

NASA Technical Memorandum 4128

A Predictive Model for Failure Properties of Thermoset Resins

James M. Caruthers
Purdue University
West Lafayette, Indiana

Kenneth J. Bowles
Lewis Research Center
Cleveland, Ohio



National Aeronautics and
Space Administration
Office of Management
Scientific and Technical
Information Division

1989

Summary

A predictive model for the three-dimensional failure behavior of engineering polymers has been developed in a recent NASA-sponsored research program. This model acknowledges the underlying molecular deformation mechanisms and thus accounts for the effects of different chemical compositions, crosslink density, functionality of the curing agent, etc., on the complete nonlinear stress-strain response including yield. The material parameters required by the model can be determined from test-tube quantities of a new resin in only a few days. Thus, we can obtain a first-order prediction of the applicability of a new resin for an advanced aerospace application without synthesizing the large quantities of material needed for failure testing. This technology will effect order-of-magnitude reductions in the time and expense required to develop new engineering polymers.

Introduction

The development of models for predicting the important engineering properties of aerospace epoxy resins has been the focus of a recent research effort at Purdue University sponsored by the NASA Lewis Research Center. The objective of this research program is to significantly reduce both the time and expense required to evaluate new candidate resins for high-performance aerospace applications. In this report we summarize our research progress to date.

The development of new polymer matrix resins for use in fiber-reinforced composites is both expensive and time consuming. A major expense in the development process is the synthesis and subsequent physical characterization of candidate resins. Specifically, in most engineering applications the resin's mechanical properties, and in particular its failure properties, are of critical importance. In order to even partially evaluate the mechanical performance, large (i.e., pound) quantities of a new resin are required; however, a polymer chemist typically synthesizes gram quantities of a new resin. The scaleup of the synthetic scheme to produce large quantities of a new resin is usually expensive and time consuming; additionally, there is no a priori assurance that the particular candidate resin selected for scaleup will have the required physical properties. Thus, a repetition of the entire process may be required. Moreover, since the deformation and failure properties of aerospace resins depend on temperature, deformation rate, mode of loading, etc., complete characterization of the

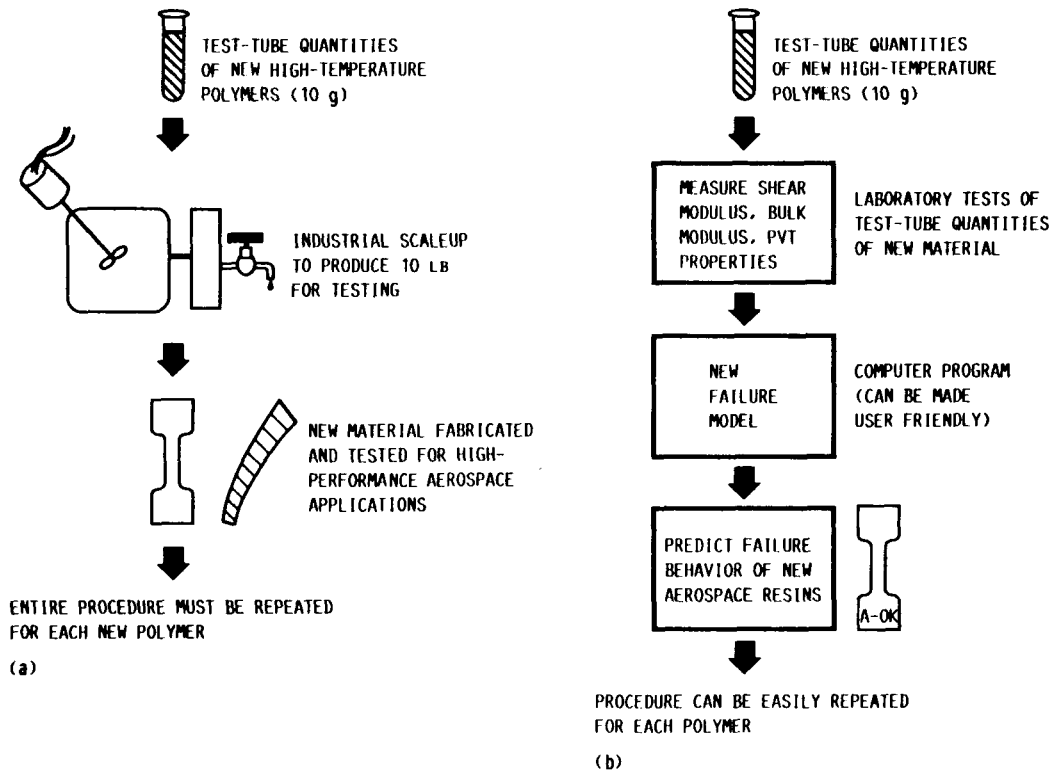
mechanical properties is quite involved, even when large quantities of a new resin can be readily obtained.

