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The Influence of Cure Pressure on Microstructure, Temperature Field and Mechanical Properties of Advanced Polymer-matrix Composite Laminates

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Abstract: Under a given curing process, various cure pressure conditions were designed to evaluate the influence of cure pressure on composite microstructure, temperature field and mechanical properties. A series of composite laminates of different technological parameters were manufactured. The locations of defect in the composite laminates were determined using phased array ultrasonic flaw detection technology. A characterization of microstructure within the composite laminates was obtained using optical digital microscope. The tensile properties test was used to establish the relationship between cure pressure and mechanical properties. Results reveal that the delamination exists in the low pressure curing stage (below 0.2 MPa), the voids mainly exist in the two forms of columnar shape and globular shape, and their number and size decrease as the cure pressure increases, the cure reaction moment occurs to delay due to the actual heating rate reduces. The tensile strength increases as the porosity deceases and the tensile modulus is insensitive to the porosity, which are consistent with previous studies.

Keywords: Polymer composites, Cure pressure, Microstructure, Temperature field, Mechanical properties

Introduction

Advanced carbon fiber-reinforced polymer-matrix composite structural components are nowadays widely applied to aerospace and high-performance automobile industries due to their high specific strength and stiffness [1]. The autoclave process is the major way of fabricating composite components, which encapsulates composite blank and honeycomb sandwich structure or adhesive banded structure on the mold, undergoing a long process of heating, pressurization, heat preservation (medium temperature or high temperature), cooling and pressure relief at the vacuum state in an autoclave, and ultimately obtains the shape and quality we need. Some drawbacks, however, include high capital investment, certain polluting and low efficiency, which also exist in the autoclave process [2-6]. Thus, some scholars tend to develop new non-autoclave technologies and have made great achievements, such as resin transfer molding process [7], vacuum film infusion [8,9] and electron beam curing [10]. But as for forming high-performance complex structures, the stringent mechanical performance is so sensitive to the internal defects (such as delamination and voids) that requires higher external pressure to increase resin fluidity and remove the voids existed in the component. Those technologies mentioned above can not often achieve the mechanical properties obtained in autoclave [6], thus in the autoclave process, some improvements should be made to optimize the curing process route so as to make it toward to the direction of energy-saving, environment-friendly and efficiency maximization.

Some complex physical and chemistry reactions are included in the autoclave curing or co-curing process, such as the exothermic chemistry in resin, resin flow, thermal transmission and so on [11]. Pressure field and temperature field are the two major physical fields, which play a crucial role of bleeding the laminate, consolidating individual plies and reducing the void content. The temperature initially reduces the viscosity of the resin, favoring the impregnation of the fibers, but it also triggers the crosslinking reactions which ultimately lead to the gelification of the resin [12]. The cure pressure has a great influence on the resin flow. In the process of forming the composite laminates, all materials used in the process are compacted on the mold by the external pressure, then, the excess resin and air bubbles are excluded out of the laminate, which ensures the forming precision and quality. If too much external pressure is applied in the process, the resin would flow faster than normal, which would also result in some unexpected defects in a partial area, for example, poor glue, rich fat and fibers' distorting etc. Due to the existence of bubbles which are mainly caused by two reasons (the entrapment of gases and volatiles arising from the resin system itself) [13-17], if the magnitude of external pressure is extremely small, the two kinds of pores mentioned above would not be excluded out of the resin matrix completely. There would be a high possibility that voids forming in the resin matrix, and have a serious effect on mechanical properties. Moreover, too small external pressure is likely to result in inadequate flow of resin in the matrix, which in turn leading to the uneven distribution of resin, the weak interlayer bonding and stress gradient. Even delamination appears in the component, which is also not acceptable. Therefore, with the exception of temperature cycle, the magnitude of external pressure is also thought to be a quite important parameter to optimize. Most scholars studied the effects of cure pressure on

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mechanical properties by void content [6,12,18-22]. They all pointed that the mechanical properties decreased as the increase of porosity (or decrease of pressure), and studied the mechanism of void size, formation and distribution in the composite. But the relationships between delamination and cure pressure are not involved, and how the influence of cure pressure works on temperature field is rarely mentioned.

