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A Study on the Properties of Resin Transfer Molding Cyanate Ester and Its T800 Grade Carbon Fiber Composites

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Abstract: The properties of resin transfer molding (RTM) cyanate ester and its T800 grade carbon fiber composites were studied with the rheometer, differential scanning calorimetry (DSC), FT-IR, dynamic mechanical analyzer (DMA), thermal gravimetric analysis (TGA), mechanical property testing, and scanning electron microscopy (SEM). The results showed that the temperature of cyanate ester suitable for RTM process was 70℃. Curing process of the resin was 130℃/2 h+160℃/2 h+200℃/2 h+220℃/4 h. Glass transition temperature and heat decomposition temperature of the cured resin are 289℃ and 415℃, respectively. Mechanical properties of T800/RTM cyanate composites are 13.5% higher than that of T700/RTM cyanate composites and equal to that of T800/Prepreg cyanate composites. T_g of T800/RTM cyanate composites was proved to be 291℃. Fracture pattern of the composites was flat, which proved excellent interface properties between fiber and resin in this composite.

Keywords: RTM cyanate ester, viscosity, glass transition temperature, heat decomposition temperature, mechanical properties.

1 Introduction

Resin Transfer Molding (RTM) is one of the most commonly used processes for high performance composites [Zhao, Sun and Li (2016)]. Parts made via this process possess unique properties such as high fiber content, excellent comprehensive mechanical properties and high precision in dimensions [He, Zhong and Li (2016); Robertson (1988)]. Comparing to prepreg hot-press process, RTM is more cost efficient, because it does not involve hot-press machine [Yi (2006)] (such as autoclave/press molding machine), prepreg manufacture/storage nor accessory materials [Kiuna, Lawrence and Fontana (2002)] (such as vacuum bags). Hence, it is widely used in aerospace, aeronautics [Sun, Kim and Daniel (2003)], automobile [Zhao, Sun, Wang et al. (2013)], voyaging [Ji, Wang, Zhao et al. (2015)] and many other applications.

Cyanate ester resin, as a newly-developed high performance resin matrix, possesses good mechanical properties [Ou, Ji, Xiao et al. (2015a)], heat resistance and dielectric properties [Nair, Mathew and Nian (2001)], low thermal expansion coefficient and

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hygroscopic rate [Faccianno (2000)]. It is widely used in aerospace structural composite materials [Li, Wang and Wang (2014)], wave absorbing/transparency composite material [FIeldly, Olsen and Rysieldal (2001)] electronic printed circuit board [Ou, Ji, Xiao et al. (2015b)] and so on. However, cyanate resins currently used for RTM process [Li, Liang and Yu (2002); Zhao, Liang, Meng et al. (2001); Zhong, Hong, Bao et al. (2006)] normally have a T_g (glass transition temperature) less than 200℃, which is not high enough for the requirement of heat endurance structural composites.

Mechanical properties of T800 Carbon fiber composites are normally 10% higher than that of T300 [Zhang, Li, Chen et al. (1998)] or T700 [Liu, Zhang, Bao et al. (2016)], which means T800 carbon fiber composites could be significant helpful for lightweight designing in aerospace applications. In view of the demand for heat endurance structural composites in aerospace field, a high T_g cyanate ester resin suitable for RTM technology has been developed, and its RTM r process and curing process have also been studied. Domestic T800 carbon fiber reinforced cyanate ester resin laminates were prepared via RTM process. The properties of stated laminates were studied and the fracture morphology and failure mode of the composites were analyzed, which provided the basis data for engineering application of RTM cyanate ester composites.

2 Experiments

2.1 Materials

RTM cyanate ester resin was made by Research Institute of special Aerospace Materials and Processing Technology, viscosity at room temperature was less than 1000 mPa·s.

T700 & T800 unidirectional fabrics with (200±10) g/m^2 areal density and 0.112 mm thickness were provided by Shan Dong Ding Sheng Technology Co., Ltd. T700 carbon fiber was made by Toray industries, Inc and T800 grade carbon fiber was produced by Zhong An Xin Technology Co., Ltd. 9518 resin is a cyanate ester for hot-melt prepreg. T800/9518 hot-melt prepreg contains resin content of 38±3% and volatile content less than 1%.