In order to significantly reduce the time and expense required to evaluate a new resin for aerospace applications, a new constitutive equation has been developed. This constitutive equation acknowledges the molecular processes that control the deformation and ductile failure in amorphous polymers. The only material properties required by the constitutive equation are the equilibrium pressure-volume-temperature (*PVT*) response and the linear viscoelastic shear and bulk moduli, properties that can be quickly evaluated from test-tube quantities of a new polymer resin. As shown schematically in figure 1, the nonlinear deformation and failure properties can be predicted via the constitutive equation, effecting order-of-magnitude reductions in the time and expense required to evaluate a new resin. In the next section of this report, we discuss briefly the constitutive equation and review some of its predictive capabilities.

The new nonlinear viscoelastic constitutive equation can effect a considerable reduction in the time and expense required to evaluate a new polymer resin; however, it would be highly advantageous if the important engineering properties of the resin could be estimated from chemical structure alone. Such predictive capabilities would allow chemists who work with synthetic polymers to screen a large number of potential molecular architectures prior to actual synthesis. Also, a model that only requires the chemical structure would provide guidance to the polymer chemist, since it is not otherwise obvious what types of molecular structures are most effective for enhancing important properties such as toughness and fatigue life. Some progress has been made in developing group contribution methods for estimating the linear viscoelastic properties required by the nonlinear constitutive equation. The research results to date are summarized in the Group Contribution Methods for Linear Viscoelastic Shear Modulus section.

Symbols

a	shift factor
a_T^α, a_T^β	shift factors for α and β mechanisms, respectively
B	material constant
E	Young's modulus
E_g	glassy tensile modulus
$E(t)$	tensile modulus



(a) Current practice: 1 to 2 years at high cost.
 (b) New methodology: 1 to 2 days at low cost.

Figure 1.—Schematic of way in which new nonlinear viscoelastic constitutive equation can significantly reduce time and expense required to evaluate new aerospace resins.

$G(t)$	linear viscoelastic shear modulus	V_0	initial volume
$G'(\omega, t)$	dynamic storage modulus	$V(t)$	volume
$G''(\omega, t)$	dynamic loss modulus	ϵ	strain
$H_{\alpha i}, H_{\beta j}$	discrete spectra values for α and β mechanisms, respectively	$\epsilon(t)$	displacement
I	identity tensor	$\dot{\epsilon}$	strain rate
$\mathbf{K}(t)$	bulk modulus	ξ	material time
P	pressure	σ	stress
$P(t)$	pressure history	$\sigma(t)$	stress response
P_{eq}	equilibrium pressure at $T(t)$ and $P(t)$	ω	experimental frequency
S	entropy		
S_0	initial entropy		
T	absolute temperature		
T_g	glass transition temperature		
T_0	initial temperature		
$T(t)$	temperature		
$T_{ref}^{\alpha}, T_{ref}^{\beta}$	reference temperatures for α and β mechanisms, respectively		
t	time		
t^*	reference time		

Nonlinear Viscoelastic Constitutive Equation

A new constitutive equation for amorphous polymers has been developed that can describe (1) the nonlinear viscoelastic behavior including yield when the polymer is in the solid state, (2) the glass transition phenomenon, and (3) the non-Newtonian flow behavior of the polymer melt. Several earlier forms of the constitutive equation have been derived intuitively (refs. 1 to 3). However, the most general form of the constitutive equation has been derived (ref. 4 and Lustig, S.R.; Shay,

R.M., Jr.; and Caruthers, J.M.: Thermodynamic Constitutive Equations With Memory Using a Material Time Scale, to be published in Journal of Rheology) via the framework of rational mechanics (refs. 5 and 6), where it was assumed that the viscoelastic dissipation occurs on a material time scale controlled by the nonequilibrium entropy. The material time scale incorporates the fact that the rate of viscoelastic relaxation changes with the thermodynamic state of the polymer (i.e., temperature, pressure, and specific volume).

