A Conceptional Approach of Resin-Transfer-Molding to Rosin-Sourced Epoxy Matrix Green Composites [†]

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[†] Dedicated to Prof. Dr.-Ing. Ortwin Hahn for his 80th birthday. Xiaosu Yi and his research team.

Abstract: In this concept-proof study, a preform-based RTM (Resin Transfer Molding) process is presented that is characterized by first pre-loading the solid curing agent onto the preform, and then injecting the liquid nonreactive resin with an intrinsically low viscosity into the mold to infiltrate and wet the pre-loaded preform. The separation of resin and hardener helped to process inherently high viscosity resins in a convenient way. Rosin-sourced, anhydrite-cured epoxies that would normally be regarded as unsuited to liquid composite molding, were thus processed. Rheological tests revealed that by separating the anhydrite curing agent from a formulated RTM resin system, the remaining epoxy liquid had its flowtime extended. C-scan and glass transition temperature tests showed that the preform pre-loaded with anhydrite was fully infiltrated and wetted by the liquid epoxy, and the two components were diffused and dissolved with each other, and finally, well reacted and cured. Composite laminates made via this approach exhibited roughly comparable quality and mechanical properties with prepreg controls via autoclave or compression molding, respectively. These findings were verified for both carbon and ramie fiber composites.

Keywords: rosin-sourced anhydrite; epoxy; viscosity; LCM process; carbon fiber composite; ramie fiber composite; in-plane mechanical properties

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1. Introduction

Due to the increasing concern about resources and environmental footprint, a large number of natural and/or bio-based polymers have been developed in the last decades to potentially replace petroleum-based polymeric materials [1]. Among the thermosetting polymers, epoxy resin is most important as an adhesive, a coating, and as a matrix resin for polymer composites, because of its superior mechanical properties, excellent thermal resistance and good processability. Epoxies can be induced to cross-link with many different curing agents. Acid anhydrides are typically used for applications in filament winding and the cross-linked epoxy composites show generally high glass transition temperature, high modulus and tensile elongation, low moisture absorption, low thermal shrink, and ease in molding [2].

Recently, rosin acid has received increasing attention as a bio-sourced form of renewable feedstock in thermosetting polymer science. From rosin acid, an anhydride-type epoxy curing agent was synthesized as maleopimaric acid (RAM) [3]. By using RAM to cure a two-component resin consisting of an E51-type epoxy and a solid phenolic epoxy, a bio-sourced epoxy matrix resin has been developed for prepreg preparation with a bio-content of about 30% [4]. As reported, the formulated resin system behaves well in film manufacturing and subsequent pre-pregging, leading to production of "green composites"

for autoclave molding. Compared with its 100% petroleum-sourced prepreg composite counterparts, the rosin-sourced green composite presents generally higher application performance [5]. Considering the increased use of polymer-based composites in aerospace industry and its eco-friendly and green needs, the rosin-sourced green composites has drawn a great deal interest from aerospace industry with the potential as quasi-structural aircraft interior parts [6,7].

However, the typical anhydride-curing epoxies, rosin-sourced epoxy cannot be used conveniently in liquid composite molding (LCM) at all, due to its intrinsically high viscosity. Among the various composites manufacturing processes, LCM has been recognized as a cost-effective and promising technology [8] due mainly to elimination of the costly pre-pregging stage. LCM summarizes a variety of process technologies such as resin transfer molding (RTM), reaction injection molding (RIM), and vacuum-assisted resin injection (VARI) that use thermoset resins and continuous fabric reinforcements to produce fiber-reinforced composites. Unlike processing of prepreg materials in autoclaves, that is generally very time consuming and expensive, LCM allows a relatively fast and high-quality production of advanced composites.

In a typical RTM process, the textile preform is placed in a closed mold; a liquid polymer with very low viscosity as the matrix resin is then either injected under pressure or drawn into the mold due to vacuum, to infiltrate and wet the fiber mat preform. The process is accompanied with a complex flow mechanism that combines macro and micro infiltration of the dry fiber preform [9]. It is obvious that the lower the resin viscosity is, the better the infiltration quality will be. The time needed for infiltration and wetting varies from a few seconds for smaller parts up to hours for very large parts such as rotor blades used for wind energy plants. The processing time for the infiltration is limited by the ultimate rise in resin viscosity as cross-linking commences. In other words, the pot life of the resin determines how much time is available for impregnation.

