Cure kinetics of epoxy resin and distributed thermal control of polymeric composite structures moulding

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*Abstract***—The goal of this work is the development of mould heating distributed control model for polymerization of the helicopter main rotor blade. Obligatory working conditions of such system control were considering of exothermal heat emanated during a polymerization of epoxy matrix, and change of a thermal capacity at transition from fluid to solid state. The kinetic model of cure epoxy resin designed on basis of DSC - experiments. It is a component of the control system synthetic model which includes also heat transfer FEM-based model of a mould with composite spar, and PID-controller model equipped by forecasting module for compensation of a mould thermal inertance. Developed model was shown the good conformity with measured dynamic temperature field in full-scale setup.**

I. Introduction

An important composite aircraft piece such spar of the helicopter main rotor blade determines the basic tactical parameters and reliability of flight vehicle. The technology of manufacturing of a fiberglass reinforcement with epoxy resin matrix composite spar include following phases: winding of a preimpregnated unidirectional glass-fiber tape on a steel mandrel; polymerization of a prepreg in a mould within approximately 16 hours; extraction of a baked spar from a mould and removal it from a mandrel.

For maintenance of high strength and fatigue characteristics of spar material it is necessary to maintain a given temperature schedule of polymerization both lengthways, and across the section of the item. The deviations from the given temperature should not be more than 5^{o} C. Accuracy of the geometrical shape and walls thickness are provided by pressure control of air insufflated to bags, placed between a mandrel and internal surface of a spar.

FEM-based dynamic computer model [1] of moulded spar polymerization distributed control was designed by authors earlier. The control system included a set of thermocouples located in a mould and electrical heaters. For the correct count of internal heat sources in the cured epoxy resin the data of exothermal heat and thermal capacity needed at all stages of solidification. The time history of a current heat quantity Q (t) at a polymerization usually is described by kinetic differential equations [2-3] linking a fractional conversion $\alpha \equiv Q(t)/Q_0$ (where $\alpha \in [0;1]$ and Q_0 is total reaction heat outflow at polymerization of a mass unit) with thermo physical constants and time.

Thus, for the adequate description of thermal processes in a molded work piece the finite element model (FEM) of a transient heat transfer should provide integration of a kinetic equation on each node of FEM mesh. In this work on the basis of DSC - results the kinetic equation of a cure process in used epoxy resin constructed. The integration of this equation on each temporary step yields value of exothermal heat and actual value of thermal capacity.

The designed synthetic model was implemented in connected software MATLAB - Comsol Multyphisics.

II. Composite Spar Cure Process. Static Model Simulation

The existing mould consists of 12 sections of 0.8 m length. Each section half contains 4 lateral heaters and 4 thermocouples. The bottom of a section is equipped with one 0.7 m long heater (see Fig. 1). Each heater is operated by one channel of automatic control system (92 channels), receiving signals from the respective thermocouples.

Because of continuous simulation 2D – models were created and analyzed separately: for longitudinal and transversal cross-sections. Geometry modeling was created by Comsol Multyphysics CAD tools. A mesh sizes was generated small enough. So, for a longitudinal section the quantity of elements made 27 500, and for transversal – 28 300 elements. For using the heat transfer application modes the thermal parameters of mould parts, crude prepreg and polymerized spar were assigned judging by the passport data of materials. Anisotropy of composite heat conductivity was neglected. At this stage of model construction the exothermal heat was not taken into account in any way.

As the basic modes of forming were exposure to constant temperature (160 - 4 hour, 180 – 2 hour), it was necessary to precisely simulate the process of heat transfer through external mould surfaces to ambient air. Simulation of irradiative and heat convection was not executed satisfactorily, that obvious explainable by complex character and temperature variation of convective flows, and also with no information about temperature of ambient bodies absorbing an infrared radiation. Therefore during manufacturing of a full-scale spar the temperature on a surface of a mould was measured and compared with the indications of thermocouples during cure cycle.