Nonlinear Stress-Strain Behavior Including Yield

Although the complete constitutive equation is quite complex, limiting forms are much simpler. For isothermal deformations in the solid, the general constitutive equation essentially reduces to the following constitutive equation, where the stress response $\sigma(t)$ to an arbitrary displacement history $e(t)$ is given by reference 2:

$$\sigma(t) = \int_0^t \left\{ G(t^* - \xi^*) \frac{\partial}{\partial \xi} \left[\mathbf{E}(\xi) - \frac{1}{3} \text{tr} \mathbf{E}(\xi) \mathbf{I} \right] + \mathbf{K}(t^* - \xi^*) \mathbf{I} \frac{\partial}{\partial \xi} \text{tr} \mathbf{E}(\xi) \right\} \partial \xi \quad (1)$$

where

$$\left. \begin{aligned} t^* &= \int_0^t \frac{\partial \xi}{a[T(\xi), V(\xi), P(\xi)]} \\ \xi^* &= \int_0^\xi \frac{\partial \xi}{a[T(\xi), V(\xi), P(\xi)]} \end{aligned} \right\} \quad (2)$$

and

$$a = \frac{B}{2.3} \left(\frac{1}{TS} - \frac{1}{T_0 S_0} \right) \quad (3)$$

and $G(t)$ and $\mathbf{K}(t)$ are the linear viscoelastic shear and bulk moduli, $\mathbf{E}(t)$ is a finite strain tensor computed from the displacement strain tensor $e(t)$, t^* and ξ^* are material times (ref. 6), and $a[T(t), V(t)]$ is a shift function that depends on the nonequilibrium entropy $S(T, V, P)$ as suggested by Adams and Gibbs (ref. 7). The equilibrium contribution to S was determined by using the Simha-Somcynsky equation of state (ref. 8). Equation (1) is quite similar to the well-known linear viscoelastic constitutive equation, except that the infinitesimal strain tensor has been replaced with a finite strain tensor and normal time t has been replaced with the material time t^* . The constitutive equation has *no adjustable parameters*, and the required material properties are (1) the equilibrium *PVT*

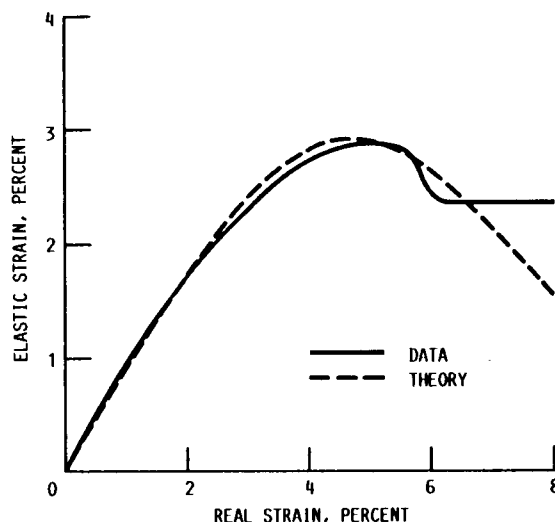


Figure 2.—Stress-strain curve for diglycidylether of bisphenol-A (DGEBA) epoxy resin cured with 4,4-diaminodiphenylsulfone (DDS) and theoretical predictions of equation (1). Temperature, 100 °C; stress divided by glassy modulus; strain rate, $\dot{\epsilon}$, 10^{-3} sec^{-1} .

behavior need to specify the Simha-Somcynsky equation of state and (2) the linear viscoelastic shear and bulk moduli.