In this study, a preform-based LCM technique [10], named ex-situ LCM, is introduced which can be applied to liquid composite molding using thermoset matrix resins of high viscosity, and allow very long flow and infiltration process time. Two rosin-sourced epoxy-matrix resin systems were developed, one for ex-situ LCM and another as prepreg material for autoclave molding. The viscosity behavior of the two resins and the associated process conditions were then compared. Carbon fiber composite laminates manufactured respectively by ex-situ LCM and autoclave using the two green epoxies were subsequently tested in terms of mechanical properties and glass transition temperature. In parallel, "greener" composites were also developed that exploited ramie fibers as reinforcement and the rosin-sourced epoxies as matrix. The ramie-fiber composites were manufactured by ex-situ LCM and compression molding, respectively. We will later demonstrate that the ex-situ LCM processed composite laminate had seemingly similar properties to the autoclaved, or compression molded controls.

2. Ex-Situ LCM Technology

As introduced, LCM is widely used for manufacturing composite parts as an affordable process technology. Any LCM process generally consists of two functional process steps, namely the impregnation of the fibrous reinforcing preform in the mold with a low viscosity liquid, and simultaneously wetting and removing of dissolved gases and moisture entrapped in the media, and then, the heat-induced crosslinking reaction to solidify the resin. Fast filling requires that the resin viscosity be as low as possible, and this low viscosity should be maintained as long as is practicable. In practice, successful infiltration requires a processing viscosity in the range of 1–100 mPa·s.

However, the low viscosity cannot be a constant and the gel point of the liquid epoxy will be determined by the mechanism of the hardener and its stoichiometry. Chemical conversion is already underway in the resin flow and infiltration stage, although its rate may be suppressed by temperature control compared to the curing phase. Consequently, the viscosity increases slowly as soon as impregnation commences, and any such changes

will influence the processing time for the flow and infiltration. The case of anhydride-curing epoxies is more challenging because of their inherently high starting viscosities and in practice impregnation may be difficult at fiber volume fractions beyond 50%, as with aerospace structural applications.

Resin viscosity depends on the chemical-physical characteristics of the polymer formulation, i.e., the pre-mixed reactive polymer compound. The viscosity increases generally over time because of both temperature variations and as consequence of chemical reactions that commence as soon as the reactive components are mixed. To tackle the process dilemma, a proprietary LCM technology is developed [10]. Instead of pre-compounding the reactive components to prepare a liquid resin, the solid curing agent is first pre-loaded on the reinforcing preform. Only the nonreactive liquid resin with intrinsically low viscosity is used for flow and infiltration. By carefully controlling the temperature, only the physical process of resin flow, infiltration and wetting occurs in the first stage with almost no chemical reaction. Then, after the mold is filled and the preform saturated, crosslinking is triggered by increasing the temperature. Thus, the two reactive components combine only after the resin saturates the preform. Diffusion and dissolution precede the crosslinking reaction, with viscosity build-up and eventual solidification. The preform-based LCM technique is designated as ex-situ LCM in the study.

There are two process benefits of ex-situ LCM. The first one is that the resins with high viscosity (or room temperature solid) hardeners can be processed via LCM. The second is that the impregnating resin is essential nonreactive and so can maintain minimum viscosity during filling. The ex-situ LCM process we investigated in this study extends the range of resin and curing agent which can be used as composite matrix in relative field such as aerospace engineering, especially for resin system with high viscosity or short gelation time. As a concept-proof study, some preliminary results of the novel technique will be presented, compared with those of the conventional molding techniques.

3. Materials and Methods

3.1. Materials

Two epoxy systems were used in the study for the ex-situ LCM and autoclave processes, respectively (Table 1). In both cases, a rosin-sourced anhydride, i.e., maleopimaric acid (RAM, white powder, >98%, acid number = 133 mg of $KOH \cdot g^{-1}$) was used as a green curing agent.

