

Analysis of the Development of Isotropic Residual Stresses in a Bismaleimide/Spiro Orthocarbonate Thermosetting Resin for Composite Materials

Mataz Alcoutlabi, Gregory B. McKenna, Sindee L. Simon

Department of Chemical Engineering, Texas Tech University, Lubbock, Texas 79409-3121

Received 30 December 2001; accepted 3 June 2002

ABSTRACT: In this article, we extend our model of isotropic residual stress development in thermosets to a novel thermosetting resin system: bismaleimide/spiro orthocarbonate. In this system, the cure shrinkage and resulting isotropic residual stresses are reduced through a ring-opening reaction that occurs independently of the addition reaction. The modeling effort includes a parametric analysis of the effects of various parameters, including the volume

changes involved in the reactions, the relative rates and orders of the reactions, the cure history, and the values of the bulk moduli and thermal expansion coefficients. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 227–244, 2003

Key words: thermoset; viscoelastic properties; residual stress; polymer cure; bulk modulus; cure shrinkage; ring opening polymerization

INTRODUCTION

Residual and internal stresses in thermosetting resins that arise because of differential shrinkage between fiber and resin during cure and subsequent thermal histories^{1–4} create a technological barrier to the successful implementation of polymer matrix composite materials in aerospace applications. For improved composite performance, it is desirable to have material models that allow the effects of the curing history and resin properties on residual stresses to be calculated. We have developed such a model for a conventional epoxy resin based on knowledge of the underlying polymer cure chemistry, the physics of thermoviscoelasticity, and the volume changes during and after cure.⁴ In this work, we model the development of isotropic (hydrostatic) residual stresses in a novel thermosetting resin consisting of a bismaleimide (BMI) monomer (Ciba–Geigy Matrimid 5292 A, Ardsley, NY) that reacts with a novel difunctional alkyl comonomer.⁵ The comonomer contains a spiro orthocarbonate (SOC) group in its backbone that undergoes a ring-opening reaction independently of the BMI addition reaction. This type of resin is expected to have reduced cure shrinkage and, correspondingly, reduced residual stresses due to the ring-opening expansion of the SOC moieties.

Over 20 years ago, Bailey and coworkers^{6–8} proposed exploiting SOC ring-opening chemistries to reduce stresses in composites. Shrinkage stresses can theoretically be reduced significantly when these expanding resins are added to epoxies as long as the ring-opening reaction occurs after gelation. Bailey and coworkers found that the composites produced from 80% dinorbornene spiro orthocarbonate and 20% epoxy had zero cure shrinkage. In addition, compared with the all-epoxy composite, the system with SOC showed increased toughness and shear strength, although it also had a lower glass-transition temperature (T_g).⁸ Lam and Piggott⁹ similarly found increases in impact resistance and toughness without a loss of shear strength in a similar epoxy/SOC copolymer containing up to 20% expanding monomer. Howell¹⁰ found improved mechanical properties for an epoxy resin when as little as 5% expanding monomer was incorporated. He and Zhou,¹¹ however, found that although a dinorbornene spiro orthocarbonate resin and an epoxy cured with boron trifluoride amine resulted in zero shrinkage, the fracture strength, T_g , and thermal stability all decreased. Ochi et al.¹² attributed the reduction in the internal tensile stress of the systems studied to the lower modulus and T_g of the modified system rather than to the reduction in shrinkage during cure. Chou and Penn¹³ similarly reported that the reduction of residual stresses in an epoxy system that contained spiro compounds was due to a decrease in T_g and modulus. The decrease in T_g was attributed to plasticization by the spiro compounds, which were found to not react during cure. Chou and Penn also calculated the residual stresses in the composite laminate as a plane stress problem.

Correspondence to: G. B. McKenna (greg.mckenna@coe.ttu.edu) or S. L. Simon (sindee.simon@coe.ttu.edu).

Contract grant sponsor: Air Force Office of Scientific Research; contract grant number: F49620-01-1-0079.

As the literature reviewed shows, it is important to understand how the addition of SOC may adversely affect properties other than cure shrinkage. In addition, it is essential that SOC can undergo ring opening in a timely fashion during the reaction. An issue with epoxy/SOC systems is that the cationic catalyst that promotes ring opening also promotes the more reactive epoxy group to polymerize. This problem is not an issue with the BMI/SOC resin⁵ that we are investigating because the two reactions involved are promoted with different catalysts. In addition to their reduced shrinkage through the ring opening of SOC, potential advantages of this BMI/SOC system are a high T_g and good thermal stability. The modeling work presented in this article directly addresses the effects of these chemistries and curing reactions on isotropic residual stress development.

THEORETICAL DEVELOPMENT

The origin of residual and internal stresses in polymer matrix composites is the differential volume change between the fiber and resin during the cure and subsequent thermal histories.^{1–4,14–16} Residual stresses have both deviatoric and isotropic (hydrostatic) components. The case of uniaxial or in-plane stresses, which include both shear and isotropic components, has been treated in detail by several groups of researchers.^{1–3,14–16} In this case, the cure temperature (T_c) is generally taken to be the stress-free temperature, and the shrinkage during cure is neglected because of the low tensile modulus in the rubbery state.^{1–3,14,15} Seferis et al.¹⁷ similarly modeled residual in-plane stresses for thermoplastic composites. The isotropic (hydrostatic) case for thermosets was treated qualitatively by Plepys and Farris.¹⁶ One recent quantitative model of the evolution of residual stresses in three-dimensionally constrained thermosets was developed by Simon et al.,⁴ and we extend that work here to predict the development of isotropic residual stresses in a novel BMI/SOC thermosetting resin under development for the U.S. Air Force.

The model used here for the development of isotropic residual stresses during the cure of composite materials incorporates six ingredients: (1) the principle of time–temperature superposition, (2) the principle of time/crosslink density (time–conversion) superposition, (3) the evolution of the viscoelastic bulk modulus during cure, (4) the point of incipient gelation, (5) the kinetics of the cure reactions in the crosslinking system, and (6) the volume change due to the cure and thermal history.⁴ We note that for the calculation of the deviatoric stresses, the theory of rubbery elasticity is also needed to account for changes in the rubbery modulus after gelation.

The principle of time–temperature superposition is widely used in the description of polymer behavior at

temperatures above T_g at which the viscoelastic response function changes with temperature by a change in the timescale (or frequency scale) by a shift factor a_T .¹⁸ The shift factors used to reduce viscoelastic data often follow the Williams–Landel–Ferry (WLF) equation¹⁹ (or the equivalent Vogel equation²⁰) or, in the case of some crosslinked polymers, the Arrhenius equation.^{21,22} This principle has been widely used in models of the evolution of the viscoelastic properties and residual stresses in thermosetting and polymer composites.^{4,23–29}

The principle of time/crosslink density superposition can be used to describe the dependence of the viscoelastic response at T_g on the extent of reaction in highly crosslinked thermosetting polymers. This principle, which was originally suggested by Plazek³⁰ for rubber, asserts that the changes in the crosslink densities of polymer networks are reflected in a timescale shift of the viscoelastic response. Time/crosslink density superposition was also used by Lee and McKenna³¹ to describe the effect of the crosslink density on stress relaxation during physical aging in model epoxy compounds. A research group at Sandia National Laboratories, in the course of studies on residual stresses in composite materials,^{23–26} has provided a slightly different method of superposing the viscoelastic functions at differing extents of reactions through a dynamic scaling theory for the viscoelasticity of crosslinked polymers near the gel point; that is, the crosslinking polymer was considered to be self-similar, with a change in the conversion resulting in a change in the timescale. In their work, to superpose the stress relaxation modulus of several epoxy systems, a vertical shift was used to account for the increase in the equilibrium modulus with cure, and a horizontal shift was used to account for the divergence of the characteristic relaxation time. More recently, the principle of time–conversion superposition was applied to a model of isotropic residual stress development by Simon et al.⁴ In that work, the stress relaxation function was assumed to depend on T_g of the material. In essence, this provides a model for the viscoelastic behavior of the material through T_g –time superposition. Then, with the relationship between T_g and conversion, time–conversion superposition is obtained.

Another ingredient needed to model isotropic residual stresses is quantitative knowledge of the time, temperature, and conversion dependence of the bulk relaxation modulus. However, there are scant data on the time or frequency dependence of the bulk modulus (K) of polymers,^{32–34} and there are no systematic studies of the evolution of K during the cure of thermosetting materials. The Sandia group implicitly ignored the viscoelastic character of K (i.e., K was not dependent on time in their model).^{25,26} In the recent work of Simon et al.,⁴ it was assumed that the relax-

ation function for K was identical to that of the shear modulus. Experimental evidence based on the work of Deng and Knauss³⁴ and Yee and Takemori,³⁵ as well as calculations based on the work of Tschoegl,³⁶ indicate that this assumption is not strictly correct, but it provides an approximation of the time dependence of K in the absence of appropriate data.

The fourth ingredient needed to calculate isotropic residual stresses in thermosetting resins is the incipient point of gelation, which is the moment at which the system starts to gel and the concentration of the network chains becomes nonzero. Of importance are both the conversion (x_{gel}) and the temperature (T_{gel}) at which gelation occurs. Knowledge of x_{gel} is necessary for calculating isotropic stresses due to shrinkage during cure because these are generally assumed to develop only after the gel point. The Sandia group^{25,26,37} calculated the curing stresses for an epoxy resin and showed that these stresses are dependent on the difference between conversion and conversion at gelation (i.e., $x - x_{\text{gel}}$). Simon et al.⁴ calculated the development of isotropic residual stresses for an epoxy resin and also explicitly stated that the curing stresses depended on $x - x_{\text{gel}}$, as well as T_{gel} .

We note that in the model of Simon et al.,⁴ the isotropic residual stresses are calculated from the integral of the product of K multiplied by the strain derivative with respect to both cure shrinkage and subsequent thermal history (discussed later). Integration is performed only after gelation (i.e., from the time at which gelation occurs, t_{gel}) because before gelation the resin can flow and the system is not three-dimensionally constrained.⁴ However, for some special processing conditions, the material may be constrained before gelation. In such a case, the integral should be evaluated from the time at which the three-dimensional constraints are imposed.

The fifth ingredient needed to calculate the residual stresses in curing materials is knowledge of the cure kinetics. This knowledge is necessary for modeling the evolution of the viscoelastic properties for thermosetting materials as a function of time during cure. Models of residual stress development during cure for thermosetting composite materials generally incorporate the cure kinetics of the material.^{4,25,26,37}

The sixth and last ingredient needed to calculate curing and thermal residual stresses is the volume shrinkage during and after cure. The curing stresses are dependent on the parameter dV/dx , which is generally considered to be a constant associated with the change in volume due to a unit change in conversion associated with the difference between the lengths of van der Waals and covalent bonds. The thermal stresses, however, are due to the differential volume change on cooling (or heating). dV/dx is constant in the model of Simon et al.⁴ and in the later work of the Sandia group.^{25,26,37} The

thermal stresses can be calculated from the integral of αKdT , where α is the thermal expansion coefficient and T is the temperature. Simon et al. used a convolution integral for calculating the thermal stresses and assumed that K varied with time, temperature, and conversion and that α varied with temperature and conversion, whereas the research group at Sandia National Labs assumed that the product of $K \times \alpha$ was constant in the rubbery and glassy regions; that is, $\alpha_g K_g = \alpha_r K_r$, where the subscripts r and g refer to rubbery and glassy regimes, respectively. However, this assumption is not necessarily valid (see McKinney and Belcher³² and Colucci et al.,³⁸ who showed that a deviation from this assumption could be as great as 60%; this is also discussed later in this work).

