Mechanical Properties of Glassy Polymer Blends and Thermosets from Atomistic Simulations

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(presented by Ray Shan)

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Outline

Introduction & Goals

Methods for Calculating Small Strain Elastic Constants

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- Glassy polymer blends
- Epoxy thermosets
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Introduction

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

Introduction

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 systems will be relatively small – even with million atom simulations – **methods for combining elastic constants of nano->microscopic domains to predict macroscopic behavior need to be investigated**.

- For quantitative property prediction, **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.

Introduction/Materials of Interest

- **Composites** contain multiple components – e.g. cured resin, coupling agents (primers), reinforcing particles or fibers. Properties of complex multiphase materials need to be studied…

- Example: Effect of primer concentration on mechanical and thermal properties
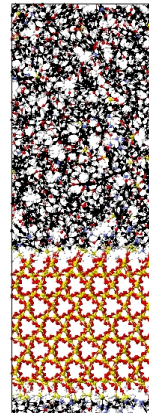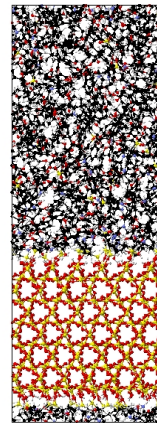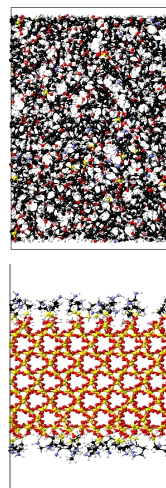
$$\begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{22} & C_{23} & 0 & 0 & 0 \\ C_{13} & C_{23} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} \end{bmatrix} \begin{bmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \\ \varepsilon_4 \\ \varepsilon_5 \\ \varepsilon_6 \end{bmatrix}$$

$$H = -kA\frac{\mathrm{d}T}{\mathrm{d}x}.$$

5
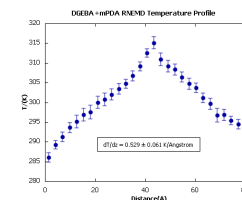
Introduction

An essential requirement for successful atomistic simulations is accordingly to assess the performance of atomistic simulation based elastic constant calculations.

Specifically, performing quantitative prediction of the properties of complex multiphase materials containing polymers first requires an assessment of both **precision** and **accuracy** achievable using today's computational materials science technology.

Here, we focus on amorphous polymer glasses, which frequently constitute the matrix material in composite materials…

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Elastic Constants - Definitions

The fourth rank stiffness tensor is formally defined as follows:

$$C_{lmnk} = \frac{\partial \sigma_{lm}}{\partial \varepsilon_{nk}}\bigg|_{T,\varepsilon_{nk}} = \frac{1}{V_0}\frac{\partial^2 A}{\partial \varepsilon_{lm}\partial \varepsilon_{nk}}\bigg|_{T,\varepsilon_{lm}\varepsilon_{nk}}$$

where *A* denotes the Helmholtz free energy σ_{ik} elements of the stress tensor and ε_{ik} the strain tensor

For small strains the generalized Hooke's law applies:

$$\sigma_{lm} = C_{lmnk}\varepsilon_{nk}$$

Conventionally the stiffness tensor is written in contracted Voigt notation as the 6x6 matrix

$$\mathbf{C} \equiv \begin{bmatrix} C_{1111} & C_{1122} & C_{1133} & C_{1123} & C_{1113} & C_{1112} \\ C_{1122} & C_{2222} & C_{2233} & C_{2223} & C_{2213} & C_{2212} \\ C_{1133} & C_{2233} & C_{3333} & C_{3323} & C_{3313} & C_{3312} \\ C_{1123} & C_{2223} & C_{3323} & C_{2323} & C_{2313} & C_{2312} \\ C_{1113} & C_{2213} & C_{3313} & C_{2313} & C_{1313} & C_{1312} \\ C_{1112} & C_{2212} & C_{3312} & C_{2312} & C_{1312} & C_{1212} \end{bmatrix}$$

Elastic Constant Methods - 1

Much of the published literature on small strain elastic properties of polymer glasses has focused on three methods as follows:

1. 'Static' methods in which a model system at mechanical equilibrium is subject to 6x tensile and 6x shear deformations, and $\Delta\sigma/\Delta\varepsilon$ calculated after restoring the state of equilibrium using minimization.

