Technological Preparation to the Manufacturing of Thick-Walled Polymer Composite Products

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Keywords: Mathematical modeling, Optimization, Polymer composites.

Abstract. The paper explores the technological problems that occur in the manufacturing of thick-walled polymer composite products. A detailed causal analysis of technological problems was carried out. We found the most vulnerable stages of the technology and outlined the ways to resolve them based on the method of mathematical modeling and optimization. The method allows to calculate the temperature-conversion fields during the curing of polymer composites and to choose the right optimization strategy of technological process molding.

Introduction

The development of modern technology requires the development and application of new structural materials that surpass traditional metals and alloys in their properties. Currently, polymer composites (PC) are one of the promising structural materials. The combination of the unique properties of polymer composites that are absent from natural materials—high strength characteristics, high chemical resistance, good tribological performance, low density, low thermal conductivity, the ability to easily and steadily stain, corrosion resistance and many other valuable properties—have ensured their widespread use in many branches of modern production [1]. As structural materials, PCs based on thermosetting epoxy, phenol-formaldehyde, polyaminomide binders, resins, adhesives that are reinforced with continuous glass, polymer, carbon fibers and fabrics, non-woven asbestos and many others are successfully used. Polymeric composite products can have various thicknesses and overall dimensions from small and thin-walled to large-sized. The wall thickness of such products can be very significant and reach 30 mm or more.

The main characteristics and quality of polymer composites are determined by the properties of the components (polymer resin and reinforcing filler), their volumetric ratio, micro and macrostructure, as well as the phase boundary. In addition, to obtain maximum physical and mechanical properties, it is necessary to comply with the requirements of the technology and optimal technological cycles of molding products [2-4]. Therefore, it is necessary to analyze the reasons associated with the development of the technology, the production cycle and the organization of the production of large-sized thick-walled PC products, including the analysis of the thermokinetic process [5, 6] and the calculation of optimal cure cycles of polymer composites depending on the thickness [2-4].

Analysis of Technological Problems

In the production of thick-walled PC products, we considered the reasons that affect the quality and properties of the finished product:

Production Technology. It includes the following important factors: temperature-time curing cycle (should be optimal for a given formulation, thickness and configuration of the product), molding method (should correspond to the shape of the product), pressure mode (should provide the necessary filling factor and solidity of the product), process time (should be minimal, but sufficient to complete the curing process), type of equipment (should correspond to the method of forming the product).

Raw Materials. The manufacturer selects the material that he needs to fulfill the technological, economic, environmental and other requirements for PC products. Raw materials also depend on the
method of molding products. When the “dry” method is used, the prepreg is used and it is important that the necessary storage conditions (temperature and duration) are not violated, the time of installation in the product does not exceed the storage time, etc. The proportions of the ingredients are also important.

**Control and Analysis.** This allows us to measure and control all the necessary process parameters, compare them with the norm, monitor and control the process. All metrological standards and measures must be observed here.

**Staff.** It directly affects the production process of PC products. Here, qualifications, experience, skills, interest and motivation of personnel, involvement in quality management processes, as well as labor organization are essential. Equally important is the training of best practice colleagues.

One of the modern ways of studying the causes and effects in the production process of obtaining PC products and managing their quality is the Ishikawa cause and effect diagram, which allows us to systematize in a simple form all the probable causes of the problems analyzed, identify the most significant and search for the root causes [7]. Based on the analysis of factors affecting the quality of thick-walled PC products, a cause and effect diagram of Ishikawa was constructed, shown in Figure 1.

![Figure 1. Cause and effect diagram of PC quality analysis.](image)

The main manifestations (consequences) of the defectiveness of polymer composite products are as follows: strength properties of PC are lower than required; resin degradation in PC; low degree of resin cure in PC; cracking of material; warpage (violation of geometry) of the finished product; product stratification, voids; places of poor impregnation; air bubbles between layers.

These manifestations are explained by the fact that the curing process of PC products based on thermosetting resins is accompanied by an exothermic reaction [1-5]. Due to the low thermal conductivity of the PC perpendicular to the reinforcement orientation layers, heat outflow from the inner layers of a thick-walled product is difficult. When using a non-optimal temperature-time curing cycle, this causes a significant heterogeneity of the temperature-conversion field \( T(x,t) \), \( \beta(x,t) \), overheating of the inner layers of the material, degradation of the resin, accumulation of internal residual stresses, leads to a decrease in the strength properties of the material, cracking and warping of the finished product. It is possible to eliminate the indicated technological problems and thereby improve the quality indicators and physicomechanical characteristics of PC products by setting the optimal temperature-time cycle \( U(t) \) on the surface of the product. This task is especially important in the manufacture of large-sized thick-walled PC products [2, 4].

