Modeling Processing of Silicone Rubber: Liquid Versus Hard Silicone Rubbers

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ABSTRACT: The processing of hard and liquid silicone rubbers (LSR) are compared by means of modeling and simulation. The curing process for both, hard and liquid silicone, are modeled using the auto-catalytic Kamal-Sourour model and a nonlinear regression method is used to find the kinetic parameters. The fitted kinetic model is then combined with the heat balance equations to simulate real processing conditions. Both resins are compared in terms of process performance and consistency of the final part. The results show that even though hard silicone rubbers are less expensive resins, its processing conditions present several issues of consistency and quality control when compared with LSR. Published 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 1864–1871, 2011

Key words: silicone rubber; cure kinetics; injection molding; finite elements

INTRODUCTION

Over the past 60 years, silicone rubbers have become increasingly popular in industry, mainly because this material maintains its mechanical and electrical properties over a wide range of temperatures. It is the natural choice in many applications ranging from aerospace to medical devices.[1–4] It is commonly used for the production of seals in the automotive and aerospace industry, connectors and cables for appliances and telecommunications, implants and devices for medical purposes, and packaging and baking pans for the food industry. Silicone rubber is a family of thermoset elastomers that have a backbone of alternating silicone and oxygen atoms with methyl or vinyl side groups. The solidification process of all heat-activated thermosets, including silicone rubber, is dominated by an exothermic and irreversible chemical reaction called cure, vulcanization or network polymerization.[5–8] The curing process forms a three-dimensional network in which each chain is connected to all others by a sequence of junction points and other chains. With low crosslink densities the product is a flexible elastomer, whereas it is a rigid material when the crosslink density is high. The curing process improves the general properties of the final product and provides resistance to heat, due to the fact that these network polymers do not melt upon heating.[5–8] Two types of reactions lead to crosslinked silicone rubber depending of the catalyst used for the curing reaction: peroxide and platinum.[9–12]

Silicone rubbers can be classified according to the polymer employed and the curing process as low-temperature-curing rubbers (RTV) and high-temperature-curing rubbers (HTV). RTV silicone rubbers come as a soft paste or a viscous liquid. HTV silicone rubbers come in two different physical states: liquid and solid. Because they exhibit a high viscosity solid silicone rubbers, commonly referred to as high consistency silicon rubbers, are processed in the same way as normal organic rubbers.[13]

Solid silicone rubbers (HSR) are formed using linear polymers with molecular weights between 400,000 and 600,000 g/mol. These polymers contain an average of 6000 siloxy units and are water clear Newtonian liquids with viscosities between 15,000 and 30,000 Pa s. Solid silicone rubbers are usually cured using two kinds of peroxide catalyst: aroyl-peroxides and alkyl-peroxides.[11,12] Aroyl-peroxides are used when the vulcanization process can be accomplished without pressure and they allow high reaction rates. Alkyl-peroxides are only used for vulcanization under pressure, as they do not form carbonic acids as decomposition products.[1,12] Liquid silicone rubbers (LSR) have the same structure as solid silicone rubbers. However, the chain length of the polydimethylsiloxane used for LSR is lower by a factor of about 6. Therefore, the viscosity of the polymer is reduced by a factor of about 1000.[1,3,12]

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The curing of liquid silicone rubber is almost exclusively carried out with a platinum-catalyzed hydrosilylation reaction, which does not generate by-products.[9,12]

For general purposes, solid silicone rubbers are less expensive resins than LSR. However, the type of reaction influences processing conditions and the quality of the final product. These factors directly determine the appropriate silicone rubber for a specific application. Solid silicone rubbers are preprocessed materials that are cured up to a certain degree and then stored in the form of foil-wrapped bars and packed cartons. To process solid rubbers a sheet is then cut or stamped to the required size and placed into a compression or transfer molder. After cure, the part is removed from the mold, deflashed and freed of the peroxide decomposition products in a postcuring process. Normally, these sequence of processes are hand-labor demanding and good quality control is hard to achieve. On the other hand, LSR are supplied in barrels or hobbocks. Because of their low viscosity, these rubbers can be pumped through pipelines and tubes to the cure equipment. The two components (A and B) are pumped to a static mixer by a metering machine were the curing process may start taking place; loss of material in the feed lines is avoided using cold runners.[9] Injection molding is one of the preferred methods to process LSR. Even though these machines can be expensive, they do not require personal during the process, whereas the quality and consistency are perfectly achieved.[9,13]

In this article, we rely on modeling and simulation to compare the performance and energy requirements of solid and liquid silicone rubber in a commonly used electrical connector. The article is organized as follows: in "Cure Kinetics" section we describe the modeling of the curing kinetics. Section "heat-transfer model" presents the balance equations used to model the process. In "Results" Section a set of results are shown. Finally, we conclude the most important remarks at the end.