In addition to the aforementioned ingredients, the relationship between T_g and conversion is needed when time- T_g superposition is used. Several equations have been used to describe the T_g -conversion relationship for thermosetting polymers.³⁹⁻⁴² The DeBenedetto⁴³ equation was employed by Simon et al.²⁹ in their model of stress development in an epoxy material. This equation, however, is not expected to be valid for this BMI/SOC system because of the chain reactions involved. Using these ingredients, Simon et al.⁴ simulated the effects of a cure history on isotropic residual stresses. The results obtained demonstrated that cure shrinkage contributes significantly to the total residual stresses and that the stress-free temperature cannot be assumed to be T_c for the isotropic case. In addition, they showed that T_{gel} is a very important parameter for minimizing isotropic residual stresses. In this case, a linear relationship between residual stresses at room temperature (RT) and T_{gel} is obtained when vitrification does not occur during cure. This result is consistent with the experimental work of Plepys and Farris¹⁶ and Madhukar and coworkers,^{44,45} as well as the modeling results of the Sandia group.^{25,26}

Here we examine how much of a reduction in the isotropic residual stresses can be obtained through a novel BMI chemistry that incorporates an independent ring-opening reaction. We use a parametric analysis that includes the effects of the volume changes involved in the BMI and ring-opening reactions, the relative rates and orders of the two reactions, the cure histories, and the product of $K \times \alpha$ in both rubbery and glassy states. The weight fractions of the monomer and polymer (w_{monomer} and w_{polymer} , respectively), the crosslink density, and the point of incipient gelation, all needed for the T_g -conversion relationship, are determined by the application of the recursive technique of Miller and Macosko^{46,47} for chain polymerization.

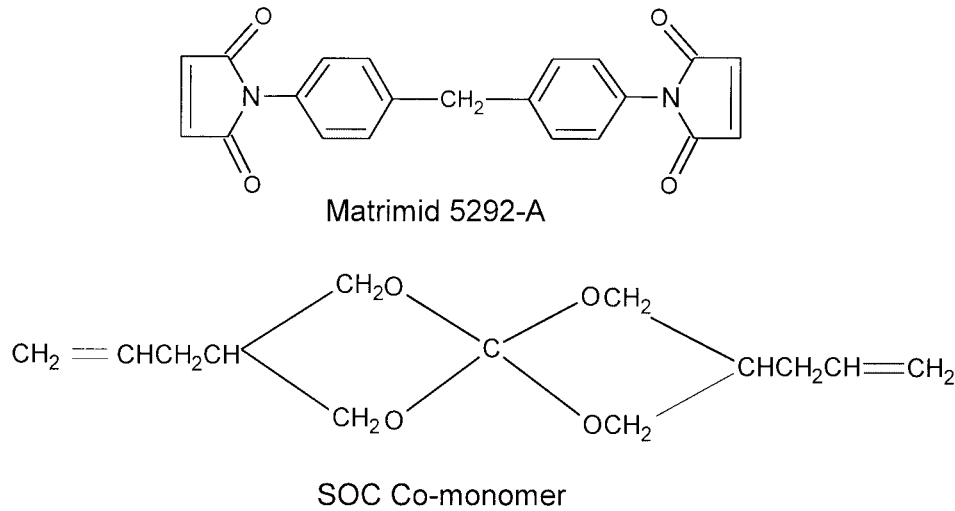


Figure 1 Chemical structure of the Matrimid 5292-A and SOC monomers.

MATERIAL CHEMISTRY

The calculations were performed for a BMI resin consisting of a Ciba-Geigy Matrimid 5292A (BMI) and an SOC comonomer, the latter of which was synthesized by Polycomp Technologies (Del Mar, CA).⁵ The chemical structures of the monomers are shown in Figure 1. Two reactions occur: the addition of the double bond in the pyrroline ring of the Matrimid BMI monomer with the allyl group on the SOC comonomer and a ring-opening reaction of the SOC group in SOC. Figure 2 shows the ideal polymeric structure when both reactions have occurred.

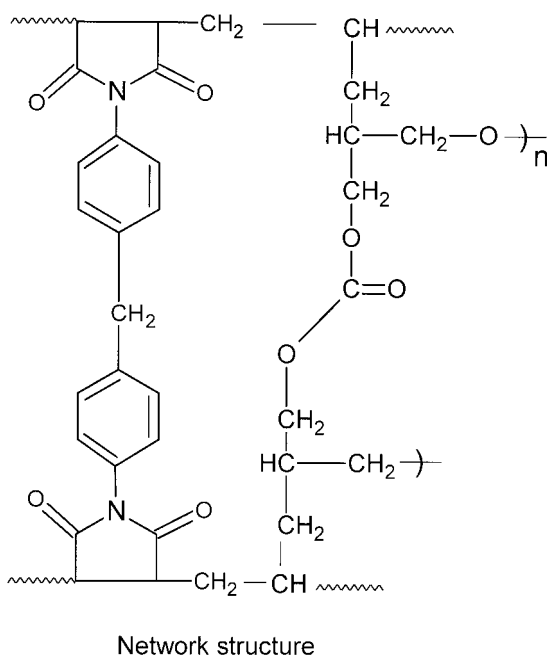


Figure 2 Chemistry of the BMI/SOC thermosetting system.

The BMI addition occurs through free-radical polymerization, whereas the SOC ring opening occurs via cationic polymerization. Therefore, the rates of the BMI addition and SOC ring-opening reactions are assumed to be independent because the initiators used to promote the two reactions can differ.

MODELING METHODOLOGY

The time evolution of the isotropic residual stresses, $\sigma_{\text{res}}(t)$, in a fully constrained resin is given by the convolution integral:

$$\sigma_{\text{res}}(t) = - \int_{t_{\text{gel}}}^t K(t - t', T, T_g) \frac{d\epsilon}{dt'} dt' \quad (1)$$

where $K(t - t', T, T_g)$ is the bulk modulus, $t - t'$ is the time elapsed from time t' of the applied strain ϵ , and T is the absolute temperature. ϵ in the resin arises from the differential shrinkage between the resin and the substrate constraining it, such as the fibers in a composite material or a mold wall. We note that eq. (1) implies linear viscoelasticity and Boltzmann superposition. If the resin is isotropic, the differential strain in the resin results from volume changes due to both cure shrinkage and temperature changes. For the BMI/SOC system, we consider the effect of both ring-opening (volume expansion) and addition (volume shrinkage) contributions to the strain evolution:

$$\frac{d\epsilon}{dt} = \frac{1}{V} \frac{dV}{dt} = \frac{1}{V} \left[\left(\frac{\partial V}{\partial x_1} \right)_T \frac{dx_1}{dt} + \left(\frac{\partial V}{\partial x_2} \right)_T \frac{dx_2}{dt} \right] + \frac{1}{V} \left[\left(\frac{\partial V}{\partial T} \right)_x \frac{dT}{dt} \right] \quad (2)$$

where dx_1/dt and dx_2/dt in eq. (2) are the reaction rates of the BMI addition and SOC ring-opening reactions, respectively. These can be calculated from knowledge of the cure kinetics (discussed later). $(\partial V/\partial x_1)_T$ and $(\partial V/\partial x_2)_T$ are constants associated with the changes in volume due to a unit change in the conversions of the addition and ring-opening reactions, x_1 and x_2 , respectively. $(1/V)(\partial V/\partial T)_x$ is α , which is a function of $T - T_g$. dT/dt text math is the change in temperature in the cure cycle or any subsequent thermal history. This equation assumes that α of the fiber array or other constraint is zero; if not, $(\partial V/\partial T)_x$ must be replaced by the differential volume change with temperature [e.g., $(\partial V/\partial T)_{\text{resin}} - (\partial V/\partial T)_{\text{fiber}}$].

K is assumed to depend on the time, temperature, and conversion in the following manner:²⁹

$$K(t, T, T_g) = K_r + (K_g - K_r) \sum_{i=1}^n g_i \exp(-(t/a_{T,T_g} \tau_i)) \quad (3)$$

where K_r and K_g are the rubbery and glassy values of K , both of which are assumed to not be a strong function of temperature or conversion, and t is time. τ_i is the i th relaxation time, and g_i is the weighting factor for τ_i , such that $\sum g_i$ is equal to 1.0. The dependence of τ_i on temperature and conversion can be explained by the principles of time-temperature^{18,19} and time- T_g ^{30,31} superposition. The shift factor a_{T,T_g} depends on temperature and T_g :

$$\log a_{T,T_g} = \log \frac{\tau_i[T, T_g(x)]}{\tau_i[T_{\text{ref}}, T_g(x_{\text{ref}})]} = \left(\frac{C}{T - T_\infty} - \frac{C}{T_g(x) - T_\infty} \right) \quad (4)$$

where C and T_∞ are constants. The subscript "ref" refers to the reference condition, either temperature T or conversion x . The general Vogel²⁰ dependence is used because it is capable of describing both the WLF equation¹⁹ (in which $T_\infty = T_g - C_2$, where C_2 is a constant) and the Arrhenius dependence^{21,22} (in which $T_\infty = 0$ K). $T_g(x)$ emphasizes that T_g is a function of conversion for thermosetting resins. The derivation of this equation assumes $T_{\text{ref}} = T_{g^\infty}$.²⁹

To use eqs. (3) and (4) to describe the evolution of K during cure, we need the relationship between T_g and conversion, as well as the cure kinetics. For the BMI/SOC system, the reactions are chain reactions, with the result that the reaction mixture will be composed of monomer and high molecular weight polymer. Consequently, T_g is assumed to depend on w_{monomer} and w_{polymer} .⁴⁸

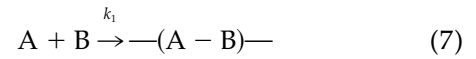
$$\frac{1}{T_g} = \frac{w_{\text{monomer}}}{T_{g0}} + \frac{w_{\text{polymer}}}{T_{g(\text{polymer})}} \quad (5)$$

where T_{g0} is the glass-transition temperature of the monomer and $T_{g(\text{polymer})}$ is the glass-transition temperature of the crosslinked polymer, which is a function of the crosslink density as described by Hale et al.⁴¹ on the basis of the work of DiMarzio:⁴⁹

$$T_{g(\text{polymer})} = \frac{T_{gu}}{1 - \frac{ZX}{1 - \psi X^2}} \quad (6)$$

where T_{gu} is the glass-transition temperature of the uncrosslinked polymer, Z and ψ are constants, and X is the crosslink density of the BMI/SOC resin.

The cure kinetics of the BMI/SOC system are assumed to be first-order reactions:



where k_1 is the rate constant of the BMI addition reaction and k_2 is the rate constant of the ring-opening reaction. A is the maleimide double bond, B is the allyl group double bond on the SOC monomer, and C is the spiro group on the SOC monomer. Therefore, for a first-order reaction, the reaction rates of the BMI addition and SOC ring-opening reactions are

$$\frac{dx_1}{dt} = k_1(1 - x_1) \quad (9)$$

$$\frac{dx_2}{dt} = k_2(1 - x_2) \quad (10)$$

The rate constants k_1 and k_2 are both temperature-dependent. The Arrhenius equation ($k_{i_a} = Ae^{-E/RT}$) describes the general temperature dependence of the rate constant k_{i_a} in the absence of diffusion control. However, when the material vitrifies during cure, diffusion control dominates the reaction, and the effective rate constant decreases. The effect of diffusion control can be incorporated into the kinetics of the reaction according to the methodology applied in the original model of Simon et al.:²⁹

$$\frac{1}{k_i} = \frac{1}{k_{i_a}} + \frac{1}{k_d} \quad (11)$$

where the rate of diffusion, k_d , is assumed to follow the form of the Doolittle equation⁵⁰ with the universal WLF parameters.¹⁹

$$k_d = k_{d0} e^{-(B/f)} \quad (12)$$

$$f = (T_c - T_g)(4.8 \times 10^{-4}) + 0.025 \quad (13)$$

where B is a constant and f is the free-volume fraction, which is considered to depend on the distance ($T - T_g$).