To study the flow behavior in comparison with RAM, benzenetricarboxylic anhydride (TMA, white flake, melting point of 164–166 °C) was chosen as a control. The molecular structure of the two curing agents, RAM and TMA is shown in Figure 1, respectively. The RAM compound was initially developed by Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences [11]. In the present study, it was dried at 120 °C for 2 h in an oven before use.
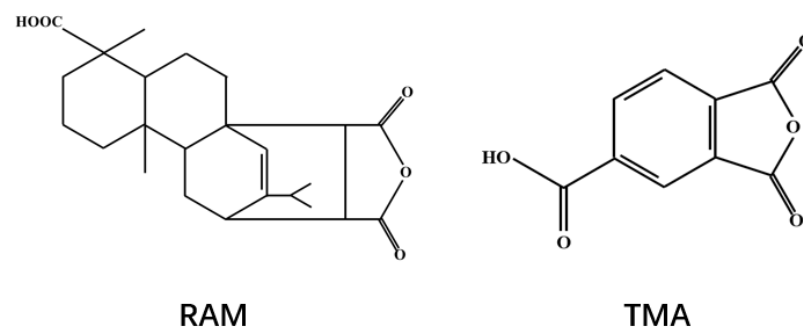
Figure 1. Chemical structures of the anhydride curing agents used in the study.

RDF–160, an E51-type bisphenol F based epoxy with an epoxide equivalent weight of 180–185 $g \cdot eq^{-1}$ was used to formulate the RTM resin system, because its viscosity at 25 °C is less than 1500 mPa·s and is thus suitable for liquid composite molding. The prepreg

matrix resin was formulated with a two-component epoxy system consisting of another E51-type liquid epoxy, i.e., 2,2-bis [4-(glycidyloxy)phenyl]propane with an epoxide equivalent weight of 171–175 g·eq^{-1} and a solid phenolic epoxy resin with an epoxide equivalent weight of 200–238 g·eq^{-1}. BC-120, a Lewis acid, is a room temperature latent, elevated temperature and confidential catalyst agent. If mixed with liquid epoxies, a clear homogeneous resin is formed with a shelf lifetime of about one year at room temperature. The catalyst was hence used to formulate the RTM resin system, whereas a two-amino imidazole salt complex, IMA (white powder) was used in the prepreg matrix formulation as accelerator. Except for RAM, all the other chemicals mentioned above were commercially available products.

Table 1. Bio-sourced epoxy system studied.

	Main Composition	Curing Temperature	Curing Method
Ex-situ LCM resin	RAM, RDF-160, BC-120	160 °C	Ex-situ LCM
Prepreg resin	RAM, two-component epoxy, IMA	130 °C	Autoclave or compression

A carbon fiber (CF) plain fabric CF3011 obtained from GuangWei Composite Material Co., Ltd. (Weihai, China) was used to produce laminate composites. It is a Chinese T300-grade CF material. The specification of CF3011 is shown in Table 2.

Table 2. Specification of carbon fiber fabrics CF3011 used.

		Specification
Weave structure		plain
Weight per unit area, g/m^2		193 ± 10
Threads per unit length, number/cm	warp	4.9 ± 0.2
	weft	4.8 ± 0.2
Tensile strength at break, N/25mm	warp	≥ 1700
	weft	≥ 1700

Ramie fiber (RF) cloth was also used as natural reinforcing material as specified in Table 3. It was obtained from Hunan Huashengdongting Ramie Co., Ltd. Yueyang, China.

Table 3. Ramie fiber cloth used as natural reinforcing material.

|		Standard Value	RP 140	RT 140
Width of the cloth, mm		1000 ± 10	995	1004
Areal density, g/m^2		140 ± 5	145	144
Water content, %		≤ 5.5	3.4	2.3
Tensile force at break, N	warp	≥ 650	685	1010
	weft	≥ 670	793	811

3.2. Sample Preparation and Experiment Setup

3.2.1. Ex-Situ LCM Process and Sample Preparation

As introduced, common LCM process uses a liquid formulated resin pre-compounded with the hardener; its chemical reaction occurs in-situ, whereas in the ex-situ LCM process, one of the reactive components is firstly surface-loaded on the reinforcing fiber preform. Only after the low-viscosity liquid resin saturates the preform, the reactive components come into contact. In principle, as the process temperature is relatively low, the solubility

and subsequent diffusion of the distributed hardener could be inhibited, resulting in an expanded processing time window. Only after full saturation is completed, the chemical reaction will be then thermally initiated. Thus, the crosslinking reaction occurs ex-situ in an ex-situ LCM process.

Following the procedure, a calculated dose of the solid rosin-anhydride RAM hardener, was firstly dissolved in acetone. The CF preform was then immersed in the solution for 30 s. After the solvent was completely volatilized, the preform was vacuum dried at 60 °C for 1 hour to produce a CF preform pre-loaded with the hardener. As calculated, the RAM mass ratio was approximately 20.4%.

