MODELING OF THICK-WALLED COMPOSITE STRUCTURE CURE PROCESS

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Abstract

A mathematical model of epoxy-based resin curing at forming of a thick-walled composite structure is presented. A differential equations system link a kinetic equation of the resin cure, that has derived from the differential scanning calorimetry investigation, with heat conduction equation taking into account a phase transfer from liquid to gel and next to solid phase. Implemented in Comsol Multiphysics software the developed model gives the spatio-temporal patterns of a curing front propagation in a moulded composite body. A possibility of using the developed model for improving the control of the molding thermal regime is discussed.

Keywords: Composite material, Thermoset resin, Curing process, Kinetic equations, Differential scanning calorimetry, Exothermal heat, Finite-element model.

Presenting Author's biography

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1 Introduction

The purpose of the kinetics - thermal cure models development is an enhancement of a composite structure geometric accuracy, stability with homogeneous mechanical properties in all points of the composite body. The complexity of this problem is caused by the fact that the cure processes occur with liberation of considerable exothermal heat, and usually very poorly controlled due to lack of means for monitoring of temperature and stress in the body at compressed thermal moulding. The presented model of the fiber reinforced composites curing processes can properly take into account the kinetics of the reactions of thermoset resin, changing its phase state and mechanical properties during cure. This largely eliminates the effect of "unobservability" of high-strength composites products technology and improves process control system, thereby providing improved quality and reliability of composite aircraft structures.

In the first section we shortly discuss the concepts, models, and experimental methods of these models verification. Next we consider the results of a thermal-kinetic study of epoxy based resin by differential scanning calorimetry (DSC), which allowed us to develop model of the resin cure. The second section shows the coupled model of the composite body cure process and its finite element implementation. The abilities of model are illustrated by a simple example for rectangular subdomain. Finally we consider the way of using this finite-element model to enhance the observability of the curing map in thick-walled composite structures.

2 Kinetic model of thermoset resin cure process

Manufacturing technology of high-polymer composites usually consist of formation of unidirectional tapes by the reinforcing fibers, dry-firing a protective layer of fibers to improve adhesion to resin, making prepreg tape by passing through a resin solution, winding or laying on the formative frame, placement of raw product in the mold and its aging for about 20 hours at a certain temperature range, ensuring the defined mechanical properties uniformly distributed in the whole product. A typical cross-section of high-strength piece made from orthotropic polymer composite is presented in Figure 1, and the temperature schedule of his mold - in Figure 2.

In turn, the temperature schedule is determined by a triple diagram of temperature - time - state (Figure 3), which link the change of the resin state during cure (liquid - gel - glass) with temperature and time of chemical reactions. A feature of such reactions is to change the phase state of resin, which occurs in the form of an initial liquefaction and reducing the viscosity of the liquid transition to the gel-like state (gelation), and the subsequent transition to the vitreous state.