Predictions made using equation (1) for the uniaxial extension at a constant strain rate of a typical aerospace epoxy resin are shown in figure 2, where the *PVT* and linear viscoelastic material properties were measured in independent experiments. By examining figure 2, we see that the constitutive equation predicted the nonlinear stress-strain curve including yield and that the predictions agreed quantitatively with the experimentally measured stress-strain response. The discrepancy between theory and experiment after yield was to be expected because the predictions assumed a spatially homogeneous deformation whereas the experimental specimen exhibited necking. In order to predict spatially nonhomogeneous deformations such as necking, equation (1) must be combined with the equation of continuity and conservation of momentum in a finite-element program. Since the yield data were not used to set any parameter in the constitutive equation, the quantitative agreement shown in figure 2 is a definitive verification of the new constitutive equation. In addition to quantitatively predicting the yield phenomenon, the constitutive equation is able to predict the effects of strain rate, temperature, and multiaxial deformations on the yield process (refs. 2 and 3).

Glass Transition Phenomenon

Another limiting form of the general constitutive equation (ref. 4 and Lustig, S.R.; Shay, R.M., Jr.; and Caruthers, J.M.: Thermodynamic Constitutive Equations With Memory Using a Material Time Scale, to be published in Journal of Rheology) is the *PVT* behavior in the glass transition region. The time-dependent volume response $V(t)$ to an arbitrary temperature $T(t)$ and pressure $P(t)$ history is given by

$$P(t) = P_{eq}[T(t), V(t)] + \frac{V_0}{3V} \left(1 + \frac{2}{3} \epsilon_{kk} \right) \int_0^t \mathbf{K}(t^* - \xi^*) \frac{\partial \epsilon_{kk}(\xi)}{\partial \xi} d\xi \quad (4)$$

where $\epsilon_{kk} = [V(t)/V_0]^{2/3} - 1$ is the voluminal strain, V_0 is the initial volume, and P_{eq} is the equilibrium pressure at $T(t)$ and $V(t)$ as given by the equation of state. Here again, there are *no adjustable parameters* and the only material properties are the equilibrium *PVT* behavior and the linear viscoelastic bulk modulus. The predictions of equation (4) for poly(vinyl acetate), as it was cooled from an equilibrium rubber, are shown in figure 3. The constitutive equation predicted a discontinuity in the slope of the volume-temperature curve that would be identified with the glass transition temperature T_g . For poly(vinyl acetate) T_g is 32 °C, in quantitative agreement with the theoretical prediction. Since T_g was not used to set any model parameter, the quantitative agreement shown in figure 3 is a definitive test of the constitutive equation's ability to describe the glass transition phenomenon. Equation (4) also accurately predicts the effects of the cooling rate on the glass transition.

Fluid Behavior

The general constitutive equation can be simplified for the case of steady shear of an uncrosslinked polymer fluid, although the form is not as simple as equations (1) and (4) and thus will not be shown here. This constitutive equation again has *no adjustable parameters* and only requires the equilibrium *PVT* response and the linear viscoelastic shear and bulk moduli. Preliminary prediction of the non-Newtonian shear viscosity for a model poly(vinyl acetate) material is shown in figure 4. The constitutive equation predicted a zero shear

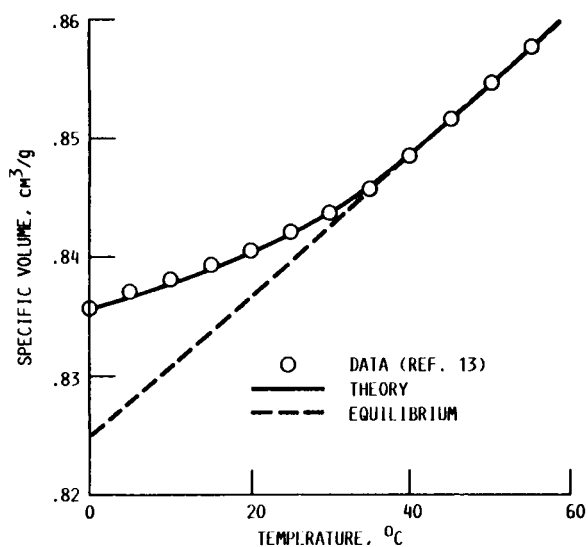


Figure 3.—Specific volume versus temperature predicted by equation (4) for poly(vinyl acetate) cooled at 5 deg C/hr. Pressure, 1 bar.