The pre-treated CF preform was placed in a closed mold (Figure 2). The epoxy liquid without hardener was then poured into a tank and de-gassed for 30–60 min. The liquid resin was then pumped into the closed mold to saturate the preform. Finally, the CF composite was cured according to the process procedure and parameters shown in Figure 3. The volume fraction of CF in ex-situ LCM molded composite was 50% and 55%.
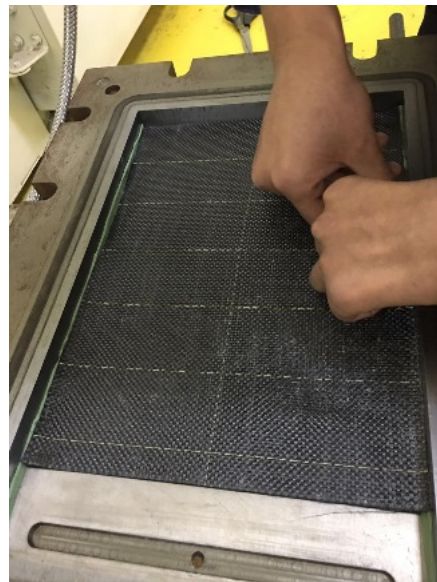

Figure 2. Lay-up process of pre-loaded carbon fiber (CF) preform in resin transfer molding (RTM) mold.
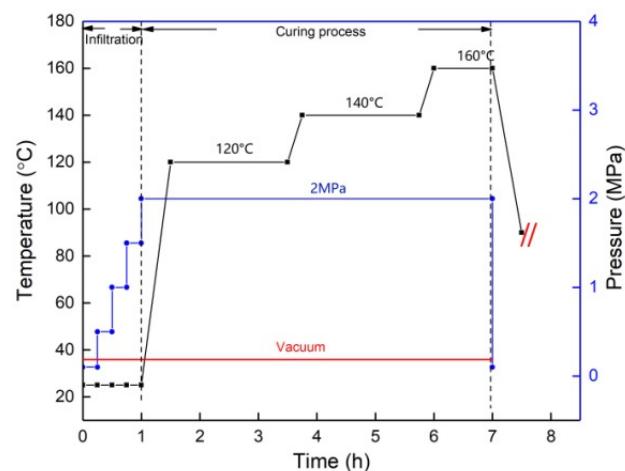
Figure 3. Process parameters and conditions for ex-situ liquid composite molding (LCM).

Ramie cloth preforms were similarly surface-loaded with RAM and resin-transfer-molded and finally cured. As demonstrated in Figure 4, the final RF composite sample

manufactured using ex-situ LCM process shows a normal appearance. The test samples were then cut from the laminate for test purpose. The volume fraction of ramie fabric in ex-situ LCM molded composite was about 41%.
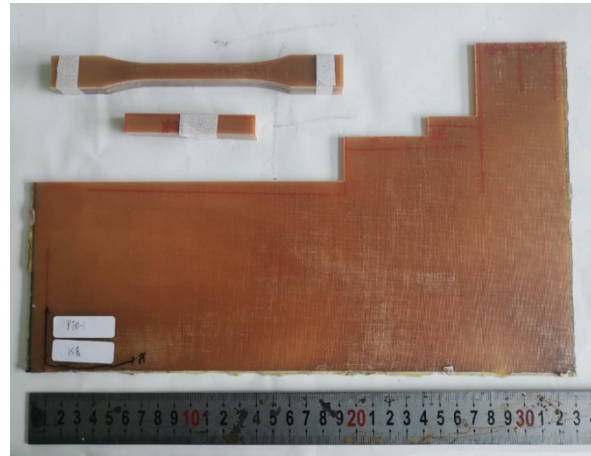
Figure 4. Ramie fiber green composites manufactured by ex-situ LCM.

