A New Process Control Method for Microwave Curing of Carbon Fibre Reinforced Composites in Aerospace Applications

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Abstract: For the fabrication of carbon fibre reinforced composites used in aerospace industry, microwave curing technologies are more effective than traditional thermal curing technologies. However, the manufacturer's recommended cure cycles used in traditional autoclave curing are directly adopted into current microwave curing technologies without thorough validation. Here, a new cyclic heating and cooling methodology for microwave curing process control of composite is proposed by analyzing mechanisms of heat conduction, stress generation and curing kinetics. The results of the experiment carried out show significant reductions in residual strain, warpage, total curing time and energy consumption, compared with both traditional thermal curing and current microwave curing technologies. The mechanical properties of samples cured by the new process are compared with the autoclave cured ones.

Keywords: A. Polymer-matrix composites (PMCs); B. Residual stress; B. Strength; E. Cure.

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1. Introduction

Carbon fibre reinforced polymer composites with high strength, stiffness and load-bearing/weight ratio have a wide range of applications [1, 2], such as in commercial and military aircrafts. Primary load bearing aerospace composites are normally fabricated using traditional thermal curing technologies [3], in which the composite material is placed in an autoclave [4, 5], and the surrounding air is heated by electric wires which transfer the heat to the material. The main problems of the traditional technology are non-uniform temperature distribution, low curing efficiency, long process cycle, and high energy consumption and cost [6]. For aerospace applications, the most serious limitation is the inability of fabricating composite materials of large and variable thickness, because of serious defects and decrease of performance induced by temperature gradients [7, 8]. More recently, microwave curing technology has been considered as a very attractive alternative to autoclave curing for the fabrication of high performance aerospace composites [9, 10].

Comparing to the conventional heating, the advantages of microwave heating include: (i) volumetric and selective heating, (ii) fast heating rates, (iii) quick start-up and stopping, (iv) reduction of curing time, (v) saving energy, (vi) higher level of safety and automation, and (vii) friendly to the environment [11]. During microwave curing, energy is supplied by an electromagnetic field directly to the composite material. This results in rapid heating throughout the material thickness with uniform temperature distribution, reduced energy consumption and cost [12]. Meanwhile, the composite performance is improved [13]. Composites cured by microwave had better impact strength [14] and stiffness [15] than that of traditional thermal cured ones. The carbon fibre in composite can effectively absorb microwave, and the interface strength of

composite was highly improved [16]. It was reported that carbon fibre screens have strong absorption of microwave in broadband frequency [17]. In addition, the microwave curing process provided higher joint strength [18], decreased the stresses deformation and total curing time of composite materials [19].

However, in the current microwave curing methods [20], the process parameters of traditional thermal heating (the manufacturer's recommended cure cycles) have been adopted without modifications and thorough validation, such as heating rate, dwell temperature and curing time. As known, the microwave can accelerate the curing rate of polymer resins at a frequency of 2.45 GHz [21], but the reaction process of resin is the same with thermal curing [22]. To take full advantage of the microwave curing, a more applicable method should be developed based on its unique heat transfer and curing mechanisms to improve the composite quality, especially in the reduction of residual stresses.

This paper introduces a cyclic heating and cooling process for microwave curing of carbon fibre reinforced composites. For conventional autoclave curing, only one cooling down during heating process can be achieved, because of the large temperature hysteresis induced by low efficiency heat transfer. And the cure-induced stresses of composites can be just slightly reduced [23]. While the use of microwave has make it possible to cyclic heat and cool composite in a fast rate. The effects on residual stresses, curing cycle and energy consumption of current microwave curing process, microwave curing with one cooling down and traditional thermal curing process are compared and analyzed. The microwave curing equipment is developed to satisfy the aim of this work. Mechanical strength of different curing processes manufactured composite samples are measured and analyzed.

2. Theories used in the new microwave curing technology

2.1 Microwave heat conduction mechanism

During traditional thermal curing of carbon fibre composite, heat is conducted via the surrounding air to the surface of the composite in an autoclave, then to the inside of the material. In comparison, during microwave curing, only high absorption materials such as carbon fibres are heated [19]. The heat is conducted from carbon fibre to resin, which results in cross-linking reaction of resin, as shown in Fig.1 (a). The composite is typically composed of over 60% volume fraction of carbon fibres. Because the composite is heated directly by microwave, the temperatures of surrounding air and tool material remain relatively low during microwave heating (Fig.1 (b)).