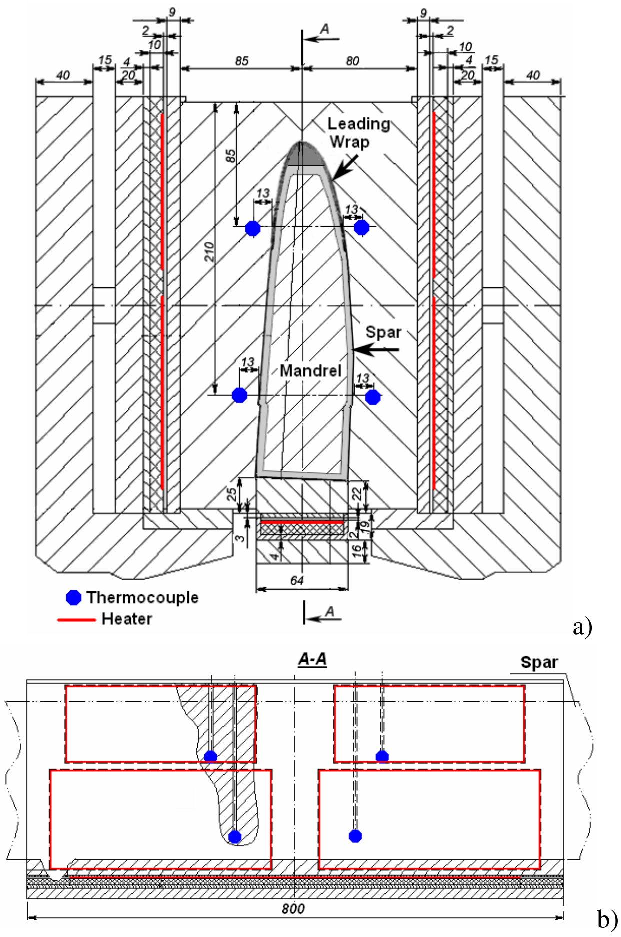

Figure 1. Cross section (a) and longitudinal view (b) on one section of mould for composite spar cure process

A comparative data analysis of simulation, the values of temperatures measured experimentally and average power of heaters has allowed to determining the seeming heat transfer parameters on a mould boundaries. These parameters were used at computer simulation. Also mean and peak power of heaters was determined this way.

For designed models the stationary solutions were found. During the analysis of stationary temperature fields (normative temperature value 160° C) some undesirable phenomena are revealed. So, in a longitudinal section of a mould the segment between two adjacent heaters had temperature 3…7 degrees lower than in a body of a spar directly under heaters. Also in cross section there were two segments with lower temperature – near leading and trailing zones of spar cross section (Fig. 2).

III. Model of Cure Kinetics

The different types of the kinetic equations for cure reactions are generalized in [3]:

$$\dot{\alpha}(T,\alpha)=\left[A_1 e^{(-E_1/RT)}+A_2 e^{(-E_2/RT)}\cdot\alpha^m\right]\cdot(\alpha_{\max}-\alpha)^n$$

$$\alpha_{\max}=B_0+B_1 T+B_2 T^2$$

where $d\alpha/dt$ is the rate of conversion $\alpha \equiv Q(t)/Q_0$, A_1, A_2 – weight factors, E_1, E_2 – activation energies, R –gas constant and T is absolute temperature.

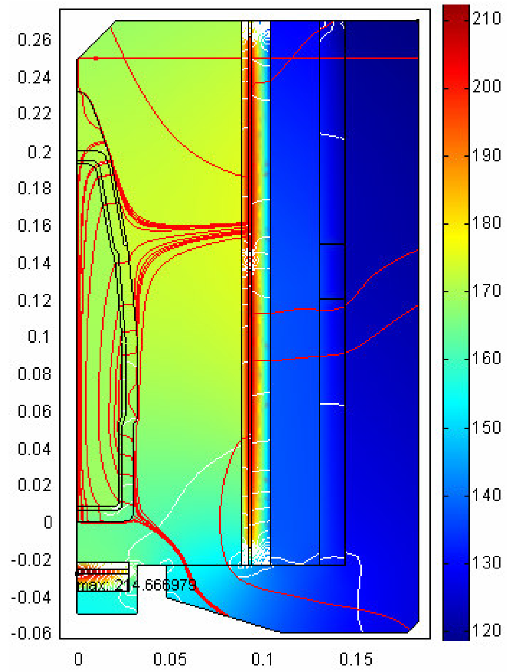

Figure 2. Simulated stationary temperature field in mould cross section

For definition of type and parameters values of the kinetic equation the thermal analysis experiment on NETZSCH DSC 204 F1 Phoenix® with PROTEUS® software was carried out. The following temperature program was utillized: 1st and 2nd heatings from 20°C up to 300°C with temperature scan rate: 5, 10, 20 K/min; cooling back to 20°C (see Fig. 3).