3.2.2. Prepreg Reference Samples Reinforced with CF and RF

Control samples of rosin-anhydride cured CF composite samples were manufactured by prepreg/autoclave method. The volume fraction of CF in the resulted composites was about 57%. In parallel, the ramie fiber control samples were produced, by prepreg/compression molding. The volume fraction of ramie fabric in compression molded composite was about 42%. The parameters of both autoclave process and compression molding are shown in Figure 5.
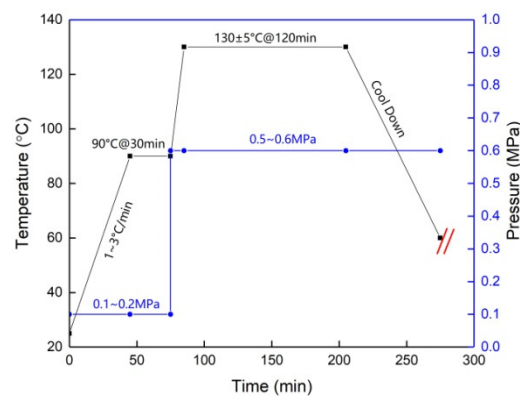
Figure 5. Autoclave and compression molding parameters for resin epoxy CF or RF laminates.

3.3. Characterization and Testing

3.3.1. Viscosity Measurement

The apparent viscosity was performed on a cone plate viscometer (CAP2000+, Brookfield, Middleborough, MA, USA) with 6th rotation spider at a rotation rate of 300 rpm and a shear rate of 1000 S^{-1}. The viscosity-of resin was tested at 80 °C, 100 °C and 120 °C, respectively.

3.3.2. C-Scanning

All samples were non-destructively tested by C-scan using a PAC UPK-T36 ultrasonic scanner (USA) prior to further mechanical tests.

3.3.3. Mechanical Testing

A universal testing machine (Instron 3365 testing machine, Instron, Norwood, MA, USA) was utilized to measure the mechanical property of the cured samples. The tensile strength test was conducted according to ASTM D3039. The three-point flexural test was performed according to ASTM D790. The short beam interlaminar shear strength was done according to ASTM D3244. A minimum of five samples were used in each test and their average values are reported below.

3.3.4. Dynamic Mechanical Testing

Dynamic mechanical analysis (DMA242E, NETZSCH Instruments, Selb, German) was used to study the thermo dynamic mechanical properties of composite sample and pure cured resin sample. The pure resin samples were fabricated by casting melted resin into the mold, after vacuum defoamation at 90 °C for 30 min in vacuum oven, and then cured following the same curing procedure of ex-situ LCM samples. The rectangular samples cutting by size of 50.0 mm × 10.0 mm × 2.0 mm were placed on a three-point bending clamp. The analysis was performed by the three-point bending mode at an oscillation frequency of 2 Hz, an oscillation amplitude of 10μm and a heating rate of 3 °C/min. The samples were heated from 30 °C to 300 °C.

4. Results and Discussion

4.1. Viscosity of the Ex-Situ LCM and Prepreg Resin

The viscosity behavior of three epoxy systems was assessed over a range of temperatures up to 160 °C, namely E51:RAM:BC120 (red), E51:TMA:BC120 (blue) and E51:BC120 (green), where the colours refer to the plots in Figures 6 and 7.
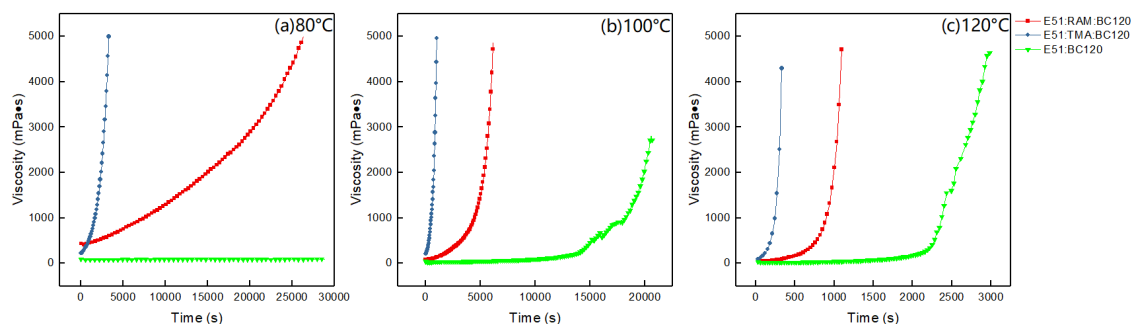
Figure 6. The viscosity-time curves for three experimental systems at (**a**) 80 °C, (**b**) 100 °C, (**c**) 120 °C.
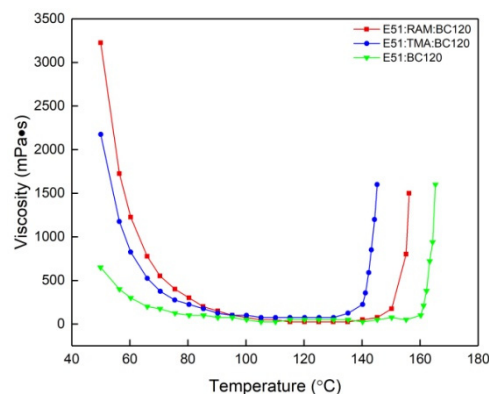
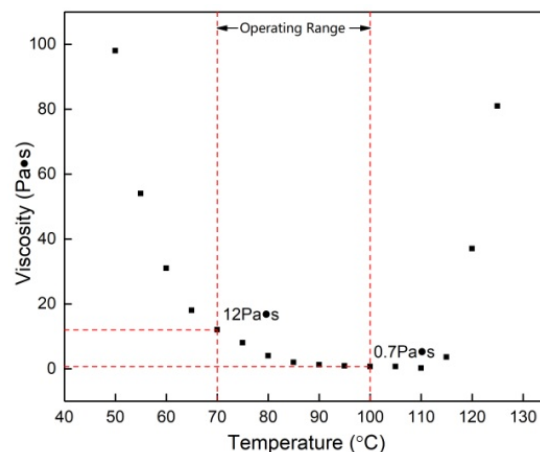**Figure 7.** Viscosity-temperature curves for the 3 model systems in comparison.