CURE KINETICS

The mechanism for crosslinking of elastomers and thermosets is very complex because of the relative interaction between the chemical kinetics and the changing of the physical properties.[14] Two distinct approaches are commonly used: phenomenological and mechanistic. The former is related to an overall reaction, the latter to a kinetic mechanism for each elementary reaction occurring during the process. The phenomenological modes are semiempirical and do not provide a clear description of the curing process and its chemistry. They are based on an evolution equation for the degree of cure or extent of reaction.[14] This approach was selected for this research because even though the individual steps of the curing process of silicone rubber can be found in literature,[1–4,12] none have a kinetic model that describes the crosslinking process in real processing conditions.

The curing process can be described as the reaction between two chemical groups denoted by A and B, which link two segments of a polymer chain. The reaction can be followed by tracking the concentration of unreacted As or Bs, C_A or C_B. The degree of cure can be then defined as follows,[5,6,13,14]

$$c = \frac{C_{A,0} - C_A}{C_{A,0}}, \tag{1}$$

where $C_{A,0}$ is the initial concentration of A. The degree of cure is zero when there has been no reaction and equals one when all As have reacted and the reaction is complete. It is difficult to physically monitor reacted and unreacted As and Bs during the reaction without costly spectroscopy analysis. However, the degree of cure can be related to the heat released during the reaction because the curing of elastomers is an exothermic process. The energy released in the exothermal reaction is proportional to the crosslinked bonds formed, as it is assumed that each bond releases the same amount of energy.[5–8] The heat released during vulcanization can be calculated by,

$$Q = \int_0^{\tau} \dot{Q} dt, \tag{2}$$

where Q is the heat released up to time τ and $\dot{Q}$ is the instantaneous rate of heat released by the sample. The total heat of reaction, Q_T, is therefore equal to,

$$Q_T = \int_0^{\tau_{final}} \dot{Q} dt, \tag{3}$$

where τ_{final} is the time at which the reaction is complete. The reaction rate, dc/dt, is then calculated as,

$$\frac{dc}{dt} = \frac{\dot{Q}}{Q_T}. \tag{4}$$

The degree of vulcanization is obtained by integration of eq. (4),

$$c = \frac{Q}{Q_T} \tag{5}$$

For this article the kinetics of cure are modeled using the nth-order Kissinger[15,16] and the $(n+m)$th-order auto-catalytic Kamal-Sourour models,[17,18] following the work of Hernandez-Ortiz and Osswald.[13,19]

The challenge of modeling the curing is to take information from the differential scanning calorimeter (DSC) and find the parameters for the kinetic models. With this information, time-temperature-transformation diagrams (TTT),[20–22] for each resin, can be obtained and processes that involve curing can be simulated.[23–27] Typically, isothermal DCS scans were used to fit the models that describe the curing reactions.[22,26,27] However, several problems arise in the isothermal experiments. First, when performing isothermal scans it is challenging to reach the desired temperature as fast as possible. Second, at realistic processing temperatures, i.e., 150°C for LSR, the reaction rate is too fast to be accurately captured in the measurement. One misses a great part of the reaction by the time the isothermal temperature is reached. Hence, one is left to perform the isothermal tests at temperatures that are significantly lower, i.e., 40–60°C lower, than the processing temperature. This results in models where the process simulation is a gross extrapolation of DSC test results. In addition, all the techniques that use isothermal DSC data solved the fitted constants for each individual temperature, and later used a cumbersome fit to determine the temperature dependence.[22,26,27] Hernandez-Ortiz and Osswald[11,19] developed a technique to use the Kamal-Sourour model to fit dynamic DSC data. The kinetic parameters were expanded with a quadratic dependence on temperature. These fitted parameters do not necessarily have physical meaning; they were simply mathematical expressions that fit the experimental data, which can be used directly in numerical simulations. For this method the Kissinger model is used in conjunction with the Kamal-Sourour to give more insight into the reaction and find a physically meaningful value for the activation energy. The use of the combined models results in a more realistic and robust model for the reaction as shown in the work of Lopez et al.[11]