At first stage of DSC-scan data processing the contribution of a material thermal capacity C in a common heat flux was separated according to relation

$$\frac{dQ}{dt}=C\cdot vT+\frac{dQ_s}{dt},$$

where Q_s – current reaction heat evolved in a dynamic DSC-scan with temperature rate vT. For this purpose the thermokinetics curves discretized and on them selected areas outlying from thermal peaks. Then on points in these areas built the regression equations expressing dependences $(C\cdot vT)$ vs time. After elimination of the thermal capacity contribution from a common heat flux the dependences of exothermal heat fluxes on temperature and on time were obtained. For build-up of $d\alpha(t)/dt$ dependence (Fig. 4) the relations

$$\frac{d\alpha(t)}{dt}\equiv\frac{1}{Q_s}\frac{dQ_s}{dt} \text{ and } Q_s=\int_0^{Tp}\left(\frac{dQ_s}{dt}\right)dt$$

have utillized approximating curves $dQ_s(t)/dt$ by 3rd order splines. On the basis of $d\alpha(t)/dt$ spline representation the dependences of the conversion rate on conversion value (Fig. 5) were constructed by numerical integration. Such way processed DSC-scan results were utilized for curing process kinetics model identification.

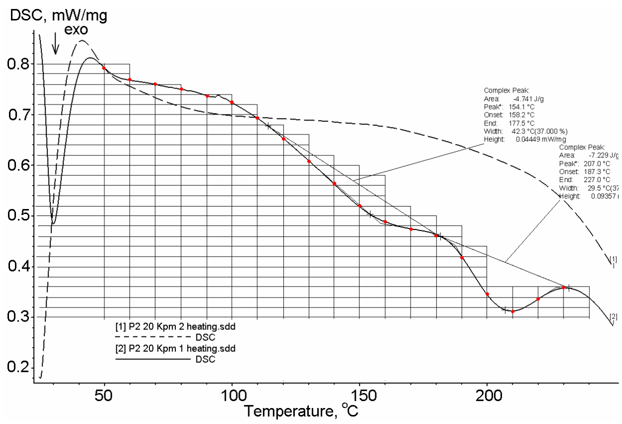

Figure 3. DSC-thermogram at temperature scan rate 20^{0}K/min

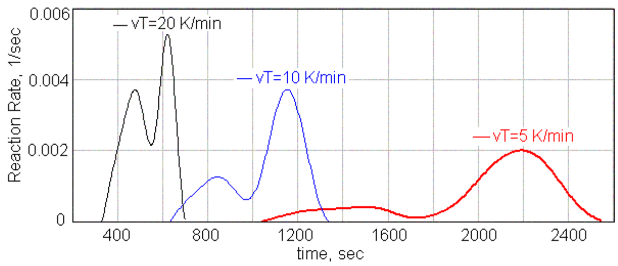

Figure 4. $\dot{\alpha}(t)$ vs time dependence at varied temperature scan rate

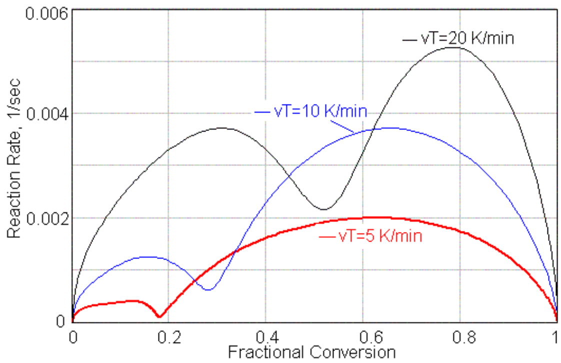

Figure 5. Empirical kinetics curve at varied temperature scan rate

As above presented generalized kinetics model not provide of good description for two modal kinetics curve (see Fig. 5) a new model were proposed:

$$\dot{\alpha} = \left[A_1 e^{-E_1/RT} e^{-\alpha/\alpha_1} + A_2 e^{-E_2/RT} \alpha^m\right] \cdot (1-\alpha)^n$$

The exponential factor depending on a fractional conversion in the first addend ensures damping of the first reaction when α becomes comparable with α_1, whereas second factor circumscribing the second reaction begins to yield the noticeable contribution only when the conversion is great enough. For constructed model all 7 parameters identified in Simulink MATLAB (see Fig. 6). Simulink realization of kinetic model provid inaccuracy of exothermal heat reproduction up to 10 %.

The significant property of the composite resin is the change of its thermal capacity during a curing reaction. The corresponding dependences constructed as a result of exothermal effect elimination from DSC-scan data, are shown in a Fig. 7.