In addition to the RAM (green) hardener and TMA, E51:BC120 was additionally chosen as a baseline without hardener. The viscosity-time curves of the 3 model systems are shown in Figure 6 for 3 constant temperatures. It is obvious that, at 80 °C, the viscosity

curve of E51:TMA:BC120 increases the fastest, followed by that of E51:RAM:BC120, whilst the viscosity of E51:BC120 at lowest level is almost a constant for the duration of the trial (around 8 h).

The viscosity-time curves of the 3 models at 80 °C, 100 °C and 120 °C are also shown in Figure 6. Under all conditions, the RAM-cured system showed a longer induction period and lower viscosity than that of the TMA, indicating the potential for a wider processing window.

Figure 7 shows viscosity-temperature curves for the 3 epoxy systems at a heating rate of 30 °C/min. Taking viscosities of 100 mPa·s as the upper limit for RTM, it is clear that, below 60 °C, neither E51:RAM:BC120 and E51:TMA:BC120, nor E51:BC120 meets the viscosity requirement, although the last combination shows the lowest viscosity of about 200 mPa·s. However, between 80 °C and 120 °C, the viscosities of all the systems are lower than 100 mPa·s which provide a good processing window for RTM.

The viscosity of the epoxy for prepreg fabrication was also studied. As mentioned in Table 1, this was a two-component system consisting of E51 with a solid phenolic epoxy, cured with RAM. Figure 8 shows the viscosity curve as a function of temperature. Increasing the temperature from 50 °C to 85 °C, the viscosity first decreased rapidly, and flattened before reaching a turning point the induction temperature of 116 °C. However, the viscosity at no point met the processability requirement for LCM.


Figure 8. The viscosity-temperature curve of the rosin-sourced prepreg epoxy system.

The rheological tests revealed that by extracting the solid RAM, the main curing agent from the formulated RTM resin system, the remaining liquid epoxy would maintain a suitably low viscosity to permit the successful impregnation of even very large structures [12].

4.2. CF Composite Sample Quality Evaluated by C-Scan

All CF samples manufactured were C-scanned to investigate the distribution of potentially dry areas prior to mechanical test. Figure 9 shows the scan results for the CF laminates produced by ex-situ LCM using the rosin-sourced green matrix resin. There appeared to be no noticeable defect in the samples, and slightly increasing the fiber volume fraction from 50% to 55% did not appear to affect the outcome significantly.
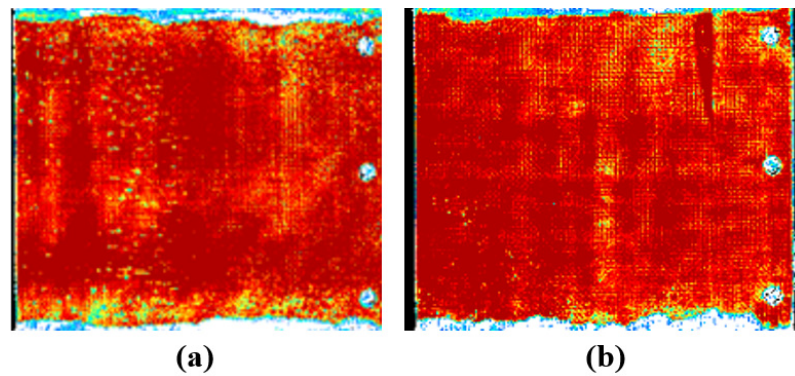
Figure 9. C-scan result of CF laminates with fiber volume content (**a**) 50%, (**b**) 55%.

