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Mechanical Properties of Glassy Polymer Blends and Thermosets

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LAMMPS Users' Workshop and Symposium,
Albuquerque, NM, August 8, 2013

Outline

Introduction & Motivation

Method Used For Calculating Small Strain Elastic Constants

Brief Summary of Early Simulation Work

Averaging Methods - Bounds

This Work
- Systems studied
- Simulation protocols
- Results

Discussion & Concluding Remarks

Introduction

Motivation: Theoretical calculation of the elastic constants of amorphous glassy materials is of increasing interest to a range of industries such as automotive and aerospace, especially in regard to predicting properties of advanced composites.

In principle, atomistic simulations can furnish a wealth of relevant mechanical property information, though in practice a number of obstacles need to be overcome, for example:

- Robust and rigorous calculation methods need to be developed.
- Since dimensions of atomistic system will be relatively small – even with million atom simulations – methods for using elastic constants of nano->microscopic domains to predict macroscopic behavior need to be more thoroughly investigated.
- Accurate force field representations are required for all materials of interest.
- Software applications need to be developed to manage and analyze the large amount of input and output data associated with the calculations.

Goals

The goal of the present study is accordingly:

“To assess the performance of atomistic simulation based elastic constant calculations reported since the 1990s, and to investigate improvements in **both** precision and accuracy achievable using today's computational materials science technology, with a particular emphasis on amorphous polymer glasses.”

Elastic Constant Method Used

Much of the published literature on small strain elastic properties of polymer glasses has focused on three methods. Here we use the so-called 'static' approach, in which a model system at mechanical equilibrium is subject to tensile and shear deformation, and $\Delta\sigma/\Delta\varepsilon$ calculated after restoring the state of equilibrium using energy minimization.

- Advantages: Conceptually straightforward
- Disadvantages:
  - Since potential energy changes only are considered, cannot capture contributions due to vibrations, or to entropy changes associated with change in conformation in polymers (so useful only for materials well below the glass temperature).
  - Requires multiple deformations and reminimizations.
  - Irreversible deformations may sometimes occur, giving rise to apparently negative elastic constants.

Review of Early Polymer Work

The pioneering calculations involving application of the static method to calculate elastic constants of polymer glasses were reported by Theodorou and Suter (Macromolecules **19**, 139 (1986)):

- Included extensive theoretical discussion to show that configurational entropy and volume dependence of vibrational frequencies can safely be neglected (max contribution of a few percent).
- System: **atactic polypropylene glass** at 233K.
- Analyzed 15 independent configurations of one 76-mer (686 atoms).
- Calculated stiffness matrix:

$$\mathbf{C} = \begin{bmatrix} 4773 \pm 498 & 3244 \pm 542 & 2047 \pm 355 & 93 \pm 242 & -243 \pm 274 & 51 \pm 231 \\ 3244 \pm 542 & 5871 \pm 772 & 2943 \pm 557 & 777 \pm 707 & -162 \pm 167 & 502 \pm 384 \\ 2047 \pm 355 & 2943 \pm 557 & 3492 \pm 497 & 695 \pm 497 & -367 \pm 191 & -31 \pm 158 \\ 93 \pm 242 & 777 \pm 707 & 695 \pm 497 & 858 \pm 472 & 8 \pm 64 & -696 \pm 477 \\ -243 \pm 274 & -162 \pm 167 & -367 \pm 191 & 8 \pm 64 & 1230 \pm 135 & 176 \pm 179 \\ 51 \pm 231 & 502 \pm 384 & -31 \pm 158 & -696 \pm 477 & 176 \pm 179 & 1221 \pm 333 \end{bmatrix} \text{MPa}$$

- Calculated tensile modulus: 2.79-2.99 GPa (expt given as 2.65 GPa)

Review of Early Work (cont'd)

Following the Theodorou-Suter work, and the appearance of commercial software packages designed for building amorphous models and performing the necessary molecular mechanics calculations, a number of other groups reported applications of the method, e.g. Fan & Hsu (1992):