The fast heating rate of composite by microwave leads to strong heat radiation and convection between part, tool and environment. Considering the balance of heat transfer, the microwave heating conduction of composite part can be expressed as [11]:

$$\rho_p \cdot C_p \cdot \frac{\partial T}{\partial t} = k_x \frac{\partial^2 T}{\partial x^2} + k_y \frac{\partial^2 T}{\partial y^2} + k_z \frac{\partial^2 T}{\partial z^2} + \rho_p Q_E + \rho_r Q_R \quad (1)$$

Where T is curing temperature, t is curing time, ρ_p and ρ_r are density of composite and resin respectively, C_p is the specific heat capacity of composite, k_x, k_y and k_z are the composite coefficients of heat conduction at x, y and z directions. Q_R is the heat generation rate density of curing reaction, and Q_E is the density of the heat generation rate of composite and has the relationship with microwave frequency, the intensity of electric field around composite and the dielectric loss tangent of material [24].

The heat of composite transfer to tool in the x, y and z directions and no heat flow in the symmetrical plane of the composite. In the boundaries of composite and tool, the

convective cooling and surface-to-ambient radiation should also be considered. The above equations are the basis for determining the parameters in the proposed new microwave curing process control method.

2.2 Residual stress induced during microwave curing

Because of the complex variation of viscoelastic properties of composites, the semi-empirical theory was developed to express the stresses induced during microwave curing. Due to the selective heating of microwave, the significant temperature difference between fibre/resin and composite/tool should be considered. Assuming there are interfaces among fibre/resin and composite/tool, respectively, as illustrated in Fig.2 (a). During heating and cooling, the interfaces suffer stresses caused by the mismatch of the Coefficients of Thermal Expansion (CTE) of different materials, as shown in Fig.2 (b). The shear stresses of these interfaces are employed to express the stresses variation during heating and cooling process. The assumption of no sliding on the interface and uniform stress distribution in the thickness (large length to thickness ratio) were adopted. Thus, the strain loads of heating and cooling process induced by thermal expansion and shrinkage were related with the temperature variation, CTE of fibre/tool and modulus of resin/composite. Considering the viscoelastic properties of composites during curing, the viscoelastic stresses are introduced. The induced stresses caused by the fibre/resin and composite/tool interactions can be expressed as below:

$$\sigma_{fiber-reisn} = \Delta T^{f} \beta_f E_f - \sigma_r(\tau) \tag{2}$$

$$\sigma_{composite-tool} = \Delta T^{t} \beta_t E_t - \sigma_p(\tau) \tag{3}$$

Where β_f and β_t are the CTEs of carbon fibre and tool. E_f and E_t are the

modulus of carbon fibre and tool, respectively. $\sigma_r(\tau)$ and $\sigma_p(\tau)$ represent the viscoelastic stresses of the resin and composite related with time, respectively. ΔT^f and ΔT^t are the temperature difference of fibre and tool in a time period. At the beginning of curing, the resin is sol liquid with an infinity value of loss modulus. As the temperature rises, it starts to gel, and the phase changes from sol-gelled rubber state to totally cured gelled glass state. Before the gelation of resin, the accumulated stresses in fibre-resin and composite-tool can be relaxed. However, after gelation, the resin starts to store stresses due to the viscoelastic properties of sol-gelled rubber phase [25]. Meanwhile, under the constraint by the outer vacuum pressure and tool friction, the elastic deformation of composite cannot be released instantaneously. Thus there is delayed elastic response to elastic deformation. The hysteresis of elastic deformation leads to the stress accumulation of composite during the continuous curing process. Because of the chemical reaction of resin, the stress will be 'locked' in the composite until curing completed and resulting in warpage of the composite.