4.3. Thermal-Mechanical Property

Glass transition behavior of the epoxy cast samples with and without rosin-sourced curing agent RAM was tested by DMA, as well as that of the CF reinforced composite samples manufactured by ex-situ LCM. Figures 10 and 11 show typical results. The T_g of the sample cured with RAM, i.e., E51:RAM:BC120, was approximately 170 °C, i.e., 33 °C higher than that of the sample without curing agent, E51:BC120. The glass transition temperature of the CF composites using the matrix resin of E51:RAM:BC120 increased with fiber volume fraction, from 177 °C to 187 °C over the V_f range 0.5–0.55.
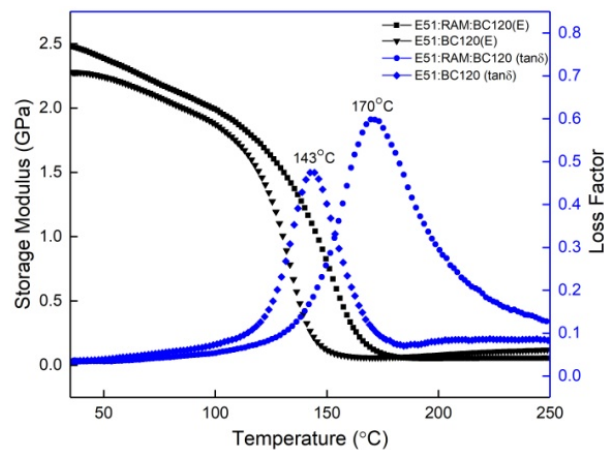

Figure 10. DMA curves for resin cast samples with or without the hardener.
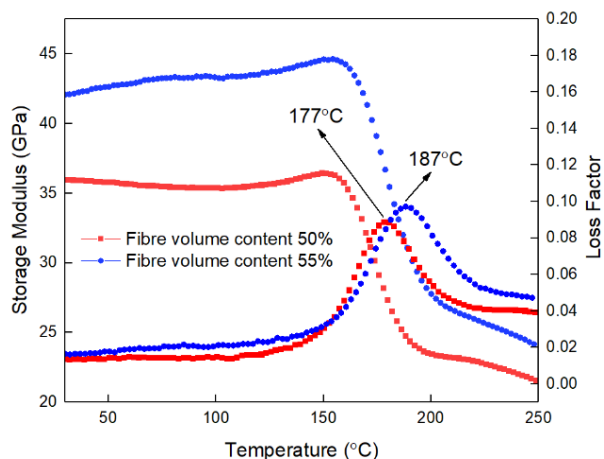
Figure 11. DMA curves for laminates with different CF volume fractions.

As shown in Figure 12, the glass transition behavior was also studied for the autoclave-molded green prepreg composite sample, i.e., RAM cured two-component epoxy system of an E51 and a solid phenolic epoxy. A T_g of approximately 182 °C can be confirmed, which is quantitatively comparable to those of the samples manufactured by ex-situ LCM, Figure 11.
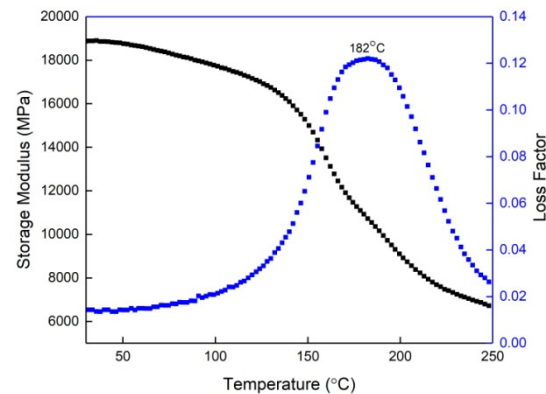
Figure 12. DMA curves for rosin-sourced epoxy prepreg laminates with 57% CF volume fraction, manufactured by autoclave.