- System: **aromatic polysulfone glass**.
- Analyzed 10 independent configurations of one 10-mer (542 atoms).
- Calculated elastic constants (note large uncertainties):

Table II
Calculated Elastic Constants of Model Aromatic Polysulfone

Lame constant, λ	1.96 ± 1.48 GPa
Lame constant, μ	1.60 ± 0.65 GPa
Young's modulus, E	3.88 ± 1.51 GPa
bulk modulus, B	3.02 ± 1.48 GPa
Poisson's ratio, ν	0.24 ± 0.15

- Experimental tensile modulus: ~2.6 GPa

Review of Early Work (cont'd)

Hutnik et al. (1993), considered another aromatic polymer containing rings in the backbone:

- System: **aromatic bisphenol A polycarbonate glass**.
- Analyzed 13 independent configurations of one 35-mer (1157 atoms); also 2 configurations of a 151-mer gave too much scatter for analysis.
- Calculated vs experimental elastic constants (again large uncertainties):

Table I
Comparison of Experimental and Predicted Values of the Elastic Constants

property	exp range[a]	pred value (±SE[b])
Lamé const, λ, MPa	4270–5550	5350 ± 1150
Lamé const, μ, MPa	800–1100	2060 ± 650
G, MPa	800–1100	2060 ± 650
E, MPa	2300–2500	5600 ± 1700
B, MPa	5000–6100	6700 ± 1600
ν	0.42–0.43	0.36 ± 0.06

Review of Early Work (cont'd)

Fan et al (1994), also considered BPA polycarbonate:

- Analyzed 6 independent configurations of one 21-mer (691 atoms)
- Calculated elastic constants (note large uncertainties):

Macromolecules, Vol. 27, No. 9, 1994

Table 7. Average Mechanical Constants of Six Model Polycarbonate Structures

Young's modulus (GPa)	5.03 ± 0.81
shear modulus (GPa)	2.02 ± 0.47
bulk modulus (GPa)	3.68 ± 0.74
Poisson's ratio	0.24 ± 0.09

- Recall Expt ~2.3-2.5 GPa

Review of Early Work (cont'd)

Finally, Raaska et al (1994), reported data for **polystyrene glass**, and compared with the earlier results for other polymers:

- Analyzed configurations of one 70-mer (1122 atoms)
- Calculated elastic constants using both the static and dynamic (stress-strain simulation) approaches, and reported a hybrid average:

polymer	Young's modulus	
	calcd value (GPa)	exptl value[21] (GPa)
polypropylene[1-3]	2.990 2.790	2.650
polysulfone[7]	3.88 ± 1.51	2.6
polycarbonate of 4,4′-isopropylidenediphenol[4-6]	5.60 ± 1.7	2.3–2.5
polystyrene this work	3.5 ± 1.7	3.2–3.3

Review of Early Work-Summary

Noteworthy features of the published work are as follows:

- System sizes are small.

- Sampling of configuration space/number of independent structures is rather limited.

- Estimated uncertainties in moduli, based on averaging Cij values are large – e.g. for tensile moduli estimated error bars lie in the range +/- 30-50% (partially as a consequence of the above).

- Force field quality, through independent validation against model compounds, is often ignored.

- Most importantly, the question of how best to analyze the raw data was not considered...

Analysis – Bounds Estimates

- As noted by Suter and Eichinger (*Polymer*, **43**, 575 (2002)), on the length scale of a few nanometers, as probed by atomistic simulations, amorphous materials are **heterogeneous**. Accordingly, elastic constants – the stiffnesses *Cij* and compliances *Sij* - are expected to differ depending on the atomic packing when small regions are considered.
- Suter and Eichinger thus addressed the question of how to obtain the best possible estimates of the elastic constants of macroscopic material based on knowledge of individual values of an ensemble of microscopic (or nanoscopic) domains.