The liquid silicone rubber, denoted as LSR and the solid silicone rubber, expressed as HRS, were analyzed via thermal analysis to determine the progression of the curing processes, using the methodology of Hernandez-Ortiz and Osswald.[10,11,19] The specific properties being studied were peak temperature, heat of reaction, and extent of reaction. A DSC equipment manufactured by Netzsch (Phox DSC 200 PC) was used to measure the heat of reaction for the samples. Sealed aluminum pans were used to analyze all reactions. The mass of the samples ranged from 10 to 30 mg. A sealed empty pan was used as a reference. The total heat of reaction was measured by a dynamic scan from 20 to 150°C using heating rates of 1.0, 2.5, 5.0, and 10.0 K/min. Multiple scanning rates were used to gain insight into the effect of time and temperature on the vulcanization reaction. Repeatability was obtained for each heating rate. All experiments were performed under nitrogen purge.

As mentioned before, the autocatalytic Kamal-Sourour model is used to model the cure kinetics. It is defined as follows,[17,18]

$$\frac{dc}{dt} = (k_1 + k_2 c^m)(1 - c)^n, \tag{6}$$

where m and n are the reaction orders and k_1 and k_2 are the rate constants described by the Arrhenius equation, i.e.

$$k_i = a_i \exp\left(\frac{-E_i}{RT}\right). \tag{7}$$

The six parameters in the model (a_1, a_2, E_1, E_2, m, and n) can be fitted to the experimental DSC data via a least-squares estimation algorithm developed by Marquardt).[28,29] Karkanas, Partridge, and Attwood[30] found that the Kamal-Sourour model accurately predicts the degree of cure during early stage of reaction, however, at the later stage; it will over predict the degree of cure.[26,27] This deviation is due to the diffusion effects.[5,6] Thus, it is necessary to modify the Kamal-Sourour model to include the diffusion-limited part of the reaction. However, for elastomeric materials it is not necessary to modify the constants of the reaction due to diffusion, because the materials cure above their glass transition temperatures. For materials that cure before the vitrification point, the model accurately predicts the total process. This condition gives sufficient free volume between the molecules to allow for freedom of movement during the molecular cross-linking process, and therefore diffusion does not play a large role.

The Kamal-Sourour reaction model has six parameters that need to be fitted. Let $\mathbf{x}$ be the unknown vector parameter defined as,

$$\mathbf{x} = \{m \;\; n \;\; a_1 \;\; E_1 \;\; a_2 \;\; E_2\}. \tag{8}$$

Hernandez-Ortiz and Osswald technique uses one or more dynamic DSC scans, avoiding the problems that arise by using isothermal DSC data. The activation energy E_1 is determined through Kissinger's model, which is then used to mathematically determine the other five parameters for the Kamal-Sourour model. This technique finds a physically meaningful E_1. The activation energy, E_2, is fitted as a constant. The four remaining parameters (m, n, a_1, a_2) in the cure model are expanded into a power series of the temperature,[11,19] that is,

$$x_i = a_{i1} + a_{i2}T + a_{i3}T^2 + O(T^3), \tag{9}$$

where $i = 1,..,4$ and a_{ij} are the new goal of the fitting. In other words, instead of looking for the six parameters using isothermal data, the new technique looks for the 13 components of the **A** matrix defined in such a way that,

$$\mathbf{x}\begin{pmatrix} m \\ n \\ a_1 \\ a_2 \\ E_2 \end{pmatrix} = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \\ a_{41} & a_{42} & a_{43} \\ E_2 & 0 & 0 \end{bmatrix} \begin{pmatrix} 1 \\ T \\ T^2 \end{pmatrix} + O(T^3). \quad (10)$$

According to eq. (10) the higher terms in the expansion are neglected, according to this the fitting must be performed in such a way that the coefficient accompanying the second order term must be small. If this condition does not satisfy an specific set of data, the expansion cannot assure that the higher order terms are small, consequently, higher order terms must be included in the expansion (i.e. third, fourth). The parameters in the model are fitted via a least-squares estimation algorithm developed by Marquardt[28,29] (see also Press et al.[31] or Dennis and Schnabel[32]). Details of the numerical method to find the **A** matrix can be found in Hernandez-Ortiz and Osswald[19] and Lopez et al.[11]

Figure 1 shows the experimental and fitted Kamal-Sourour model for Liquid Silicone Rubber at rates from 1 K/min to 10 K/min. The figure illustrates the good performance of the nonlinear fitting technique. The values for the a_{ij} coefficients are summarized in Table I.[11]

Solid silicone rubbers present lower repeatability than liquid silicone rubber, because the material is prevulcanized up to a certain degree before storing. During storage, the rubber continues to crosslink at different proportions. The results of solid silicone rubber and one type of liquid silicone rubber were also compared. Various material samples were taken from one HSR batch and tested.[13] Because of the variation in the initial degree of cure between the samples, only one was chosen to fit the model. Figure 2 presents the fitted data and compares it to a LSR for similar applications. The fitted parameters for HSR are taken from a previous work[13] and are summarized in Table II. It should be noted that for this fitting the Kissinger equation was not used to compute the activation energy.