**Cure Cycle Optimization**

Determining the optimal temperature-time curing cycles of polymer composite products is a complex and critical problem. The problem of determining the optimal temperature-time curing cycles of thick-walled products can be solved on the basis of mathematical modeling and optimization of the
PC curing process, which guarantees the creation of a high-quality finished product in a minimum time and low cost [2]. The key problems that need to be addressed in determining the optimum cure cycle for thick-walled PC products are as follows [2-4]: reduction in the duration of the curing cycle; reduction of temperature-conversion inhomogeneities in PC; complete curing of the resin.

The mathematical model necessary for solving the optimization problem for each molding method and technological process has its own specifics, and yet the same structure. Therefore, the model is built in accordance with the used method of forming products [4]. The mathematical model of the PC hot curing process is a system of differential equations of heat and mass transfer, curing kinetics, resin flow (extrusion), material compaction during molding, and rheological equations of state. The regulating effect here is the temperature of the mold $U(t)$.

The parameters necessary to solve the equations of the mathematical model are determined from experiments using special methods and settings that reproduce conditions close to the technological process, i.e. study of the filled composite, the presence of technological pressure, close to the regulation of the heating rate, etc. [4, 5].

One of the paramount parameters of the mathematical model of the curing process are the characteristics of the composite, both in the cured state and in the uncured state, as well as in the curing process. These include: the thermophysical characteristics of the material, i.e. volume heat capacity $C(T, \beta, \gamma)$ and thermal conductivity $(T, \beta, \gamma)$ depending on temperature $T$, degree of cure and resin content the heat release rate $W(t)$, the total thermal effect $Q$, the kinetic characteristics, i.e. the activation energy of the curing process $E(\beta)$ and the kinetic function $q(\beta)$, which includes the rate and the order of the chemical reaction, and when needed rheological characteristics i.e. the activation energy of the viscous flow $E_{\mu}$ and the effective viscosity of the resin during curing and flow [4]. To determine the above characteristics of the material and other parameters of the mathematical model, we created a data-measuring device (DMD) for studying the curing process of composites [8, 9].

When calculating the optimal cure cycles, the criterion of the optimality of technological process $I$ is first selected. The objective function of the task of optimizing the curing cycle can be to minimize the duration of the process $t_m$. The mathematical formulation of the problem of optimizing the curing process of PC products is to search for the temperature-time cycle $U$ on the surfaces of the heated and cured product, which is the control action

$$U(t; \min t_m) = \{T_0(t), T_L(t)\},$$

which delivers a minimum to some optimality criterion $I$ and ensures the creation of a high-quality finished product with a minimum process time $t_m$ when making connections in the form of mathematical models [4] that correspond to the considered technological method of forming products, as well as subject to restrictions in the form inequalities imposed on the process, taking into account the temperature-time cycles allowed by the equipment.

The desired temperature-time curing cycle is calculated as a piecewise linear function

$$U_i(t) = \begin{cases} \tilde{T}_i - \tilde{K} i, & t_{i-1} < t < t_i, \\ \tilde{T}_i, & t_i \leq t \leq t_{i+1}, \end{cases} \quad i = 1, 2, ..., k_{st},$$

where $\tilde{K} -$ is a heating rate of the surface of the product, K/s; $k_{st} -$ is a number of heating stages; $\tilde{T} -$ is the temperature of isothermal hold at the $i$-th heating stage, K.

The restrictions in the optimization problem are follows: the maximum allowable temperature $T_{\max}$ inside the product, above which side undesirable reactions begin to occur in the resin, causing the destruction of the resin; the maximum allowable temperature difference across the thickness of the product $\Delta T$, not causing heterogeneity of the curing process of the material; the maximum allowable temperature gradient during curing $\frac{\partial T}{\partial z}$, not causing the accumulation of residual stresses in the material. The restrictions, which are associated with the mechanical characteristics of polymer
composites, we determined experimentally or as a result of a numerical analysis of residual stresses in a joint solution of the equations of the mathematical model.