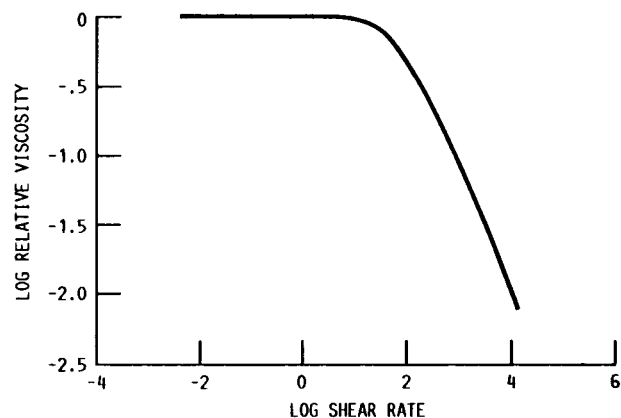


Figure 4.—Predictions of nonlinear viscoelastic constitutive equation of strain-rate-dependent shear viscosity for single-relaxation-time idealized poly(vinyl acetate) material at 80 °C.

viscosity at low shear rates and shear thinning viscosity at higher shear rates. The shear thinning viscosity could be described by a power law with a slope of approximately $-1/2$, which was in qualitative agreement with experimental data. The constitutive equation also predicted a primary normal stress that was also shear thinning and in qualitative agreement with experimental data. Although much work remains before the non-Newtonian fluid predictions of the constitutive equation are fully evaluated, the initial results shown in figure 4 look quite promising.

Group Contribution Methods for Linear Viscoelastic Shear Modulus

An extensive experimental study of the linear viscoelastic shear modulus was performed for a series of diglycidylether of bisphenol-A (DGEBA) epoxy resins cured with 4,4-diaminodiphenylsulfone (DDS). The dynamic linear viscoelastic storage and loss moduli, G' and G'' , were measured as functions of frequency from liquid nitrogen temperatures to well above T_g (ref. 9). The complete linear viscoelastic response is usually determined by time-temperature superposition of the frequency- or time-dependent isotherms (ref. 10); however, time-temperature superposition is not applicable for the DGEBA/DDS materials, since they exhibit multiple relaxation mechanisms.

A novel procedure has been developed (ref. 11) to extract the linear viscoelastic shear response when there are two relaxation mechanisms: the α mechanism in the glass-to-rubber transition and a sub- T_g β mechanism. We assumed that the viscoelastic response of the material was a linear combination of the α and β response; that is,

$$G'(\omega, T) = G'_\alpha \left(a_T^\alpha \omega, T_{ref}^\alpha \right) + G'_\beta \left(a_T^\beta \omega, T_{ref}^\beta \right) \quad (5)$$

and

$$G''(\omega, T) = G''_{\alpha} \left(a_T^{\alpha} \omega, T_{\text{ref}}^{\alpha} \right) + G''_{\beta} \left(a_T^{\beta} \omega, T_{\text{ref}}^{\beta} \right) \quad (6)$$

where $a_T^{\alpha}, a_T^{\beta}$ and $T_{\text{ref}}^{\alpha}, T_{\text{ref}}^{\beta}$ are the shift factors and reference temperatures for the α and β mechanisms, respectively; T is the experimental temperature; and ω is the experimental frequency. It is implicitly assumed in equations (5) and (6) that the relaxation spectra of the α and β mechanisms are additive but that the time-temperature shifts are different. For discrete spectra of α and β relaxation times, the $G''(\omega)$ isotherms are given by

$$G''(\omega, T) = \sum_{\text{all } i} G''_{\alpha i}(\omega, T) + \sum_{\text{all } j} G''_{\beta j}(\omega, T) \\ = \sum_{\text{all } i} H_{\alpha i} \frac{\omega a_T^{\alpha} \tau_i}{1 + (\omega a_T^{\alpha} \tau_i)^2} + \sum_{\text{all } j} H_{\beta j} \frac{\omega a_T^{\beta} \tau_j}{1 + (\omega a_T^{\beta} \tau_j)^2} \quad (7)$$

where $H_{\alpha i}$ and $H_{\beta j}$ are the discrete spectra values for the α and β mechanisms. The $G''(\omega, T)$ response is experimentally measured at a variety of frequencies and temperatures. Subsequently, equation (7) is written in a matrix form, where $H_{\alpha i}$ and $H_{\beta j}$ are elements of an unknown column vector H . By using the a_T^{α} and a_T^{β} shift functions determined from

shifting the G'' data, the vector H can be determined from the experimental G'' isotherms.