To release the 'locked' stress, a cyclic heating and cooling method is proposed and shown in Fig.3. $g(t)$ is defined as the temperature variation of composite under the cyclic heating-cooling process ($P(t)$, $A(t)$ and $\varphi(t)$ denote the average temperatures, amplitude and variation frequency respectively). Compare with the traditional autoclave curing methods, the curing temperature in the reaction process remain invariable (dwell stage), or only one cooling down and re-heating can be achieve [23]. While in the case of traditional autoclave curing methods, it is impractical to realize the cyclic heating and cooling process due to the high temperature of surrounding air and tool which gives rise to a bad control ability of composite temperature. According to Eq.1, the strong heat dissipation of composite can lead to fast

cooling down rate. Meanwhile, the volumetric heating of microwave provided fast heating rate of composite. Through cyclic heating and cooling, the stress 'locked' in the previous stage (e.g., heating in Fig.2 (b)) will be reduced in the next stage (e.g., cooling in Fig.2 (b)) by the almost same value but opposite direction stresses. Base on the Maxwell viscoelastic mode, the relationship between stresses and strains can be expressed as:

$$\sigma(t) = \varepsilon E(t) \tag{4}$$

According to the Bolzmann superposition principle, the integral representation of $\sigma(t)$ and $\varepsilon(t)$ is shown below:

$$\sigma(t) = \int_0^t E(\alpha, t-\tau)\frac{d\varepsilon(\tau)}{d\tau}d\tau \tag{5}$$

Where, $E(\alpha, t-\tau)$ is the relaxation modulus related to the degree of curing and curing time. According to the basic viscoelastic mechanics theory, the relaxation modulus can convert to exponential function:

$$E(\alpha, t-\tau) = E(a)\exp(-\frac{t-\tau}{\xi(\alpha)}) \tag{6}$$

Where, $\xi(\alpha)$ is the relaxation time, which related with the degree of curing.

$$\xi(\alpha) = \frac{\eta(\alpha)}{E(\alpha)} \tag{7}$$

The heating or cooling process is the same as applying strain with constant rate on the material.

$$\varepsilon(t) = \kappa t \tag{8}$$

Thus, the above Eq. (5) can be written as:

$$\begin{aligned}\sigma(t) &= \int_0^t E(\alpha)\exp(-\frac{t-\tau}{\xi(\alpha)})\frac{d\varepsilon(\tau)}{d\tau}d\tau \\ &= \int_0^t E(\alpha)\exp(-\frac{t-\tau}{\xi(\alpha)})\kappa d\tau \\ &= \kappa\left[E(\alpha)\xi(\alpha)\exp(-\frac{t-\tau}{\xi(\alpha)})\right]_0^t \\ &= \kappa E(\alpha)\xi(\alpha)\left[1-\exp(-\frac{t}{\xi(\alpha)})\right]\end{aligned} \tag{9}$$

For the fibre and resin interaction stresses, the fibre shrinkage/expansion during heating/cooling process can be considered as applying loads on the resin matrix. The fibre has nearly constant modulus as the variation of curing temperature, but the elasticity modulus of resin changes with the curing state. The relationship between modulus and degree of curing can be expressed as follows [26]:

$$\begin{aligned}E_r(\alpha) &= E^0 \qquad 0 \le \alpha < \alpha_{gel} \\ E_r(\alpha) &= E^0 + (E^\infty - E^0)\alpha \qquad \alpha_{gel} \le \alpha\end{aligned} \tag{10}$$

Where, E^0 is the elasticity modulus of resin at the initial state, E^∞ is the modulus of fully cured resin. Because of the resin is liquid at the room temperature, the initial elasticity modulus of resin is approximately equal to zero ($E^0 \approx 0$), before the gelation point. α_{gel} is the degree of curing of resin at the gelation point. On account of the time temperature equivalence principle, raising the temperature and increasing the time has the same influence on the viscoelastic properties of resin. The viscoelastic parameters at different temperature of resin can be transferred by the shift factor a_T. According to the free volume theory and WLF (Williams-Landel-Ferry) equation, the shift factor is calculated as follows:

$$\lg a_T = \frac{-C_1(T-T_g)}{C_2+(T-T_g)} \tag{11}$$

Where, C_1 and C_2 are the constants related with resin. For the reference temperature of resin (T_g, glass-transition temperature), the C_1 and C_2 have value of 17.4 and 51.6 respectively [27]. Under a certain heating rate ($T = qt$), the relationship between shift factor and relaxation time is:

$$\xi_r(t) = \frac{1}{\omega \alpha_T(qt)} \tag{12}$$

With regard to the tool-part interaction during curing, the mechanical properties of tool remain constant, but the composite material exhibits obvious viscoelastic characteristic. The relaxation modulus of carbon fibre reinforced composite materials is related to its dynamic thermal mechanical properties, the relaxation modulus is determined from:

$$E_p(t) = \frac{E_p^{'}(t)(1+\omega^2 \xi_p^2(t))}{\omega^2 \xi_p^2(t)} \tag{13}$$