The algorithm for solving the problem of searching for optimal cure cycles of PC products of various thicknesses is based on a special method that includes phased optimization of each heating stage [4]. The condition for completing the solution of the optimization task of the curing cycle is to achieve a given final degree of curing throughout the entire volume of the product. As a result of the calculation, we obtain the optimal cure cycle, which guarantees the creation of a high-quality finished product.

Results and Discussion

As an example, we considered the process of manufacturing carbon fiber reinforced products (CFRP). In the initial state, the carbon prepreg is a unidirectional carbon fiber tape coated on one side with a resin layer. The existing standard cure cycle of CFRP is one-stage and includes raising the temperature at a speed of 3 K/min to 190 °C, holding at \( T = 190 \) °C and a vacuum of 0.7-0.9 atm. during \( t_1 = 30 \) min, then the pressure is supplied up to \( P = 2 \) atm. and holding for \( t_2 = 150 \) min. The total time of isothermal hold at \( T = 190 \) °C is \( t = 180 \) min. The duration of the curing process is \( t_m = 230 \) min. Then the product is cooled to room temperature. This cycle was determined using thermal analysis methods for thin products.

To calculate and analyze the curing cycle, by means DMD we studied the CFRP characteristics needed to simulate the curing process. Using the studied characteristics of CFRP, numerical studies and analysis of the existing standard curing cycle designed for the manufacture of products with a thickness of up to 5 mm were carried out, its suitability for the manufacture of more thick products, for example, with a thickness of 30 mm or more was estimated, and optimal cycles of curing of products with thickness up to 30 mm were also calculated. To analyze the standard cycle, the temperature conversion fields were calculated, i.e. the temperature on the surfaces of the plate \( T_0 \) and in the middle of \( T_{L/2} \), respectively, the degree of cure \( \beta_0 \) and \( \beta_{L/2} \), the power of heat release \( W_0 \) and \( W_{L/2} \), the maximum temperature gradient modulus \( \chi \) in the process of curing for plates with a thickness of \( L = 30 \) mm. The effect on the calculated curing cycle of the set value of the temperature spike \( \Delta T \) and the set value of the temperature gradient \( \chi \) was studied. In a one-stage curing cycle with an isothermal holding of 190 °C, the maximum temperature inside a flat product with a thickness of \( L = 30 \) mm reaches \( T_{L/2} = 213 \) °C (\( \Delta T = 23 \) K), and the temperature gradient is \( \chi = 2.9 \) K/mm, which leads to destruction resin and the formation of a stressed structure of the material. Therefore, the standard curing cycle designed for curing thin-walled products up to 5 mm thickness is not suitable for the manufacture of more thick PC products.

![Figure 2. Optimal cure cycles for different thickness of CFRP products with minimum process time.](image)

The final step is to calculate the optimal cure cycles of the studied CFRP. The calculated optimal curing cycles with the minimum duration are shown in Figure 2. The calculations of the optimal cure
cycles were performed with the following restrictions: allowable temperature gradient in thickness \( \Delta T = 0.2 \text{ K/mm} \) and allowable overheating of inner layers \( \Delta T = 5 \text{ K} \). As a result of the calculations, curing cycles were obtained that differ from the standard by lower temperature differences in thickness, significantly lower temperature gradients and a gradual increase in the degree of cure. An analysis of the graphs shows that with an increase in the thickness of PC products, the duration of the curing process significantly increases, and the temperature of the first and subsequent isothermal holding decreases markedly, while the internal power of heat release and temperature of the inner layers at the first stages of the process also decrease. This, to specified levels, reduces the heterogeneity of the temperature-conversion field and leads to an increase in the quality indicators of polymer composite products, which allows the use of calculated curing cycles for the production of large-sized thick-walled PC products.

**Summary**

Based on the cause-and-effect analysis, the main technological and organizational problems that arise during the technical preparation of manufacturing thick-walled polymer composite products are identified. One of the ways to improve the quality of PC products is to organize research in order to determine the optimal temperature-time cycles for curing thick-walled products, taking into account the capabilities of the equipment available in the technological process and strict adherence to these cycles in the manufacture of PCs. An example of the choice of optimal curing cycles for CFRP plates of various thicknesses based on the method of computer simulation and optimization is given. The actions taken will eliminate technological problems in the production of large-sized thick-walled products for PCs and improve their quality indicators.

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