Using the methodology presented previously, we can calculate the isotropic residual stresses in the BMI/SOC resin system as follows:

$$\sigma_{\text{res}}(t) = - \int_{t_{\text{gel}}}^t K(t - t', T, x_1) \times \left(\frac{1}{V} \left[\frac{\partial V}{\partial x_1} \frac{dx_1}{dt'} + \frac{\partial V}{\partial x_2} \frac{dx_2}{dt'} \right] + \frac{1}{V} \frac{\partial V}{\partial T} \frac{dT}{dt'} \right) dt' \quad (14)$$

The model parameters needed to apply this equation include the cure kinetics, the relative volume shrinkage per unit conversion for each reaction ($\partial V/\partial x_1$ and $\partial V/\partial x_2$), the thermal expansion in glassy and liquid regimes ($(1/V)(\partial V/\partial T)_g$ and $(1/V)(\partial V/\partial T)_r$), K_g and K_r , and the T_g -conversion relationship, as well as the parameters g_i , τ_i , C , and T_∞ . The integration in eq. (14) is performed only after gelation because before gelation the resin can flow and the system is assumed to not be three-dimensionally constrained. Because the BMI addition reaction results in a crosslinked structure, whereas the SOC ring opening results in a flexible linear linkage, gelation is assumed to occur when the crosslink density arising from the BMI addition reaction becomes nonzero. The extent of the addition reaction at gelation, $x_{1,\text{gel}}$, determined with Miller and Macosko's recursive method, as described in the appendix, was found to be just greater than zero because of the nature of the chain reaction. The conversion of the SOC ring opening at the gelation of the system, however, varies from 0 to 100%, depending on the relative rates of the addition and ring-opening reactions.

PARAMETER ESTIMATION

To evaluate the influence of the cure chemistry and resin properties on the development of isotropic residual stresses in the BMI/SOC resin, we need to estimate some particular parameters, such as the relative volume changes involved in the ring-opening and addition reactions, the volume changes due to the thermal history (i.e., the thermal expansion coefficients), K_r and K_g , and the dependence of T_g on the network formed (i.e., T_g -conversion relationship). We emphasize that, although these parameters can be measured, the focus of this work is on development of the methodology to predict isotropic stresses in the

absence of measured material properties. The primary goal is to examine the predicted effect of the SOC reaction on the isotropic stresses. In the course of the work, additional insights concerning possible strategies for isotropic residual stress mitigation were obtained, and these are discussed later.

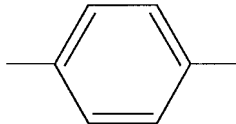


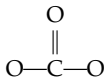
The relative volume shrinkage per unit conversion for each reaction in the BMI/SOC system, $(1/V)(dV/dx_i)$, was determined from the Van Krevelen group contribution method, which allows the molar volume of a monomer (or polymer) to be estimated as a function of its structure.⁵¹ This method assumes that the molar volumes of the constituent groups are additive. For some constituent groups, the molar volume contributions were not tabulated by Van Krevelen. We assumed for these groups that the molar volume contribution was equivalent to 1.5 times the van der Waals volume. Table I shows the constitutive group molar volumes used. The values are for the rubbery state at RT. The molar volumes of BMI and SOC are estimated to be 277.85 and 220.69 cm³/mol, respectively, and the total volume of the reactants is 249.27 cm³/mol. In the same way, the total molar volume value, V_{total} , of the fully reacted system (SOC and BMI) was calculated; this value is 235.75 cm³/mol on the basis of the moles of monomer units in the system. Table II shows the values of monomer molar values and the percentage change in the BMI/SOC reaction. As shown in Table II, the relative volume shrinkage for the addition reaction is $(1/V)(dV/dx_1) = -5.4\%$, whereas the relative volume shrinkage for the SOC reaction in the BMI/SOC networks is $(1/V)(dV)/(dx_2) = \nu_{\text{SOC}}(\Delta V_{\text{ring-opening}}/V_{\text{SOC}}) = 0.9\%$ to the total volume of the polymer. Here, ν_{SOC} is the volume fraction of the SOC comonomer, and it is equal to 0.477 for a 1:1 stoichiometric ratio of BMI and SOC, $\Delta V_{\text{ring-opening}}$ is the volume change in SOC when undergoing ring opening, and V_{SOC} is the molar volume of the SOC monomer. The total (relative) volume change on full conversion for both reactions can then be calculated as follows:

$$\frac{\Delta V_{\text{total}}}{V_{\text{total}}} \approx \frac{\Delta V_{\text{addition}}}{V_{\text{total}}} + \nu_{\text{SOC}} \frac{\Delta V_{\text{ring-opening}}}{V_{\text{SOC}}} \approx -0.045 = -4.5\% \quad (15)$$

$\Delta V_{\text{addition}}$ is the volume change in BMI when undergoing an addition reaction, and V_{total} is the total volume of the reactants. At full conversion, the SOC ring-opening reaction is estimated to decrease shrinkage due to cure by 17% $[(0.054 - 0.045)/0.054 \times 100\%]$.

The values of α for the BMI/SOC resin in the glassy and liquid regimes, $(1/V)(\partial V/\partial T)_g = \alpha_g$ and $(1/V)(\partial V/\partial T)_r = \alpha_r$, were estimated by the averaging of the experimental data of several polymers reported in the literature.⁵² These polymers are polycarbonate,

TABLE I
Constituent Group Molar Volumes (V_R) and Group Contributions (m_i and $Y_{g,i}$) Used in the Calculations of the Volume Change and T_g during Cure of the BMI/SOC Resin

Groups	V_R (cm ³ /mol) ^a	m_i (g/mol) ^a	$Y_{g,i}$ (K kg/mol) ^a
—CH=CH—	27.75	N/A	N/A
—CH ₂ —	16.45	14.03	2.7
=CH—	13.87	N/A	N/A
—CH— 	9.85	13.02	17.7 ^b
—C— 	4.75	N/A	N/A
	61.4	76.09	29
—O—	8.5	N/A	N/A
=CH ₂	17.9 ^c	N/A	N/A
	17.55 ^c	28.01	9
	24 ^c	N/A	N/A
—N— 	N/A	14	17.7 ^b
	N/A	60	20

The values are for the rubbery state at room temperature. N/A = not applicable.

^a From ref. 51 unless otherwise noted.

^b These values were not tabulated in ref. 51 and were estimated from the relationship with some similar groups.

^c V_R estimated from $1.5 V_W$, where V_W is the van der Waals volume from ref. 51.

poly(methyl methacrylate), polystyrene, poly(vinyl acetate), polysulfone, and poly(2,6-dimethylphenylene ether). The values of α for the BMI/SOC resin are, therefore, taken to be $\alpha_g = 2.55 \times 10^{-4} \text{ K}^{-1}$ and $\alpha_r = 6.00 \times 10^{-4} \text{ K}^{-1}$. In the same way, the values of K_g and K_r of the BMI/SOC system were calculated from the averages of the values for the same six polymers as reported in ref. 52. These values are calculated to be K_r

$= 1.75 \times 10^9 \text{ Pa}$ and $K_g = 3.10 \times 10^9 \text{ Pa}$. It is important to note here that $\alpha_g K_g = 0.79 \text{ MPa/K}$ and $\alpha_r K_r = 1.05 \text{ MPa/K}$; this illustrates that αK is not constant in traversing the glass transition. We remark that these average values of αK were chosen to be representative. However, without better group additivity methods or data, we acknowledge that they may not be correct for the specific system modeled here. Therefore, our model is expected to be qualitative in this sense. However, the specific influence of αK on the magnitudes of the residual stresses is examined subsequently, and the insights from the relevant results are discussed.

In addition to the aforementioned parameters, the dependence of T_g on the crosslink density (or on the conversion) must be established. In this work, T_g of the BMI/SOC networks is calculated from Fox's equation [see eqs. (5) and (6)], in which T_g depends on w_{monomer} and w_{polymer} , T_{g0} , and $T_{g(\text{polymer})}$, which, in turn, depends on X . w_{monomer} and w_{polymer} were cal-

TABLE II
Monomer Volume Values (V_i) and Percentage Change on the BMI/SOC Reaction

Name	V_i (cm ³ /mol)	% Change
Matrimid (BMI)	277.85	N/A
SOC comonomer	220.69	N/A
BMI/SOC addition polymer	235.75	-5.4
SOC ring-opening polymer	224.99	1.9
Copolymer addition and ring opening	N/A	-4.5

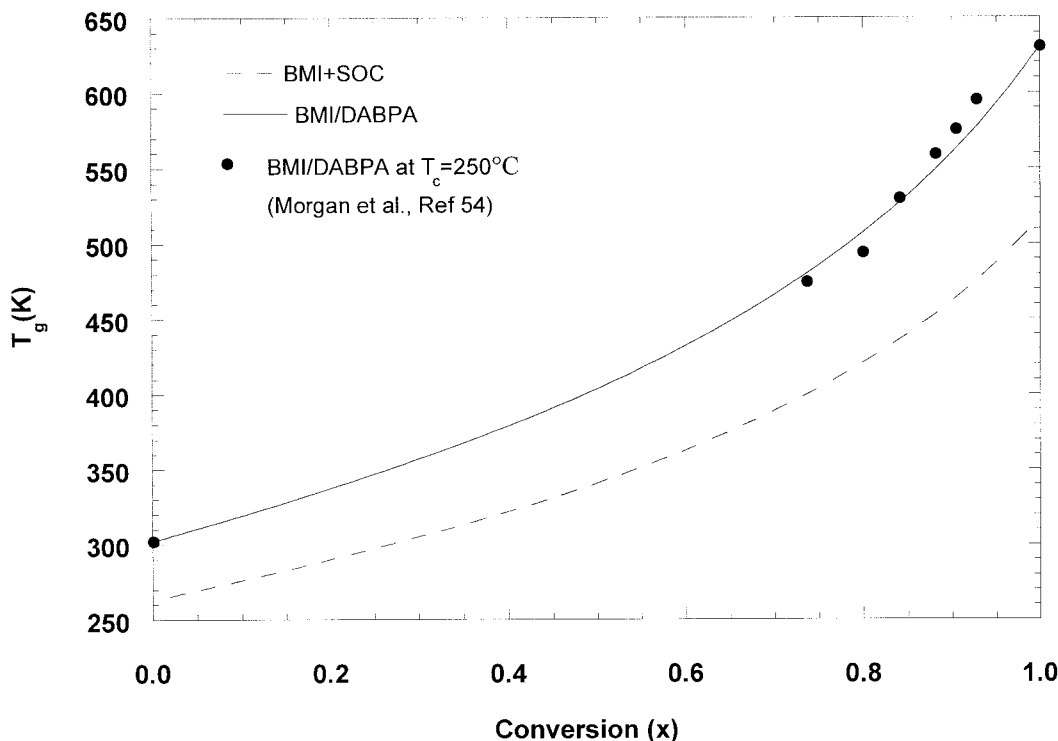


Figure 3 Relationship between T_g and conversion for a BMI/DABPA resin as measured at $T_c = 250^\circ\text{C}$ by Morgan et al.⁵⁴ The best fit of eqs. (6) and (7) is given by the solid line. The dashed line is the estimated T_g -conversion relationship for the BMI/SOC resin studied here. The constants used for both calculations were $Z = 0.218$ and $\psi = 0.10$.

culated by the application of the recursive technique of Miller and Macosko^{46,47} to chain reactions (see the appendix).