The research presented in this paper mainly aimed at obtaining an optimal cure cycle as well as assessing the influence of cure pressure on microscopic structure, temperature field and mechanical properties of composite component. The influence mechanism between cure pressure and microscopic structural defects was established, and the cure temperature field and pressure field were coupled effectively to evaluate the effects on defects so as to develop favorable preventive measures. All of these were favor of providing theoretical support for the best curing process. Phased array ultrasonic flaw detection and optical digital microscope (ODM) techniques were combined to study the microscopic structure. The tensile properties test was used to establish the relationship between cure press and mechanical properties.

Experimental

Materials

The experimental composite material used in the research is MCF100UD epoxy prepreg (purchased from Yubo Composites Co., Ltd., China). The resin (designation: YPH-23) is a solvent-free epoxy resin which has a high thermal variation and impact resistance, especially developed for carbon fiber or glass fiber prepreg manufacturing. The initial fiber volume fraction of 66 vol% and the 100 g m^{-2} prepreg areal density are all supplied by the manufacturer.

Fabrication of Unidirectional Composite Laminates

In order to measure the influence of cure pressure on curing quality (included microscopic structure and mechanical properties) of composite, seven unidirectional composite laminates were made by applying different kinds of external pressures in the autoclave process. These kinds of pressures were set as 0.0, 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 MPa, the temperature route was as shown specifically in Figure 1. Every kind of cure pressure was controlled precisely by pre-set system program of autoclave. To exclude the resin bubbles so as to improve the curing quality, always the moment of applying pressure is chosen when the temperature reaches 30 °C in each manufacturing process. 20 plies of each plate was designed and manufactured by manual paving for each cure route considered, respectively. The designed laminates dimension was 300 mm (length)×200 mm (width)×2 mm (thickness), and the final thickness was approximately 2.0-2.2 mm after curing.

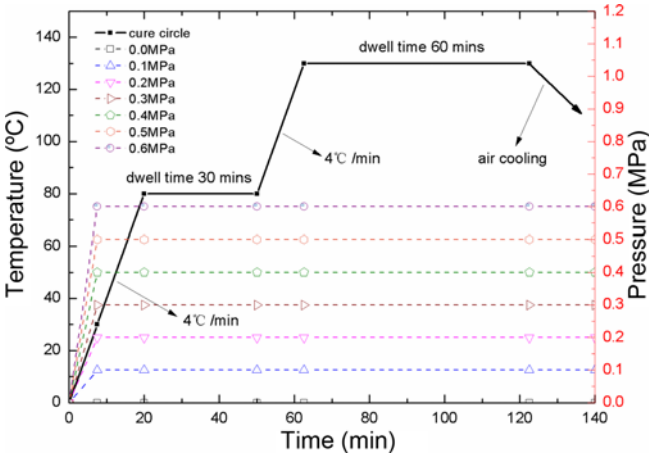

Figure 1. Plot of temperature versus time and pressure.

Phased Array Ultrasonic Flaw Detection

The defects of composite laminates may occur in the forming process were studied by phased array ultrasonic flaw detection (Omni Scan MX2). The probe (5L64-A2) frequency was 5 Hz, using 64 chips arranged in a one-dimensional style, the wedge (SA2-AL) material was plexiglass. Zero linear focal law and A+S-scan display mode were employed in the test. The electronic scanning step was set as 1, the depth of focus was 2.5 mm, and the longitudinal wave sonic speed was 3000 m s^{-1}. Water was selected as the coupling agent and coupled together with the composite laminates. In the A-scan display area, the gate A was placed between the initial wave and the bottom wave. And thus, ensured the signal collected from the gate A to convert into corresponding S-scan images.

Optical Digital Microscopy

For each piece of composite laminates cured at different pressures, samples were taken from them of 10×10 mm, respectively. According to the national standard GB3365-82, the samples were mosaic, polished, polishing and ultrasonic cleaning. The optical digital microscope (ODM, model: OLYMPUS DS×500) and metallurgical microstructure image analysis systems were employed to study the microscopic structure of composite laminates.