TABLE I
Fitted Parameters for a LSR Resin[11]

Parameter	O(1)	O(T)	$O(T^2)$
m	1.5533E + 02	−0.7588E + 00	9.3349E−04
n	1.7499E + 02	−0.8911E + 00	1.1426E−03
a_1	1.6554E + 15	2.8889E + 12	−1.8655E + 10
a_2	−5.8582E−05	2.4736E−07	−2.3529E−10
E_2	−36,800.93	0	0
E_1	124,850.53	0	0

As shown in Figure 2, silicone rubber vulcanizes at higher temperatures than liquid silicone rubber leading to larger cycle times and energy costs. In addition, the vulcanization rate of liquid silicone rubber is higher than the one of hard silicone rubber. A higher reaction rate will significantly reduce the cycle time, as it will be illustrated later.

HEAT-TRANSFER MODEL

To compare the process performance of LSR and HSR, we developed a model for the heat transfer of the curing process inside a mold. This simulation can be representative of transfer molding for HSR or injection molding for LSR.[13] We selected the

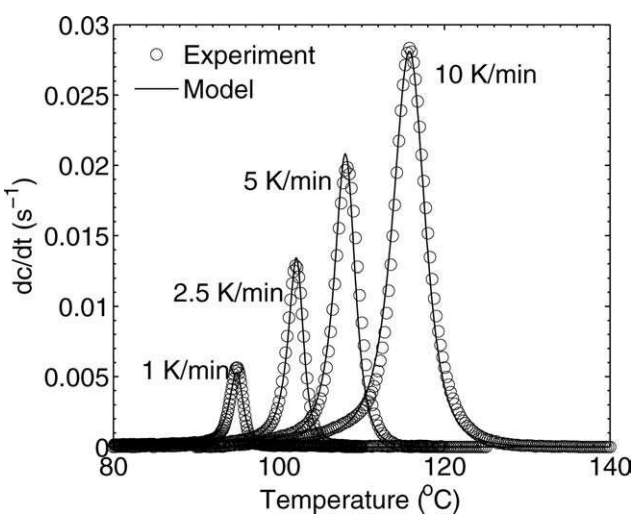


Figure 1 Fitted model and experimental data for a LSR resin.

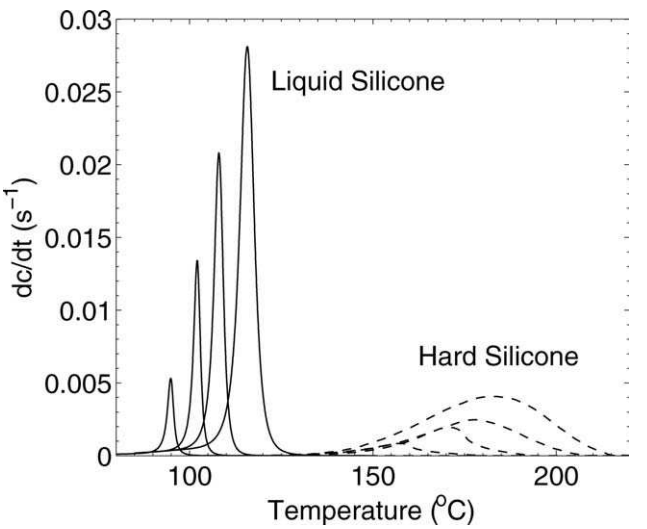


Figure 2 Comparison of degree of cure for liquid and solid silicone rubber.

TABLE II
Fitted Parameters for a HSR Resin[11,19]

Parameter	O(1)	O(T)	$O(T^2)$
m	8.4455E + 01	−5.5926E−01	9.0122E−04
n	2.0456E + 01	−1.0317E−01	1.2983E−04
a_1	1.6682E−22	−7.1679E−21	1.8524E−23
a_2	−1.5320E + 03	6.6209E + 00	−7.1566E−03
E_1	1.1447E + 05	−6.5515E + 02	2.1787E−01
E_2	−2.2411E + 05	1.4717E + 01	1.0666E + 00

electrical connector shown in Figure 4. The model will be restricted to analyzing the heat transfer during cure, in other words the process of injection will be neglected based on the fact that during injection of LSR the cure is avoided (cool running system).