The C-scan result, together with T_g data of the CF samples manufactured by ex-situ LCM suggests that the CF preform was fully infiltrated and wetted by the liquid epoxy, and the two reactive components have diffused and dissolved with each other, with a homogenous degree of conversion across the laminate.

4.4. Mechanical Properties of CF Composites

CF volume fraction dependent mechanical properties were studied for the composite samples manufactured by ex-situ LCM. Table 4 lists the flexural properties and interlaminar shear strength (ILSS). As the CF volume fraction increased from 50% to 55%, the flexural properties increased whereas the ILSS decreased.

Table 4. Typical mechanical properties of CF composites produced by ex-situ LCM and autoclave in comparison.

CF vol %	Flexural Strength, MPa	Flexural Modulus, GPa	ILSS, MPa	Manufacturing Method
50	734 ± 68	48.8 ± 1.0	49.0 ± 2.1	Ex-situ LCM
55	772 ± 69	57.5 ± 1.1	45.6 ± 2.0	
57	883 ± 77	56.8 ± 1.1	55.7 ± 2.2	Prepreg autoclave-molded

For comparison purpose, the flexural and ILSS properties were also tested on the CF reinforced green prepreg composite samples produced by autoclave-molding. The test result is also listed in Table 4. It is common and usual that the mechanical properties of the laminated CF composites produced by autoclave are generally higher than those of the RTM composites [13].

4.5. Mechanical Properties of Ramie-Fiber Composites

Similarly, tensile and flexural mechanical properties of the RF composite samples manufactured by ex-situ LCM were tested and reported in Table 5, as well as those of the compression-molded prepreg material. The fluctuation in the data came likely from the inaccuracy in control of the process parameters due to the preliminary study.

Table 5. Typical mechanical properties of RF composites produced by ex-situ LCM and compression in comparison.

Manufacturing Method	Tensile Strength, MPa	Tensile Modulus, GPa	Flexural Strength, MPa	Flexural Modulus, GPa
Ex-situ LCM	91.0 ± 8.0	9.1 ± 0.1	165.8 ± 4.7	7.3 ± 0.3
Prepreg/Compression molding	86.5 ± 3.4	6.5 ± 0.2	133.0 ± 5.4	8.5 ± 0.3

From the results reported above, it is believed that the ex-situ LCM technique is not only applicable to many other high viscosity resins but can also be used for the production of very large composite part demanding very long resin pot life.

5. Conclusions

A novel process concept, i.e., ex-situ LCM for liquid molding using high viscosity matrix resins was first proposed. In the study, it was a rosin-sourced green epoxy that had an inherent high viscosity, thus was conventionally not able to be used for RTM. Rheological study revealed that the liquid resin without the solid anhydride-curing agent could maintain the low viscosity and high flow ability for a very long time. It was demonstrated that, by means of the ex-situ LCM technique, the high-viscosity green epoxy could be used for RTM.

Consider the growing requirement for polymer composite in aerospace industry, the development of this ex-situ LCM process provides new perspective for composite manufacturing which allows to process high viscosity epoxy systems at a cheaper and less time-consuming fabrication technologies and to obtain homogeneous laminates with comparable mechanical properties. It also extends the potential resin system with high intrinsically viscosity or short gelation time in aerospace industry, can be applied as composite matrix by ex-situ LCM technology.

The comparative study from the DMA, C-scan, and mechanical tests yielded important information about composite quality and properties between the samples manufactured by ex-situ LCM and autoclave or compression molding. Both carbon and ramie fiber composite samples were manufactured, studied and compared. For the 55 vol% CF composites fabricated by ex-situ LCM, the flexural strength and ILSS were 72 MPa and 45.6 MPa, respectively, as compared with the 57 vol% compression molded CF samples, which has a flexural strength of 83 MPa and ILSS of 55.7 MPa. However, the flexural modulus of samples fabricated by two process were at similar level. Regarding the RF composites, the tensile strength and flexural strength of ex-situ LCM molded samples were 91.0 MPa and 165.8 MPa, respectively. These properties were marginally higher than those of prepreg/compression molded composite. The preliminary experiment shows that the resulting material quality and mechanical properties were generally comparable with those manufactured by prepreg/autoclave, or prepreg/compression molding.

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