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Effect of rapid curing process on the properties of carbon fiber/epoxy composite fabricated using vacuum assisted resin infusion molding

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A B S T R A C T

Long processing cycle makes vacuum assisted resin infusion molding (VARIM) only suitable for low and medium volumes of production, and shortening of curing time is critical to improving the processing efficiency of automotive composite parts. In this paper, unidirectional carbon fiber reinforced composite laminates were fabricated by VARIM. Three different processes (namely quick, quick-post and preheating) were employed, in which a kind of rapid curing epoxy resin is used. The preheating of mold and fiber was conducted to shorten the filling time compared with that of quick process. Quick-post process with a post cure stage was investigated to verify the composite properties fabricated by quick process. The cycle time was 16 min for preheating process, about 30% shorter than that of quick process, simultaneously, flexural strength and interlaminar shear strength (ILSS) were respectively improved by 29% and 7% compared with those of quick process. The non-uniformity of mechanical properties at different positions along resin flow direction under preheating process was found, but the processing quality of composite was good. The preheating process is confirmed to be suitable for the improvement of processing efficiency of VARIM with good mechanical properties. In addition, the composite fabricated by quick-post process has better mechanical properties, which is attributed to the alleviation of residual stress during post curing process.

1. Introduction

The current trend in advanced composite materials, especially carbon fiber reinforced polymer matrix composite (CFRP), is to expand the use from aeronautic and defense industries to civil industries, such as automotive, wind turbine blade and building reinforcement. It requires a significant improvement in processing efficiency of composite and a sharp reduction in cost of composite in order to realize large scale usage. This calls for the development of new processing technology and materials. For thermoset composite, the curing stage generally takes a long time (several hours) to complete the crosslink of resin for obtaining excellent mechanical properties, and it is far beyond the targeted manufacturing cycle (several minutes per part) in automotive industry. Therefore, shortening of curing time is critical to improvement of processing efficiency [1–3].

Liquid composite molding (LCM) is one of the key low-cost manufacturing methods and is regarded as an alternative to prepreg technology [4,5]. In the process, layers of fibrous reinforcement are laid on mold to create a preform, and then thermoset resin is injected into the mold cavity and impregnates the reinforcement. The mold is usually heated to initiate a curing reaction, which is an exothermic polymerization phenomenon that crosslinks the resin, and obtains a composite structure. Vacuum assisted resin infusion molding (VARIM), which uses low-cost tooling, has been a most widely used LCM process for large structures, including boat hull, wind turbine blade and automobile chassis components, where rigid tool processes are economically or technically unfeasible because of part size or volume of production. However, its long cycle time makes it only suitable for low and medium volumes of production, and the application of VARIM for high volumes of production is restricted.

In recent years, new LCM resin systems with low viscosity, good impregnation with fiber and fast curing properties have been developed. Kame et al. developed a rapid curing epoxy resin system composed of 2-methylimidazole and an alcoholic type chain transfer agent. Using this resin system, CFRP automobile panel was successfully fabricated in 10 min by an isothermal resin transfer molding (RTM) process at 105 °C [6]. Resin 05127/curing agent 05443, the product of Hexion Specialty Chemicals, has been applied for high-volume RTM in particular for truck application with curing time of 23 min [7]. In addition to the development of fast curing resin system, there are some works to reduce the time of

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processing by improving process conditions, such as preheating mold and fiber [8–11] and using high speed RTM injection system [12,13]. Preheating mold can aid to facilitate resin flow as a consequence of viscosity reduction at elevated temperature [10]. On the other hand, M.Yamasaki et al. [12] developed a rapid injection RTM process based on multi-gate resin injection system. They controlled resin injection time of a 700 mm × 1200 mm × 150 mm automobile inner door panel within three minutes. Mathieu Devillard et al. [14] shortened the curing time by 20–25% by continuously varying the percentage of curing agent during injection, where sophisticated liquid meter and injection equipment were needed to complete the process. These techniques for LCM with rapid curing resin obtained short cycle time, but nonuniform curing degree and processing quality along resin flow direction might occur for the variation in thermal history, which would result in residual stress and degradation of mechanical properties of composite. Therefore, the relationship between the processing conditions of LCM and the performances of composite using rapid curing resin need be further understood.

In our previous work, a rapid curing epoxy resin system, diglycidyl ether of bisphenol-A (DGEBA) epoxy resin/modified imidazole/aliphatic amine, was developed for VARIM process, which exhibited less than 5 min curing time under 120 °C and good flowing characteristics [15]. In order to further enhance fabricating efficiency, the processing conditions should be optimized and the effects on the properties of composite need be studied. In this paper, unidirectional CFRP laminates were fabricated under three kinds of cure schedules which were labeled as quick, quick-post and preheating processes, respectively. A post cure process (quick-post) was adopted to verify the composite properties fabricated by quick process. The preheating of mold and fiber was conducted to shorten the cycle time compared with that of quick process. The effects of different cure cycles on void percent, fiber volume fraction, heat resistance, flexural properties and interfacial bonding of the composite were investigated. The efficiency of preheating process and the uniformity of composite properties were analyzed.