The heat balance states that the accumulated energy must be equal to the conduction plus the heat generated during the curing process, i.e.

$$\frac{\partial}{\partial t}(\rho C_p T(\mathbf{x},t)) = \nabla \cdot (k \nabla T(\mathbf{x},t)) + \rho \dot{Q} \qquad (11)$$

where $T(\mathbf{x},t)$ is the temperature field, ρ is the density, C_P is the specific heat and k is the thermal conductivity. The heat release during cure is related to the cure kinetics from the definitions of eqs. (1)–(5). The boundary conditions are set to Dirichlet boundary condition for the points in contact to the mold:

$$T(\mathbf{x},t) = T_{\text{mold}} \quad \text{when} \quad \mathbf{x} \in \text{Mold}, \qquad (12)$$

and homogeneous Newmann conditions for the symmetry planes,

$$\nabla T(\mathbf{x},t) \cdot \mathbf{n} = 0 \quad \text{when} \quad \mathbf{x} \in \text{Symmetry}, \qquad (13)$$

where $\mathbf{n}$ is the normal vector.

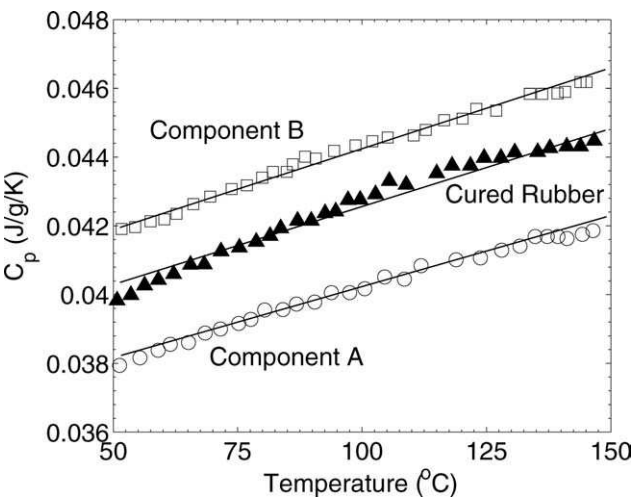


Figure 3 Specific heat for LSR: each component and cured rubber.

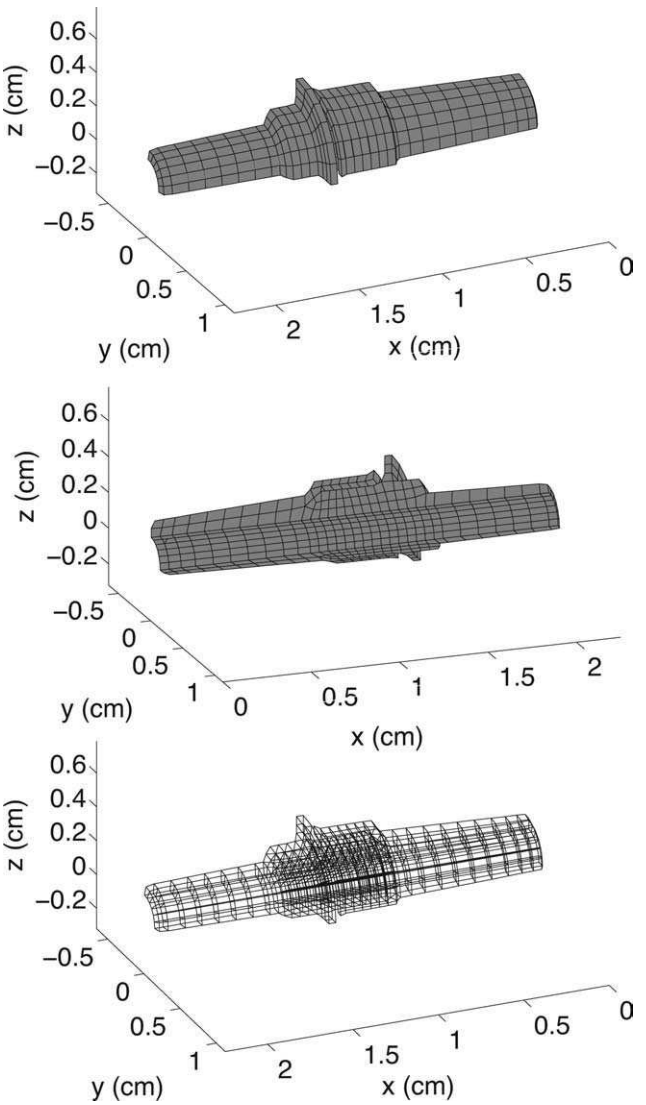


Figure 4 Analyzed geometry and FEM mesh: 3100 nodes and 2481 elements.