  In composite theory, the extreme upper and lower bounds – the Voigt and Reuss bounds – are obtained based on the assumption that during deformation each domain is subject to the same strain or the same stress, respectively. The Voigt bound is thus obtained by averaging individual stiffness matrices, while the Reuss bound is obtained by averaging the compliance matrices, i.e.

$$< C >_{Voigt} = \frac{1}{n} \sum_i C_i \qquad < S >_{Reuss} = \frac{1}{n} \sum_i S_i$$

  where n denotes the number of samples (cells) with,

$$< C >_{Reuss} = < S >^{-1}_{Reuss}$$

Analysis – Bounds Estimates

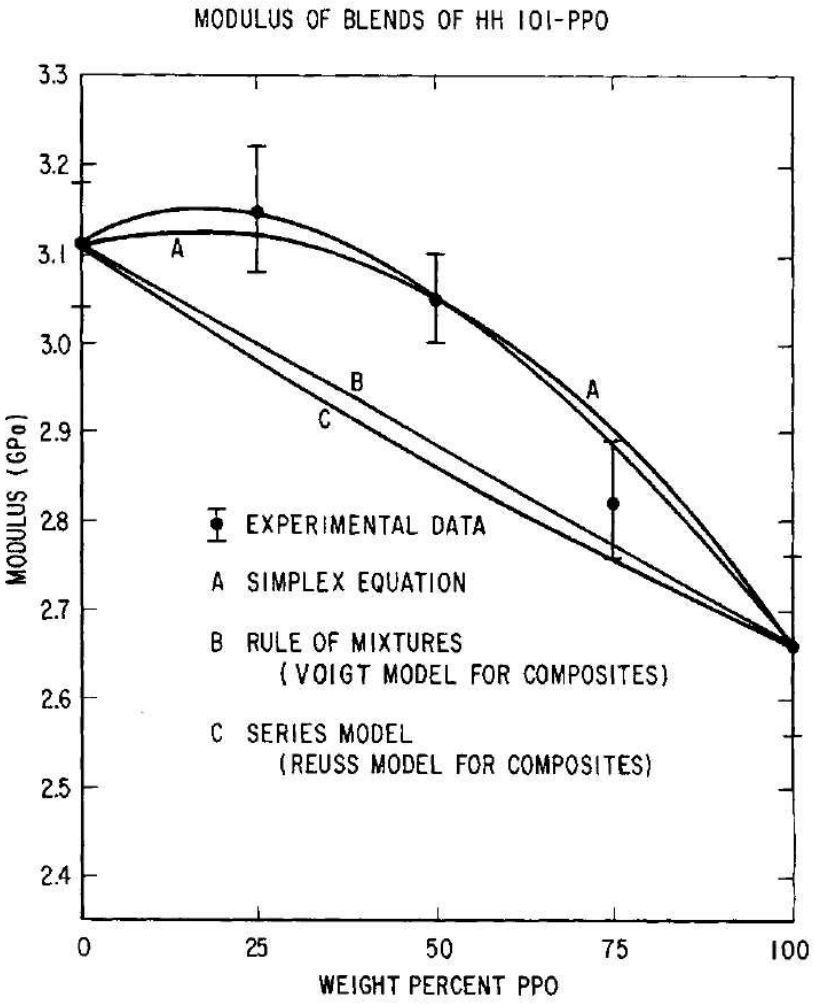
- Note that the Voigt and Reuss bounds also give rise to an unphysical picture of the assumed 'composite', since in the case of the Voigt average the forces between the array of domains will not be in equilibrium, while for the Reuss average the strained domains will not fit together.

- Also, in practice, for nanometer sized domains, these bounds are **too widely separated to be of any use in comparing materials**. Moreover, while Hill's suggestion that the midpoint of the range provides a useful estimate is reasonable, Hill and Walpole were able to derive a more precise method for estimating bounds, which Suter & Eichinger showed is much more meaningful for estimating macroscopic elastic constants.

- These authors tested the effectiveness of the treatment by 'synthesizing' stiffness matrices generated by adding 'random noise' to the stiffness matrix appropriate for a material possessing the same moduli as a typical atactic polystyrene glass (namely G=1.2 GPa, E=3.4 GPa, B=5 GPa, and ν=.38). The amplitude of the noise was chosen to represent typical and extreme simulation behavior.

