THE APPLICABILITY OF NONLINEAR MELT RHEOLOGY CONCEPTS TO THE
NONLINEAR SOLID RHEOLOGY OF DGEBA/m-PDA EPOXY RESIN IN THE
GLASSY REGION

Gale A. Holmes, Richard C. Peterson, Donald L. Hunston, and Walter G. McDonough

National Institute of Standards and Technology, Polymers Division, Gaithersburg, Maryland 20899

Abstract

Most ductile polymers exhibit nonlinear viscoelastic behavior above 1% strain. In structural applications where matrix deformation may play an important role in the performance and failure process of a part, very little has been done to characterize the solid state nonlinear viscoelastic behavior of polymers. In this paper we use melt rheology concepts and a standardized testing regime to develop a nonlinear constitutive equation that describes the nonlinear behavior of a polymer above 1% for single-step stress relaxation experiments. The nonlinear constitutive equation is then used to characterize the multi-step stress relaxation behavior of the same polymer. When compared with actual behavior, the model prediction was found to under predict the response of the polymer at strains above 1%. This suggests the presence of a path dependent mechanism, not accounted for in single-step stress relaxation tests, that alters the response of the matrix material during the test. Therefore, the single-step stress relaxation test must be augmented with other characterization techniques to account for the response of the matrix during multi-step stress relaxation tests.

Introduction

Rheology is the study of the way materials deform under applied forces. Except for elastomers, rheology has usually been restricted to the study of fundamental relations, termed constitutive relations, between force and deformation in liquid and liquid-like materials, e.g., molten polymers. Over the years, considerable knowledge and understanding has been amassed about the response of molten polymers to linear and nonlinear deformation regimes (e.g., in extrusion). Although polymers are widely used in structural applications (e.g., composites), relatively little research has been done to equate the nonlinear response of polymeric structures to the molecular architecture and nonlinear deformation behavior of the glassy polymer. From a materials engineering viewpoint, failure in any material is related to the strain on the microscopic scale. Although the failure criteria for metals, yielding, can be expressed in terms of stress since the constitutive behavior of metals is a linear multiple of strain, the failure criteria for polymers cannot be expressed this way because of their nonlinear constitutive behavior. The engineering design criteria for polymers must be expressed in terms of limiting values of stress and strain, which are in general independent of each other. Therefore, a more detailed analysis is needed for polymers to conform to these limiting values. McKenna and Knauss suggested that melt rheology concepts provide a useful starting place for elucidating nonlinear constitutive behavior in glassy polymers.

In fibrous composites, the deformation behavior and adhesion of a polymer at the fiber-matrix interface is critical to composite structure performance. In addition, macroscopic failure of composites is often preceded or accompanied by localized nonlinear deformation behavior in the matrix. The architecture of a polymer has been shown to influence its glass transition temperature, yield, and fracture behavior. In addition, physical aging, hydrostatic pressure, degree of plasticization, and the confining geometry as imposed by the reinforcement in the composite have a significant influence on the deformation response of a polymer matrix. Although the confining geometry is important in traditional fiber composites, it is of particular importance in hybrid composites, composed of two types of fibers (i.e., carbon and glass) embedded in a thermoset resin. Hybrid composites are finding increasing use in applications where the
performance properties of carbon fibers and the damage tolerance and cost effectiveness of glass fibers are desired. The large differences in thermal expansion coefficients and Young's moduli of the matrix and fibers comprising the hybrid composite lead to severe thermal and/or residual stresses not found in fiber composites with only one type of fiber. These mismatches give rise to large interfacial shear stresses at the fiber-matrix interface and axial stresses in the fiber and matrix which result in deformation responses that cannot be predicted (Hybrid Effect) by the simple rule of mixtures of components. In addition, localized nonlinear deformation behavior may be occurring in the matrix when the global response of the composite is linear. Ongoing research in this laboratory has shown that the matrix strain between fiber breaks in a test specimen that contains a single E-glass fiber (unit composite tests specimen) can be an order of magnitude higher than the global macroscopic strain. Thus, the key to understanding the deformation behavior, performance characteristics, and failure of composites rests in understanding the response of the matrix material in these composite structures. Success in this endeavor will allow the development of design criteria and guidelines that will be useful in predicting the deformation behavior and life expectancy of composite structures.