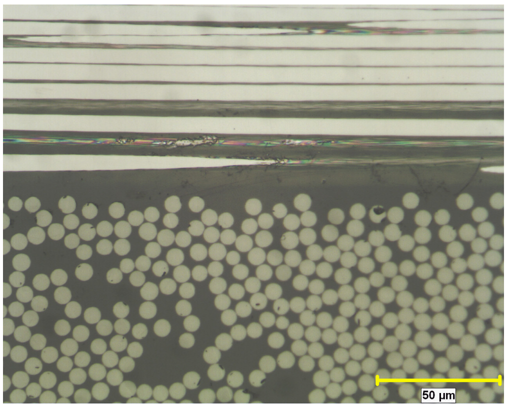

Fig. 1 The slice of glass-fiber reinforced epoxy based composite

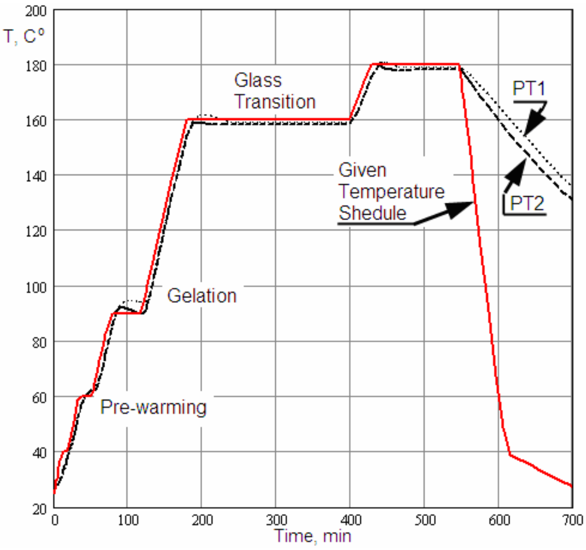

Fig. 2 The typical temperature schedule for curing of epoxy based composite

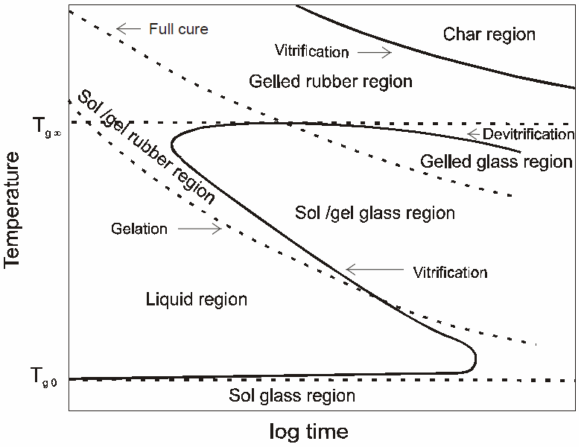

Fig. 2 Generalized isothermal cure phase diagram of time-temperature transformation [1]

It is important to note that, unlike crystalline materials, all epoxy based polymers change its state at a certain temperature range, and the location of this range may vary at the studying of thermal and rheological characteristics of the material. Therefore, accepted in the scientific literature and used herein the terms "gel transition", "glass transition" refers to a range of temperatures (see Figure 4) rather than to a strictly fixed temperature, as is the case in crystalline solids. Another feature of the thermoset cure reaction is the discharge of the exothermal heat. And the maximum of the exothermic heat can occur at single (one-step reaction) or more (two-stage reaction) temperatures (see Figure 5).

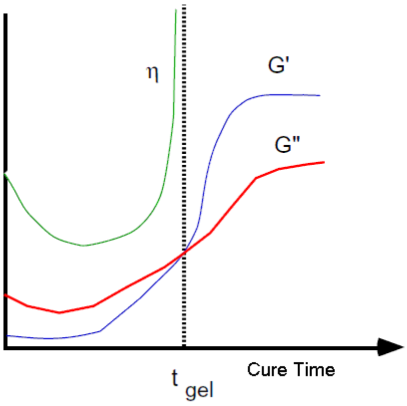

Fig. 4 The change of viscosity η, shear modulus G' and loss modulus G" at thermosetting resin curing [2]

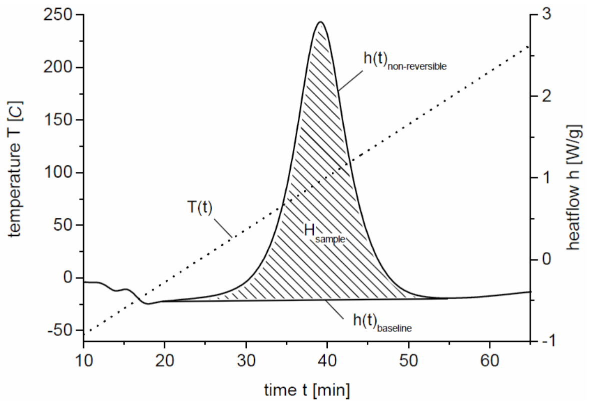

Fig. 5 Data of a DSC scanning of polymer

It is considered that the amount of evolved heat during the exothermic reaction at a time characterizes the degree of polymerization of the material. Quantitative assessment of the degree of cure (or, equivalently, conversion) is $\alpha \equiv Q(t)/Q_0$ $(\alpha \in [0;1])$, where $Q(t)$, Q_0 – an actual and the total amount of heat during the polymerization unit of mass. A crucial role in describing the cure process is the dependence of conversion rate on conversion, known as the kinetic curve, which is a visual representation of the kinetics of polymerization reactions for a given composition of the polymer and the temperature schedule. The necessary apparatus for the quantitative description of the cure process gives the kinetic equation, the first of which [4] is applied to cure epoxy system. Overview of types of these equations is given in [1, 2, 5-7], and in [5] is given a generalized form of the kinetic equation for the cure reactions