The value of T_{g0} for the BMI/SOC system is determined from the values of the glass transition of BMI and SOC monomers according to the following equation:⁴⁸

$$\frac{1}{T_{g0}} = \frac{w_1}{T_{g01}} + \frac{w_2}{T_{g02}} \quad (16)$$

where w_1 and w_2 are the mass fractions of the BMI and SOC monomers, respectively. The values of T_{g01} and T_{g02} are estimated by the application of the relationship between T_g and the melting temperature (T_m), as reported in the literature.⁵³ This relationship assumes that the ratio T_{g0}/T_m lies between 0.5 and 0.8. For the BMI/SOC system, we chose $T_{g0}/T_m = 0.75$. The T_m values of the Ciba-Geigy Matrimid 5292A (BMI) and the SOC monomers are reported to be 425.56 and 303 K, respectively.⁵ With these values, the values of T_{g01} and T_{g02} are calculated to be 319 and 227 K, respectively. By the application of eq. (16), the value of T_g of the BMI/SOC monomer is estimated to be 265 K.

However, the glass transition at full conversion, $T_{g\infty}$, and $T_{g(\text{polymer})}$ in eq. (5) of the BMI/SOC resin depend on the glass transition of the uncrosslinked BMI/SOC resin, T_{gu} , and on the parameters Z and ψ from eq. (6).

T_{gu} can be calculated with the Van Krevelen additive (group contribution) techniques:⁵¹

$$T_g = \frac{Y_g}{M} = \frac{\sum_i Y_{gi}}{\sum_i m_i} \quad (17)$$

where m_i is the molecular weight of the i th group, M is the molecular weight of the structural unit, Y_{gi} is the molar glass-transition function of the i th group, and Y_g is the molar glass transition of the structural unit. The group contributions m_i and Y_{gi} of the uncrosslinked BMI/SOC resin are summarized in Table I. Some groups were not tabulated in the original reference of Van Krevelen,⁵¹ and we estimated them from their relationship with other groups. From Table I, the value of T_{gu} is calculated to be 392 K.

To estimate parameters Z and ψ in eq. (6) for our BMI/SOC system, we first fit the experimental data of Morgan et al.⁵⁴ [of a model for BMI and diallyl bisphenol (DABPA) resin cured at 250°C] to the equation. T_{gu} was estimated for this BMI/DABPA system in a manner similar to that described previously for our BMI/SOC resin. We calculated the values of Z and ψ to be 0.218 and 0.10, respectively. By applying eq. (6) and using these values, we calculated $T_{g(\text{polymer})}$ of the BMI/SOC resin to be 517 K (244°C) at full conversion (i.e., $T_{g\infty}$). In Figure 3, we show the experimental and

TABLE III
Model Parameters Used in Eqs. (4) and (11)–(13)

Parameter	Value
C (K)	42.420
T_∞ (K)	0.0
E/R (K)	6,000
k_{d0} (s^{-1})	5,566
B	0.2

calculated dependencies of T_g on conversion for Morgan et al.'s data. This figure also shows the calculated relationship between T_g and conversion for our BMI/SOC resin based on the same values of Z and ψ . We note that BMI systems often undergo several reactions and that these result in a T_c dependence of the T_g –conversion relationship. We chose to model Morgan et al.'s data for $T_c = 250^\circ\text{C}$, which is slightly above the estimated $T_{g\infty}$ of our system.

Finally, some estimates of the activation energies are required to carry out the modeling work. The activation energies of both reactions are assumed to be 50 kJ/mol, the value reported by Mijovic and Andjelic⁵⁵ for the BMI/DABPA system. The parameters B and k_{d0} used in eqs. (11)–(13), and the parameters C , T_∞ , g_i , and τ_i are those published by Simon and co-workers^{4,29} and are given for the sake of completeness in Tables III and IV.

SIMULATIONS

The aim of the model calculations performed in this work is to estimate how much the isotropic residual stresses in the BMI/SOC resin can be reduced through the ring-opening reaction. In addition, we demonstrate how the relative reaction rate, cure history, and material parameters influence isotropic residual stresses. Two cure histories are simulated: a one-step isothermal cure and a ramp/hold cure, both followed by cooling to RT. Table V gives a description of the two histories and also lists the range of parameters used. For the one-step cure, T_c , the cure time (t_c), the relative reaction rate (k_2/k_1), and the product of $\alpha \times K$ ($\alpha_r K_r$ above T_g and $\alpha_g K_g$ below T_g) were varied. For the ramp/hold cures, the ramp rate was varied, and nominal values for the other parameters were used.

We note that the higher values of the product αK result in higher values of the residual stresses, which, in turn, can result in cavitation leading eventually to fracture. Therefore, it is important to reduce the cavitation stress, which is directly related to K and α of the material.^{56–58} This is discussed later.

RESULTS

Evaluation of the effect of the ring-opening reaction on the isotropic residual stresses

We calculated the cure-induced isotropic residual stresses for the BMI/SOC resin by first assuming that

the addition and ring-opening reactions had identical rates. Figure 4 shows the evolution of isotropic residual stresses during isothermal cure and subsequent cooling for two cases, one in which ring opening occurs and the other in which it does not. The simulations were performed for an isothermal cure at $T_c = 250^\circ\text{C}$ for approximately 60 min followed by cooling to RT at $10^\circ\text{C}/\text{min}$. In this simulation, $k_1 = k_2 = 0.0025 s^{-1}$, and the conversion at the end of the isothermal cure was greater than 0.99 for both reactions. Figure 4 shows that the isotropic residual stresses begin to increase immediately at zero time because gelation occurs as soon as the BMI addition reaction begins. The stress levels off as full conversion is reached. With cooling (which begins at approximately 60 min), the hydrostatic residual stresses again increase. It can be seen in Figure 4 that the stresses that arise because of shrinkage during cure are significant and that the ring-opening reaction reduces the cure stresses by 18.5 MPa or about 17% at T_c . This reduction of 17% is obtained when the addition and ring-opening reactions have identical rates and if T_g is unaffected by the ring-opening reaction [i.e., the contribution of the thermal stresses to the total magnitude is unaffected by the ring-opening reaction because it depends on $\alpha_r K_r (T_c - RT)$. Therefore, at RT, the residual stresses are still 21.3 MPa lower when ring opening occurs, but this is now only a 6% decrease of the total residual stress with respect to the case in which ring opening does not occur.

TABLE IV
Relaxation Time Spectrum Used in Eq. (1)
(After Refs. 4 and 29)

g_i	$\log(\tau_i/s)$
0.0215	-7.0
0.0215	-6.5
0.0215	-6.0
0.0215	-5.5
0.0267	-5.0
0.0267	-4.5
0.0375	-4.0
0.0405	-3.5
0.0630	-3.0
0.0630	-2.5
0.1054	-2.0
0.1160	-1.5
0.1160	-1.0
0.1653	-0.5
0.0561	0.0
0.0561	0.5
0.0199	1.0
0.0119	1.5
0.0055	2.0
0.0028	2.5
0.0008	3.0
0.0002	3.5
0.0003	4.0
0.0003	5.0

TABLE V
Simulated Cure Histories

	Description	T_c (°C)	t_c (min)	m (°C/min)	k_1 (s ⁻¹)	k_2 (s ⁻¹)	$\alpha_r K_r$ (GPa/K)	$\alpha_g K_g$ (GPa/K)
One-step cure	Isothermal hold at T_c for time t_c until x_1 reaches 99%. Cool to RT at 10°C/min.	220–310	60–600,000	N/A	0.0025	0 to 2.50 × 10 ¹	2.25 × 10 ⁻⁴ to 19.25 × 10 ⁻⁴	4.00 × 10 ⁻⁴ to 15.75 × 10 ⁻⁴
Ramp/hold cure	Ramp at m (°C/min) to $T_c = 250$ °C and hold isothermally at T_c for t_c until the conversion reaches 99%. Cool to RT at 10°C/min.	250	6000	0.1–10	0.0025	0.0025	10.50 × 10 ⁻⁴	7.90 × 10 ⁻⁴

N/A = not applicable.

We note that the ring-opening reaction will increase the flexibility of the structure while increasing the number of crosslink junctions at the same time. We make the assumption that these effects approximately cancel. Therefore, we do not include the flexible crosslink points in X when we calculate T_g . However, if the net effect of the ring-opening reaction is a decrease in T_g , the result is an increase in thermal stresses on the order of $[\alpha_r K_r - \alpha_g K_g] \Delta T_g$.

To show how the isotropic residual stresses during cure depend on the sequencing of addition and ring-opening reactions in the BMI/SOC resin, we varied the relative reaction rates. Figure 5 shows the development of the isotropic residual stresses as a function

of time for relative reaction rate ratios k_2/k_1 of 0.001, 1.00, and 1000 ($k_1 = 0.0025$ s⁻¹). When the ring-opening reaction is slower than the addition reaction ($k_2/k_1 = 0.001$), the stresses increase about 19% in the isothermal cure region, but these stresses also increase by about 18% when the ring opening is significantly faster than the addition reaction ($k_2/k_1 = 1000$). The effect of the relative reaction rate on the development of isotropic residual stresses can be summarized in Figure 6. This figure shows the effect of the relative reaction rate ratio on the isotropic residual stresses in the BMI/SOC system for a one-step cure held for 60 min at 250°C. The stresses are shown both at T_c and after cooling to RT. The isotropic residual stresses at T_c

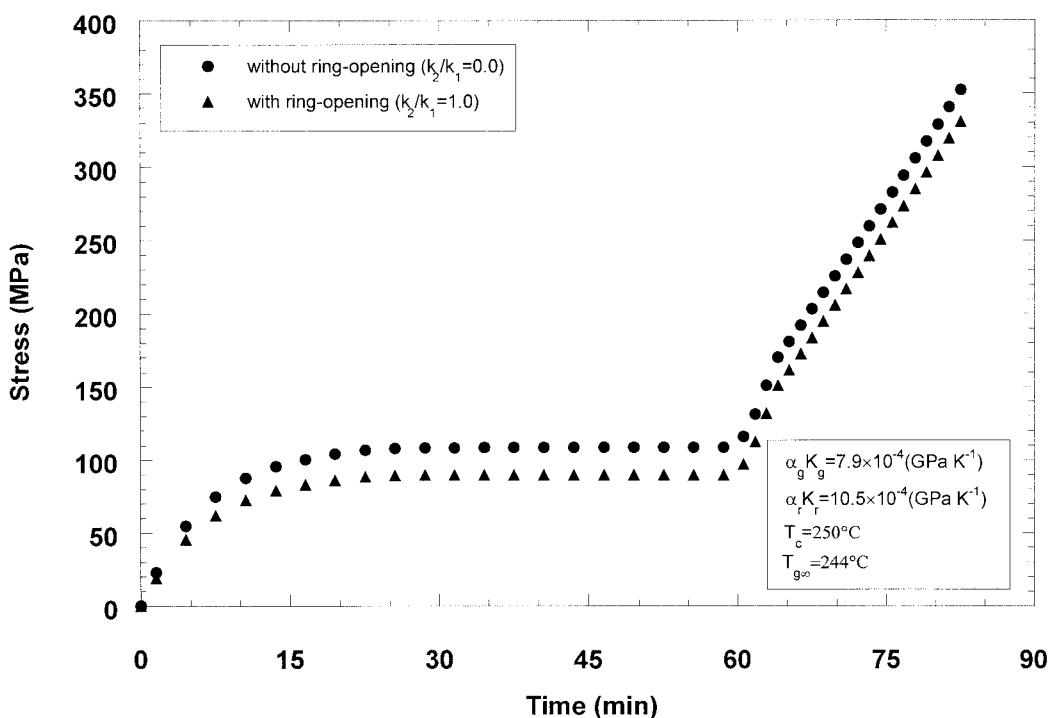


Figure 4 Evolution of the isotropic residual stresses during the cure at 250°C and subsequent cooling to RT as a function of t_c for the BMI/SOC resin with and without ring opening ($k_1 = 0.0025$ s⁻¹). Cooling was initiated at approximately 60 min. x_1 was 0.99.