Where, $E_p(t)$ and $E_p^{'}(t)$ are the relaxation modulus and storage modulus of composite material, respectively. ω is the testing frequency of dynamic thermal mechanical analyzing of composite. Also, the relaxation time $\xi_p(t)$ of Maxwell model can be expressed as:

$$\xi_p(t) = \frac{1}{\omega \tan_p(t)} = \frac{E_p^{''}(t)}{\omega E_p^{'}(t)} \tag{14}$$

Here, $\tan_p(t)$ is the loss tangent of composite, $E_p^{''}(t)$ is the loss modulus of composite. Base on the above analysis, the temperature variation value of one heating or cooling down process can be calculated by considering the accumulation and release of thermal stresses in the cyclic process.

As shown in Fig.3, if the first cooling down at the gelation point is to reduce the

curing reaction rate to nearly zero, the point at t_0 time is considered as the start point of the cyclic heating-cooling and the cure-induced stresses is also nearly zero. The temperature should be raised to cure the composite, but this process will induce thermal stresses from the CTE mismatch of fibre/resin and tool/part. The heating time $t_1 - t_0$ and temperature at this point is the initial values of stresses calculation. After the heating process, the cooling down is implemented to reduce the thermal stresses accumulated in $t_1 - t_0$ time period. For fibre/resin and tool/part interaction stresses, the applied strains on the resin and composite are:

$$\varepsilon_{u1}^{f} = \Delta T_{t_1-t_0}^{f} \beta_f , \quad \varepsilon_{u1}^{t} = \Delta T_{t_1-t_0}^{t} \beta_t \tag{15}$$

Here, ε_{u1}^{f} is the strain of fibre applied on the resin, and ε_{u1}^{t} is the strain of tool applied on the composite part. From t_0 to t_1 time period, the stresses of fibre/resin and tool/part at the heating process are analyzed separately, as shown below. The stresses accumulate from t_1 to t_2 can be determined by using the same equations.

$$\begin{aligned}
\sigma_{fibre-resin}^{t_1-t_0} &= \Delta T_{t_1-t_0}^{f} \beta_f E_f - \sigma_r(t)\Big|_{t_0}^{t_1} \\
&= \Delta T_{t_1-t_0}^{f} \beta_f E_f - \varepsilon_{u1}^{f} \left[E_r(\alpha)\xi_r(t)(1-\exp(-\frac{t}{\xi_r(t)})) \right]\Big|_{t_0}^{t_1} \\
&= \Delta T_{t_1-t_0}^{f} \beta_f E_f - \Delta T_{t_1-t_0}^{f} \beta_f \left[E_r(\alpha)\xi_r(t)(1-\exp(-\frac{t}{\xi_r(t)})) \right]\Big|_{t_0}^{t_1}
\end{aligned} \tag{16}$$

$$\begin{aligned}
\sigma_{tool-part}^{t_1-t_0} &= \Delta T_{t_1-t_0}^{t} \beta_t E_t - \sigma_p(t)\Big|_{t_0}^{t_1} \\
&= \Delta T_{t_1-t_0}^{t} \beta_t E_t - \varepsilon_{u1}^{t} \left[E_p(t)\xi_p(t)\exp(-\frac{t-\tau}{\xi_p(t)}) \right]\Big|_{t_0}^{t_1} \\
&= \Delta T_{t_1-t_0}^{t} \beta_t E_t - \Delta T_{t_1-t_0}^{t} \beta_t \left[E_p(t)\xi_p(t)(1-\exp(-\frac{t}{\xi_p(t)})) \right]\Big|_{t_0}^{t_1}
\end{aligned} \tag{17}$$