2.2 Sample preparation and property tests

2.2.1 Clear casting preparation

Certain amount of resin was weighted out and put into a clean mold. The mold with the resin was heated to 70℃ by oven and then the defoaming was operated via vacuum for 30-40 mins until there was no air bubbles observed on clear casting surface. The resin was cured by the protocol of 130℃/2 h +160℃/2 h+200℃/2 h+220℃/4 h in which 130℃/2 h meant the resin was heated under 130℃ for 2 h. The sample was prepared and tested according to GB/T 2567.

2.2.2 Laminates preparation

T700 & T800 unidirectional fabrics were cut according to the inner dimension of RTM molding. The fabrics were laid into the cleaned RTM molding with the one fiber direction of all layers. The designed thickness of laminates was 2 mm and the designed fiber content was (60±3)%. The mold together with resin injection tank were placed into oven and heated up to 70℃. Before injection, the resin was then poured into the

injection tank and the defoaming was operated via vacuum for 30-40 min. The laminates were cured according to following steps, 130℃/2 h +160℃/2 h+200℃/2 h+220℃/4 h. The cured laminates were demold after the mold cooling down to the room temperature.

16 pieces of T800/9518 prepregs were cut according to the inner dimension of the compression mold. Laminates with 2 mm thickness were hot-pressed according to the following protocols, 130℃/0.5 h+160℃/0.5 h (Hot-Press/Close mold)+200℃/2 h+220℃/4 h. The mold cooled down to the room temperature before demolding. Three types of laminates were then prepared and tested according to representative standards.

2.2.3 Property tests

Viscosity tests were conducted with the instrumentation of BrookField DV-II. The Temperature range of dynamic viscosity test was 30-200℃ with 10℃ each step and isothermal viscosity tests were analyzed at 50℃, 60℃ and 70℃.

Differential scanning calorimetry (DSC) tests were conducted on the Mettler Toledo DSC822e. With the nitrogen gas protection, the heat flow vs time relation was measured with a temperature range of 25-350℃ at 5℃/min, 10℃/min and 15℃/min heating rate.

The FT-IR spectra were measured on Nicolet iS50 infrared spectrometer. The absorption peaks were scanned between 4000 cm^{-1}-400 cm^{-1} for samples before and after curing by pressed disc method, the resolution is 4 cm^{-1}.

The dynamic mechanical analysis (DMA) was performed using the Mettler Toledo DMA/SDTA861e from 25-350℃ at a heating rate of 5℃/min. And displacement control method with a three-point bending fixture was used with a frequency of 1 Hz.

The thermal gravimetric analysis (TGA) was conducted using the Mettler Toledo TGA/SDTA851e analyzer at a heating rate of 5℃/min. With the nitrogen gas protection, the testing temperature ranges from 25-600℃.

Mechanical properties testing was conducted on the AG-I 250 KN test machine supplied by Shimadzu Corporation according to the corresponding standards.

The fracture morphology of the tensile samples was observed under the scanning electron microscope (SEM).

3 Results and discussion

3.1 Cyanate ester resin and its RTM process

3.1.1 Resin rheology

The resin rheology of cyanate ester was shown as Fig. 1. Fig. 1(a) showed that the resin viscosity changed according to the system temperature. As temperature increased, resin viscosity decreased at first and then increased, making a “U” shape. For analysis, Fig. 1(a) could be divided into three phases and each phase represented different reaction mechanism. Phase 1, 50~80℃ and the viscosity ranged from 830 mPa·s to 60 mPa·s. In phase 1, system temperature was relatively low hence low degree of curing reaction. Reactivity of the resin functional groups was also low at this stage, activity of molecular chain increased as temperature increases. Movements of molecular chain

lead to the system viscosity decreasing rapidly. Phase 2, 90~180℃ and the viscosity ranged from 20 to 45 mPa·s. Temperature continued to rise up at this stage, hence the reactivity of the resin functional groups increased, system energy kept increasing while not high enough to surpass required energy barrier for curing. Degree of curing of the resin was still low at this stage and movements of molecular chain had reached maximum at around 80℃, so the viscosity maintained stable. Phase 3, 190~200℃ and the viscosity ranged from 90 to 560 mPa·s. At this stage, reactivity of the resin functional groups continued to increase as temperature increased, system energy finally surpassed required energy barrier for cuing. Degree of curing increased rapidly in short time, the resin system started gelling and the viscosity started to soar.