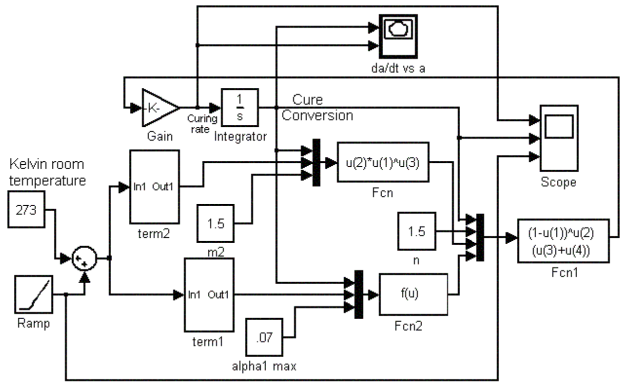

Figure 6. Simulink model realizing the new kinetics equation

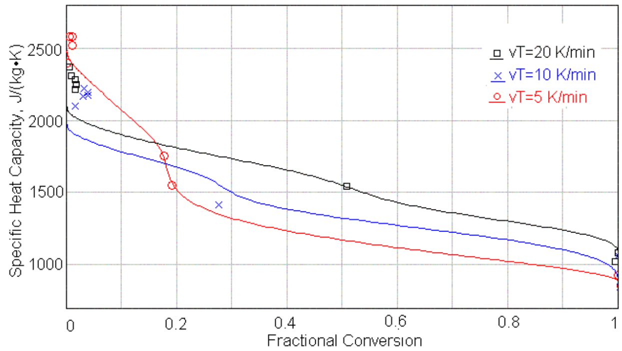

Figure 7. Specific heat capacity dependence on conversion at varied temperature scan rate

It is well visible that at increase of heating rate the phase transition becomes less expressed and is shifted in area of late polymerization. However, since a conversion greater than 0.6 the behavior of a thermal capacity practically does not depend on heat rate.

The constructed kinetic model utilized as a component of dynamic computer model of spar polymerization distributed control.

IV. Automatic Control of Distributed Heating

For the system of distributed heating analysis in dynamics, temperature of points, where the thermocouples were installed in the mould itself, was exported in Simulink - model of automatic control system (Fig. 8). Besides, temperature in several points of a molded spar is registered. The Simulink - model submit to the input of Comsol Multyphisics - subsystem the values of heaters power and the temperature of ambient air, which varied randomly stipulated by movements of large mass of air in a spacious production facility.

For speed up of linked Simulink and Comsol models simulation the initial finite-element models were subject to a reduction as follows. The volumetric heat sources were replaced by surface sources with the conforming intensity. The sandwich structure of a mould was replaced by a homogeneous body (Fig. 9), the parameters of which were recalculated according to

$$\overline{C\rho} = \frac{1}{l}\sum_i C_i \rho_i l_i\,; \qquad \bar{k} = l\left(\sum_i l_i / k_i\right)^{-1};$$