2.3. Microwave curing kinetics

For the purpose of controlling the curing process and ensuring the complete curing of composites, the microwave curing kinetics of composite should be studied. As microwave heating does not change the structures of the cured products [28], the methods for analyzing the kinetics of the traditional thermal heating are still applicable. The degree of curing composite is denoted as α, which is the ratio of the extent of exothermic reaction at certain curing temperature. According to the Arrhenius law [29], the microwave curing kinetics of reaction is expressed as:

$$d\alpha/dt = K\exp(-E_a/RT)(B+\alpha^m)(1-\alpha)^n \tag{18}$$

Where, K is the frequency factor, E_a is the activation energy, R is the universal gas constant, B is a temperature independent parameter, m and n are the orders of the autocatalytic and non-catalyzed polymerization reactions, respectively. For microwave curing kinetics, the activation energy E_a is lower than the conventional thermal curing. Thus higher curing reaction rate in a microwave process can be expected [30]. At the beginning of curing, the reaction rate is very low. After the curing temperature reaches a certain level, the reaction rate accelerates quickly to arrive the gelation point. Gelation is a sudden and irreversible transformation of resin from a viscous liquid to an elastic gel glass. The cyclic heating-cooling process leads to the variation of curing rate. The curing reaction rate at the heating stage is the fastest, and is the lowest in the cooling stage.

3. New process control method for microwave curing

Instead of commonly using the manufacturer's recommended cure cycles of

traditional thermal process in the current microwave curing technologies, the proposed new method is based on the cyclic heating-cooling process as illustrated in Fig.4, which reduces the cure-induced stress through the alternating stress reduction of repeating heating and cooling during the curing process. For example, the stresses 'locked' in the heating stage will be calculated based on the semi-empirical equations of Eq. 16 and Eq. 17. Then, the calculated stresses can be devoted to calculate the temperature variation at next cooling stage, which can reduce the accumulated stresses. It is noted that at the cooling stage, the degree of curing and viscoelastic properties of composite are already changed. Thus, the cooling down process will not be the same with the heating stage.

In current microwave curing methods, there is slightly temperature fluctuation in the dwell stage. Because of the heat strongly dissipates from composite to surrounding environment and leads to difficulties of temperature control. However, the new microwave curing method actively controls the fluctuation of temperature during the 'dwell' stage in order to reduce cure-induced stresses. Traditional autoclave curing with quick heating rate normally results in uneven temperature distribution in the composite [31]. In comparison, the fast heating rate of microwave curing can maintain a more even temperature distribution across the composite and the tool, and can reduce residual stress [19]. The results of the experiment carried out in this project indicated that fast cooling rates using the new microwave curing method can further reduce the induced stress. Therefore, heating rate H_r and cooling rate C_r should be controlled within the maximum heating and cooling capability of the microwave curing equipment. The long dwell period in current microwave curing methods can be reduced, as there is no need for stress relaxation by long dwell time in the new cyclic heating-cooling method. The dwell temperature and time parameters change with time, and can be expressed as:

$$H_r \times t_{heating} + D_t \geq t_{\alpha=1.0} \tag{19}$$

$$P(t) + A(t)/2 \leq T_{\text{char}} \tag{20}$$

Eq.19 means that the degree of curing should arrive nearly 1.0 before the final cooling process at least. Eq.20 means that the maximum heating temperature cannot exceed the char temperature of resin (T_{char}). In order to improve the quality of composite, the excessive resin in the prepreg will be extruded at the lowest viscosity where the holding time is R_t. Fig.4 shows the whole microwave curing cycle with technical parameters using the new cyclic heating-cooling method for composites that meet the requirements of aerospace applications.

After the first (Heating) stage and when the resin reaction rate reaches the highest values, temperature T_p at that point should be 'maintained' (but with controlled cyclic variation) to allow resin extrusion for improving the compaction degree until the gelation point. The controlled temperature variation before the gelation point aims to release the stresses accumulated during heating stage, and to control the cross-linking reaction rate. To ensure nearly no new stresses are induced, the temperature should be reduced, from the gelation point to the temperature ($T_{d\alpha/dt\approx 0}$) at which the resin reaction rate is nearly zero. The next heating stage is to rekindle the curing reaction, and the following cooling stage will reduce the stresses accumulated during the preceding heating stage. The cyclic heating-cooling process continues until the composite totally cured. Since the thickness of the composite is far smaller than the other two dimensions, the stress imposed by the tool along the thickness direction of composite is ignored. As shown in Fig.4, the temperature profile accordingly changed as exponential, because of the exponentially variation of the loss tangent and curing degree of composite.