Mechanical Testing

To assess the effects of cure cycle pressure on mechanical properties of composite laminates, the tensile strength and tensile modulus of elasticity (GB1447-2005) were employed for mechanical evaluation. The mechanics performance test was conducted on CMT5105 tensile testing apparatus (produced by Sansi Taijie Co., Ltd., China). The tensile specimen size was of 250 mm (length)×25 mm (width) and, the thickness of samples was the full thickness of composite laminates, respectively. The stretching rate was 0.5 mm min^{-1}. The aluminum alloy sheet (thickness: 1-3 mm) was selected as clamping pieces, and a team of typical tensile specimens

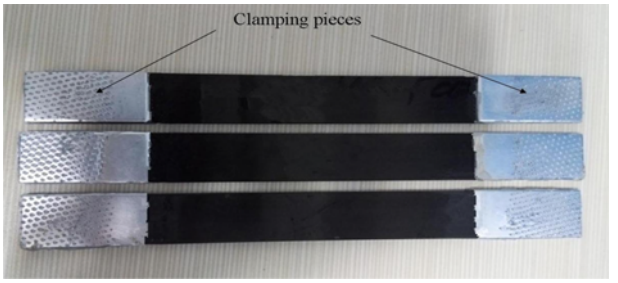

Figure 2. Tensile specimens.

were shown in Figure 2. The tensile strength σ_t (MPa) of the composite samples was determined according to equation (1):

$$\sigma_t = F_{max}/(d \cdot b) \quad (1)$$

where F_{max} is the yield load, a breaking load or the maximum load (N), b is the sample width (mm) and d is the sample thickness (mm).

The tensile modulus of elasticity E_t (GPa) of the composite samples were calculated according to equation (2):

$$E_t = \Delta P \cdot L/(d \cdot b \cdot \Delta L) \quad (2)$$

where ΔP (N) is the incremental load on the initial line segment of load-deformation curve, ΔL (mm) is the increment of deformation corresponding to ΔP within the L gauge, and L (mm) is the measuring gauge.

Results and Discussion

Microscopic Structural Analysis

Phased array ultrasonic flaw detection technology can accurately assess the presence and location of possible defects in the composite laminates. The principle of this technology mainly bases on the defects such as delamination and voids, which absorb the ultrasonic and cause ultrasonic attenuation. In certain heating process, the ultrasonic testing results caused by different pressures are shown in Figure 3. When the laminate was flawed (0.0 MPa), the amplitude of interlaminar echo was the highest, and the bottom wave almost disappeared. A-scan image (Figure 3(a)) also showed that the defects located along the depth direction of 0.7 mm and 1.2 mm. According to the corresponding S-scan images, a clear source of ultrasonic attenuation (namely defects) appeared between surface echo and bottom wave. The defects absorbed and reflected partial sonic wave, made the amplitude of interlaminar echo increase as well as made the bottom wave seem to be not obvious. With the increase of cure pressure, the amplitude of bottom wave increased and interlaminar echo deceased sharply. When the external pressure reached to 0.6 MPa, the amplitude of bottom wave raised nearly 80 %. At the moment, the intensity of bottom waves and surface waves was almost unanimous according

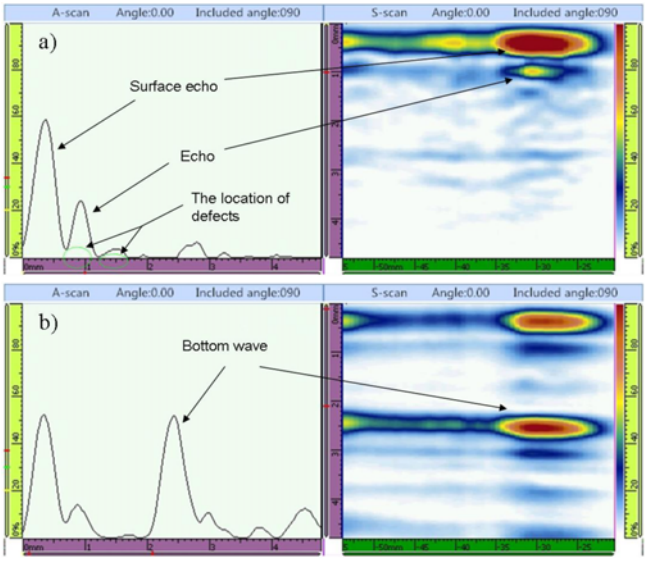

Figure 3. Ultrasonic flaw detection with different cure pressure; (a) 0.0 MPa and (b) 0.6 MPa.