The density (ρ = 1800 kg/m^3) and conductivity (k = 50 W/m/K) of the materials we considered constant during the curing process while the specific heat was measured with DSC (see Fig. 3 for an LSR example) and its dependence to the cure and temperature was done by regular polynomial interpolation.[13] The numerical scheme use to solve the heat and cure kinetics equations was Finite Differences (FDM) with an Explicit Euler scheme for the time derivatives and Finite Elements (FEM) for the space gradients. Quadratic 20-noded brick elements were used for the FEM discretization[13,33] (see Fig. 4).

RESULTS

We start with the simulation of LSR processing. The mold temperature, after injection, is set to T_{mold} = 150°C at time zero. Because the two components were mixed before reaching the cavity at room

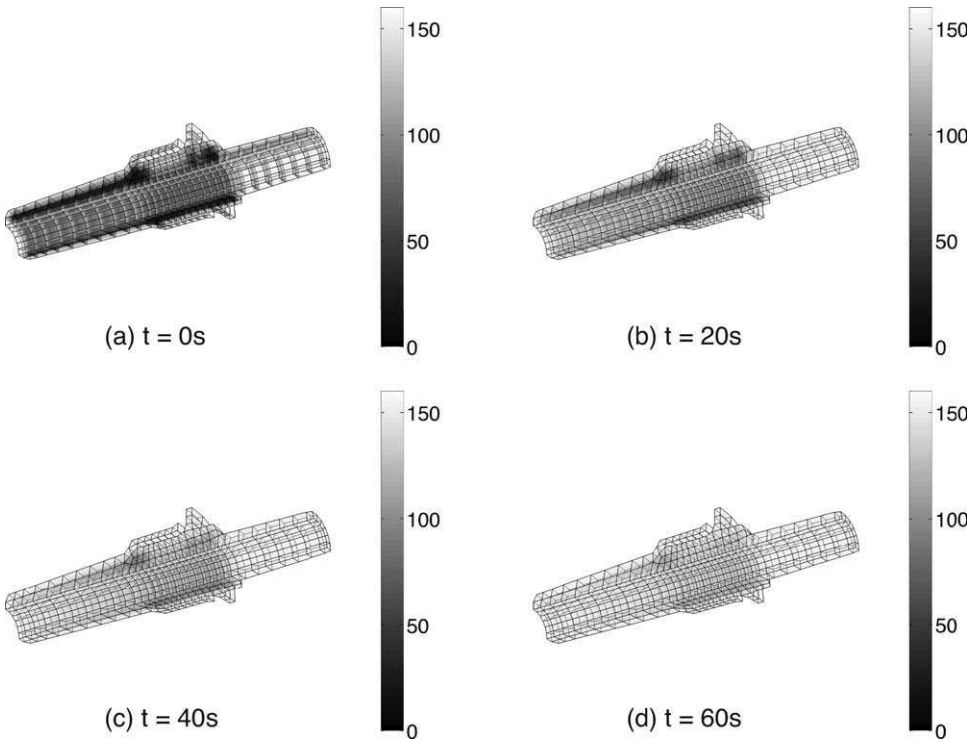


Figure 5 Temperature field as a function of time for LSR, $T_{\text{mold}} = 150°\text{C}$.

temperature the initial degree of cure is zero for all nodes. Figure 5 illustrates snapshots of the temperature field for different times, whereas Figure 6 shows the corresponding degree of cure. These results indicate that due to the kinetics of LSR, the processing goes smoothly and the curing is achieved