4. Materials and experiment methods

Carbon fibre reinforced bismaleimide composite samples of 200mm×200mm× 2.3mm size were fabricated by ply 18 plies of T700/QY9611 (carbon fibre T700 reinforced bismaleimide resin QY9611) unidirectional prepreg with the matrix volume fraction of 35.7%. This kind of prepreg has high usage temperature and strength, usually applied in primary load bearing composites in aircrafts. The ply sequence is $[0_2/-45/0/45/0/90/0_4/90/0/45/0/-45/0_2]$ and generally used in parts bearing tensile loads. For comparison, the composite samples were fabricated using the traditional thermal curing, the current microwave curing, the microwave curing with one cooling down and the proposed new microwave curing technology respectively. Each curing technologies tested three different samples respectively and the statistical results were analyzed.

Experiment of the new method is shown in Fig.5 (a). Three Fibre Bragg Grating (FBG) sensors are embedded in the middle of the sample to measure the strains during curing (note: strain can be converted to residual stress) [32, 33]. The aluminium foil is stuck on the edge of the prepreg to avoid arcing of carbon fibre, and a capillary tube is applied to compensate the temperature change according to the reading of the FBG sensor as shown in Fig.5 (b). The air tube is connected to the compressed air bag to control the cooling rate. The advanced microwave curing system (octagon chamber, 2.45GHz, 20 kW power, 16 microwave sources and antennas of waveguide slots) were designed and manufactured by the authors. The Labview-PCI data acquisition (two PCI-1727U card) was developed to separately control each microwave sources, which can provide uniform temperature distribution of composite during curing process. Two optical fiber fluorescent sensors are placed on the surface of a vacuum bag to measure the microwave curing temperature. The dynamical thermal mechanical properties of

four composite samples were measured by using DMA 242 E (NETZSCH). The mechanical strength of composite samples were measured by using MTS C45 electronic universal testing machine. The ZEISS EVO18 scanning electron microscope was applied to observe the fracture surface of tested samples (surface gold plating).

One of the tested sample's dynamic mechanical analyzing (DMA) result is shown in Fig 6. The storage modulus ($E^{'}$) of composite changes from 7GPa to 30GPa and decreases after the char temperature. The loss modulus ($E^{''}$) represents the viscoelastic properties of composite and quickly goes down after heating process. At the gelation point, the loss modulus occurs a peak at about 240 ºC, and the corresponding degree of curing is about 0.78. For the new curing process, the first heating stage is aiming at increasing the degree of curing of composite (after gelation point, as shown in Fig. 4) and the temperature should not be too high to cause the over-reaction of resin. As a result, the boundary conditions of the above equations can be expressed as:

$$t_0 = 0,\ \ t_1 = 16\min,\ \ \Delta T^{f}_{t_1 - t_0} = 90^{o}C,\ \ \Delta T^{t}_{t_1 - t_0} = 40^{o}C \tag{21}$$

Here, $\Delta T^{f}_{t_1 - t_0}$ and $\Delta T^{t}_{t_1 - t_0}$ are calculated by the thermal heat conduction equation and verified by the experiment. The experiment frequency of dynamic mechanical analyze is $\omega = 2$, heating rate is 5.5 ºC/min ($T = 130^{o}C + 5.5t$). The properties of materials provided by the material suppliers are shown in Table 1. According to the results calculated by Eq. 16 and Eq. 17, the ΔT of the following equations from t_1 to t_2 time period can be determined. The equation of storage and loss modulus of composite were acquired by fitting the experimental data:

$$E_p^{'}(T)=\begin{cases}\left(9\times10^3-78.8T+0.27T^2\right)\times10^6 & 20^oC\le T<175^oC\\ \dfrac{3.3\times10^{10}}{1+\exp(14.6-0.06T)} & 175^oC\le T<325^oC\end{cases} \quad (22)$$

$$\tan_p(T)=\begin{cases}0.58-3\times10^{-3}T-1.2\times10^{-6}T^2 & 20^oC\le T<175^oC\\ \dfrac{0.15}{1+\exp(20-0.08T)} & 175^oC\le T<325^oC\end{cases} \quad (23)$$