$$\frac{d\alpha}{dt} = \left[A_1 \exp\left(-\frac{E_1}{RT}\right) + A_2 \exp\left(\frac{E_2}{RT}\right) \cdot \alpha^m\right] \cdot (\alpha_m - \alpha)^n \quad (1)$$

$$\alpha_m = B_0 + B_1 T + B_2 T^2$$

where: A_1, A_2 - scale factors (reactions weights), E_1, E_2 - the activation energy, R - gas constant, α_m - maximum conversion value for fully polymerized material, m, n - constants (order) of the reaction cure. This generalized model has 9 constants, allowing a good flexibility. Simplified form of this model, in which the notation $k_{1,2} = A_{1,2} \cdot \exp\left(-E_{1,2}/RT\right)$ used, is the Kenny model [8]. Modern means of constructing the experimental kinetic curves is DSC method that implements the monitoring of thermal processes during polymerization. These curves (thermograms) provide information on the specific heat of the sample at different temperatures, enthalpy and temperature of polymerization processes.

We used a DSC scanning at the following temperature program:
1st and 2nd heating in a nitrogen atmosphere: 20 ^{0}C .. 300 ^{0}C;
Cooling from 300 ^{0}C to 20 ^{0}C;
Heating rate: 5, 10, 20 K / min.

These DSC scans were numerically processed to obtain dependencies $d\alpha(\alpha,T)/dt, C(\alpha,T)$. On the basis of these data for investigated material which has the two-modal kinetic curves (see Fig. 6) a new kinetic model and empirical dependence for heat capacity have been proposed

$$\frac{d\alpha}{dt} = \left[A_1 \cdot e^{\left(-\frac{E_1}{RT}\right)} \cdot e^{-\frac{\alpha}{\alpha_t}} + A_2 \cdot e^{-\left(\frac{E_2}{RT}\right)} \cdot \alpha^m\right] \cdot (1-\alpha)^n \quad (2)$$

$$C_r = \left[C_f - \left(C_f - 1.145 C_s\right) \cdot H\left(\alpha - \alpha_t, \delta\alpha\right)\right] \cdot \left(.8 + .2e^{-\alpha}\right) \quad (3)$$

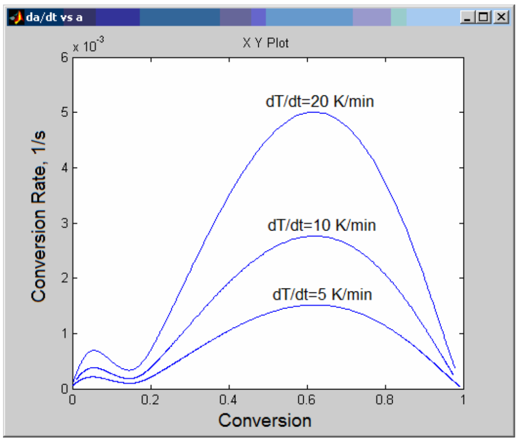

Fig. 6 The kinetic curves calculated according to the Eq. (2)

where C_f and C_s are the specific heats of uncured (liquid) and fully polymerized (solid) resin respectively; conversion α_t corresponding to jump of heat capacity at phase transition, and the width of the jump in the smoothed Heaviside function H have defined by the relations

$$\alpha_t = .05 + .45\tanh^2\left(\frac{dT/dt}{12}\right), \tag{4}$$

$$\delta\alpha = .1 + .4\left[1 - \exp\left(\frac{dT/dt}{15}\right)\right]. \tag{5}$$

Equation (3) satisfactorily describes the jump of the heat capacity at the transition, and "broadening" of this jump with increasing heating rate. Relation similar to Eq. (3) is used for the actual value of the resin thermal conductivity. To do this, simply replace $k_r \to C_r$; $k_f \to C_f$; $k_s \to C_s$. The empirical dependencies of the specific heat and thermal conductivity on the degree of cure are shown on a Figure 7. The dependence of the thermal conductivity was "tied" to the data of the manufacturer, who reported the value at 20 ^{0}C, at the start of gelation and in the solid state.