Fig. 1(b) showed the isothermal viscosity changes *vs.* time. Under isothermal condition 50~70℃, system viscosity slowly increased as time went by. The viscosity was still below 500 mPa·s even after 8 h and it meant that this resin system possessed an eight-hours-processing window for RTM injection which met the resin viscosity requirement for a typical RTM process [Yi (2001)]. Within this processing window, the required injection pressure was relatively low due to the low viscosity, which was good for fiber wetting and air elimination in preforms and was good for obtaining low porosity composites. Based on the data above and careful considerations, 70℃ was identified as the ideal injection temperature for this cyanate ester resin system during RTM process.

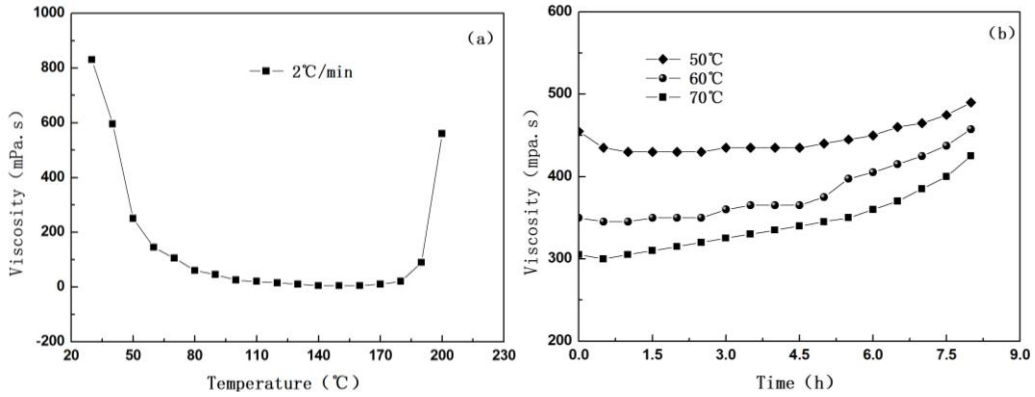

Figure 1: Dynamic viscosity (Fig.1(a)) and isothermal viscosity (Fig.1(b)) of cyanate ester

3.1.2 Curing reaction of cyanate resin

Fig. 2 showed DSC curves for cyanate ester resin. As a typical cyanate ester resin, only one exothermic peak was observed during resin curing process, indicating all steps of curing took place within a confined temperature range. The peak shifted towards higher temperature as the heating rate increased, generating a larger integral area with baseline. Amount of heat release was represented by the integral area. The larger the integral area is, the more heat was released due to higher degree of curing.

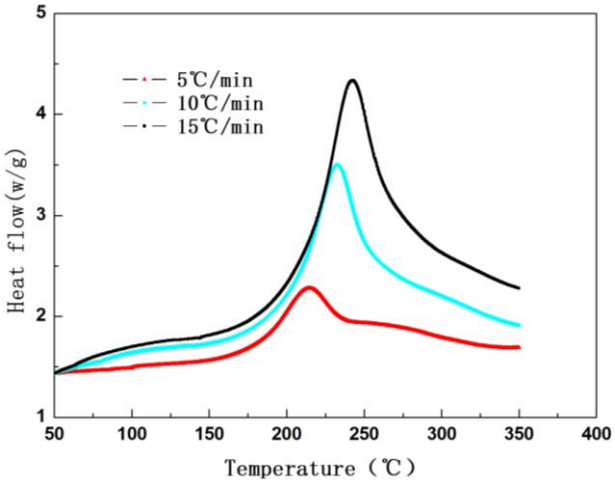

Figure 2: DSC curves of cyanate ester for RTM

3.1.3 Curing process and characterization

Fitting curves in Fig. 3 were drawn by using characteristic temperatures (Initiating temp=T_i, Exothermal peak=T_p and Finished temperature=T_f) as *y* and heating rate (β) as *x*. In an isothermal condition, the characteristic temperatures (T_{i0}=167℃, T_{p0}=203℃ and T_{f0}=219℃) of the cyanate ester resin was calculated via the extrapolation method. For all fitted curves, the correlation coefficients (R-square) were above 0.999, indicating the equation had good reliability for application.