In composite research, the single fiber fragmentation test (SFFT) is widely used to characterize the fiber-matrix interface shear strength. As noted by Piggott, the SFFT is the test that most realistically accounts for the impact of interfacial pressure on the interfacial shear strength parameter. Since the fiber is neither pushed nor pulled directly, Poisson effects between the fiber and matrix are similar to those occurring in a fiber composite. In the SFFT, a dogbone is made with a resin having a high extension to failure and a single fiber embedded along the axis of the dogbone. The sample is pulled in tension and stress is transmitted into the fiber through the fiber-matrix interface. Since the fiber has a lower strain to failure than the resin, the fiber breaks at the weakest flaw as the strain is increase. This process continues until the remaining fiber fragments are all less than a critical transfer length, which is the length below which the fragments are too short for sufficient load to be transmitted into them to cause failure. This point is termed saturation. The fragment lengths at saturation are measured and a micromechanics model is used to convert the average fragment length into a measure of the interface strength. Thus, the interface strength is determined indirectly from experimental data and theoretical models. Ongoing research in this laboratory has shown that fiber fragmentation during this test occurs when the deformation response of the matrix material is nonlinear viscoelastic. Hence, nonlinear models are required to assess the fiber-matrix interfacial shear strength. Therefore, characterization of the nonlinear viscoelastic behavior of the matrix resin will facilitate the development of an accurate standardized test methodology and enhance or understanding of the interfacial shear strength test. Since the matrix used in the SFFT test is typical of resin systems utilized in filament wound composites, this information will provide a basis for understanding the deformation behavior of the matrix material in full composite applications.

In this paper, DGEBA/m-PDA epoxy resin will be characterized by single step-strain stress relaxation data obtained at various strain levels up to 6%. The data from this fundamental test will be used to formulate a nonlinear constitutive model based on concepts developed in melt rheology and recently used by Matsuoka to explore the nonlinear deformation behavior of polycarbonate. The nonlinear constitutive model will then be used to predict the multi-step stress relaxation response of the DGEBA/m-PDA epoxy resin. This deformation regime is utilized in the single fiber fragmentation test and hence provides a measure of the predictability of polymer response functions derived from fundamental test data.
Experimental

Sample Preparation

To make test specimens, eight-cavity molds were made out of RTV-664 from General Electric following the procedure described by Drzal. All molds were post cured at 150 °C and rinsed with acetone prior to use. 100 grams of diglycidyl ether of bisphenol-A (DGEBA, Epon 828 from Shell Chemical Co.) and 14.5 grams of meta-phenylenediamine (m-PDA, Fluka Chemical Co.), were weighed out in separate beakers. To lower the viscosity of the resin and melt the m-PDA crystals, both beakers were placed in a vacuum oven (Fisher Scientific Isotemp Vacuum Oven, model 281 A) set at 75 °C. After the m-PDA crystals were completely melted, the silicone molds are placed into another oven (Blue M Stabiltherm, model OV-560A-2) that was preheated to 100 °C. With this preheated oven (Blue M Stabiltherm, model OV-560A-2) turned off, the silicone molds were warmed in the oven for approximately 20 minutes. This last procedure dries the molds and minimizes the formation of air bubbles during the curing process.

At approximately 9 minutes before the preheated molds were removed from the oven, the m-PDA was poured into the DGEBA and mixed thoroughly. The mixture was placed into the vacuum oven and degassed for approximately 7 minutes. The preheated molds were removed from the oven after 20 minutes and were filled with the DGEBA-m-PDA resin mixture using 10 cc disposable syringes. The filled molds were then placed into a programmable oven (Blue M, General Signal, model MP-256-1, GOP). A cure cycle of two hours at 75 °C followed by two hours at 125 °C was used.

Multi-Step Stress Relaxation Tests

The multi-step stress relaxation tests were carried out on a small hand-operated loading frame similar to that described by Drzal. The loading frame was mounted on a Nikon Optiphot polarizing microscope. The image was viewed using a CCD camera (Optronics LX-450 RGB Remote-Head microscope camera) and monitor (Sony, PVM-1344Q). The sample was scanned by translating the loading frame under the microscope with a micrometer. The position of the load frame was monitored by an LVDT (Trans-Tek, Inc. model 1002-0012) connected to an A-to-D board (Strawberry Tree, Inc.) in a computer. To determine the strain, two lines were made in the gauge section of the test specimen using a “green” Staedtler Lumocolor 317 permanent marker pen. The strain was determined by measuring the same point on each line at each strain increment. The location of the point of interest on each line was aligned with a cross hair in the microscope as seen on the video monitor, and the position of the LVDT was digitized into the computer. The standard instrument uncertainty in measuring a point is ± 0.3 μm. The standard uncertainty in relocating a point reproducibly is ±1.1 μm. The load was also monitored during the experiment using a 2,224 N (500 pound) load cell connected to a bridge (load cell and AED 9001A bridge, Cooper Instruments). The expected standard uncertainty of the load measurements is 3% of the load. The bridge was attached to the same computer via a serial connection. A custom program was developed to continuously record the load and any LVDT measurements that are made. The average application time of each strain step was (1.10 ± 0.17)s and the average deformation was (14.45 ± 3.11) μm. The strain was found to increase by 0.0034% for each 1 N change in load. Finite rate corrections were not performed on the step-strain data.