$$\bar{h} = \sum_i h_i (T_i + T_{i-1}) l_i \Big/ (T_0 + T_n) l$$

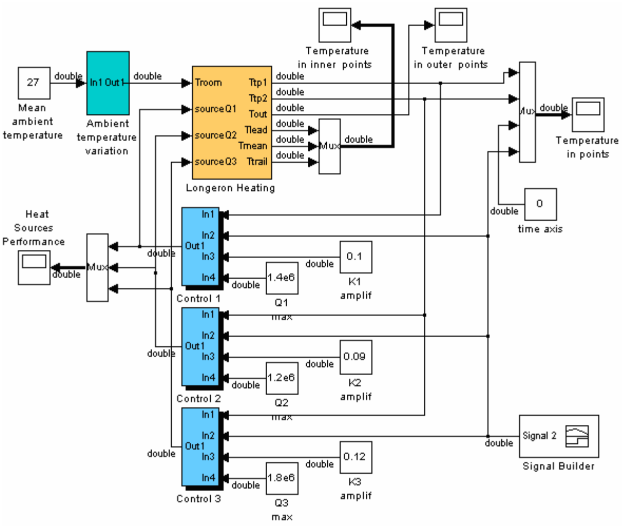

Figure 8. Simulink-model of one channel automatic heating control

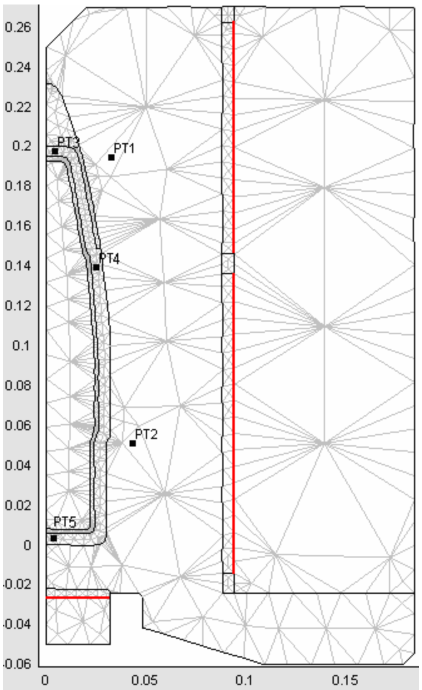

Figure 9. The simplified FEM-model of mould cross-section

where: $C,\ \rho,\ k$ - heat capacity, density and thermal conductivity respectively, h - lateral boundary heat transfer coefficient; l - thickness of sandwich; T_i, T_0, T_n - temperature on interior, heated and cooled boundary respectively; subscript i - number of layer; line above letters means fitting to homogeneous body.

The simplified model has demonstrated in a static schedule a temperature field, matched to experiment on external surfaces of a mould and in its part, nearest to a molded spar. At given temperature schedule (see Fig.10) the simplified model has yielded a maximum deviation from experimentally measured temperature in the item $\pm 2^{o}$ C. The reduced FEM model of a mould cross section included 1720 elements and was imported in Simulink as the general dynamic model. The heating control system (Fig. 8) represented a proportional - integral control system including as part the kinetics model (see Fig.6).

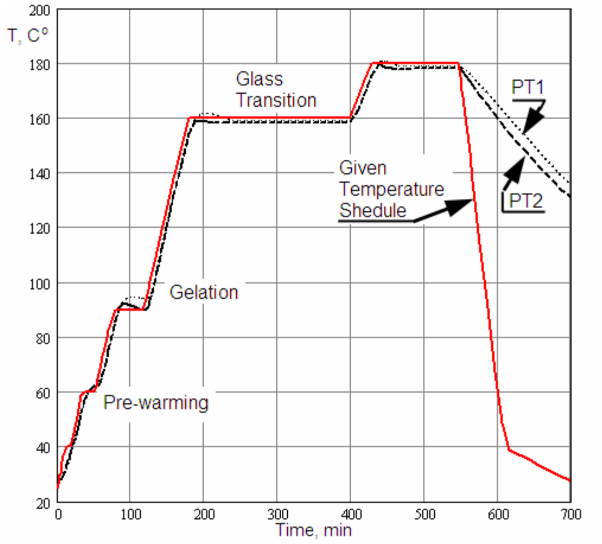

Figure 10. Temperature registered by thermocouples during a cure cycle (results of simulation)

To take into account a thermal inertia effect of a mould the prediction-correction of the thermocouples indications by polynomials of the 2nd order was used.

The machining time necessary for simulation of a complete cure cycle (Fig. 11) made 30…180 min that has allowed executing necessary adjusting of automatic control system and mould design.

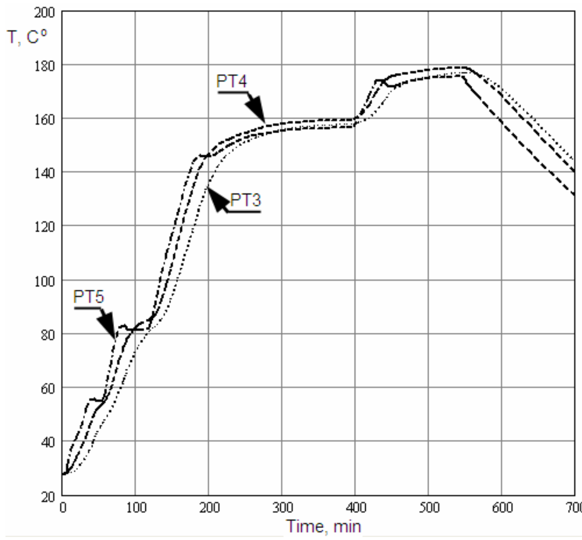

Figure 11. Temperature in inner points of spar (results of simulation)

ACKNOWLEDGMENT

The authors wish to acknowledge the financial support of RFBR (Grants 05-01-00690, 06-01-08041).

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