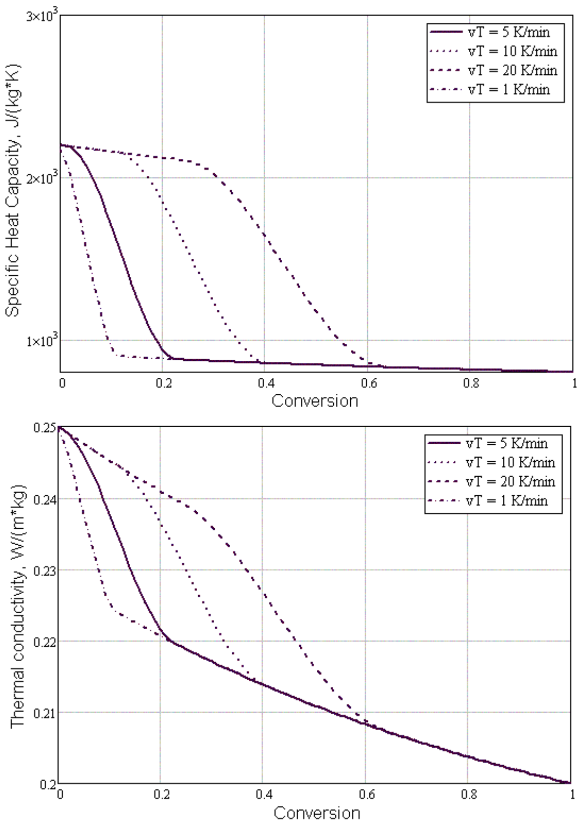

Fig. 7 The dependencies of specific heat (top) and coefficient of thermal conductivity (bottom) on the conversion at different heating rates. Calculation of empirical formulas (3) - (5) for investigated epoxy resin

3 The coupled model of the heat propagation and the curing process in a glass fibers reinforced epoxy based composite, and its finite element implementation

Recent attempts (e.g. [9]) to the analytical solving of the Stefan problem, to which the problem considered here can be reduced, have showed that mathematical complexity allow to obtain some qualitative results in the simplest areas under very restrictive assumptions. Much more efficient finite element approach were used in [1, 5, 10 and others] for solving problems related to the thermo-kinetic and mechanical processes of composites curing. This approach was used in this work.

The prototype for the problem formulation was the curing of spar for helicopter rotor blades in mold. The product is the tube-like structure length of 8 m; the shape and thickness of the cross section varies from root to tip. Near the blade root a wall thickness is about 20 mm, and close to the blade tip diminishes to ~ 5 mm. A raw prepreg wounded on a mandrel cures in the mold, whose outside surfaces are heated by electric heaters. After pre-heating and dilution of resin creates pressure, clamping prepreg to the forming surfaces. The excess resin can be freely moved away the mold. Thus, the front of polymerized material, moving from the external hot surfaces, is not constrained by a liquid phase. Consideration of the finished product cooling and formation of the residual thermal stress is beyond the scope of this article, therefore, not discussed below. Problem is examined for an arbitrary section of a composite body, heated on one side and exchange heat with a steel mandrel, and illustration of the process is presented on a simple rectangular area on a Fig. 8.

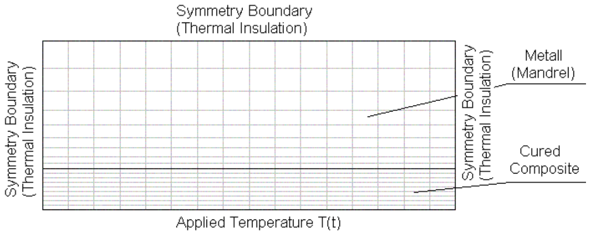

Fig. 7 The geometry of the simplified FEM-model of the composite cure process

Here is a full problem statement for a two-dimensional case.

