Research on Compression Molding Process of Carbon Fiber Reinforced Polymer

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Abstract. The compression molding process of CFRP (Carbon Fiber Reinforced Polymer) is a multi-parameter coupled system, and its molding mechanism is very complex. Based on the Gel point and the glass transition temperature of the matrix material, the compression molding process of CFRP is divided into three sub-processes: thermal-chemical process, flow-compaction process and residual stress-deformation process, and the mathematical constitutive model of each sub-process is established. On the basis, the interaction and calling relationship of each sub-process are determined, which lays a foundation for the molding process simulation of CFRP and further analysis of its multi-parameter coupling effect mechanism.

1. Introduction

Due to the characteristics of CFRP (Carbon Fiber Reinforced Polymer) such as high specific strength, high specific modulus, fatigue resistance, good molding process, good breakage safety, and strong performance designability, the CFRP are increasingly applied in aerospace, wind turbine blades, sports equipment, and automotive parts, etc. It is the mainstream material for lightweight products in the 21st century [1-3]. The compression molding method has the advantages of low cost, high efficiency, low internal stress, small warpage, good mechanical stability, and high repeatability in the batch production of product parts, especially on a large scale [4,5].

The compression molding process of CFRP is a multi-parameter coupling system, with the interaction and coupling disturbance of heating, chemical reaction, matrix flow, thermal expansion and so on. Scholars worldwide have conducted a lot of research based on the molding mechanism of the CFRP and achieved rich results, and proposed the linear elastic constitutive model and the viscoelastic constitutive model [6-11], which has played an important role in revealing the molding mechanism. However, the constitutive models above can not accurately describe the various stages of the molding Process for CFRP.

Based on the previous research, in order to reveal the molding process mechanism for CFRP under multi-parameter coupling, the Gel point and glass transition temperature of the matrix material are comprehensively considered, and which taken as the judging condition, the molding process is divided into three sub-processes: thermo-chemical process, flow-compaction process and residual stress-deformation process. Because the influences of each sub-process to each other, the influence relation between each sub-process and the calling relation between each sub-process are established. The research which lays a foundation for the compression molding process simulation of CFRP and further analysis of its multi-parameter coupling effect mechanism.
2. Compression Molding Sub-processes of CFRP

Taking the gel point and glass transition point of the CFRP matrix during the curing process as the criteria, the compression molding process was divided into three sub-processes: thermal-chemistry, flow-compacting, and residual stress-deformation.

2.1. Thermo-chemical Sub-process

In the compression molding process of CFRP, the temperature field distribution inside the material not only affects its curing degree and uniformity but also directly leads to the formation of residual stress. The temperature field of compression molding is essentially a nonlinear superposition of internal and external heat sources. The internal heat source mainly comes from the non-linear heat source generated by the chemical reaction in the melting process of the matrix, and the external heat source is from the mold temperature during the compression molding process[12,13]. Using the Fourier heat conduction law and energy balance relationship, a mathematical model of heat conduction was constructed. Considering the anisotropic characteristics of the composite materials, the governing equation of transient heat conduction is shown as:

\[ \rho c T = K_x \frac{\partial^2 T}{\partial x^2} + K_y \frac{\partial^2 T}{\partial y^2} + K_z \frac{\partial^2 T}{\partial z^2} + \dot{q} = \rho c \frac{\partial T}{\partial t} \]

(1)

where, \( \rho \), \( c \), \( T \) and \( t \) represent the density of the composite, specific heat, temperature and time respectively; \( K_x \), \( K_y \), and \( K_z \) are the thermal conductivity coefficients in the overall coordinate system of the material;

Formula (1) includes the heat conduction equation and the homogenization equation, where the right side of the equation is the heat required by the temperature rise of the micro element body, and the left is the heat introduced into the micro element body in the direction of X, Y and Z respectively.