Because the set of equations is nearly singular, the conventional least-squares solution procedure produces oscillatory spectra. The technique of regularization with quadratic programming (RQP) is an appropriate method for solving ill-posed problems such as equation (7) (ref. 10). We have used the RQP method with proper scaling of the variables in equation (3) to accurately determine $H_{\alpha i}$ and $H_{\beta j}$. Details of the method are presented elsewhere (ref. 9). The $\log a_T^{\alpha}$ and $\log a_T^{\beta}$ shift factors are shown in figure 5 for the series of epoxy resins. The individual G'' responses, as determined from the spectra for the α and β mechanisms, are shown in figure 6 for the series of epoxy resins.

An examination of the $\log a_T^{\alpha}$ data in figure 5 shows that the α -mechanism shift factor is the same for all the epoxy materials when referenced to T_g . The difference in $\log a_T^{\alpha}$ below T_g is a consequence of different thermal histories during formation of the glass rather than an effect of the chemical structure. The G'' response for the α -mechanism is essentially identical for all the epoxy resins, with the exception of the two most tightly crosslinked materials, which have greater strength at high frequencies. Further, the G'' response for the β mechanism was essentially the same for all the epoxy resins investigated. The data shown in figures 5 and 6 are the beginnings of a group contribution method for the linear viscoelastic shear modulus of DGEBA epoxy resins. Group methods for other diepoxide systems have also been investigated (ref. 12).

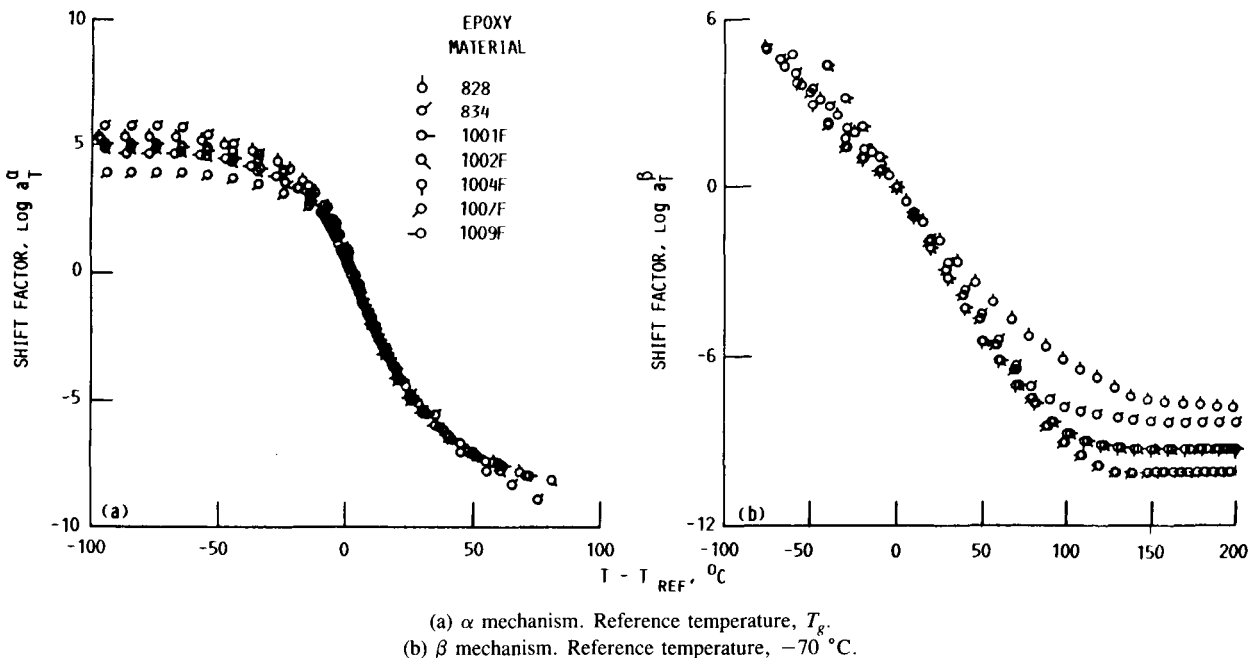


Figure 5.—Independent $\log a_T^{\alpha}$ and $\log a_T^{\beta}$ shift factors for series of DGEBA/DDS epoxies.