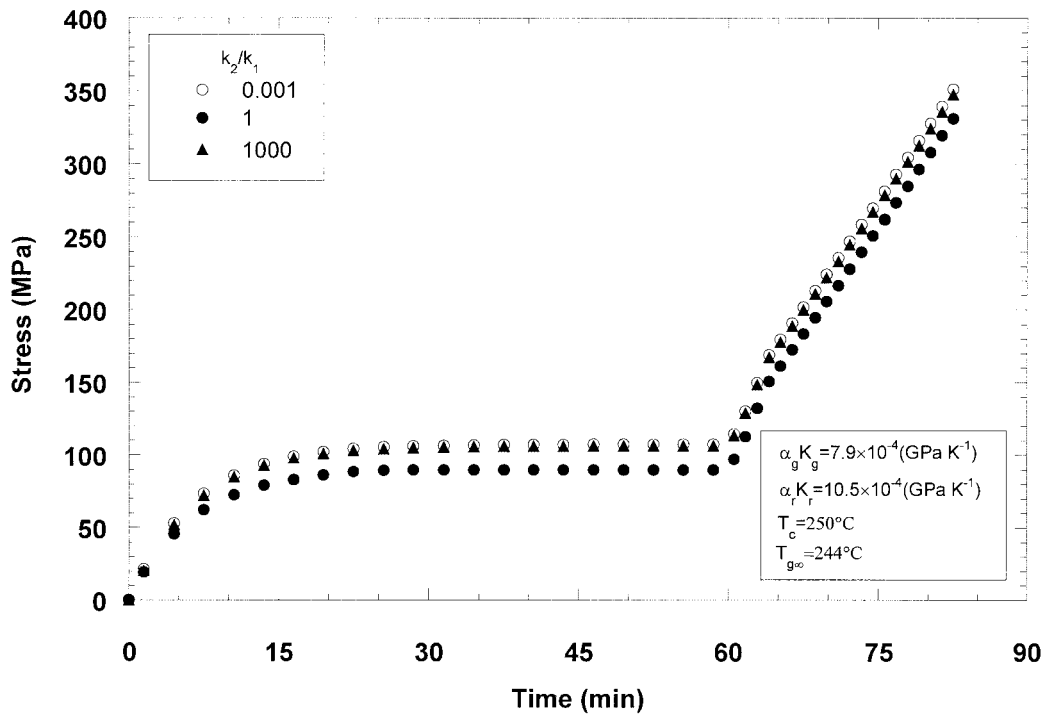


Figure 5 Evolution of the isotropic residual stresses during the cure at 250°C of BMI/SOC resins for three values of the relative reaction rate ratio ($k_1 = 0.0025 \text{ s}^{-1}$). Cooling was initiated at approximately 60 min. x_1 was 0.99.

are always less than the stresses at RT, but for the parameters chosen for these calculations, the residual stresses due to the cure shrinkage (i.e., those at T_c) may contribute 25–30% of the total stresses. The shape

of the curves in Figure 6 is related to the extent of the ring-opening reaction that occurs after gelation. There is a minimum in the cure stresses at intermediate values of k_2/k_1 . If the ring-opening reaction is too slow

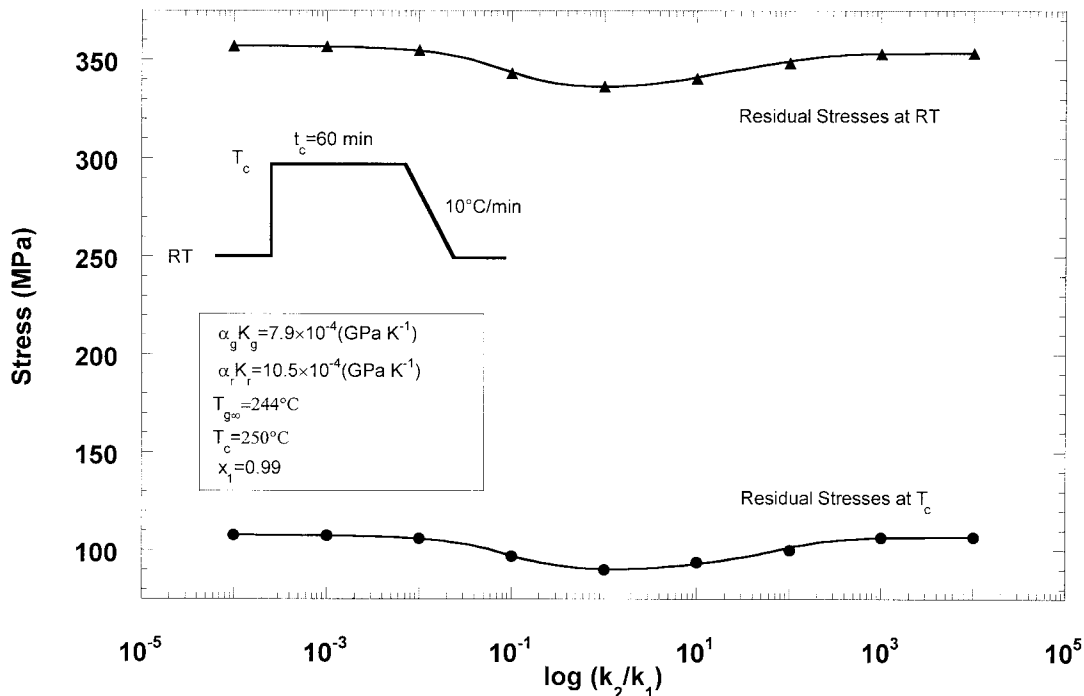


Figure 6 Isotropic residual stresses after a 60-min cure at T_c and at RT as a function of the relative reaction rate ratio k_2/k_1 ($k_1 = 0.0025 \text{ s}^{-1}$).

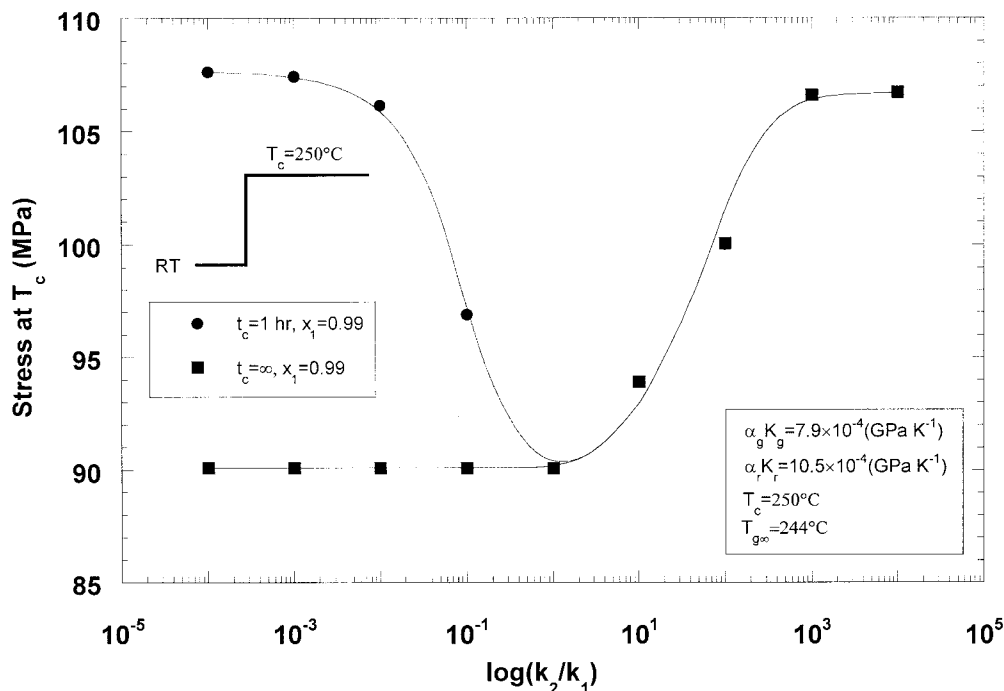


Figure 7 Isotropic residual stresses at the end of the cure at T_c at two t_c 's as a function of the relative reaction rate ratio k_2/k_1 ($k_1 = 0.0025 \text{ s}^{-1}$).

and does not occur in the timescale of the isothermal cure (very low k_2/k_1), no expansion will occur after gelation, and the isotropic residual stresses will be high. At intermediate k_2/k_1 values, there is a regime in which the ring-opening reaction occurs on a timescale comparable to or slightly slower than that of the addition reaction, fast enough to achieve significant cure in the timescale of the isothermal cure but slow enough that much of the ring opening occurs after gelation of the system. However, if the ring-opening reaction is too fast and expansion occurs before gelation of the system (very high k_2/k_1), again the isotropic residual stresses will be high.

For the case in which the ring-opening reaction is slow with respect to the addition reaction, longer t_c 's will result in lower residual stresses. This is shown in Figure 7, in which we compare the isotropic residual stresses at the end of the cure at T_c for $T_c = 250^\circ\text{C}$, for $t_c = 60 \text{ min}$, and for long enough for us to ensure greater than 99% conversion of the ring-opening reaction (designated ∞ in the figure). When the ring-opening reaction occurs after gelation of the system and ring opening proceeds to full conversion, the residual stresses are minimized.

Evaluation of the effect of the cure history on the isotropic residual stresses

We investigated how residual stresses in the BMI/SOC resin are affected by the cure history by varying T_c for a one-step cure. The relative reaction rate

k_2/k_1 was taken to be 1.0, and t_c 's were such that 99.0% conversions of both reactions were obtained. Figure 8 shows the isotropic residual stresses at T_c at the end of cure and at RT after cooling. The residual stresses at T_c are essentially independent of T_c because the shrinkage that occurs during cure is independent of T_c . There is a slight increase at the two lowest T_c 's (130 and 140°C) because when T_c is less than T_{g^∞} (244°C), the material vitrifies during the cure, and this results in an increase in K (from K_r to K_g) and a concomitant increase in the residual stresses. However, the magnitude of the residual stresses at RT increases with increasing T_c . This is due to the fact that the thermal stresses are significantly larger for the higher T_c 's because of the greater temperature change during cooling from T_c to RT.