To accurately predict the internal temperature field in the homogenization of the CFRP, it is necessary to accurately describe \( \dot{q} \), which can be expressed as

\[ \dot{q} = \rho (1 - \nu_f) H_g \frac{da}{dt} \]

(2)

Among them, \( \nu_f \) is the fiber volume content, \( H_g \) is the total heat released by the chemical reaction of the matrix per unit mass; \( a \) is the degree of curing, which indicates the degree of progress of the curing crosslinking reaction, and is the ratio of the current heat released and the total heat released, and \( \frac{da}{dt} \) is the curing reaction rate. The phenomenological curing kinetics can be used to represent the functions of temperature and curing degree:

\[ \frac{da}{dt} = g(T, a) = kf(a) \]

(3)

where, \( f(a) \) is the function expression whose independent variable is the degree of curing, \( k \) is the reaction rate constant, which can be expressed as an exponential function of temperature, and conform to the Arrhenius formula:

\[ k = A e^{\Delta E / RT} \]

(4)

where, \( A \) is the frequency factor, \( \Delta E \) is the activation energy of viscous flow, \( R \) is the universal gas constant, and \( T \) is the absolute temperature.

The specific forms and values of \( f(a) \), \( A \), and \( \Delta E \) are measured through the DSC experiment.
2.2. Flow-compaction Sub-process

After the heat-chemical process, the matrix of CFRP is in a flowing state after melting, and the continuity equation of the matrix flow is shown as:

\[
\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} + \Delta v = \frac{\partial}{\partial t} \left( \frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} \right)
\]  

(5)

where, \(v_x, v_y, v_z\) and are the micro-flow velocity of the matrix in the x, y, and z directions;

\(\Delta v\) is the volume change of the matrix under melting and pressure; \(u, v, w\) are the displacement of the reinforcing fibers in the x, y, and z directions.

The left of the formula is the volume of the matrix flowing into the micro-units in a unit time, and the right is the volume change of the micro-units in a unit time. The seepage flow motion equation of the matrix material is established by Darcy’s law. In three-dimensional flow, Darcy is expressed as:

\[
\begin{cases}
    v_x = -\frac{s_x}{\mu} \frac{\partial p_x}{\partial x} \\
    v_y = -\frac{s_y}{\mu} \frac{\partial p_y}{\partial y} \\
    v_z = -\frac{s_z}{\mu} \frac{\partial p_z}{\partial z}
\end{cases}
\]

(6)

where, \(s_x, s_y, \text{and } s_z\) are the permeability of the matrix in the x, y, and z directions of the fiber network; \(\mu\) is the resin viscosity; \(p\) is the resin pressure

Ignoring the carbon-fiber-reinforced material in the CFRP, its matrix can be regarded as porous medium, and the continuity of matrix impregnation is shown as:

\[
\begin{bmatrix}
    \frac{\partial}{\partial x} \left( s_x \frac{\partial p_x}{\partial x} \right) + \frac{\partial}{\partial y} \left( s_y \frac{\partial p_y}{\partial y} \right) + \frac{\partial}{\partial z} \left( s_z \frac{\partial p_z}{\partial z} \right) - \frac{\partial}{\partial t} \left( \frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} \right) \right) + \Delta v = 0
\]

(7)

In the flow-compacting stage, it’s assumed that the fibers are incompressible and unstretchable, the resin flows between the fibers in a saturated state, and the fiber quality remains unchanged. At this time, the total stress is the effective stress of the fiber and the resin pressure, namely:

\[
\sigma_{ij} = \sigma^f_{ij} - \delta_{ij} p_r
\]

(8)

where, \(\sigma^f_{ij}\) is the effective stress of the fiber, \(\delta_{ij}\) is kronecker delta, and \(p_r\) is resin pressure.

According to Dancy’s law, the compaction equation of the composite material is expressed as:

\[
\frac{K_w}{V_f} \frac{\partial^2 p_r}{\partial x^2} + \frac{K_w}{V_f} \frac{\partial^2 p_r}{\partial y^2} + \frac{1}{V_0} \frac{\partial}{\partial z} \left( V_f K_{ij} \frac{\partial p_r}{\partial z} \right) = \mu \frac{\partial}{\partial t} \left( \frac{1-V_r}{V_f} \right)
\]

(9)

where, \(V_0\) is the fiber volume fraction under zero load; \(V_f\) is the fiber volume fraction, \(\mu\) is the resin viscosity, and \(K_{ij}\) is the composite permeability.

Permeability is related to fiber volume fraction, fiber diameter and fiber structure, generally expressed by empirical formula:

\[
K_{ij} = \frac{r_f^2}{4K_0} \left( \frac{1-V_f}{V_f} \right)^2
\]

(10)

In this formula, \(V_f\) is the fiber radius, \(K_0\) is the Kozeny constant, changing with the fiber structure
and the flow direction of the matrix.