* Certain commercial materials and equipment are identified in this paper to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply necessarily that the product is the best available for the purpose.
Single-Step Stress Relaxation Tests

For step-strains above 0.8%, the SFFT apparatus described above was used. For small strains, grips identical to those for the SFFT apparatus were constructed for a Dynastat® testing machine. The displacement of the grips was found to be inadequate for calculations of the strain, so an extensometer was used to monitor strains. Loading by the Dynastat® required approximately 10 ms; therefore, data from 0.1 s to 10 s was obtained. The relative increase in strain at each strain step for the Dynastat® was found to be negligible, since the loading frame is very stiff.

Results and Discussion

Single-Step Relaxation Data

Plots of selected modulus relaxation curves for the DGEBA/m-PDA epoxy resin are shown in Figure 1. Readily apparent from Figure 1 is the decrease in the instantaneous modulus, $E_0$, with increasing step-strains. This behavior is consistent with nonlinear viscoelastic behavior and has been termed by some to be strain-softening of the elastic component (i.e., modulus). In melt rheology, this change in relaxation modulus with increasing strain has been modeled using an equation of the following form:

$$E(\varepsilon) = E_0 h(\varepsilon) = E_0 \exp(-\eta \varepsilon)$$

where $E(\varepsilon)$ is the strain dependent modulus, $h(\varepsilon)$ is a damping function, $\varepsilon$ is the strain, and $\eta$ is a fitting parameter.

From Equation 1, a plot of $\ln(E(\varepsilon))$ (i.e., at a constant time after each strain increment) versus $\varepsilon$ allows the determination of $E_0$ and $\eta$ by linear regression analysis. Such a plot is shown in Figure 2 for the 100 s modulus data.
Figure 1. Plot of single-step relaxation behavior for DGEBA/m-PDA epoxy resin.
Polymer materials that undergo strain-softening are either time-strain separable or time-strain nonseparable in their constitutive behavior. For time-strain separable materials, the relaxation behavior of the polymer does not change with increasing step-strains. In Figure 1, the relaxation behavior of the DGEBA/m-PDA epoxy resins transitions from the time-strain separable to nonseparable behavior between 1.26% and 2.5% strain. This is best seen by dividing the relaxation modulus $E(t)$, by the modulus at 100 s, $E_{100s}$ and plotting the relative relaxation with time for each step-strain, as shown in Figure 3. The gradual change in relative relaxation with increasing step-strains above 1.3% is apparent. Also apparent is the lack of change in relaxation behavior below 1.3% strain. Since, fragmentation in the SFFT typically occurs at strains greater than 1.5%, over most of the strain range of interest, DGEBA/m-PDA exhibits nonseparable behavior with respect to time and strain. Hence, a nonseparable time-strain constitutive equation can be used to model the behavior for the material.

Matsuoka, Williams, and Schapery have noted that for some polymers well below the glass transition temperature, $T_g$, the relaxation behavior can be approximated by power law expressions. Schapery has also shown that the modified power law is often a good approximation for crosslinked polymers with a
broad distribution of relaxation times. Using the results from the linear regression analysis in Figure 2, the
nonseparable relaxation modulus for the DGEBA/m-PDA epoxy resin is represented by the following form:

\[ E(\varepsilon,t) = E_0 \exp(-\eta \varepsilon)(\alpha + t/\tau)^{\delta(t)} = 3.07 \exp(-14.92\varepsilon)(\alpha + t/100\varepsilon)^{\delta(t)} \] (2)

Figure 3. Relative relaxation behavior of DGEAB/m-PDA epoxy resin with increasing strain.

where

- \( \alpha = 0 \) represents the standard power law form
- \( \alpha = 1 \) represents the power law form
- \( \tau \) represents the characteristic relaxation time
- \( \delta(\varepsilon) \) characterizes the change in relaxation behavior of the polymer with increasing strain

From the data in Figure 1 and similar data not shown, the variation \( \delta(\varepsilon) \) of with strain is shown in Figure 4.