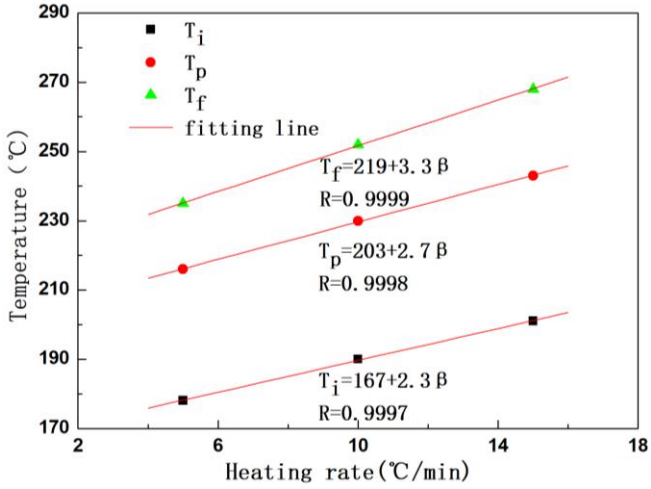

Figure 3: Relationship between the characteristic temperatures and the heating rate of cyanate ester

The first isothermal platform was usually set to a little bit lower than initiating temperature, so that thermographic of the composites could be homogeneous, and all parts of the composites could cure at the same time, which would minimize the stress

during curing. Considering instrumentation and molding influences, the actual curing temperature was normally 10℃ different from the calculated temperature. As a result, the curing process was determined to be 130℃/2 h+160℃/2 h+200℃/2 h+220℃/4 h.

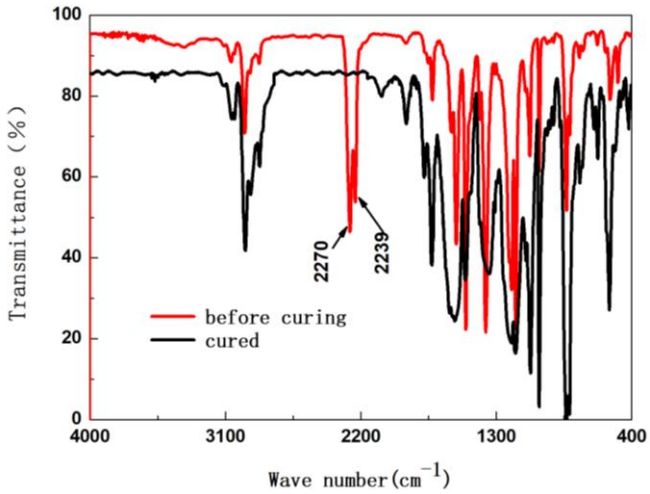

Figure 4: FT-IR of cyanate ester for RTM

The above curve with red color in Fig. 4 was IR spectra for uncured cyanate resin while the below curve with black color was that of cured cyanate resin following the curing process aforementioned. The fact that absorbance peak for cyanide (-OCN) was observed in red curve but not in black curve indicated that cyanate ester resin had been completely cured, which verified the effectiveness of the determined curing process and the reliability of the extrapolation method.

3.1.4 Thermal behavior of RTM cyanate ester

The TGA curve of RTM cyanate ester resin was shown in Fig. 5. No obvious weight loss can be observed before 415℃. The subtle weight loss mainly comes from the volatilization of moisture and small molecules gradients in the resin. When the temperature rises to 428℃, the weight drops suddenly and the decomposition rate increases rapidly. The sudden weight loss is caused by the decomposition of methyl group, carbonization and pyrolysis of the molecular chains. The weight loss rate slows down above 428℃ when the molecular chains have been carbonized, and the weight loss mainly comes from the deep cracking of the main chains. The initial thermal decomposition temperature of RTM cyanate ester resin is 415℃, and the peak temperature at the maximum weight loss rate is 428℃. It can be concluded that the resin has an excellent resistance of short-time high temperature.