According to Kozeny-German theory, the material pores are expressed as:

\[ e = \frac{Vol - Vol_f}{Vol_f} = \frac{1}{V_f} - 1 \]  

(11)

where, Vol and Vol_f are the total volume of the composite material and the volume occupied by the reinforcing fibers, respectively.

During the matrix infiltration process, the thickness h of the composite laminate changes as:

\[ -\frac{d(hS)}{dt} = \frac{KP_r}{\mu h} \]  

(12)

And, S is the layering area of the composite material.

2.3. Residual Stress-deformation Sub-process

The residual stress-strain of the CFRP compression molding mainly consists of two parts: thermal strain and chemical shrinkage strain.

Thermal strain is mainly due to thermal expansion and contraction caused by temperature changes during curing. It’s expressed as:

\[ \varepsilon^th = \alpha_i \Delta T \ (i = x, y, z) \]  

(13)

where, \( \alpha_i \) is the equivalent thermal expansion coefficient of the composites in three directions.

Considering that the CFRPs are anisotropic materials, it’s assumed that x is the fiber direction and y-z is the isotropic plane, and then the thermal expansion coefficient in each direction is given as:

\[ \alpha_x = \alpha_{sf} \frac{E_v V_f + \alpha_m E_m V_m}{E_{sf} V_f + E_m V_m} \]  

\[ \alpha_y = \alpha_z = \left( \alpha_{sf} + v_{sf} \alpha_{sf} \right) V_f + \left( \alpha_m + v_m \alpha_m \right) \left( 1 - V_f \right) - \left[ v_{sf} V_f + v_m \left( 1 - V_f \right) \right] \frac{\alpha_{sf} E_v V_f + \alpha_m E_m \left( 1 - V_f \right)}{E_{sf} V_f + E_m \left( 1 - V_f \right)} \]  

(15)

where, \( m \) and \( f \) in the subscript are the matrix and the reinforcing fiber respectively; \( \alpha_{sf} \) and \( \alpha_{sf} \) are the thermal expansion coefficients of the fiber parallel to the fiber axis and perpendicular to the fiber direction; \( E_{sf} \) and \( V_{sf} \) are the elastic modulus of the fiber in the fiber axis and the Poisson's ratio on the x-y surface respectively; \( E_m, v_m, \) and \( \alpha_m \) are the elastic modulus, Poisson's ratio and thermal expansion coefficient of the matrix.

For the chemical shrinkage strain, assuming the same amount of shrinkage in all directions, the chemical shrinkage strain of the matrix is expressed as:

\[ \varepsilon^c_m = \sqrt{1 + \Delta v} - 1 \]  

(16)

The matrix volume change rate \( \Delta v \) is related to the degree of curing and the total volume shrinkage \( V_{sh} \) after complete curing, and can be expressed as:

\[ \Delta v = \Delta \alpha \cdot V_{sh} \]  

(17)

The chemical shrinkage strain of composite materials can be expressed as:

\[ \varepsilon^c_x = \varepsilon_{sf} \frac{E_{sf} V_f + \varepsilon_m E_m V_m}{E_{sf} V_f + E_m V_m} \]  

(18)
\[ e_v^e = e_x^e = (e_{yy} + v_{yy} e_{yy}) V_f + (e_{xx} + v_{xx} e_{xx}) (1 - V_f) - \left[ v_{yy} V_f + v_{xx} (1 - V_f) \right] \frac{e_{yy} E_{yy}}{E_{yy} V_f + E_{xx} (1 - V_f)} \] (19)

3. Mutual Influence and Calling Relationship Between Sub-processes

During the compression molding process of the CFRP composites, the physical and chemical phenomena described in each sub-process may occur simultaneously, and there is also mutual influence. This relationship is reflected in the data exchange between the sub-process models, as shown in Figure 1.

![Figure 1. Data exchange between sub-processes.](image)

The matrix in a liquid state has no fiber deformation or residual stress. After a gelation transition, its modulus gradually increases, and the residual stress caused by curing shrinkage is released due to the viscoelastic effect of the resin. When the matrix changes to the glass state, the residual stress caused by curing shrinkage increases linearly with the degree of curing[14,15]. Therefore, the gel point and the glass transition temperature were used as criteria in this study.
Figure 2. shows the calling relationship between sub-processes at different moments.

