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## CONSTITUTIVE MODELING OF EPOXY USING THE MULLIKEN-BOYCE MODEL FOR GLASSY POLYMERS

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# CONSTITUTIVE MODELING OF EPOXY USING THE MULLIKEN-BOYCE MODEL FOR GLASSY POLYMERS

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## ABSTRACT

Polymers are increasingly common in aerospace structural applications where they experience complex, non-static loads. Correspondingly, the high strain rate mechanical properties are of increasing importance. This paper gives results from an initial investigation of the properties of bisphenol-A/diethanolamine epoxy (Epon 826/DEA) across strain rates from  $10^{-3}$  to  $10^5$  s<sup>-1</sup>. The samples were tested using Instron, traditional split Hopkinson pressure bars (SHPBs) and a miniaturized SHPB for ultra-high strain rates and dynamic mechanical analysis to look at the effects of time-temperature superposition on the strain rate effects in the samples. The Mulliken-Boyce constitutive model for glassy polymers is used to describe the mechanical properties of epoxy across the range of strain rates tested.

## 1 INTRODUCTION

Epoxyes such as bisphenol-A/diethanolamine epoxy (Epon 826/DEA) are ubiquitous materials for structural applications, including those with high-rate, large-strain dynamic loads. The mechanical properties of polymers are greatly affected by both the strain rate and the temperature of the testing. For example, Bauwens and colleagues investigated polycarbonate (PC) in compression over a range of temperatures, and found a bilinear relationship between stress and strain [1, 2]. This behavior was attributed to the different molecular relaxations in the material. At high temperatures or low strain rates only the  $\alpha$  relaxation (glass transition) plays a role in the polymer behavior, while at low temperatures and high strain rates, the effect of the  $\beta$  relaxation is superimposed on that of the  $\alpha$  transition. The authors developed a model to explain the yield stress behavior, which was also used by Rietsch and Bouette [3]. More recently, Siviour, et al. [4, 5] performed experiments on PC and PVDF and identified the effect of different molecular transitions on the strain rate-dependent material strength using temperature-strain rate equivalence. Mulliken and Boyce [6] further showed how shifting data from dynamic mechanical analysis (DMA) curves can be used to develop the physically based understanding behind a predictive model for high strain rate behavior of polymers.

The mechanical and thermal properties of epoxy, even with the same epoxy resin, can vary greatly depending on curing agent [7, 8] and curing regime [8]. Hu, et al. [9, 10] found that under shear loading Epon 826 cured with Epi-cure 9551 exhibited strain rate dependence independent of hydrostatic pressure (up to 17 MPa). This paper presents initial results and analysis from recent experiments investigating the quasi-static and high strain rate compressive properties of Epon 826 epoxy resin cured with diethanolamine (DEA) hardener. The effects of time-temperature superposition on the mechanical properties of the epoxy material will be investigated in the extended version of this paper [11].

## 2 EXPERIMENTAL PROCEDURE

### 2.1 Thermomechanical Analysis

Dynamic mechanical analysis was performed in a single cantilever configuration at 1, 10, and 100 Hz over temperatures from 148 K to 473 K. The Epon 826 resin was mixed at 80°C with the DEA hardener and vacuum cast (also at 80°C) in a rectangular pan. The epoxy was cured at 80°C for a minimum of 12 hours. After curing, the samples were machined from the large block of material. These samples were then tested across a range of strain rates from  $10^{-2}$  to  $10^4$ , at room temperature and at 1470 s<sup>-1</sup> across a range of temperatures (213-333 K). An Instron model 2630 was used for quasi-static loading, in which the samples were nominally 8 mm diameter by 3.5 mm thick. In these experiments, samples with dimensions identical to those used for the split Hopkinson pressure bar were tested. The strain in the sample was determined from crosshead displacement, and the stress was determined from the load cell output. All data was acquired using Instron's Merlin software.