The effect of the ramp rate on the residual stresses is shown in Figure 9 at the end of the cure at T_c and at RT for ramp/hold cures consisting of a ramp to 250°C , isothermal cure at 250°C to 99% conversion, and cooling to RT at $10^\circ\text{C}/\text{min}$. Figure 9 shows that residual stresses, at the end of the cure at T_c and at RT, are lower at lower ramp rates. This is due to the fact that T_{gel} (i.e., T_c at which x first becomes nonzero) is lower for lower ramp rates. Therefore, there is more thermal expansion during the ramp after gelation for lower ramp rates, and this partially compensates for the shrinkage due to cure and cooling. In fact, for the cases in which the stresses at the end of the cure at T_c are

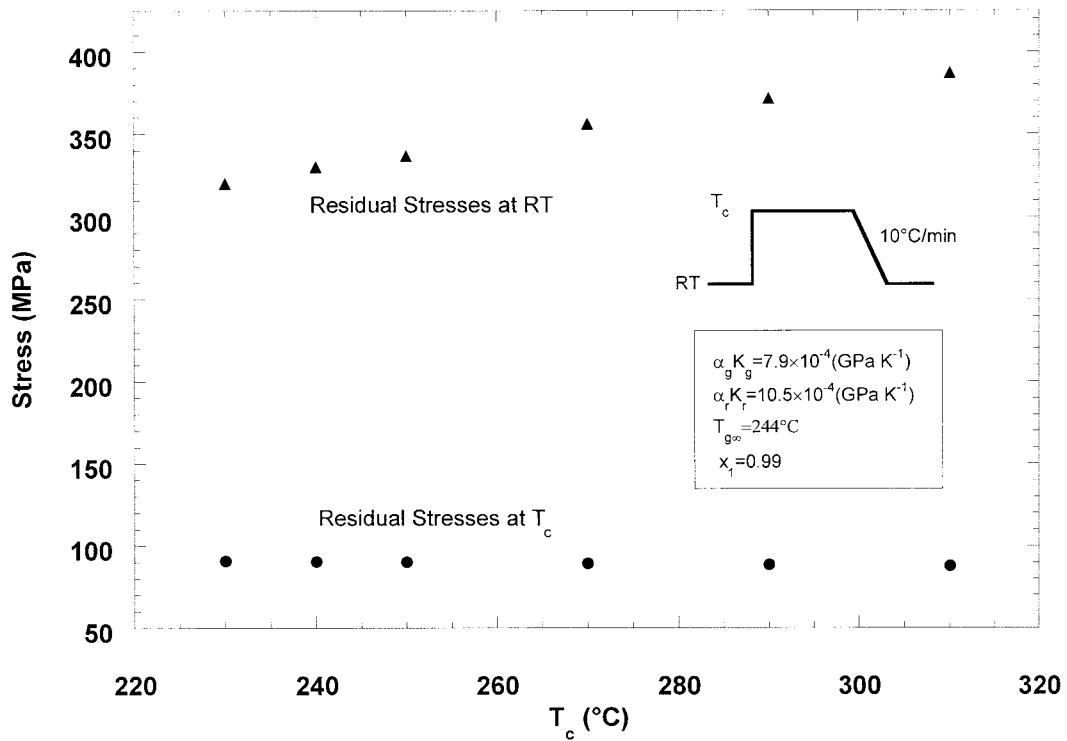


Figure 8 Isotropic residual stresses at the end of the cure at T_c and at RT for one-step isothermal cure histories as a function of T_c ($k_1 = k_2 = 0.0025 \text{ s}^{-1}$).

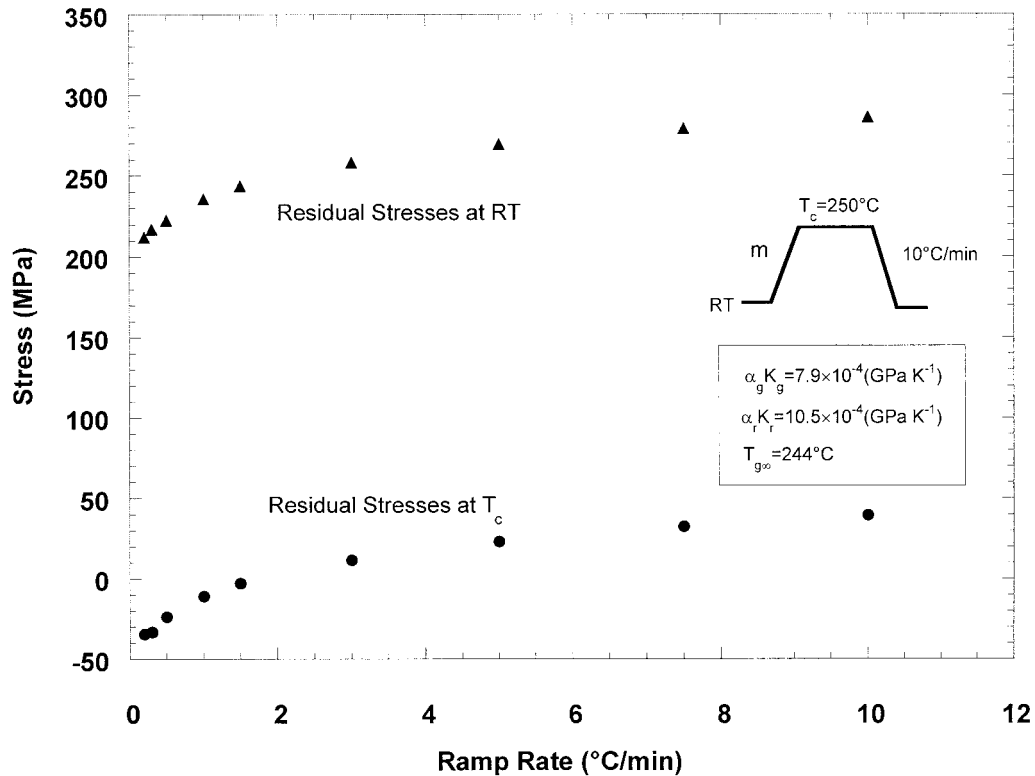


Figure 9 Isotropic residual stresses at the end of the cure at the final T_c (250°C) and at RT for ramp/hold cure histories as a function of the ramp rate ($k_1 = k_2 = 0.0025 \text{ s}^{-1}$).

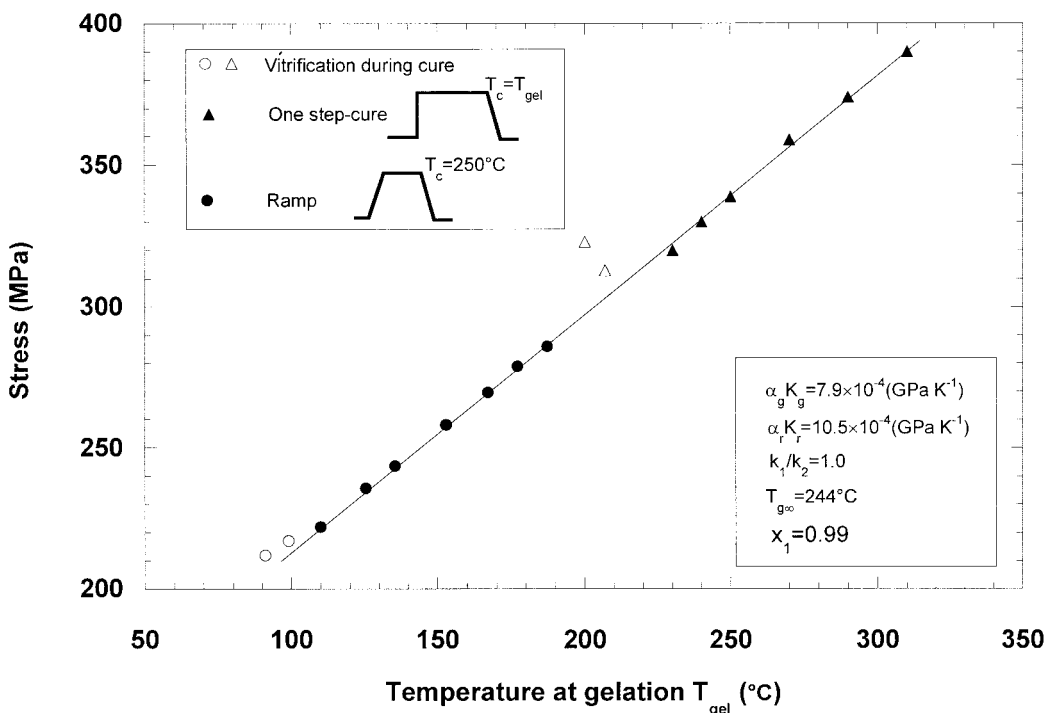


Figure 10 Isotropic residual stresses at the end of the cure at RT for one-step isothermal cure and ramp/hold cure histories as a function of T_{gel} ($k_1 = k_2 = 0.0025 \text{ s}^{-1}$). The filled and unfilled symbols indicate the cure histories in which vitrification did not and did occur during the cure, respectively. The line represents the relationship obtained in the absence of vitrification.

negative, the thermal expansion after gelation more than compensates for cure shrinkage.

The results of these simulations are summarized as a function of T_{gel} in Figure 10. A linear relationship between the residual stress and T_{gel} is obtained if vitrification does not occur during the cure, that is, if during the cure K can relax to its rubbery value in the timescale of the cure. These results demonstrate that T_{gel} is an important parameter for optimizing cure histories in efforts to reduce isotropic residual stresses.

Evaluation of the effect of the material parameters

Figures 11 and 12 show the effects of varying the products $\alpha_g K_g$ and $\alpha_r K_r$, respectively, on the magnitude of the isotropic residual stresses in the fully cured material at RT for one-step cure cycles. The value of $\alpha_g K_g$ influences the magnitude of the thermal stresses, and decreasing the value significantly reduces the isotropic residual stresses at RT. However, the value of $\alpha_r K_r$ influences primarily the magnitude of the shrinkage-induced cure stresses. The thermal stresses are only slightly affected by the change in $\alpha_r K_r$ because cooling occurs in the rubbery state over only a few degrees (i.e., from T_c to $T_{g\infty}$). However, because reducing $\alpha_r K_r$ reduces cure stresses, reducing $\alpha_r K_r$ reduces stresses both at T_c and at RT.

In addition to the simulations presented in Figures 11 and 12, we show in Figure 13 the effect of $\alpha_g K_g$ on the isotropic residual stresses at RT [calculated from eq. (14)] for several thermosetting resins and thermoplastics reported in the literature. The thermosetting resins are diglycidyl ether of bisphenol A/polyoxy polypropylentriamine,¹⁶ diglycidyl ether of bisphenol A/(metaphenylene diamine/methylene diamine),²⁵ Hexcel 8551-7,⁴ diglycidyl ether of bisphenol A/(trimethylene glycol-di-*p*-aminobenzoate),⁵⁹ and phenoxy epoxy.⁶⁰ The thermoplastics are poly(methyl methacrylate)⁵² and poly(2,6-dimethylphenylene ether) (PXE).⁵² Also, this figure shows the value of residual stresses calculated in this article for our BMI/SOC resin. As expected, the higher values of residual stresses are due to the higher values of $\alpha_g K_g$. In addition, the lower values of the residual stresses for the epoxies reported in the work of Simon et al.⁴ and Iza et al.⁵⁹ indicate that one possible reason for the successes of these resins in commercial applications may be related to the low values of $\alpha_g K_g$. This is an area that merits further examination.