A linear regression analysis of the data and a power law fit of the data (not shown) were comparable.

Hence, \( \delta(\varepsilon) \) is assumed to have the following functional form:

\[ \delta(\varepsilon) = (d\delta/d\varepsilon)\varepsilon + \kappa = 0.4677\varepsilon + 0.0140 \] (3)

where \( \kappa \) is the intercept.
Model predictions of the step-strain data given in Figure 1 are shown in Figure 5. With the exception of the 1.26% strain increment, the prediction of the relaxation behavior at each step-strain up to 4.97% strain by Equation 2 and Equation 3 are reasonable. As previously noted, the data in Figure 3 indicates that the DGEBA/m-PDA epoxy resin transitions from time-strain separable behavior to time-strain nonseparable behavior above 1.26% strain. Therefore, the poor fit at 1.26% strain arises from this assumption. The poor fit by Equation 2 and Equation 3 of the stress relaxation data at 5.90% strain is consistent with the lack of fit of the 100 s modulus data point at 5.90% by linear regression analysis in Figure 2. In Figure 6, the multi-step relaxation behavior of the DGEBA/m-PDA epoxy resin is predicted from the nonseparable relaxation modulus derived from the single step-strain relaxation data. Although reasonable agreement is obtained for the initial strain increments, above 0.0081 strain the model systematically underpredicts the load. At the final increment, the load predicted by the model relative to the actual data is lower by approximately 15%.

\[ \theta \{ \epsilon \} = a \epsilon + b = 0.4677 \epsilon + 0.0140 \]

Figure 4. Variation of theta values with increasing strain. Solid symbols correspond to experimental data shown in Figure 1.
Figure 5. Model prediction of single-step relaxation behavior of DGEBA/m-PDA epoxy resin using the standard power law form of Equation 2, $\alpha=0$, with $\theta(\varepsilon)$ obtained from Equation 3.
Figure 6. Prediction of multi-step relaxation behavior for DGEBA/m-PDA specimen strain at 1 h time intervals using nonseparable relaxation modulus obtained from single step-strain data.

Conclusions

Experimental data is presented which shows that the DGEBA/m-PDA epoxy resin exhibits time-strain separable relaxation behavior below 1.3% strain and time-strain nonseparable behavior above this value. The nonlinear constitutive equation derived from the single step stress relaxation data was shown to under predict the load of the DGEBA/m-PDA epoxy resin in the multi-step step-strain deformation regime. Although the DGEBA/m-PDA epoxy resin exhibits strain-softening in both deformation regimes, the rate of strain-softening is less in the multi-step step-strain test. This suggests the presence of a second relaxation regime that is dependent of the history of the deformation process. Research is underway to accurately model the multi-step step-strain relaxation behavior.
References


## Contents

### Physical Chemistry

<table>
<thead>
<tr>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitron as a Potential Chemical Sensor for Stratospheric Nitric Acid</td>
<td>1</td>
</tr>
<tr>
<td><em>Kapres Meadows and Vernon R. Morris</em></td>
<td></td>
</tr>
<tr>
<td>The CSTEA Howard Oxidants and Air Quality Experiment (CHOAQE)</td>
<td>15</td>
</tr>
<tr>
<td><em>Vernon R. Morris</em></td>
<td></td>
</tr>
</tbody>
</table>

### Polymer/Material Science

<table>
<thead>
<tr>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanophase Materials Synthesis via Clathrate Hydrate Co-Nucleation</td>
<td>23</td>
</tr>
<tr>
<td><em>G. C. Irvin Jr., S. Li, S. Banerjee, and V. T. John</em></td>
<td></td>
</tr>
<tr>
<td>Modeling the Evolution of Structure in a Meltblowing Process</td>
<td>33</td>
</tr>
<tr>
<td><em>Kyra D. Dorsey, Prashant Desai, and Agaram S. Abhiraman</em></td>
<td></td>
</tr>
<tr>
<td>The Applicability of Nonlinear Melt Rheology Concepts to the Nonlinear Solid Rheology of DGEBA/m-PDA Epoxy Resin in the Glassy Region</td>
<td>47</td>
</tr>
<tr>
<td><em>Gale A. Holmes, Richard C. Peterson, Donald L. Hunston, and Walter G. McDonough</em></td>
<td></td>
</tr>
<tr>
<td>Materials Synthesis via Water-in-Dense CO₂ Microemulsions: A Novel Reaction Medium</td>
<td>59</td>
</tr>
<tr>
<td><em>G. C. Irvin Jr. and V. T. John</em></td>
<td></td>
</tr>
<tr>
<td>Phase Transitions of a Bacterial Polyhydroxyalkanoate from a Novel Source</td>
<td>69</td>
</tr>
<tr>
<td><em>Tima M. McGuthry-Banks, Folahan O. Ayorinde, Broderick E. Eribo, and William E. Collins</em></td>
<td></td>
</tr>
</tbody>
</table>