2. Materials and experimental methods

2.1. Materials

The epoxy resin used in this study was DGEBA E51 (supplied by Blue star New Chemical Materials Co. Ltd.). The cure agents included modified aliphatic amine (home-made) and modified imidazole (supplied by Bluestar New Chemical Materials Co. Ltd.). The weight ratio of epoxy/imidazole/aliphatic amine was 100:6:6. The reinforcement was T700SC unidirectional carbon fiber fabric with an areal density of 200 g/m^2 (supplied by Jiangsu Tianniao High Technology Co. Ltd.).

2.2. Preparation of composites

The composite laminates were prepared by means of VARIM method, as illustrated in Fig. 1. Nine layers of T700SC unidirectional carbon fiber fabrics (320 mm × 160 mm) were stacked along longitudinal direction on a mold to form a 2 mm thick laminate. Peeling ply, highly permeable medium and distribution mesh were laid over the surface of the fabric successively. The distribution mesh was terminated at a gap 30 mm from the end of the fabric preform, preventing resin race-tracking as it flows through the medium and the fiber preform.

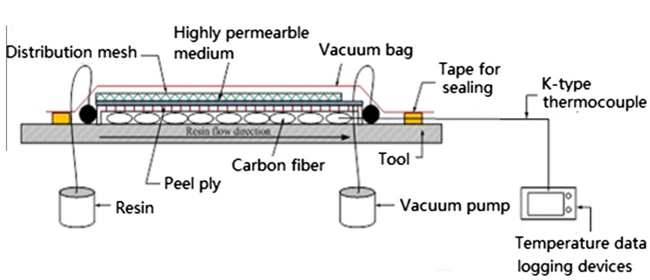

Fig. 1. Schematic diagram of VARIM process.

The curing cycle included three stages: injection stage, curing stage and cooling stage, referring to resin injection, cross-link reaction and cooling of the laminate, respectively. In this paper, three different curing conditions were used with different injection stage and curing stage. For the first curing cycle, named quick process, vacuum pressure (0.098 MPa) was applied to the preform for making resin flow into the preform at 25 °C, and then the assembly is put directly into an oven under 120 °C until the temperature of laminate came to a peak and began to reduce. After that, the assembly was taken out from the oven to cool down. The second curing cycle (named quick-post process) had the same injection stage and cooling stage as those in the quick process, but a post cure at 120 °C for 1 h was added in its curing stage after the temperature of laminate came to a peak in an oven under 120 °C. The third curing cycle was called as preheating process, during which preheating mold and fiber were used and epoxy resin flowed into the preheated assembly (80 °C, 0.098 MPa vacuum pressure) in the injection stage. And then, temperature of the oven was elevated to 120 °C within 5 min to complete curing stage. Its cooling stage was the same as that in the quick process. A preheating temperature of 80 °C was employed in preheating process because the lower viscosity and sufficient gel time of the resin system were both obtained under the temperature. All of the laminates were naturally cooled down to 60 °C and then demolded. In order to monitor the temperature history inside the laminates during the curing process, K-type thermocouples were embedded in the middle of preform in longitudinal directions, as show in Fig. 2.

2.3. Testing method

2.3.1. Rheological analysis

Rheological measurements were carried out in parallel plate mode with a Gemini rheometer (Bohlin Instruments), and resin complex viscosity was generated with the disc oscillating at 1.0 HZ. The dynamic viscosities versus temperature were determined from 25 °C to 200 °C at the heating rate of 5 °C/min, and isothermal tests were performed at 30 °C, 60 °C, 80 °C and 90 °C, respectively.

2.3.2. Differential scanning calorimetric analysis

Differential scanning calorimetry (DSC) was performed on a thermal analyzer (Mettler Toledo) to obtain the curing degree of the laminate. Firstly, uncured epoxy resin mixed with curing agent was subjected to a scanning rate of 10 °C /min from 25 °C to 250 °C, to calculate the total heat of reaction of the resin system (H_T). The residual reaction heat (H_r) of the resin sample cut from the cured composite was obtained with a scanning rate of 5 °C /min from 25 °C to 200 °C, and then the curing degree of the composite was calculated as follows:

$$\alpha = \frac{H_T - H_r}{H_T} \quad (1)$$

2.3.3. Dynamic mechanical thermal analysis

Dynamic mechanical thermal analysis (DMA Q800) was performed in a three-point bending mode at a frequency of 1 Hz with a strain of 0.04%. The composite samples (30 mm × 8 mm × 2 mm) were heated from 25 °C to 200 °C at 5 °C/min with an assigned strain of 9 μm. The storage modulus (E') of the composite specimen