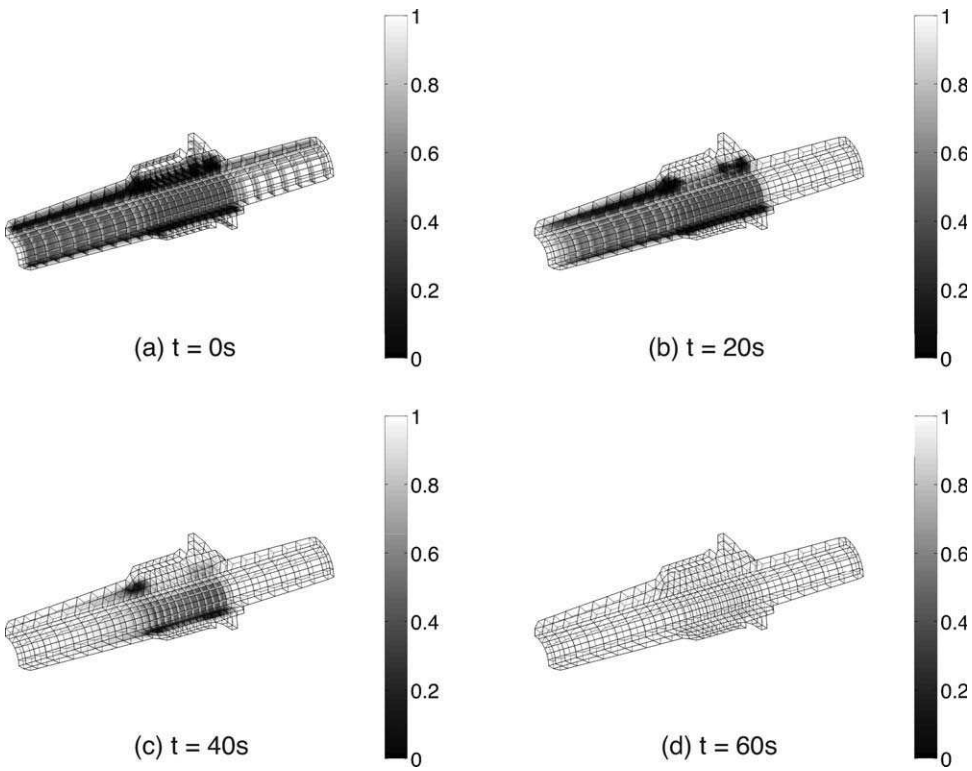


Figure 6 Degree of cure as a function of time for LSR, $T_{\text{mold}} = 150°\text{C}$.