Based on the semi-empirical equations of Eq. 16 and Eq. 17, the calculation results of cure-induced stresses at the heating stage can be divided as elastic portion (stresses from fibre and tool) and viscoelastic portion (stresses from resin and composite). The fibre/resin interaction stress should be considered more than tool/part interaction stress, because of high percentage of the fibre/resin CTE mismatch influence on composite's deformation. For the elastic stresses reduction, the temperature cooling down is better to be the same as heating stage. However, the viscoelastic stresses from resin and composite raised exponentially, so the temperature profile accordingly changed as exponential variation. The calculation results are shown in Fig.8, and degree of curing of composite is also calculated based on the equation of composite curing kinetics of reaction (parameters are measured in [34]) during the cyclic heating-cooling process.

5. Discussion of Results

The samples for traditional thermal curing were heated in an autoclave with the same vacuum pressure and conditions of microwave curing. The autoclave heating process followed the manufacturer's recommended cure (MRC) cycle. The samples for current microwave curing were heated using parameters basically the same as traditional thermal curing, except that the dwell time at 200°C was cut down, because of the fast microwave curing rate. The comparison of measured curing temperature curve

of a set of the experimental samples can be seen in Fig.7. The new microwave curing process and degree of curing of composite are shown in Fig.8, the fluctuation of curing degree at 185°C is ignored. The microwave curing process with one cooling down at the gelation point has been tested to verify the effectiveness of the new microwave curing. It is clear that the new microwave curing method reduced the total curing time to 45% of the traditional autoclave curing. In order to verify the reliability of the results, three samples of each curing technologies were tested respectively and the statistical results are shown in Fig. 9 and Fig. 10. The measured strains with standard deviations corresponding to the temperature of different curing process are shown in Fig.9. In Fig. 10, the residual stress converted from the residual strain and modulus of totally cured composite (200GPa) are compared with standard deviations.

As shown in Fig. 9, the demould strains of the displayed set of samples were measured when they were demoulded from the tool and marked with solid dots in the figure. Then, the statistical residual strains were obtained after 12 hours of demoulding (placed at room temperature with no constraint) and marked in 1320 minute in Fig. 9. The measured stress of the sample cured by the new microwave curing technology is positive (tensile), whilst the stresses of the samples cured by the traditional thermal, current microwave curing and microwave curing with one cooling down are negative (compressive), as shown in Fig. 10. The compressive stresses of the samples cured by traditional thermal and current microwave methods increased after 12 hours, and this is caused by the imposed stresses of tool. However, for the sample cured by the new method, the tensile stress is further reduced since the compressive stresses of tool are released after 12 hours. The results shown in Fig. 10 of four different curing processes exhibit that the maximum warpage of the new microwave curing technology is smaller

than other curing process. This interesting results indicate that the microwave curing with one cooling down has lower strain but higher warpage than current microwave curing. The reason may be due to the tool-part interaction.

As shown in Table 2, the mechanical strength of three different curing processes are measured according to American Society for Testing Material (ASTM) standards. The tensile strength of the new microwave cured samples are lower than the current microwave and autoclave cured ones. The flexural strength and tensile modulus of microwave cured samples are higher than the autoclave cured ones. In order to analyzing the reasons, the SEM micrographs of samples cured by different process showing the fracture surface after tensile and three-point flexural test are illustrated in Fig.11. For the tensile strength, the fracture surface of tensile test samples have different amount of residue resin. The new and current microwave process cured sample have more residue resin on the surface of fibres. The autoclave cured sample has a relatively clean fibre fracture section. This indicate that the microwave cured composites have stronger interfacial bonding than the autoclave cured one. However, the microwave cured composite showed lower tensile strength than the autoclave specimens may due to greater void content [35]. The main reason is that the fast reaction rate of microwave leads to the impurities can hardly be extruded from resin.