Analysis – Bounds Estimates

- **In summary**, it appears that the improved Hill-Walpole bounds analysis, in conjunction with more rigorous sampling of configurations, may be useful for making precise and quantitative predictions of small differences in elastic constants e.g. as measured in the polystyrene-poly(2,6-dimethyl-1,4-phenylene oxide study of Kleiner et al (Polym. Eng. Sci. (1979)) where extreme values differ by perhaps < 20%.



This Work – Systems Studied

Two examples of glassy polymer systems are considered as follows:

- The compatible blend system polystyrene – poly(2,6-dimethyl-1,4-phenylene oxide) – aka PS-PPO

- 4,4' Diaminodiphenylsulfone (DDS)-crosslinked thermosets with resins whose molecular architecture is varied:
  - 'Type RA_2': Diglycidyl ether of bisphenol-A (DGEBA)
  - 'Type RA_3': Triglycidyl p-amino phenol (TGAP)
  - 'Type RA_4': Tetraglycidyl diaminodiphenylmethane (TGDDM)

This Work – Simulation Protocols

For elastic constants of polymer glasses:

- Typical systems contain 3000-5000 atoms.

- Building, equilibration, elastic constant calculation and analysis performed using 4-5 batches of 20-25 configurations each, managed using a single MedeA® Flowcharts protocol with the following stages:
  - Create 'nstruct' independent amorphous configurations
  - For Each Structure:
    - All calculations use extension to pcff force field (“pcff+”).
    - Apply initial equilibration stage, using atom based cutoffs and employing NPT dynamics to compress to target density.
    - Second NVT equilibration stage, using PPPM or ewald nonbond method, cooling from 600K to ambient, followed by 200ps NVT at ambient, and final minimization for 2500 steps or until a gradient of .000001 kcal $mol^{-1}A^{-1}$ is reached.
    - Minimize undeformed and 12 deformed structures (strain=.001) to gradient of .000001 kcal $mol^{-1}A^{-1}$ to extract Cij from $\Delta\sigma i/\Delta\varepsilon j$
    - Apply Hill-Walpole bounds analysis using ~100 independent structures at each composition.

This Work – Simulation Protocols

Additional details of elastic constants simulations for polymer mixture studies:

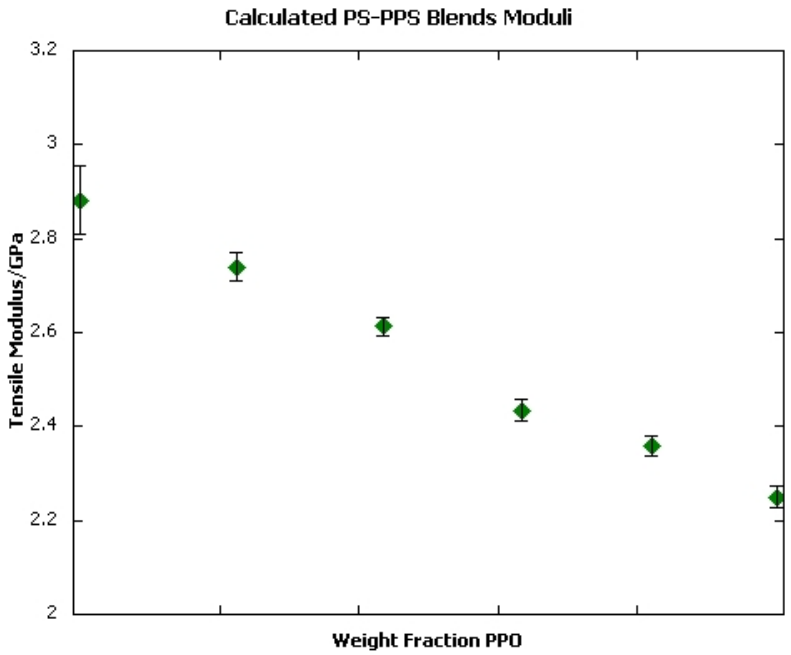
- Densities used were either:
  - the ideal density calculated from the known densities of the pure components and mixture composition (i.e. assuming zero excess volume of mixing)

    or,

  - the density as measured during the experimental tensile modulus studies.