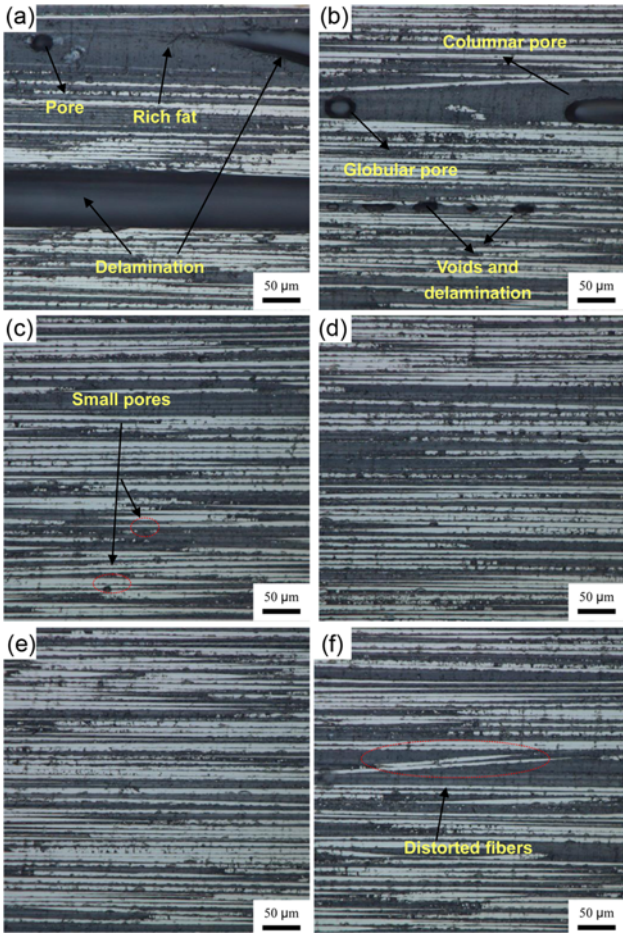

Figure 4. The ODM morphology of composites with different cure pressures; (a) 0.0 MPa, (b) 0.1 MPa, (c) 0.2 MPa, (d) 0.4 MPa, (e) 0.5 MPa, and (f) 0.6 MPa.

to the corresponding S-scan image. Meanwhile, the defects existed in the composite laminates nearly disappeared, shown in Figure 3(b). Therefore, the cure pressure is indispensable to restrain the emergence of solidification defects.

Basing on the ultrasonic flaw detection, the application of optical digital microscopy (ODM) can help us clearly observe the microstructure morphology of defects. The microscopic morphology of different cure pressures applied on composite laminates was shown in Figure 4. As can be seen from it, serious delamination in the composite laminates appeared when the cure pressure was 0.0-0.1 MPa, and a large size and considerable number of voids occurred mostly at the ply interface. Which also indicated that the main types of defect detected in Figure 3(a) were delamination and big voids, and the result of Figure 3(a) was consistent with the result of Figure 4(a). Therefore, the combination of ultrasonic flaw detection and ODM can characterize the morphology, distribution and size accurately. Meanwhile, the resin liquidity was poorer than other cure pressure conditions owing to the deficient pressures. The voids mainly existed in the two forms of columnar shape and globular shape. There are two major reasons of voids formation: firstly, the entrapment of gases during impregnation of fiber reinforcement with resin or during the lay-up, which are not excluded timely due to lower external pressure, this portion of bubbles form into columnar voids; and secondly, volatiles arising from the resin system itself owing to the crosslinking reaction are also stuck in the resin matrix, and develop to globular voids. Furthermore, some serious influences caused by low pressure appeared. Firstly, the fibers infiltrate incompletely in the resin; Secondly, the distribution of fibers along the thickness direction is uneven; Thirdly, the resin offset the partial holes left by the removed bubbles, this may also lead to new uneven distribution of resin. As a result, the phenomenon of resin rich fat appeared around the voids (Figure 4(a), Figure 4(b)). With the improvement of cure pressure, the number and size of voids decline significantly, although the phenomenon of lamination disappeared when the cure pressures were larger than 0.2 MPa, the voids still existed in the resin matrix. As the cure pressure reached to the scope of 0.4-0.6 MPa, the number and size of voids reduced dramatically, which were hardly observed in the metallograph. However, a small angle offsets took place in some fiber areas (Figure 4(f)), that was because the resin flowed so fast in the partial area due to the excessive pressure that the distribution of resin and fibers were extremely uneven. In conclusion, in term of the experimental composite, the defects of lamination and big voids occurred when the cure pressures were below 0.2 MPa, and the voids mainly existed in the two forms of columnar shape and globular shape. The lamination disappeared when the cure pressure exceeds 0.2 MPa, and a lower porosity can be obtained within the cure pressure range of 0.4-0.6 MPa. But too large pressure may cause new defects in some partial areas of component, which was also not to be ignored.