### 2.2 Split Hopkinson Bar Testing

The split Hopkinson pressure bar (SHPB) is a well-known technique for rate-dependent materials characterization and has been reviewed by many authors [12, 13]. Compression experiments at

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intermediate strain rates ( $10^3 - 10^4$ ) were conducted using two split Hopkinson pressure bars (SHPB) [12, 13], a schematic diagram of which can be seen in Figure 1.

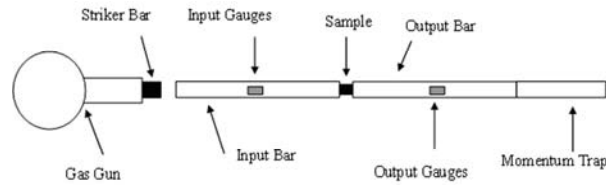


Figure 1. Schematic of split Hopkinson pressure bar (SHPB) experimental setup.

The experiments varying strain rate were conducted using the SHPB system located at AFRL/RWME, Eglin AFB, FL, which is comprised of 1524 mm long, 19 mm diameter incident and transmitted bars of 440-HT stainless steel or 6061-T6 aluminum. The striker is 305 mm long and made of the same material as the other bars. The experiments with varying temperature were performed using the SHPB system at the Cavendish Laboratory, University of Cambridge, which consists of 500 mm long, 12.7 mm diameter incident and transmitted bars with a 200 mm striker bar of grade 300 maraging steel. The samples, which were nominally 8 mm diameter by 3.5 mm thick or 5 mm diameter by 2.5 mm thick, depending on strain rate, are positioned between the incident and transmitted bars. The bar faces were lightly lubricated with paraffin wax to reduce friction.

Experiments at ultra-high strain rates ( $10^4 \text{ s}^{-1}$ ) were conducted using a miniaturized split Hopkinson pressure bar (MSHPB), which is, in principle, identical to the full sized SHPB. However, the bars are 300 mm long and 3–3.2 mm in diameter. Samples tested in this apparatus are nominally 1.5 mm diameter by 0.6 mm long. The MSHPB at Eglin AFB provides the opportunity to test materials up to strain rates of  $10^5 \text{ s}^{-1}$ , with tungsten carbide (WC) and titanium alloy (Ti-6Al-4V) bar materials available.

### 3 THEORY, ANALYSIS AND PROPERTY ESTIMATION

#### 3.1 Mulliken-Boyce Model

Although the Mulliken-Boyce model is a full three-dimensional model appropriate for implementation in a finite element code, such as ABAQUS, in this work the model was adapted to one dimension and implemented in MATLAB. Since the available data from this study was compressive stress-strain curves at varying rates and temperatures, this simplification allows the model to be explored for application to epoxy systems. A detailed presentation of the one-dimensional theory will be given in another article [11].

#### 3.2 Model-Based Estimation

The properties of the sample are estimated from experimental data using a rigorous model-based estimator. Due to the large number of parameters, stiffness (i.e., solution instability) of the problem, and weak sensitivity to several parameters, use of a stochastic estimator is indicated. A genetic algorithm (GA) [14, 15] is used to generate initial estimates for the 11 material parameters using population sizes of 20 to 50 individuals (with 4-5 elites). For each individual, the 1-D Mulliken-Boyce model is calculated for multiple strain rates (for example,  $1 \times 10^{-3}$  and  $1.3 \text{ s}^{-1}$  in Fig. 1). The fitness (figure of merit) of each individual for a given generation is calculated using the converged value from a solution to the system of differential equations (again using MATLAB routines); the fitness then governs the likelihood of those estimates continuing to the next generation. The “optimal” estimate is the individual with the maximum fitness.

### 4 RESULTS AND DISCUSSION

Using the 1D Mulliken-Boyce, the GA is used for several different combinations of strain rate. The estimates of one example, using strain rates of  $1 \times 10^{-3}$  and  $1.3 \text{ s}^{-1}$ , are shown in Fig. 2 and Table 1. The converged estimates show some qualitative agreement with the stress-strain behavior, especially in the linear domain. However, there is significant disparity in the  $\alpha$ - and  $\beta$ -components of the stress behavior. This is because the model has very low sensitivity to the estimation parameters related to the  $\alpha$ -transition, notably the activation energy and shear strain rate. However, the relative contribution of the  $\beta$ -relaxation is lower in magnitude. Therefore, the  $\alpha$ -transition with the lower sensitivity is driving the model convergence. Coupled with the intrinsic solution instability (from the model stiffness), the initial estimates have relatively low confidence but do provide some insight into the challenge in estimating the parameters.