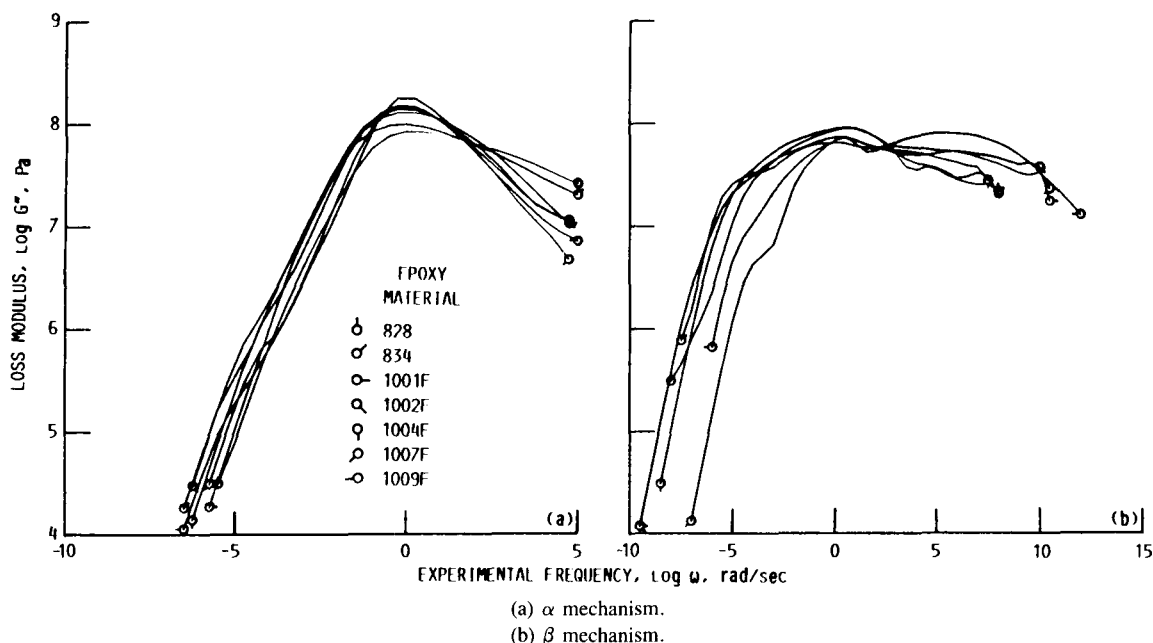


Figure 6.—Loss modulus response for α and β mechanisms for series of DGEBA/DDS epoxies.

Summary of Results

From this study to develop models for predicting the important engineering properties of aerospace epoxy resins, the following results have been noted:

1. A new constitutive equation has been developed that can describe (a) the nonlinear viscoelastic behavior including yield when the polymer is in the solid state, (b) the glass transition phenomenon, and (c) the non-Newtonian flow behavior of the polymer melt.

2. The new constitutive equation has no adjustable parameters and the required material properties are (a) the equilibrium pressure-volume-temperature behavior needed to specify the Simha-Somcynsky equation of state, and (b) the linear viscoelastic shear and bulk moduli.

3. The constitutive equation predictions for a typical epoxy resin agreed quantitatively with the experimentally measured stress-strain response.

4. The specific volume versus temperature response for poly(vinyl acetate) agreed quantitatively with measured data and accurately predicted the glass transition temperatures T_g .

5. The constitutive equation accurately predicted the strain-rate-dependent shear viscosity for single-relaxation-time poly(vinyl acetate) material.

6. A novel procedure has been developed to extract the linear viscoelastic shear response when there are two relaxation mechanisms (α and sub- T_g β) operating.