Results – Calculated PS-PPO Moduli

PS-PPO tensile moduli with Hill-Walpole bounds (ideal densities):

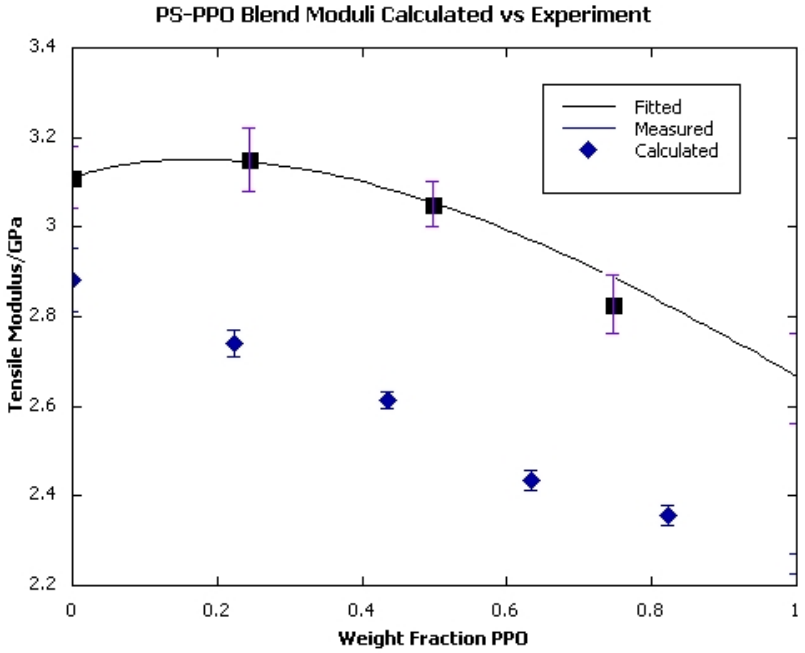


Points to note:

- Bounds represented by upper and lower extremes of error bars
- Small differences of a few percent can be resolved!!!
- Zero excess volume assumption leads to almost linear decrease in modulus with composition
- Percent decrease in modulus ~21% compared with ~15% experiment

Results – Calculation vs Experiment

Comparison with experimental data of Kleiner et al (1979)



Notes:

- Uncertainties from H-W are mostly smaller than experiment.
- Calculated moduli are lower. However, note that the Kleiner data refer to much higher molecular weight polymers (PS is highly polydisperse with DP_n ~900, DP_w ~2700, and PPO has DP_n ~140, DP_w ~285; compare with DP=30 in this work), both with higher density.

Results – Experimental Densities

Mixture densities were also measured by Kleiner et al (1979)