DISCUSSION

The simulations presented in this work indicate that the SOC ring-opening reaction plays a significant role

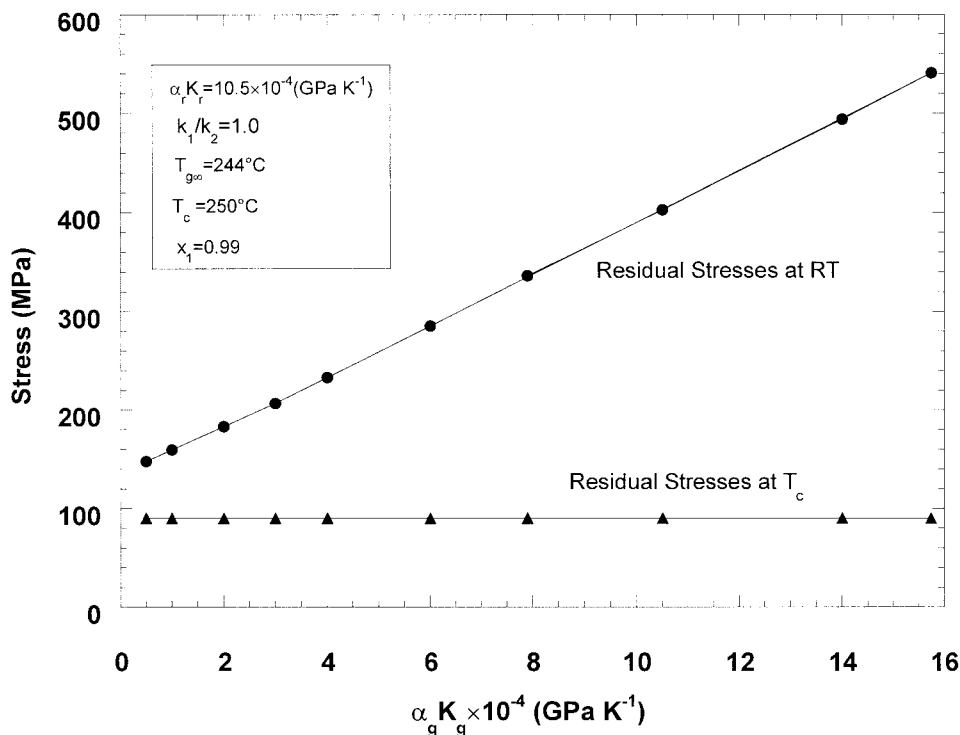


Figure 11 Effect of the product $\alpha_g K_g$ on the isotropic residual stresses at the end of the cure at T_c and at RT for the cure at 250°C for 1 h followed by cooling at 10°C/min to RT.

in reducing cure shrinkage and residual curing stresses in the SOC/BMI copolymer. In addition, we predict that the ring-opening reaction reduces the

shrinkage due to the cure of the BMI/SOC resin by 17% when the addition and ring-opening reactions have identical rates. The isotropic residual stresses at

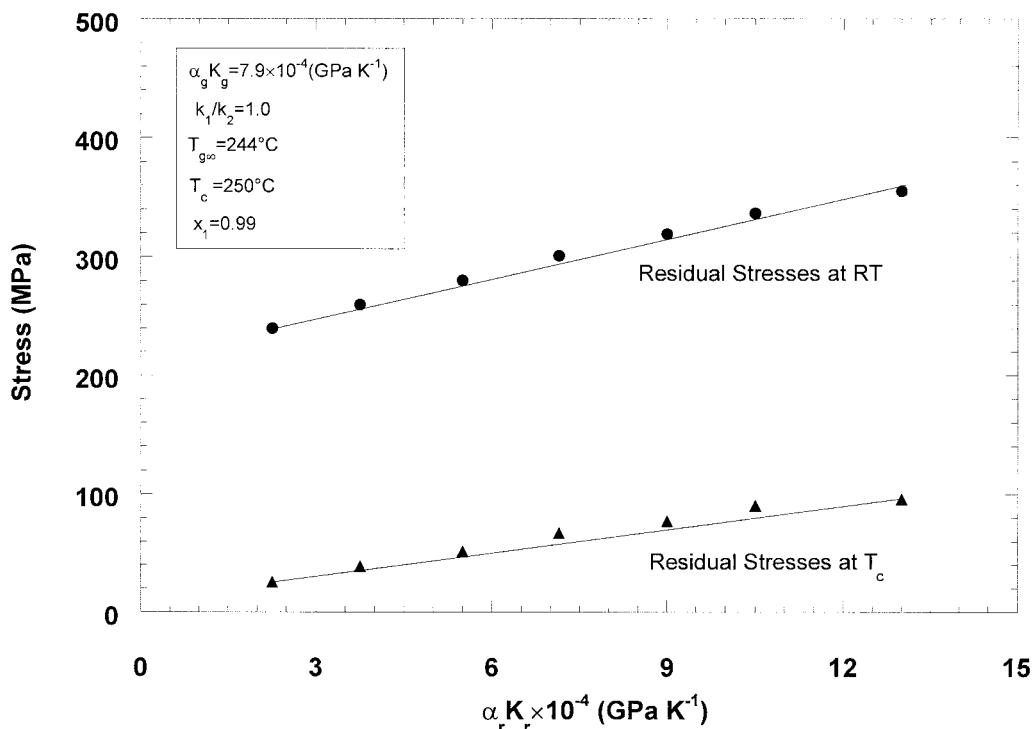


Figure 12 Effect of the product $\alpha_r K_r$ on the isotropic residual stresses at the end of the cure at T_c and at RT for the cure at 250°C for 1 h followed by cooling at 10°C/min to RT.

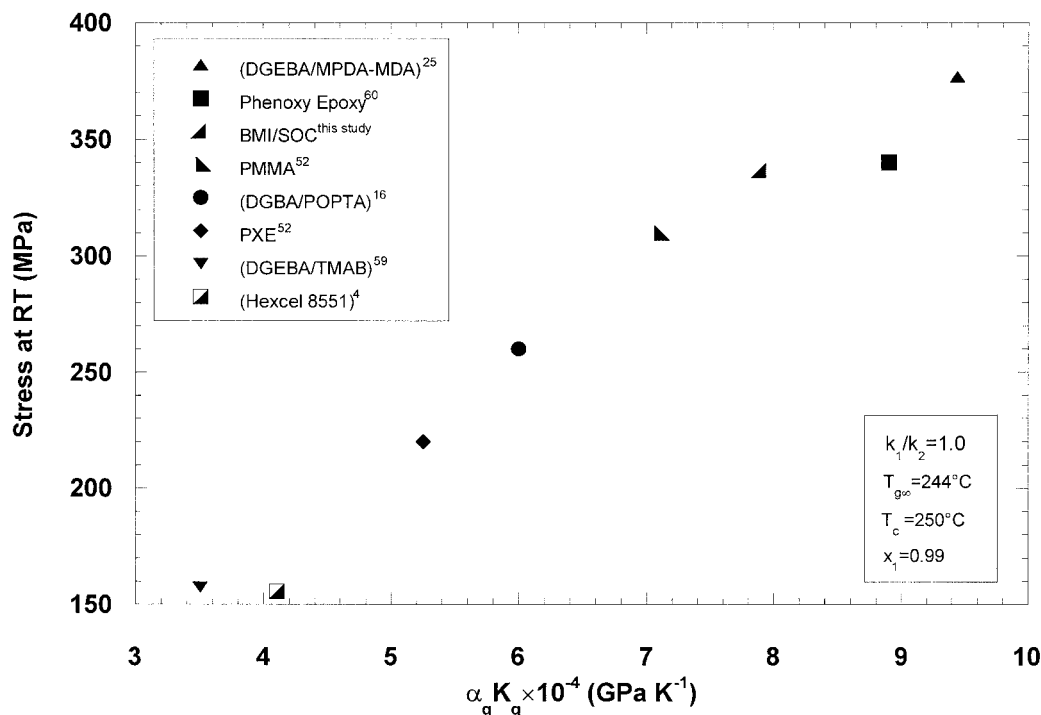


Figure 13 Effect of the product $\alpha_g K_g$ on the isotropic residual stresses for the end of the cure at T_c and at RT for different polymers reported in the literature. The thermal history used for the simulations was the same as that used for Figures 11 and 13.

RT decrease by about 6% for the same set of parameters. Other simulations show that the ring-opening reaction is able to reduce cure stresses if the reactions are sequenced optimally such that (1) the ring-opening reaction occurs after the gelation of the system and (2) the ring-opening reaction reaches full conversion by the end of the isothermal cure.

The cure history also plays a significant role in the magnitude of the isotropic residual stresses observed after cure at RT. Our results indicate that T_{gel} is an important parameter for minimizing isotropic residual stresses in thermosetting resins. The lowest residual stresses are achieved when T_c equals the lowest T_c at which gelation will still occur. This temperature is designated ${}_{gel}T_g$, the glass-transition temperature of the material at the fixed conversion at which gelation occurs, in the time-temperature-transformation isothermal cure diagram of Gillham.^{61,62} For our system, ${}_{gel}T_g$ is approximately T_{g0} because gelation occurs as soon as reaction occurs. However, we note that lowering T_{gel} results in longer and slower cure cycles and, therefore, increases the cost of manufacturing. Obviously, gelling the system at T_{g0} may be impractical.

Reducing residual curing stresses in the BMI/SOC copolymer is expected to enhance mechanical properties and improve the long-term performance of the matrix composite. Although the reduction of the residual stresses appears small (ca. 6% at RT), the impact on durability should be greater. For example, Mc-

Kenna and Penn^{63,64} and Crissman and McKenna⁶⁵ found that the time-dependent failure of several polymers and rubbers follows a very strong power law in the applied stress. According to that body of work, decreasing applied stresses by 6% increases the time to failure (t_{fail}) by approximately a factor of 4 (e.g., $t_{fail} = t_0 \sigma^{-19.4}$ for PMMA, where t_0 is a prefactor and σ is the applied stress). A similar analysis of the fatigue lifetime of an epoxy resin⁶⁶ yields an exponent of -13 such that t_{fail} would increase by a factor of 2.2 for a 6% reduction in residual stresses. Therefore, the apparently small change in residual stresses when the ring-opening chemistry is used is anticipated to have a significant effect on material durability.

In addition, our simulations provide a quantitative illustration of the importance of the product of K and α , $K\alpha$, to the magnitude of the isotropic residual stresses that develop in thermosetting resins. As mentioned previously, high isotropic residual stresses can result in cavitation of the resin. This, in turn, can lead to fracture and failure of the composite. Reducing the magnitude of the residual stresses in the material will reduce the likelihood of cavitation. This might be achieved by a reduction in the value of K . However, a reduction in K is also normally associated with a reduction in the shear modulus, which can reduce the compression strength and yield stress of the composite.^{1,67} For example, fiber buckling or global instability in the composite can occur as a result of the reduction

in K of the polymer matrix.^{1,67} Therefore, it would be desirable to have a means of reducing K of a resin system without a significant reduction in the shear modulus. One possibility would be through the development of auxetic materials that have high shear modulus combined with a low K value (i.e., negative Poisson's ratio).^{68–70} Clearly, this is a speculative point at this time. However, it suggests that alternative paths may be available for mitigating residual stress other than the chemistries examined in this work. These merit further investigation.

CONCLUSIONS

A thermoviscoelastic model of isotropic residual stress development in thermosets has been extended to a novel thermosetting resin system, BMI/SOC. The influence of the cure chemistry and resin properties on the buildup of isotropic residual stresses has been evaluated. The simulations performed show that for the case in which the addition and ring-opening reactions have identical rates, the isotropic residual stresses after cure at T_c and at RT are reduced by 17 and 6%, respectively. The optimal sequencing of the addition and ring-opening reactions in the BMI/SOC system is such that the ring-opening reaction should be slow enough that it occurs only after gelation of the system, yet it should be fast enough to achieve full conversion in a reasonable time frame. Our calculations also show that isotropic residual stresses can be mitigated through gelling at lower temperatures and through a reduction of the product of $\alpha \times K$, αK . This latter observation suggests that new strategies could be developed beyond these ring-opening chemistries that could also enhance composite material performance.

APPENDIX: APPLICATION OF MILLER AND MACOSKO'S RECURSIVE THEORY TO CHAIN POLYMERIZATION IN THE BMI/SOC SYSTEM

One necessary ingredient in the model is the dependence of T_g on the conversion in the BMI/SOC resin. This relationship is assumed to depend on w_{monomer} and w_{polymer} in the system and the crosslink density, all of which can be obtained by the application of the recursive technique of Miller and Macosko.^{46,47} For our BMI/SOC resin, we make the following assumptions:

1. No termination reactions occur.
2. A double bond is said to be reacted when it has chains extending from both sides.
3. No intramolecular reactions occur in finite species.