Temperature Field Analysis

The influence of cure pressure on curing process depends that, it is not only to compact the component tightly on the mold surface and to exclude the excess of resin and air bubbles generated in the curing reaction. But also, on the other hand, it is an important factor of affecting the heat transfer between component and air. The higher the cure pressure is, the better the heat transfer and the fluidity of resin are, which in turn, the bubbles generated in the curing process are more easily to be moved away. Effects of cure pressure on the heat transfer were studied by specific experiments [23], the following relationships existed between the convective heat transfer coefficient and cure pressure were obtained according to equation (3):

$$h \propto (P/T)^{4/5} \tag{3}$$

where, h is the convective heat transfer coefficient, P is the pressure, T is the temperature.

Equation (3) demonstrates that the heat transfer coefficient is proportional to the cure pressure in a certain temperature condition. The experimental seven pieces of composite laminates were formed in the same autoclave, and in addition to the cure pressure, other process conditions were completely consistent. Therefore, the cure pressure had a direct influence on the heat transfer of the test process. The composite laminates center temperature curves of different pressures applied in the curing process were shown in Figure 5. The curing reaction moment was delayed about three minutes as the magnitude of cure pressure decreased by 0.2 MPa. The higher the cure pressure, the closer to the curing process curve the actual center temperature curves were. This implied that increasing the heat transfer was beneficial to adequate exchange between component and air in the autoclave, and would facilitate temperature field to be homogeneous. Furthermore, with the increasing of cure pressure, the actual heating rates in the composite structure

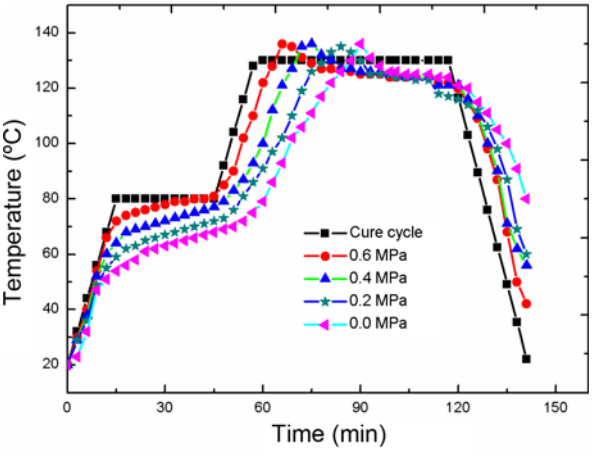

Figure 5. The actual temperature curves with different cure pressures.

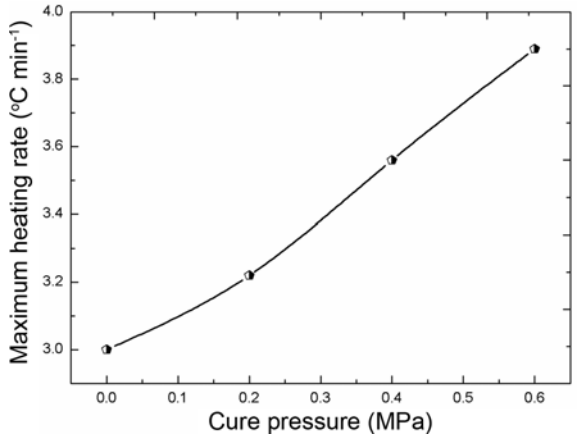

Figure 6. The relationship between actual maximal heating rate and cure pressure.