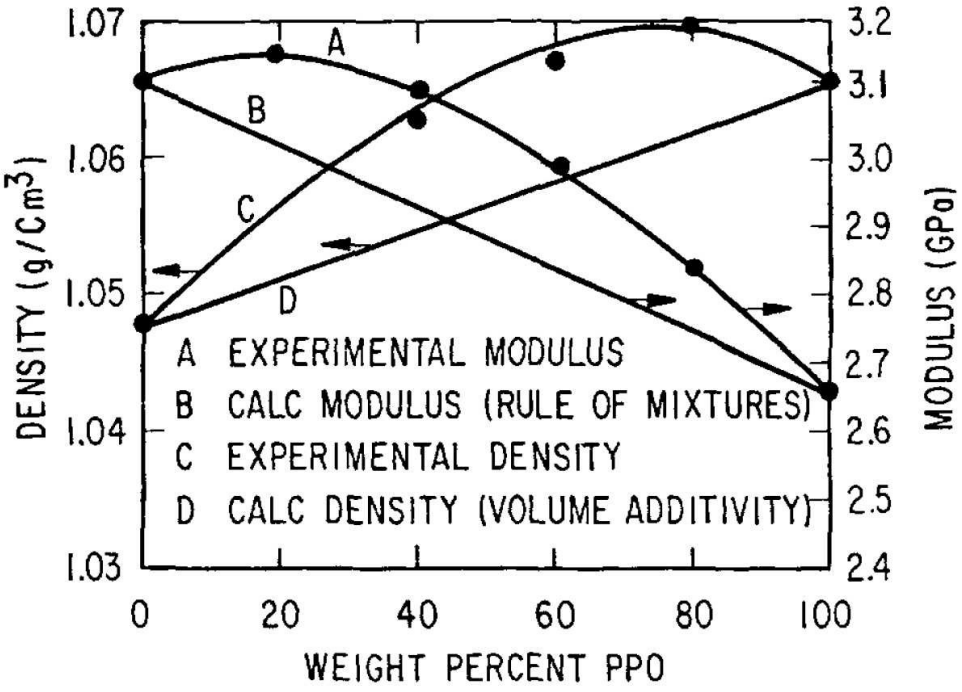


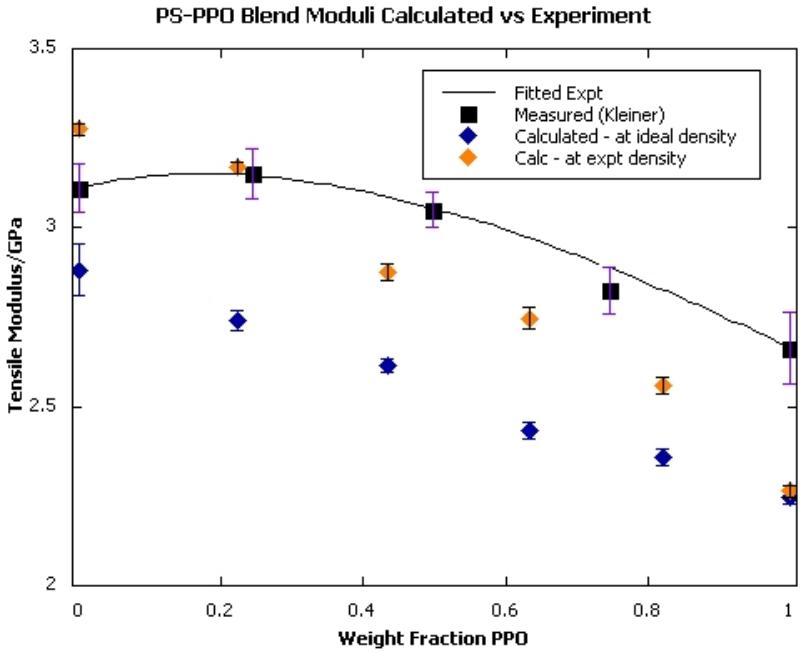
Fig. 3 Dependence of modulus and density upon composition.

Notes:

- PS density (this work) = 1.0334; Kleiner et al. = 1.048
- PPO density (this work) = 1.06; Kleiner et al. = 1.066
- Studies of density effect have also been performed...

Results – PS-PPO Density Effect

Comparison with experimental data after performing addidional calculations using Kleiner et al. PS and PPO densities.



Notes:

- Moduli somewhat sensitive to density
- Possible synergistic effect? (but weak)
- n.b. Kleiner data actually refer to higher MW polymers (may also need to investigate molecular weight effect)