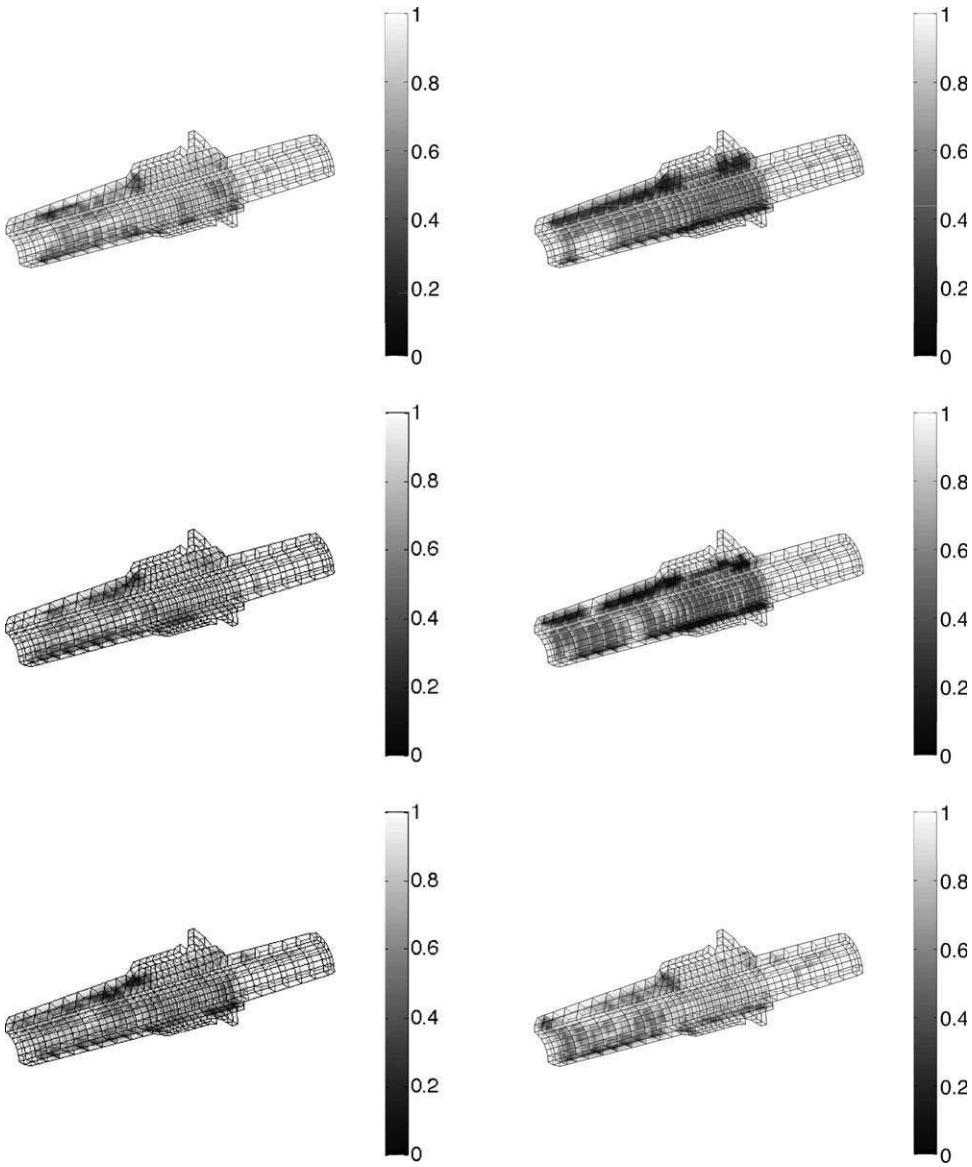


Figure 7 Degree of cure after 3 min for HSR, $T_{mold} = 250°C$.

in a minute with the given temperature. The curing time can be reduced using a higher mold temperature.

The simulation of HSR has additional inconvenients. The resin is not totally uncured at the beginning of the process and we can not control this initial degree for all the points in the geometry. Therefore, to make an approximation of real processing conditions, we start the simulation from a randomly distributed degree of cure between 0 and 0.05. Additionally, the mold temperature is increased to achieve an acceptable performance accordingly with the cure kinetics (see Fig. 2). Figure 7 illustrates the degree of cure for six different cure degree distributions at time zero, for a mold temperature of $T_{mold} = 250°C$. The results are after 3 min of processing. As indicated in these results, the curing of HSR does not evolve smoothly in time as LSR. The initial cure distribution affects the evolution and final stages of the cure process. To even the cure distribution the mold temperature must be increased further and probably also the processing time. Meaning that, in addition to the cumbersome process that HSR presents, in the sense that the precured sheets must be cut and placed in the mold by hand, the temperature and cycle time requirements are higher than LSR processing. Any increase in temperature and cycle time increases the energy requirement and decreases process performance.

The most intriguing result of Figure 7 is the poor capacity that processing HSR has in controlling the consistency of the final part. In some cases the cure degree is even lower than 0.5, which implies that postcuring is necessary.

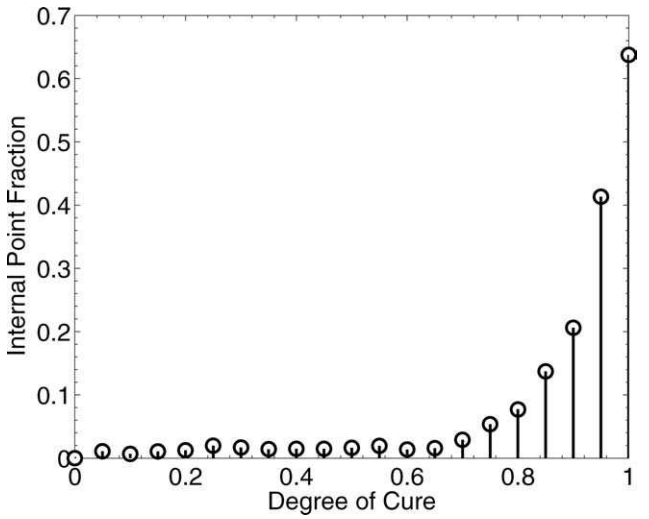


Figure 8 Average degree of cure distribution for 10 different runs.

We cannot rely on the postcuring during storage of the final parts due to the low kinetics that HSR presents at room temperature. This, in fact, will increase the hand-labor and energy requirements for HSR processing. Figure 8 shows the average degree of cure distribution, after 3 min of HSR, for 10 different runs. Even though most of internal points are fully cure, there are more than 30% uncured internal points. This is a direct indication of the difficulty of quality control in this type of processing.

CONCLUSIONS

Processing LSR has best performance, quality control and less energy requirement than HSR processes. The main problem of HSR comes from its cure kinetics, needed for the precured requirements of such processes. The accelerated kinetics at low temperatures of LSR, increases the processing performance, efficiency and control, which ensures that the final parts have a perfect consistency. LSR must be selected over HSR despite the cost of the resins.

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