- The heat transfer equation

$$\rho_c C_c\, \partial T/\partial t + \nabla(-h_c \nabla T) = Q_{exo} \tag{6}$$

- the kinetics equation (2) for conversion $\alpha(x, y, T, t)$ which is a function of space coordinates, temperature, and time;

- composite density

$$\rho_c = \rho_f \nu_f + \rho_r (1 - \nu_f) \qquad (7)$$

- the heat transfer coefficient of composite

$$k_c = k_r \cdot \frac{(1+\nu_{fb})\cdot k_{fb} + (1-\nu_{fb})\cdot k_r}{(1-\nu_{fb})\cdot k_{fb} + (1+\nu_{fb})\cdot k_r}, \qquad (8)$$

where actual value of the resin matrix heat transfer coefficient k_r is defined by a function of conversion

$$k_r = \left[k_f - (k_f - 1.145 k_s)\cdot H(\alpha - \alpha_t, \delta\alpha)\right]\cdot\left(.8 + .2e^{-\alpha}\right), \quad (9)$$

- the specific thermal capacity of composite

$$C_c = C_{fb}\nu_{fb} + C_r(1 - \nu_{fb}) \qquad (10)$$

where C_r is defined by Eqs. (3) - (5);

- an intensity of the internal heat sources

$$Q_{exo} = Q_{tot}\left(\frac{\partial T}{\partial t}\right)\cdot\frac{\partial \alpha}{\partial t} \qquad (11)$$

and all used numerical values were obtained from DSC experiments. In the above equations index fr indicates the material of reinforcing fibers, and the index r - resin matrix.

The developed model has been numerically implemented in the Heat Transfer and PDE (partial differential equation) modules included into Comsol Multiphysics finite element software. The system of two coupled equations (6) and (2) was solved inside the modeling domain (usually with zero initial conditions). At each integration step the values of specific heat, thermal conductivity, and the intensity of heat sources for all points of the modeled domain were calculated according to the presented equations.

Here are the results of solving the non-stationary problem of the composite cure in a rectangular area (lower half). The composite thickness of 10 mm, the lateral sides of the composite layer insulated (assumed infinitely long layer), the bottom side is heated at a rate of 3.6 ^{0}C / min, top - the metal layer thickness of 30 mm (mandrel). Duration of heating is 1 hour up to 218 ^{0}C.

Figure 8 shows how the front of polymerized material is formed, and move deeper into the body of prepreg. But heating for one hour is not enough for complete cure of the material throughout the section. This is due to the large mass and heat capacity of metal mandrel. Indeed, after an hour of heating the metal temperature reaches only 60 C. This result revealed the cause of incomplete polymerization products in the area of thickening, which was established experimentally at investigation the full-scale pieces.

Figure 9 also shows the front appearance of the curing rate after about 1/2 hour of heating (up to 105 ^{0}C), and its movement toward the colder material.

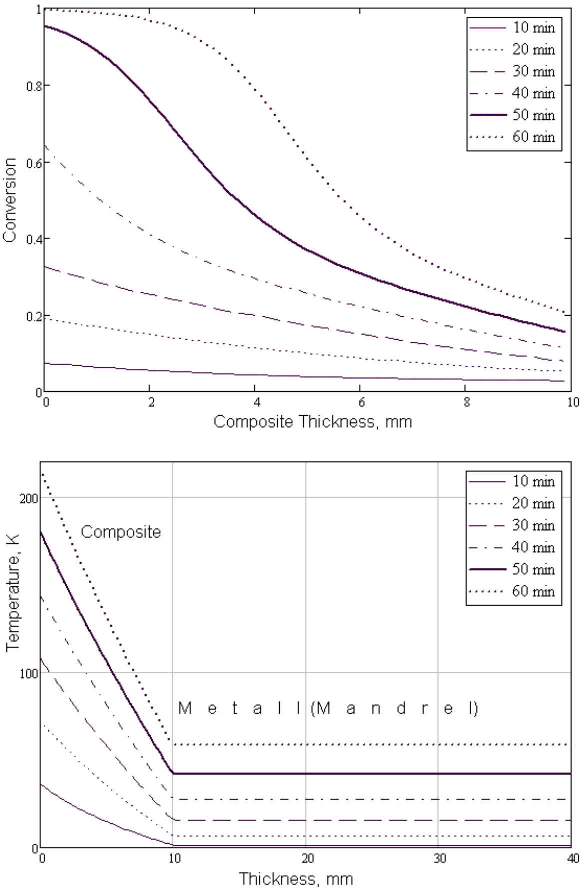

Fig. 8 Distribution of conversion (top) and temperature (bottom) inside composite cross section during heating with constant temperature rate