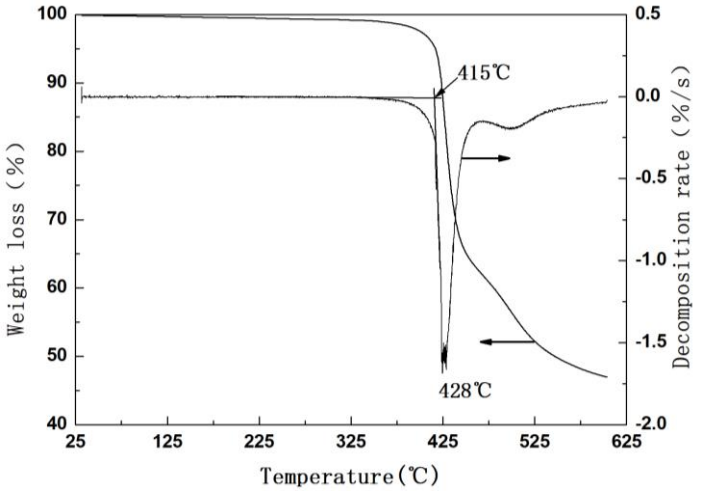

Figure 5: TGA curves of cyanate ester for RTM

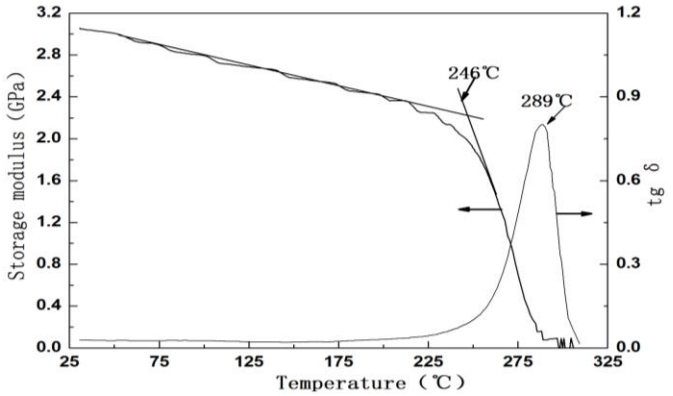

Figure 6: DMA curves of cyanate ester for RTM

The Fig. 6 plots the DMA curve of the RTM cyanate ester resin. Within the temperature range of 25 to 246℃, the storage modulus of the resin declines slowly with the temperature increasing. At this time, the elevated temperature only enhances the movement ability of some chain segments but has marginal effect on the mechanical properties of the material. With the temperature increasing higher than 246℃, the storage modulus declines significantly due to the increased mobility of the entire molecular chain causing the loss of load bearing capacity of the material. The inflection point of the storage declination along with the temperature is 246℃, and the corresponding tg δ peak temperature is 289℃, showing that that RTM cyanate ester possess high temperature stability which makes it suitable for the elevated temperature structures.

3.2 Composites and its properties

3.2.1 Mechanical properties

Three types of composites were prepared for comparison. T800/RTM (T800 carbon fiber reinforced cyanate resin for RTM process), T700/RTM (T700 carbon fiber reinforced cyanate resin for RTM process), and T800/Prepreg (T800 carbon fiber reinforced 9518, a modified cyanate resin).

Mechanical properties of three types of composites were displayed in Tab. 1. Mechanical properties of T800/RTM were observed 13.5% higher than that of T700/RTM, but similar to that of T800/Prepreg, which meant that T800/RTM possessed good comprehensive mechanical properties. Thus, T800/RTM could be considered as a promising material to replace T700/RTM for structural weight reduction.

Table 1: Mechanical properties of T800 grade carbon fiber RTM cyanate ester composites

Item	T800/RTM	T700/RTM	T800/Prepreg	Increment*(%)
0°Tensile strength /MPa	2751	2240	2774	22.8
0°Tensile modulus /GPa	158	123	169	28.5
0°Compression strength/MPa	1362	1200	1350	13.5
0°Compression modulus/GPa	148	130	150	13.8
0°Flexural strength/MPa	1850	1608	1860	15.0
0°Flexural modulus/GPa	157	124	155	26.6
0°Interlaminar shear strength/MPa	106	92	108	15.2

*The increment is defined by the increasing rate of RTM T800/cyanate ester composites compared to RTM T700/cyanate ester composites

3.2.2 Thermo-mechanical properties of T800/RTM cyanate composites

From DMA curve in Fig. 7, T_g of T800/RTM composites can be obtained as 291℃. If highest working temperature was 56℃ less than its T_g, which can be calculated as 235℃, indicating that this material possessed excellent heat endurance properties. Comparing Fig. 6 (DMA for clear casting) with Fig. 7 (DMA for composite), it was observed that T_g for composites was also higher than that of clear casting. Good interfacial properties between fiber and resin (due to good fiber wetting properties) provided better thermomechanical properties.