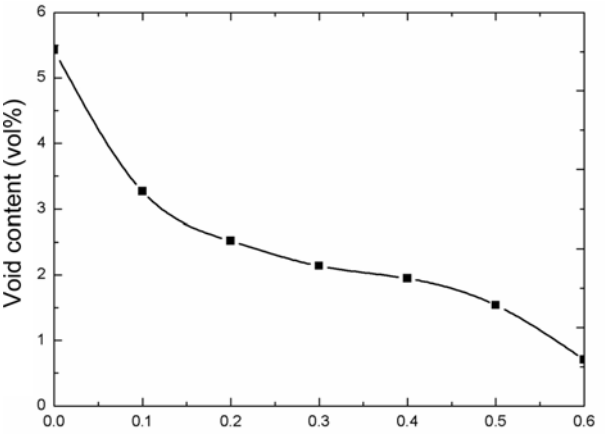

Figure 7. The relationship between void content and cure pressure.

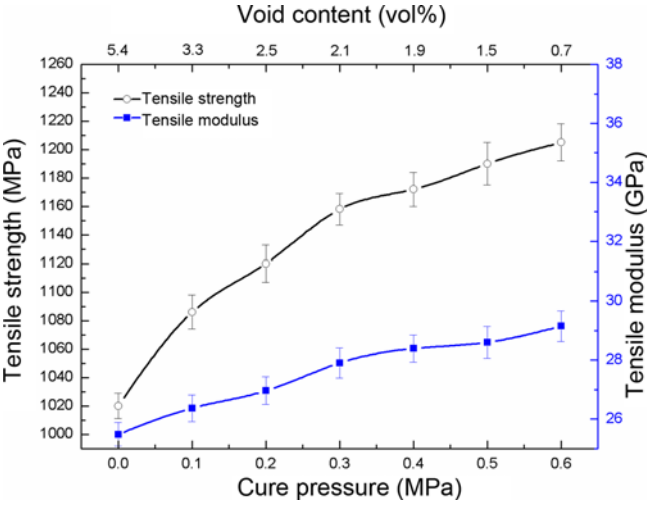

Figure 8. The relationship between tensile properties and cure pressure.

were accelerated (as shown in Figure 6) when the cure pressures increased from 0.0 MPa to 0.6 MPa, and the added value of heating rates was 0.22-0.34 ^{o}C min^{-1} corresponding to the actual heating rate. Improving cure pressure can make the curing reaction occur earlier, and the overshoot temperatures were lower in the curing insulation stage. This demonstrated that increasing the heat transfer can help the internal temperature of composite enhance before curing, and release internal temperature when curing. But in the later period of curing, as the increase of cure pressures, the trends of the two phenomenon mentioned above started to reduce owing to the composite laminates center temperature was constrained by the thermal conductivity and their thickness. In the curing process of composite, therefore, if the temperature cycle is definite, increasing the curing pressure can benefit the temperature transmission between component and air, and reduce the internal temperature difference of component, which in turn improve the forming quality.

However, it is not that the forming quality could be improved by the growing pressure, the selection of pressure should be a balanceable criterion. Under the experimental conditions and for the identical temperature environment, with the increase of cure pressure, the heat transfer is also accelerated. But if the heat transfer is too fast, the heat transfer phenomenon of cure temperature field will turn to be fiercely and unsteadily, leading to an increasing of component temperature gradient and a decreasing of internal uniformity of component. In such a situation, the uneven distribution of partial resin and the distortion of fibers in some area appeared, as shown in Figure 4(f). So the cure pressure should be taken within a reasonable range, which is conducive to the internal resin uniformity, but not to enlarge the temperature difference of components.

Tensile Properties Analysis

As previously mentioned, the cure pressure has important influence on voids, delamination and internal temperature field of composite, which affects the mechanical properties of materials indirectly by affecting the porosity (as shown in Figure 7) and the internal resin flow uniformity. Unlike the interlaminar shear properties and bending properties which are so sensitive to the impact of internal defects caused by cure pressure [18], the sensitivity of tensile properties is lower. The results of tensile property measurements were reported in Figure 8, the tensile strength σ_t decreased by 15.3 % and the tensile modulus E_t by 12.6 % as the value of cure pressure decreased from 0.6 MPa up to 0.0 MPa, while the corresponding porosity increased from 0.7 % to 5.4 %. But the actual difference of tensile modulus was quite small (only about 4 GPa). The decrement of tensile strength accelerated as the value of cure pressure was below 0.2 MPa, this was mainly related to the delamination and large size of voids. Such defects made partial fibers shift and the actual number of bearing fibers reduce. Under higher pressure conditions, the delamin ation disappeared and the irregular

distribution of small pores became the main defects in the composite, which had little effect on the axial location of fibers. Thus, the strength and modulus changed more gently.