4. The density of rigid crosslinks (X_{rigid}) is due to crosslink sites arising only from the addition reaction.

With the recursive method, we determine the probabilities of finding a finite rather than infinite chain on looking out or into species i , $P(F_i^{\text{out}})$ and $P(F_i^{\text{in}})$, respectively. Following the notation of Miller and Macosko, we find^{46,47}

$$\begin{aligned} P(F_A^{\text{out}}) &= P_{AB}P(F_A^{\text{out}}|A_{\text{reacts with B}}) \\ &+ (1 - P_{AB})P(F_A^{\text{out}}|A_{\text{does not react with B}}) = x_1(0) \\ &+ (1 - x_1)(1) = 1 - x_1 \quad (\text{A.1}) \end{aligned}$$

$$P(F_A^{\text{in}}) = P(F_A^{\text{out}}) = 1 - x_1 \quad (\text{A.2})$$

$$\begin{aligned} P(F_B^{\text{out}}) &= P_{BA}P(F_B^{\text{out}}|B_{\text{reacts with A}}) \\ &+ (1 - P_{BA})P(F_B^{\text{out}}|B_{\text{does not react with A}}) = x_1(0) \\ &+ (1 - x_1)(1) = 1 - x_1 \quad (\text{A.3}) \end{aligned}$$

$$\begin{aligned} P(F_C^{\text{out}}) &= P_{CC}P(F_C^{\text{out}}|C_{\text{reacts with C}}) \\ &+ (1 - P_{CC})P(F_C^{\text{out}}|C_{\text{does not react with C}}) = x_2(0) \\ &+ (1 - x_2)(1) = 1 - x_2 \quad (\text{A.4}) \end{aligned}$$

$$P(F_B^{\text{in}}) = P(F_B^{\text{out}})P(F_C^{\text{out}}) = (1 - x_1)(1 - x_2) \quad (\text{A.5})$$

where A is the double bond on the BMI monomer, B is the allyl group on the SOC monomer, and C is the spiro group on the SOC monomer. P_{ij} refers to the probability of having group j react with i to yield an i - j link.

The weight fraction of the monomer (w_{monomer}) is equal to the weight fraction of sol (w_{sol}) or finite species in the system:

$$\begin{aligned} w_{\text{sol}} = w_{\text{monomer}} &= \frac{[P(F_A^{\text{out}})^2 + P(F_B^{\text{out}})^2P(F_C^{\text{out}})]}{2} \\ &= \frac{(1 - x_1)^2(2 - x_2)}{2} \quad (\text{A.6}) \end{aligned}$$

The weight fraction of the polymer (w_{polymer}) is then given as follows:

$$w_{\text{polymer}} = 1 - w_{\text{monomer}} = 1 - \frac{(1 - x_1)^2(2 - x_2)}{2} \quad (\text{A.7})$$

X_{rigid} in the BMI/SOC material can be expressed as follows:

$$X_{\text{rigid}} = \frac{M_0}{2} [(1 - P(F_A^{\text{out}}))^2 + (1 - P(F_B^{\text{out}}))^2] = M_0 x_1^2 \quad (\text{A.8})$$

where M_0 is the initial concentration of the monomer. $x_{1\text{gel}}$ can be calculated from eq. (A.8) and is the value when the crosslink density becomes nonzero. Because of the nature of the chain reaction, gelation occurs as soon as x_1 is greater than zero.

References

1. Tsai, S. W.; Hahn, H. T. *Introduction to Composite Materials*; Technomic: Westport, CT, 1980.
2. White, S. R.; Hahn, T. H. *J Commun Mater* 1992, 26, 2402.
3. Weitzmann, Y. J. *J Appl Mech* 1979, 46, 563.
4. Prasatya, P.; McKenna, G. B.; Simon, S. L. *J Comp Mater* 2001, 35, 826.
5. Leung, C. *Symposium Proceedings of High Temple Workshop XX*, San Diego, CA, Jan 24–27, 2000.
6. Bailey, W. J.; Sun, R. L.; Katsuki, H.; Endo, T.; Iwama, H.; Tsushima, R.; Saigou, K.; Bitritto, M. M. In *Ring Opening Polymerization*; Suegusa, T.; Goethals, E., Eds.; ACS Symposium Series 59; American Chemical Society: Washington, DC, 1977; p 38.
7. Bailey, W. J. U.S. Pat. 4,387,215 (1983).
8. Bailey, W. *Mater Sci Eng A* 1990, 126, 271.
9. Lam, P. W. K.; Piggott, M. R. *J Mater Sci* 1989, 24, 3189.
10. Howell, B. F. *J Commun Technol Res* 1992, 14, 169.
11. He, P.; Zhou, Z. *J Mater Sci* 1991, 26, 3792.
12. Ochi, M.; Yamazaki, K.; Shimbo, M. *J Mater Sci* 1989, 24, 3189.
13. Chou, C. T.; Penn, L. S. *J Commun Mater* 1992, 26, 171.
14. Lange, J.; Toll, S.; Manson, A.-J. E.; Hult, A. *Polymer* 1997, 38, 809.
15. Brahatheeswaran, C.; Gupta, V. B. *Polymer* 1997, 38, 809.
16. Plepys, A. R.; Farris, R. J. *Polymer* 1990, 31, 1932.
17. Chapman, T. J.; Gillespie, J. W., Jr.; Pipes, R. B.; Manson, J.-A. E.; Seferis, J. C. *J Commun Mater* 1990, 24, 616.
18. Ferry, J. D. *Viscoelastic Properties of Polymers*; Wiley: New York, 1980.
19. Williams, M. L.; Landell, R. F.; Ferry, J. D. *J Am Chem Soc* 1955, 77, 3701.
20. Vogel, H. *Phys Z* 1921, 22, 645.
21. Kitoh, M.; Suzuki, K. *Kobunshi Ronbunshu* 1975, 32, 147.
22. Suzuki, K.; Miyano, Y. *J Appl Polym Sci* 1977, 21, 3367.
23. Martin, J. E.; Adolf, D.; Wilcoxon, J. P. *Phys Rev Lett* 1988, 61, 2620.
24. Adolf, D.; Martin, J. E. *Macromolecules* 1990, 23, 3700.
25. Adolf, D.; Chambers, R. S. *Polymer* 1997, 38, 5481.
26. Adolf, D.; Martin, J. E.; Chambers, R. S.; Burchett, S. N.; Guess, T. R. *J Mater Res* 1998, 13, 530.
27. Lawrence, W. E.; Manson, J.-A. E.; Seferis, J. C.; Gillespie, J. W.; Pipes, R. B. *Am Soc Compos Mater Tech Conf* 1990, 5, 401.
28. Woo, E. W.; Seferis, J. C.; Schaffnit, R. S. *Polym Comp* 1991, 12, 273.
29. Simon, S. L.; McKenna, G. B.; Sindt, O. *J Appl Polym Sci* 2000, 76, 495.
30. Plazek, D. J. *J Polym Sci Part A-2: Polym Phys* 1966, 4, 745.
31. Lee, A.; McKenna, G. B. *Polymer* 1988, 29, 1812.
32. McKinney, J. E.; Belcher, H. V. *J Res Natl Bur Stand Sect A* 1963, 67, 43.
33. Goldbach, G.; Rehage, G. *Rheol Acta* 1967, 6, 30.
34. Deng, T. H.; Knauss, W. G. *Mech Time-Depend Mater* 1997, 1, 33.
35. Yee, A. F.; Takemori, M. T. *J Polym Sci Polym Phys Ed* 1982, 20, 205.
36. Tschoegl, N. W. *The Phenomenological Theory of Linear Viscoelasticity*; Springer-Verlag: Berlin, 1989.
37. Adolf, D.; Martin, J.-E. *J Commun Mater* 1996, 30, 13.
38. Colucci, D. M.; McKenna, G. B.; Filliben, J. J.; Lee, A.; Curliss, D. B.; Bowman, K. B.; Russell, J. D. *J Polym Sci Part B: Polym Phys* 1997, 35, 1561.
39. Pascault, J. P.; Williams, R. J. J. *J Polym Sci Part B: Polym Phys* 1990, 28, 85.
40. Majovic, J.; Wijaya, J. *Macromolecules* 1990, 23, 3671.
41. Hale, A.; Macosko, C. W.; Bair, H. E. *Macromolecules* 1991, 24, 2610.
42. Gan, S.; Seferis, J. C.; Prime, R. B. *J Therm Anal* 1991, 37, 463.
43. DiBenedetto, A. T. *J Polym Sci Part B: Polym Phys* 1987, 25, 1949.
44. Madhukar, M. S.; Kosuri, R. P.; Bowles, K. J. *Proceedings of ICCM-10*, Whitler, Canada, Aug 1995.
45. Genidey, M. S.; Madhukar, M. S.; Russell, J. D. *Proceedings of ICCM-11*, Gold Coast, Australia, July 1997.
46. Miller, D. R.; Macosko, C. W. *Macromolecules* 1976, 9, 200.
47. Miller, D. R.; Macosko, C. W. *Macromolecules* 1976, 9, 206.
48. Fox, T. G. *Bull Am Phys Soc* 1958, 1, 123.
49. DiMarzio, E. A. *J Res Natl Bur Stand Sect A* 1964, 68, 611.
50. Doolittle, A. K. *J Appl Phys* 1951, 22, 1471.
51. Van Krevelen, D. W. *Properties of Polymers: Correlations with Chemical Structure*; Elsevier: Amsterdam, 1972.
52. Orwoll, R. A. In *Physical Properties of Polymers Handbook*; Mark, J. E., Ed.; American Institute of Physics: New York, 1996; Chapter 7, p 81.
53. Cowie, J. M. G. *Polymers: Chemistry and Physics of Modern Materials*; Blackie: London, 1973.
54. Morgan, R. J.; Shin, E. E.; Rosenberg, B.; Jurek, A. *Polymer* 1997, 38, 639.
55. Majovic, J.; Andjelic, S. *Macromolecules* 1996, 29, 239.
56. Naqui, S. L.; Robinson, I. M. *J Mater Sci* 1993, 28, 1421.
57. Dijkstra, K.; Wal, A. V. D.; Gaymans, R. J. *J Mater Sci* 1994, 29, 3489.
58. Lazzeri, A.; Bucknall, C. B. In *Toughening of Plastics: Advances in Modeling and Experiments*; Pearson, R. A.; Sue, H.-J.; Yee, A. E., Eds.; American Chemical Society: Washington, DC, 2000; Chapter 2.
59. Iza, M.; Simon, S. L.; McKenna, G. B. *Society of Plastics Engineers, ANTEC 2002*, 755.
60. Zoller, P.; Walsh, D. *Standard Pressure–Volume–Temperature Data for Polymers*; Technomic: Westport, CT, 1995.
61. Gillham, J. K. *Polym Eng Sci* 1986, 26, 1425.
62. Enns, J. B.; Gillham, J. K. *J Appl Polym Sci* 1983, 28, 2567.
63. McKenna, G. B.; Penn, R. W. *Polymer* 1980, 21, 213.
64. McKenna, G. B.; Penn, R. W. *J Biomed Mater Res* 1980, 14, 689.
65. Crissman, J. M.; McKenna, G. B. *J Polym Sci Part B: Polym Phys* 1987, 25, 1667.
66. Hahn, H. T. *ASTM STP* 1979, 674, 383.
67. Schultheisz, C. R.; Wass, A. M. *Prog Aerospace Sci* 1996, 32, 1.
68. Lakes, R. S. *Science* 1987, 235, 1038.
69. Chan, N.; Evans, K. E. *J Mater Sci* 1997, 32, 5925.
70. Chan, N.; Evans, K. E. *J Mater Sci* 1997, 32, 5945.