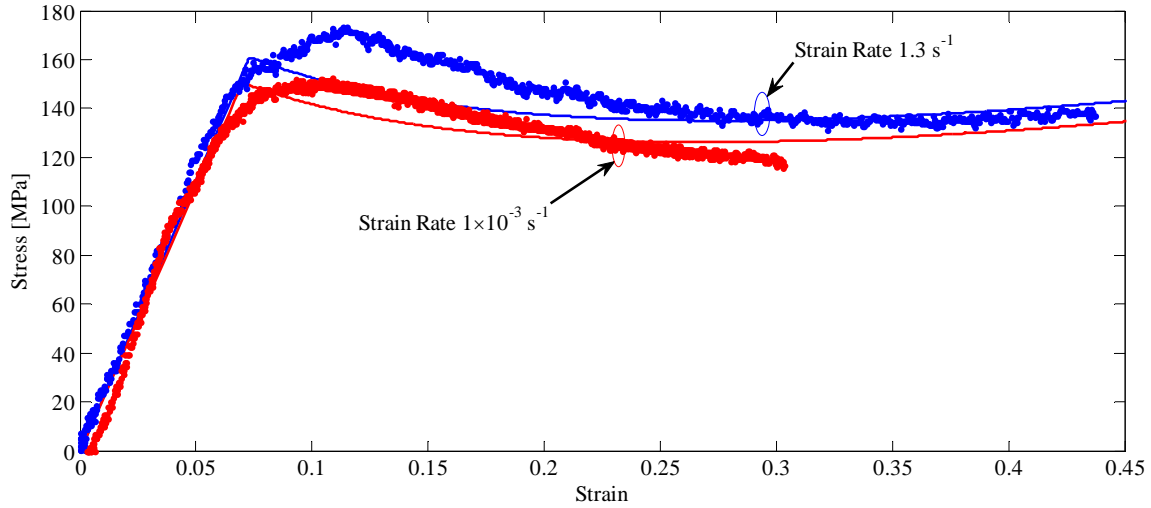


Figure 2. Experimental data ( $\bullet$ ) and 1D Mulliken-Boyce model output ( $-$ ) using best estimates (Table 1).

Symbol	$s_{ss,\alpha}$	$\dot{\gamma}_{0,\alpha}$	$\dot{\gamma}_{0,\beta}$	$\Delta G_{\alpha}$	$\Delta G_{\beta}$	$\alpha_{p,\alpha}$	$\alpha_{p,\beta}$	$h_{\alpha}$	$C_R$	$N$	$\sigma_{\beta}$
Units	MPa	$10^{15} \text{ s}^{-1}$	$10^6 \text{ s}^{-1}$	$10^{-18} \text{ J}$	$10^{-21} \text{ J}$	—	—	MPa	MPa	$\text{m}^{-1/2}$	MPa
Min	0.5	1	0.01	0.01	1	0.1	0.1	100	13	1	0.01
Max	1	1000	1	1	10000	0.3	0.3	300	15	3	1
Est.	0.670	178	0.542	0.967	834	0.224	0.378	263	13.9	2.02	0.283

Table 1. Estimation properties (symbolic), range, and converged estimates from Fig. 2.

## 5 CONCLUSIONS

Using a one-dimensional version of the Mulliken-Boyce model, data from DMTA and SHPB experiments was analyzed using a genetic algorithm-based to estimate the constitutive parameters that drive the stress-strain behavior of the epoxy. While in agreement with the linear region, the parameter estimates do not capture all of the experimental features since the  $\alpha$ -transition dominates the stress but has weaker parametric sensitivity. However, the approach shows promise and will be expanded in future efforts.

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