Conclusion

Under a given curing process, the carbon fiber resin matrix composite laminates were fabricated using variable pressure parameters. The influence of cure pressures on composite microstructure and temperature field of composite laminates were assessed. The influence mechanism of cure pressure on composite microstructure defects, mechanical properties and temperature field were illustrated. The specific location of curing defects was detected using phased array ultrasonic flaw technology. A better characterization of pore shape, size, and location in the composite was obtained using optical digital microscope.

Results showed that the curing reaction moment can be delayed about three minutes as the cure pressure magnitude decreased by 0.2 MPa, the actual ratio of heating in the composite can improve 0.22-0.34 ^{o}C min^{-1} by increasing the cure pressure from 0.0 MPa up to 0.6 MPa, tensile strength decreased 15.3 % when the porosity increased from 0.7 % up to 5.4 %, while the sensitivity of tensile modulus was much smaller.

Through the study found that, it is not that the forming quality can be improved by the growing pressure. It is bad for the normal flow of resin and complete infiltration of fibers if the cure pressure is too low. But if the magnitude of cure pressure is too large, which is apt to leading to unevenness of resin and increasing temperature gradient. Hence, there should be a balanceable criterion.

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References

1. L. W. Davies, R. J. Day, D. Bond, A. Nesbitt, J. Ellis, and E. Gardon, *Compos. Sci. Technol.*, **67**, 1895 (2007).
2. M. G. Bader, *Compos*., **A33**, 924 (2002).
3. S. L. Agius, K. J. C. Magniez, and B. L. Fox, *Compos*., **B47**, 235 (2013).
4. C. Nightingale and R. Day, *Compos*., **A33**, 1025 (2002).
5. L. K. Grunenfelder and S. R. Nutt, *Compos. Sci. Technol*., **70**, 2306 (2010).
6. S. Hernández, F. Sket, J. M. Molina-Aldareguía, C. González, and J. L. Lorca, *Compos. Sci. Technol*., **71**, 1338 (2011).
7. T. S. Lundström and B. R. Gebart, *Polym. Compos*., **15**, 27 (1994).
8. F. Y. C. Boey, *Polym. Test*., **9**, 373 (1990).
9. D. Abraham, S. Mathews, and R. McHaahagger, *Compos*., **A29**, 799 (1998).
10. A. Singh, C. B. Saunders, J. W. Barnard, V. J. Lopata, W. Kremers, T. E. McDougall, M. Chung, and M. Tateishi, *Radiat. Phys. Chem.*, **48**, 160 (1996).
11. W. I. Lee, A. C. Loos, and G. S. Springer, *J. Compos. Mater*., **16**, 516 (1982).
12. S. Hernández, F. Sket, C. González, and J. L. Lorca, *Compos. Sci. Technol.*, **85**, 77 (2013).
13. J. L. Kardos, M. P. Dudukovic, and R. Dave, *Adv. Polym. Sci*., **80**, 116 (1986).
14. J. Muric-Nesic, P. Compston, and Z. H. Stachurski, *Compos*., **A42**, 324 (2011).
15. T. Naganuma, K. Naito, J. Kyono, and Y. Kagawa, *Compos. Sci. Technol*., **69**, 2430 (2009).
16. F. Y. C. Boey and S. W. Lye, *Compos.*, **23**, 263 (1992).
17. J. M. Tang, W. I. Lee, and G. S. Springer, *J. Compos. Mater*., **21**, 430 (1987).
18. L. Liu, B. M. Zhang, D. F. Wang, and Z. J. Wu, *Compos. Struct.*, **73**, 306 (2006).
19. K. Bowles and S. Frimpong, *J. Compos. Mater*., **26**, 1489 (1992).
20. L. Liu, B. M. Zhang, and Z. J. Wu, *J. Mater. Sci. Technol*., **21**, 89 (2005).
21. J. Yu, J. C. Chen, Z. J. Hong, and J. Feng, *Acta Mater. Compos. Sinica*, **28**, 150 (2011).
22. P. Olivier, J. P. Cottu, and B. Ferret, *Compos*., **26**, 511 (1995).
23. J. Andrew, Ph.D. Dissertation, University of New Brunswick, New Brunswick, 1992.