### Organic Chemistry

<table>
<thead>
<tr>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>A Synthetic Approach to Amphidininolide A: A Novel Macrolactone with Anti-Leukemic Activity</td>
<td>79</td>
</tr>
</tbody>
</table>

*Proceedings: NOBCChE '98, Volume 25, August 1998*
### Poster Session for Undergraduates

**The Chemical Characterization of Titanium Alloy (Ti-15-3) Surface Treatments for Adhesive Bonding to Form Composite Structural Materials**  
Ivy L. Badger, Khadija Dugan, Joseph C. Williams, Sharon Lowther, and Terry St. Clair  
87

### The NOBCChE Rohm and Haas Company Undergraduate Research Award Competition

**The Effects of Solutes on Liquid Crystal Stability**  
Charles A. Jones III, Sueng K. Kang, and Edward T. Samulski  
95

**Progress Towards the Solid State Polymerization of Poly(Bisphenol A Carbonate) in Supercritical Carbon Dioxide**  
Devin Flowers, Steven Gross, and Joseph M. DeSimone  
101

**The Regiochemistry of Alkyne Hydrostannylations under Palladium Catalyzed and Free Radical Conditions**  
Susan L. Whitehead, Michael B. Rice, Ina Terstiege, and Robert E. Maleczka Jr.  
107

**Characterization of Amphiphilic Dendritic Diblock Copolymer Solutions**  
Kala Fleming, Paula Hammond, Jyostna Iyer, and Cathy Bambenek  
117

**Growth of Vascular Cells on Bioactive Polysaccharide Surfaces**  
Angela Foster and Howard W. T. Matthew  
127

**CVD Ir Film Growth and Vapor Pressure Analysis with Iridium Tris-acetylacetonate**  
Clover E. Sweeney, Yang-Ming Sun, J. Ekerdt, and J. M. White  
131

### Speakers' Forum

**Opening Session**  
Pamela B. Jackson  
137

**Preparing Our Youth for the Next Millennium Workshop**  
Yolanda George and Saundra Y. McGuire  
143

**A Second American Century? Opportunities and Challenges in the 21st Century**  
Mary Good  
149

**Matrix Metalloproteases: A Link Between Tumor Cell Metastasis and Angiogenesis?**  
Linda Meade-Tollin  
159

*Proceedings: NOBCChE '98, Volume 25, August 1998*
<table>
<thead>
<tr>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tools for the Transition to the New Millennium</td>
<td>165</td>
</tr>
<tr>
<td><em>Saundra Y. McGuire and Leon O. Spencer</em></td>
<td></td>
</tr>
<tr>
<td>The Impact of Changes on Affirmative Action Forum</td>
<td>171</td>
</tr>
<tr>
<td><em>James E. Evans</em></td>
<td></td>
</tr>
<tr>
<td>The Impact of Changes on Affirmative Action Forum</td>
<td>177</td>
</tr>
<tr>
<td><em>Shirley McDavid</em></td>
<td></td>
</tr>
<tr>
<td>The Impact of Changes on Affirmative Action Forum</td>
<td>181</td>
</tr>
<tr>
<td><em>Halcolm Holliman</em></td>
<td></td>
</tr>
<tr>
<td>The Impact of Changes on Affirmative Action Forum</td>
<td>187</td>
</tr>
<tr>
<td><em>Sylvester J. Gates Jr.</em></td>
<td></td>
</tr>
<tr>
<td>Annual Awards Banquet</td>
<td>191</td>
</tr>
<tr>
<td><em>Frank L. Douglas</em></td>
<td></td>
</tr>
<tr>
<td>Friday Luncheon</td>
<td>197</td>
</tr>
<tr>
<td><em>Freeman A. Hrabowski III</em></td>
<td></td>
</tr>
</tbody>
</table>