4. Conclusions
In this paper, the compress molding process of CFRP is studied and it is divided into three sub-processes: thermal-chemical process, flow-compaction process, and residual stress-deformation process. The mathematical constitutive model of each sub-process is established and the interaction and calling relationship of each sub-process are determined. All the above lay a foundation for the molding process simulation of CFRP and further analysis of its multi-parameter coupling effect mechanism.

5. Acknowledgments
The research of this paper is made possible by the generous support from Tianjin Sino-German University of Applied Sciences, and the authors are grateful to Tianjin Natural Science Foundation 20JCYBJC00290 and 20YDTPJC01620, and Jinnan Project 2019ZD21.

6. References
[1] S Y Du. Advanced Composite Materials and Aerospace Engineering[J]. Acta Materiae Compositae Sinica, 2007, 24(1):12-12.
[2] A X Ding, S X Li, A Q Ni, et. al.. A Review of Numerical Simulation of Cure-Induced Distortions and Residual Stresses in Thermoset Composites[J]. Acta Materiae Compositae Sinica, 2017, 34(3):471-485.
[3] Molchanov E S , Yudin V E , Kyrdalieve K A , et al.. Comparison of the thermomechanical characteristics of porcher carbon fabric-based composites for orthopaedic applications[J]. Mechanics of Composite Materials, 2012, 48(3):343-350.
[4] Q Wang, J H Lv, Z Liu, et al.. A Lightweight Design of Carbon Fiber Reinforced Plastic Auto Bumper[J]. Journal of Shanghai Jiao Tong University, 2017, 51(2):136-141.
[5] X Zhang, Y Liu, B Yang, et al.. Effect of Carbon Fiber Surface Modification on Properties of Composites[J].Journal of Functional Polymers, 2017, 30(4):444-449.
[6] Corbridge D M , Harper L T , De Focatiis D S A , et al. Compression moulding of composites with hybrid fiber architectures[J]. Composites Part A: Applied Science and Manufacturing, 2017, 95:87-99.
[7] H. S. Mali, R. K. Misra. Investigation of the Thermo-mechanical behavior of a 2 × 2 TWILL
weave fabric advanced textile composite[J]. Mechanics of Composite Materials, 2015, 51(2): 253-264.

[8] Q Wang, H J Lu, Z Liu, et al. A Lightweight Design of Carbon Fiber Reinforced Plastic Auto Bumper[J]. Shanghai Jiaotong Daxue Xuebao/journal of Shanghai Jiaotong University, 2017, 51(2):136-141.

[9] Y Pan, Y Chen, Q Shen, et al. Effect of Carbon Fiber Surface Modification on the Flexural Mechanical Properties of Carbon Fiber Reinforced Polyetheretherketone Biocomposites[J]. Journal of Polymer Engineering, 2015, 35(7):657-663.

[10] J M Xie, S Y Wang, Z B Cui, et al. Research on Anisotropic Viscoelastic Constitutive Model of Compression Molding for CFRP[J]. Materials, 2020.

[11] Cheung A , Yu Y , Pochiraju K . Three-Dimensional Finite Element Simulation of Curing of Polymer Composites[J]. Finite Elements in Analysis and Design, 2004, 40(8): 895-912.

[12] Twardowski T E, Lin S E, Geil P H. Curing in Thick Composite Laminates: Experiments and Simulation. Journal of Composite Materials, 1993, 27 (3): 216-250.

[13] Zvetkov V L. Mechanistic Modeling of The Epoxy-Amine Reaction: Model Derivations. Thermochimica Acta, 2005, 435(1): 71-84.

[14] Zocher M A, Groves S E, Allen D H. A Three-Dimensional Finite Element Formulation for Thermo-Viscoelastic Orthotropic Media. International Journal for Numerical Methods in Engineering, 1997, 40(12): 2267-2288.

[15] Toudeshky H H, Sadighi M, Vojdani A. Effects of Curing Thermal Residual Stresses on Fatigue Crack Propagation of Aluminum Plates Repaired by FML Patches. Composite Structures, 2013, 100(5): 154-162.