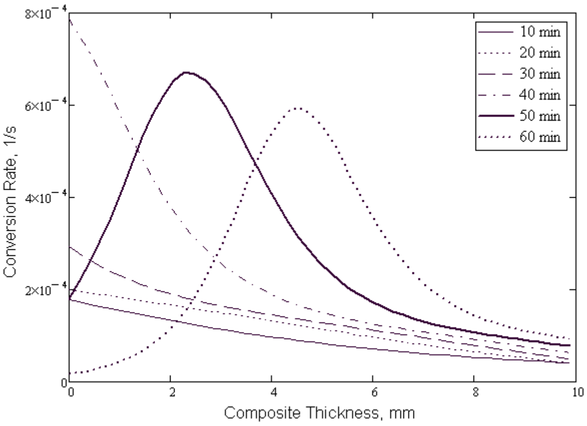

Fig. 9 Spatial distribution of conversion rate inside composite cross section

Dependence shown in Figure 10 has been obtained by integrating a differential exothermal heat flow in the region occupied by the composite. It illustrates the nature of the heat peaks which appeared during cure of the resin matrix. The first, less powerful exothermal heat peak corresponds to the first stage of the polymer chains formation, and the second peak - formation of a continuous polymerization front, moving inside a cross section of the composite material.

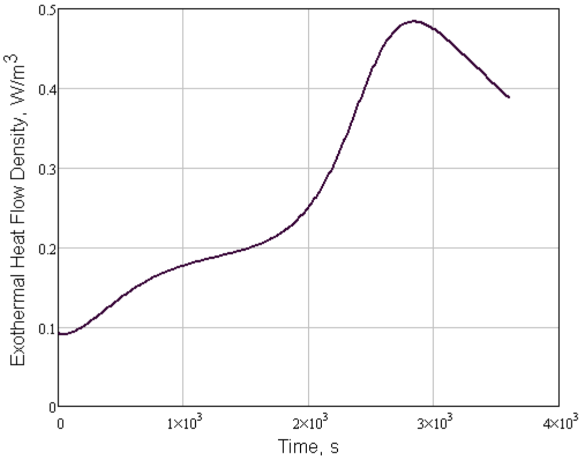

Fig. 10 Time chart of the exothermal heat flow during cure

The amount of heat consumed on heating the metal (see Fig. 11) is comparable to the amount of heat consumed on the formation of the polymer structure. Fully cured material has a much lower thermal conductivity. The regime of heating should be modified so as not to create overheat the outer layers of the composite, evaporation inside micropores of the matrix, which leads to degradation of the composite mechanical properties.

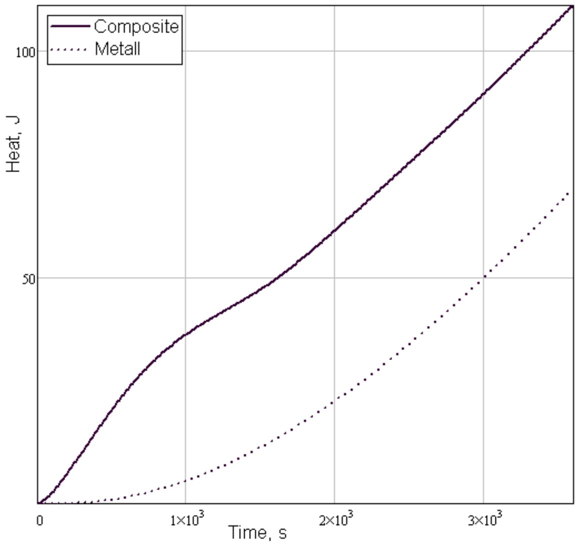

Fig. 10 The comparative time chart of the supplied heat which consumed by metal and by polymeric composite during cure

4 Conclusion

The model of spatially distributed curing process of epoxy matrix polymeric composite was developed and implemented using the finite element method. Developed model implementation allowed us to determine the critical factors controlled the quality parameters of the composite material, to ensure homogeneity of the matrix properties inside the cross section of products that defines a set of the material mechanical properties.

In order to avoid formation the internal peel and cavities due to overgrowth heating rate a problem of optimal heating control can be formulated using the developed FEM model. To do this we need to postulate some control law, depending on the group of parameters, as well as the cost function and technological constraints which ensure the minimal thermal stresses and distortions.

5 Acknowledgments

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