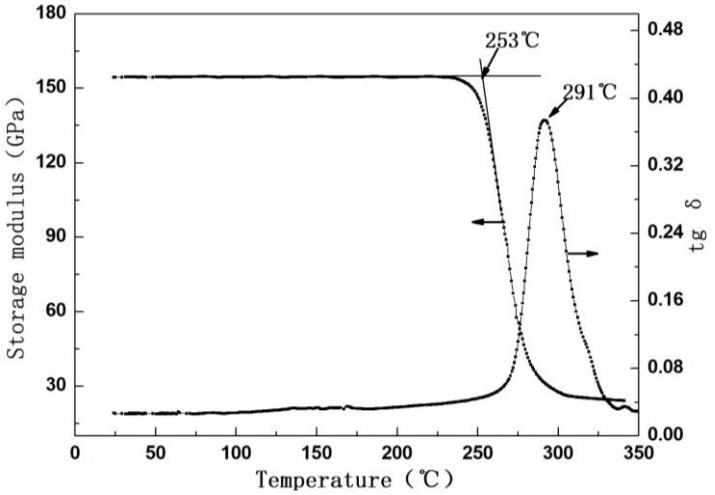

Figure 7: DMA curves of T800 grade carbon fiber RTM cyanate ester composite

3.2.3 Fracture morphology analysis of T800/ RTM composites

SEM images were taken from the fracture surface of composites. In Fig. 8(a), fragile fracture morphology was observed at breaking points while few pulled out fibers were observed. This indicated good interfacial properties between resin and fibers, which was beneficial for good mechanical properties. In Fig. 8(b), resin was observed to be sticking to the pulled out fiber, demonstrating high bonding strength between resin and fibers. Thus, high strength and modulus of T800 fiber could be easily transferred from resin matrix, generating high loading probabilities.

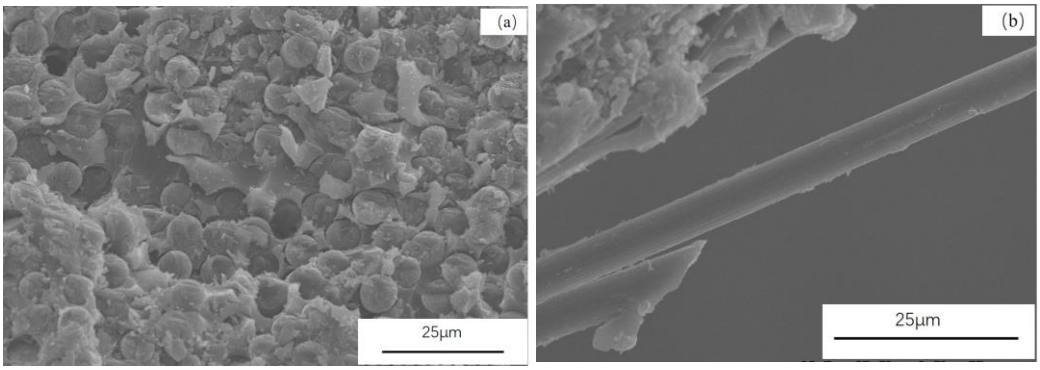

Figure 8: SEM images of T800 grade carbon fiber RTM cyanate ester composites

4 Conclusion

Cyanate ester resin for RTM process, could be cured completely via following process, 130℃/2 h+160℃/2 h+200℃/2 h+220℃/4 h. The resin injection temperature was chosen 70℃. The cured clear casting possessed high heat endurance property. T800/RTM composites possessed great comprehensive physical properties, and its

highest working temperature can reach 235℃ (T_g=291℃) which indicated the potential application for heat endurance structural parts.

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