.; Falzon, B. G.; Tan, W. Experimental and numerical studies on the impact response of damage-tolerant hybrid unidirectional/woven carbon-fibre reinforced composite laminates. *Compos. B. Eng.* **2018**, 136, 101–118. <https://doi.org/10.1016/j.compositesb.2017.10.016>
- Menard, K. P. *Dynamic mechanical analysis: A practical introduction*. CRC Press. 1999. <https://doi.org/10.1201/9781420049183>
- Mesogitis, T.; Kratz, J.; Skordos, A. A. Heat transfer simulation of the cure of thermoplastic particle interleaf carbon fibre epoxy prepregs. *J. Compos. Mater.* **2018** 53 (15), 2053–2064. <https://doi.org/10.1177/0021998318818245>
- Mphahlele, K.; Ray, S. S.; Kolesnikov, A. Cure kinetics, morphology development, and rheology of a high-performance carbon-fiber-reinforced epoxy composite. *Compos. B. Eng.* **2019**, 176, 107300. <https://doi.org/10.1016/j.compositesb.2019.107300>
- Newcomb, B. A. Time-Temperature-Transformation (TTT) diagram of a carbon fiber epoxy prepreg. *Polym. Test.* **2019**, 77, 105859. <https://doi.org/10.1016/j.polymertesting.2019.04.006>
- Nixon-Pearson, O. J.; Belnoue, J. H.; Ivanov, D. S.; Potter, K. D.; Hallett, S. R. An experimental investigation of the consolidation behaviour of uncured prepregs under processing conditions. *J. Compos. Mater.* **2017**, 51 (13), 1911–1924. <https://doi.org/10.1177/0021998316665681>
- Oishi, S. S.; Rezende, M. C.; Origo, F. D.; Damião, A. J.; Botelho, E. C. Viscosity, pH, and moisture effect in the porosity of poly(furfuryl alcohol). *J. Appl. Polym. Sci.* **2013**, 128 (3), 1680–1686. <https://doi.org/10.1002/app.38332>
- Paiva, J. M.; Costa, M. L.; Rezende, M. C. Evaluation of thermal stability and glass transition temperature of different aeronautical polymeric composites. *Polym. Plast. Technol. Eng.* **2006**, 45 (2), 157–164. <https://doi.org/10.1080/03602550500373915>
- Paris, C.; Olivier, P. A.; Bernhart, G. Modelling of the thermokinetic behaviour and the phases transitions of a carbon/polymeric composite submitted to high heating rate ramps. *Int. J. Mater. Form.* **2010**, 3 (1), 639–642. <https://doi.org/10.1007/s12289-010-0851-8>
- Paris, C.; Bernhart, G.; Olivier, P. A.; Almeida, O. Influence of fast curing cycles on aeronautical prepreg M21/T700: polymerization control and mechanical properties. *Mater. Tech.* **2012**, 100 (6–7), 611–622. <https://doi.org/10.1051/mattech/2012010>
- Ribeiro, B.; Nohara, L. B.; Oishi, S. S.; Costa, M. L.; Botelho, E. C. Carbon nanotubes/polyamide 6.6 nanostructured composites crystallization kinetic study. *J. Thermoplast. Compos. Mater.* **2013**, 26 (7), 893–911. <https://doi.org/10.1177/0892705711430532>
- Sánchez-Soto, M.; Pagés, P.; Lacorte, T.; Briceño, K.; Carrasco, F. Curing FTIR study and mechanical characterization of glass bead filled trifunctional epoxy composites. *Compos. Sci. Technol.* **2007**, 67 (9), 1974–1985. <https://doi.org/10.1016/j.compscitech.2006.10.006>
- Silverstein, M.; Webster, F. X.; Kiemle, D. J. *Spectrometric identification of organic compounds*. John Wiley & sons. 2000.
- Ștefanov, T.; Ryan, B.; Ivanković, A.; Murphy, N. Dynamic mechanical analysis of carbon black filled, elastomer-toughened ethyl cyanoacrylate adhesive bulk films. *Int. J. Adhes. Adhes.* **2020**, 101, 102630. <https://doi.org/10.1016/j.ijadhadh.2020.102630>
- Ueda, M.; Yokoo, T.; Nakamura, T. Synthesis of poly (ether-sulfone-amide)s by palladium-catalyzed polycondensation of aromatic dibromides containing ether sulfone structure, aromatic diamines, and carbon monoxide. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, 32 (15), 2989–2995. <https://doi.org/10.1002/pat.4328>
- Urban, V. M.; Machado, A. L.; Vergani, C. E.; Jorge, E. G.; Santos, L. P.; Leite, E. R.; Canevarolo, S. V. Degree of conversion and molecular weight of one denture base and three relines submitted to post-polymerization treatments. *Mat. Res.* **2007**, 10 (2), 191–197. <https://doi.org/10.1590/S1516-14392007000200016>

Vyazovkin, S.; Burnham, A. K.; Criado, J. M.; Pérez-Maqueda, L. A.; Popescu, C.; Sbirrazzuoli, N. ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data. *Thermochim. Acta.* **2011**, *520* (1–2), 1–19. <https://doi.org/10.1016/j.tca.2011.03.034>

Vyazovkin, S.; Chrissafis, K.; Di Lorenzo, M. L.; Koga, N.; Pijolat, M.; Roduitf, B.; Sbirrazzuoli, N.; Suñol, J. J. ICTAC Kinetics Committee recommendations for collecting experimental thermal analysis data for kinetic computations. *Thermochim. Acta.* **2014**, *590*, 1–23. <https://doi.org/10.1016/j.tca.2014.05.036>

Wang, Y.; Chea, M. K.; Belnoue, J. P.-H.; Kratz, J.; Ivanov, D. S.; Hallett, S. R. Experimental characterisation of the in-plane shear behaviour of UD thermoset prepregs under processing conditions. *Compos. - A: Appl. Sci. Manuf.* **2020**, *133*, 105865. <https://doi.org/10.1016/j.compositesa.2020.105865>

Wetton, R. E.; Marsh, R. D. L.; Van-de-Velde, J. G. Theory and application of dynamic mechanical thermal analysis. *Thermochim. Acta.* **1991**, *175* (1), 1–11. [https://doi.org/10.1016/0040-6031\(91\)80240-J](https://doi.org/10.1016/0040-6031(91)80240-J)