The tensile modulus mainly depends on the toughness of resin matrix, and the microwave cured resin has higher tensile modulus than autoclave cured one [36]. As the cyclic microwave heating and cooling process, the curing reaction also occurs cyclic acceleration and deceleration phenomenon. This can affect the curing of resin and reduce the influence of microwave on resin reaction in the cooling down stage, lead to lower tensile modulus of composite. Fig. 11(b), (d) and (f) exhibit the breakage section

after flexural test of new microwave process, current microwave process and autoclave cured samples, respectively. The microwave cured samples have more resin on the carbon fibres compare with the autoclave cured samples. More clean fibres and smooth grooves of resin can be founded on the breakage section of autoclave cured samples. It is known that the flexural strength of composites are determined by the interfacial strength between fibre and resin [37]. The previous research exhibited that microwave curing process can effectively improve the interfacial strength between carbon fibre and matrix resin [20, 38]. The reason is that the chemical mechanism of the fiber/matrix interface is essentially identical for microwave and thermal curing, but the selective heating of microwave leads to the prioritized heating of carbon fibre and can significantly increase the interfacial strength. However, for the new microwave process, the amount of heat conduct from fibre to resin during the cooling stage decreased. Therefore, the new cyclic heating and cooling curing process can effectively release the cure-induced stresses of composite, but may reduce the interfacial strength of fibre and resin compared with the traditional microwave curing process.

The tensile strength above 1200 MPa can satisfy the requirements of aircrafts. However, the engineers desire to obtain high flexural strength and appropriate tensile modulus (from 150GPa to 170GPa) to cover the shortage of composite parts. Thus, the new microwave curing process has enormous potential in aerospace applications. Through recording the electrical power of the three experiments, the energy consumption results are: for the same volume of curing chamber (2000L), the energy consumption is 52 kWh for the new microwave curing, 105 kWh for current microwave curing, and 1800 kWh for autoclave (1m diameter and 2m length) curing respectively. This means that the energy consumption of the new microwave curing technology is

only 3% of the traditional autoclave curing, and 50% of current microwave curing.

6. Conclusion

This paper presented a new microwave curing technology based on a cyclic heating-cooling process control method by considering the unique characteristics of microwave heating. The experimental results demonstrated that: (i) cure-induced residual strains and warpage of composites can be significantly reduced by the new microwave curing process; (ii) total curing time can be reduced to 45% of traditional thermal curing and 56% of current microwave curing technologies and (iii) energy consumption can be reduced to 3% of autoclave curing and 50% of current microwave curing. The flexural strength and tensile modulus of samples cured by the new microwave curing process are higher than the autoclave cured ones, and the differences were analyzed by using SEM micrographs. Preliminary industrial validation has been carried out for primary load bearing aerospace composites. Further work is to develop recommendations and guidelines for using the new method and select technical parameters.

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Artwork and Tables with Captions

Fig.1. (a) Heat conduction between carbon fibre and resin; (b) Heat conduction between the composite and surrounding air and tool.

Fig.2. (a) Assumed Interfaces between fibre-resin and composite-tool; (b) Changes in stress direction during heating and cooling.

Fig.3. The proposed new cyclic heating and cooling method.

Fig.4. The designed new microwave curing method of composites.

Fig.5. (a) Sample preparation with FBG sensors; (b) Microwave curing in an octagon microwave chamber.

Fig.6. Dynamic thermal mechanical analyzing results and degree of curing of composite sample.

Fig.7. The comparison of measured temperature variations of four curing technologies.

Fig.8. Zoomed portion of the curve in Fig.7 for the new microwave curing process showing parameters.

Fig.9. The measured strains of samples cured by four process technologies.

Fig.10. Comparison of residual stresses and maximum warpage of different curing technologies.

Fig.11. SEM micrographs of samples cured by different process showing the fracture surface after tensile and three-point flexural test. (a) and (b) tensile and flexural test samples cured by new microwave process; (c) and (d) tensile and flexural test samples cured by current microwave process; (e) and (f) tensile and flexural test samples cured by autoclave.

Table 1. Mechanical properties of composite material and tool.

Table 2. Mechanical strength of three different curing processes.