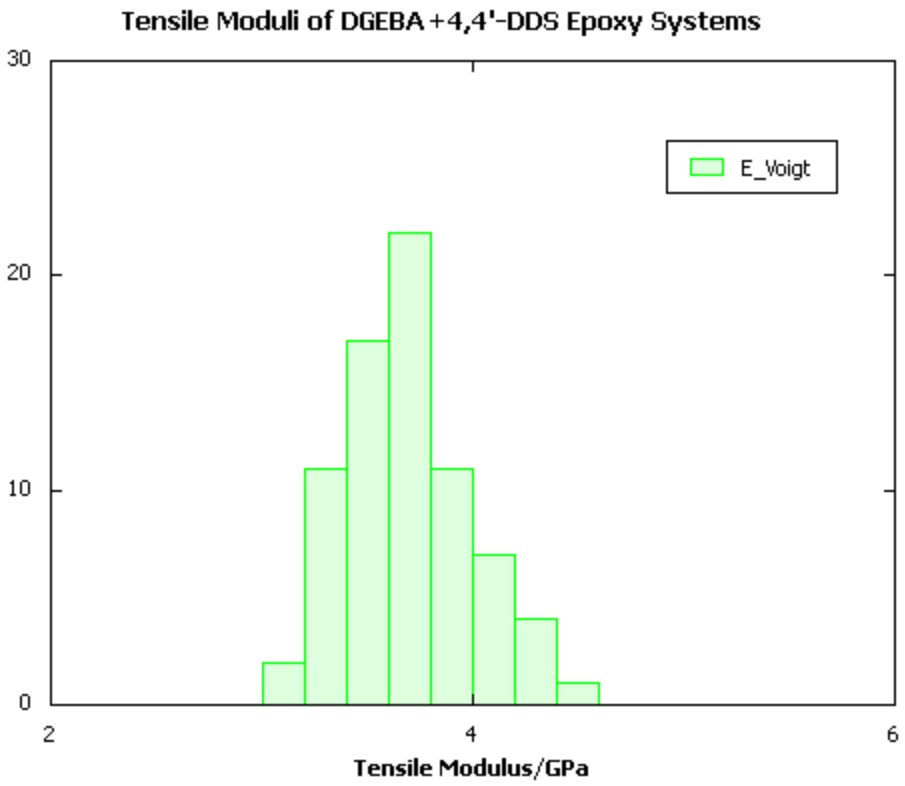
Thermosets

- Batches of ~100 samples, each crosslinked to ~90-95% extent of reaction, prepared for 4,4'-DDS-cured resins:
  - DGEBA
  - TGAP
  - TGDDM

- Subjected to mechanical property calculation with HW bounds analysis...

Results - Thermosets

- Typical distribution of individual epoxy model tensile moduli is quite broad (units:GPa; is actually similar for PS-PPO blends)



Results - Thermosets

- Application of Hill-Walpole analysis shows considerably narrower bounds, and correctly reproduces network architecture effect on tensile moduli.

Type	Resin	Calculated Bounds (GPa)	Experiment (GPa)
RA_4+RB_2	DGEBA	3.49-3.53	2.4-3.2[a]
RA_4+RB_3	TGAP	4.42-4.45	4.396±.027[b]
RA_4+RB_4	TGDDM	5.18-5.19	5.103±.033[c]

a. Extents of reaction 0.5-1.0; ~300K; using dynamic mechanical analysis at 1Hz (White, 2002)
b. Extent of reaction 0.93; 295K; strain rate 1.67 $x10^{-2}s^{-1}$ (Behzadi, 2005)
c. Extent of reaction 0.88; 295K; strain rate 1.67 $x10^{-2}$ s^{-1} (Behzadi, 2005)

Summary

- Investigated LAMMPS-based elastic constant calculation using MedeA®-Flowcharts (includes modification of LAMMPS line search to fine tune performance of minimizer).
- Force field parameter validation using small molecule model compounds shows no particular issues that would adversely affect elastic constants.
- Successfully demonstrated that use of H-W bounds calculation in conjunction with improved configurational averaging (~100 samples) allows resolution of changes in tensile moduli amounting to a few percent.
- Can (almost quantitatively) reproduce variation in tensile moduli as a function of composition of the well-understood PS-PPO blend system.
- Can similarly reproduce network architecture effects using crosslinked thermosets (~90% conversion).
- Quantitative prediction is very good and may be improved still further with proper attention to effects of glass density, polymer molecular weight, etc.

Acknowledgements

Valuable discussions with Prof. B.E. Eichinger (U. Washington) on the implementation of the Hill-Walpole method for obtaining bounds on elastic constants are gratefully acknowledged.