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio, March 30, 1989

References

1. Shay, R.M., Jr.; and Caruthers, J.M.: A Free Volume Model for Yield Stress. *Advances in Rheology*, Vol. 1: Theory, B. Mena, A. García-Rejón, and C. Rangel-Nafaile, eds., National University of Mexico, 1984, pp. 549-556.
2. Shay, R.M., Jr.; and Caruthers, J.M.: A New Nonlinear Viscoelastic Constitutive Equation for Predicting Yield in Amorphous Solid Polymers. *J. Rheology*, vol. 30, no. 4, 1986, pp. 781-827.
3. Shay, R.M., Jr.; and Caruthers, J.M.: A Nonlinear Viscoelastic Constitutive Equation—Yield Predictions in Multiaxial Deformations. *Developments in Mechanics*, Vol. 14(b), Purdue University, 1987, pp. 493-498.
4. Lustig, S.R.; and Caruthers, J.M.: Thermodynamic Constitutive Equations With Memory Using a Material Timescale. *Xth International Congress on Rheology*, Vol. 2, P.H.T. Uhlherr, ed., Australian Society of Rheology, 1988, pp. 100-102.
5. Truesdell, C.; and Noll, W.: *The Non-Linear Field Theories of Mechanics*, *Handbuch der Physik*, Vol. III, Pt. 3, H.S. Flugge, ed., Springer-Verlag, New York, 1965.
6. Hopkins, I.L.: Stress Relaxation or Creep of Linear Viscoelastic Substances Under Varying Temperature. *J. Polym. Sci.*, vol. 28, no. 118, Apr. 1958, pp. 631-633.
7. Adam, G.; and Gibbs, J.H.: On the Temperature Dependence of Cooperative Relaxation Properties in Glass-forming Liquids. *J. Chem. Phys.*, vol. 43, no. 1, July 1, 1965, pp. 139-146.
8. Simha, R.; and Somcynsky, T.: Statistical Thermodynamics of Spherical and Chain Molecule Fluids. *Macromolecules*, vol. 2, no. 4, 1969, pp. 342-350.
9. Curliss, D.B.: Linear and Non-Linear Viscoelastic Behavior of a Series of DGEBA Epoxy Resins. M.S. Thesis, Purdue University, 1987.
10. Ferry, J.D.: *Viscoelastic Properties of Polymers*. Third Ed., Wiley, 1980.
11. Wiff, D.R.: RQP Method of Inferring a Mechanical Relaxation Spectrum. *J. Rheology*, vol. 22, no. 6, Dec. 1978, pp. 589-597.
12. Gibson, F.W.: The Effect of Chemical Structure of Linear Viscoelastic Properties of Epoxy Resins. M.S. Thesis, Purdue University, 1988.
13. McKinney, J.E.; and Goldstein, M.: Pressure Volume Temperature Relations for Liquid and Glassy Poly(vinyl Acetate). *J. Res. Nat. Bur. Stand., Sect. A.*, vol. 78, no. 3, 1974, pp. 331-353.



Report Documentation Page

1. Report No. NASA TM-4128	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle A Predictive Model for Failure Properties of Thermoset Resins		5. Report Date July 1989	
		6. Performing Organization Code	
7. Author(s) James M. Caruthers and Kenneth J. Bowles		8. Performing Organization Report No. E-4572	
		10. Work Unit No. 510-01-0A	
9. Performing Organization Name and Address National Aeronautics and Space Administration Lewis Research Center Cleveland, Ohio 44135-3191		11. Contract or Grant No.	
		13. Type of Report and Period Covered Technical Memorandum	
		14. Sponsoring Agency Code	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546-0001			
15. Supplementary Notes James M. Caruthers, Purdue University, West Lafayette, Indiana 47907 (work funded under NASA Grant NAG3-599); Summer Faculty Fellow. Kenneth J. Bowles, NASA Lewis Research Center.			
16. Abstract <p>A predictive model for the three-dimensional failure behavior of engineering polymers has been developed in a recent NASA-sponsored research program. This model acknowledges the underlying molecular deformation mechanisms and thus accounts for the effects of different chemical compositions, crosslink density, functionality of the curing agent, etc., on the complete nonlinear stress-strain response including yield. The material parameters required by the model can be determined from test-tube quantities of a new resin in only a few days. Thus, we can obtain a first-order prediction of the applicability of a new resin for an advanced aerospace application without synthesizing the large quantities of material needed for failure testing. This technology will effect order-of-magnitude reductions in the time and expense required to develop new engineering polymers.</p>			
17. Key Words (Suggested by Author(s)) Polymers Properties Model Failure		18. Distribution Statement Unclassified - Unlimited Subject Category 24	
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No of pages 8	22. Price* A02