- Advantages: Conceptually straightforward
 (well-established for computing elastic constants of metals, inorganic crystals, etc.)
.
- Disadvantages: Cannot capture vibrational contributions; Requires multiple deformations and re-minimizations; Irreversible deformations may occur, giving rise to apparently negative elastic constants (structures must be detected and discarded).

Elastic Constant Methods - 2

1. Generating 'stress-strain' curves by performing MD simulation of systems subjected to an applied load, e.g. Brown & Clarke (1991)
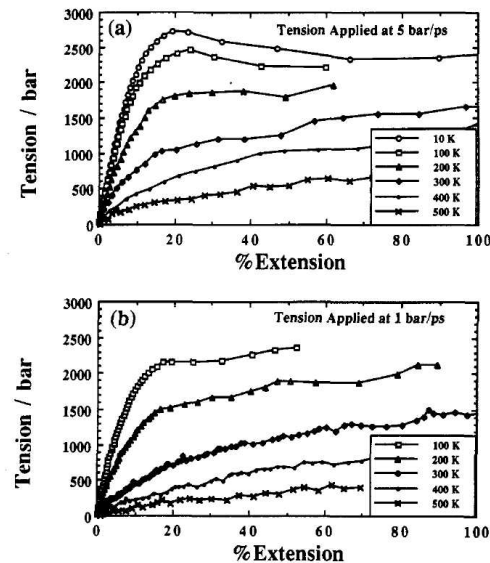
• Advantages: Simple to implement; can also be used to study behavior at large strains.

• Disadvantages: Difficulty of identifying initial linear region of stress-strain curves (results in poor reproducibility). Not always reversible (non-elastic).

Elastic Constant Methods - 3

1. Use of statistical mechanical fluctuation formulae.

- Advantages: In principle requires a single MD simulation

- Disadvantages: Convergence is usually <u>extremely slow</u>, and in practice may still require using multiple independently generated models to adequately sample configuration space in the case of glassy materials

Since the static method <u>does not require subjective input</u>, such as estimating the limit of the elastic region or judgments of convergence, and since the method has been applied to a relatively broad range of glassy materials, **we have selected this approach for assessment of the precision and accuracy with which elastic constants can be determined using atomistic simulations**.

Some Early Polymer Work

The pioneering calculations involving application of the static method to calculate elastic constants of polymer glasses was 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.

• System: atactic polypropylene glass at 233K.

• Analyzed 15 independent configurations of one 76-mer (686 atoms).

• Calculated stiffness matrix:

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

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

Some 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:

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

Some 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 and experimental elastic constants were compared:

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

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

Some 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:

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 experimentally-measured ~2.3-2.5 GPa

Some Early Work (cont'd)

Finally, Raaska et al (1994), reported data for polystyrene, and summarized 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

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 C_{ij} 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, which might be assessed through validation against model compounds, is largely ignored.

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

Averaging Methods – 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 C_{ij} and compliances S_{ij} - are expected to differ depending on the atomic packing when individual 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.

where n c $< C >_{Voigt} = \frac{1}{n} \sum_i C_i$ mber of samples $< S >_{Reuss} = \frac{1}{n} \sum_i S_i$

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

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Analysis – Bounds Estimates

- Note that the Voigt and Reuss bounds also give rise to an <u>unphysical picture</u> 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 <u>too widely separated</u> 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.

- Suter & Eichinger 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. Representative results are summarized on the following slide...

Analysis – Bounds Estimates

Typical distribution of tensile moduli obtained for a collection of individual nanoscopic models of a polymer glass

Tensile Moduli of 80:20 PS-PPO Blend Systems
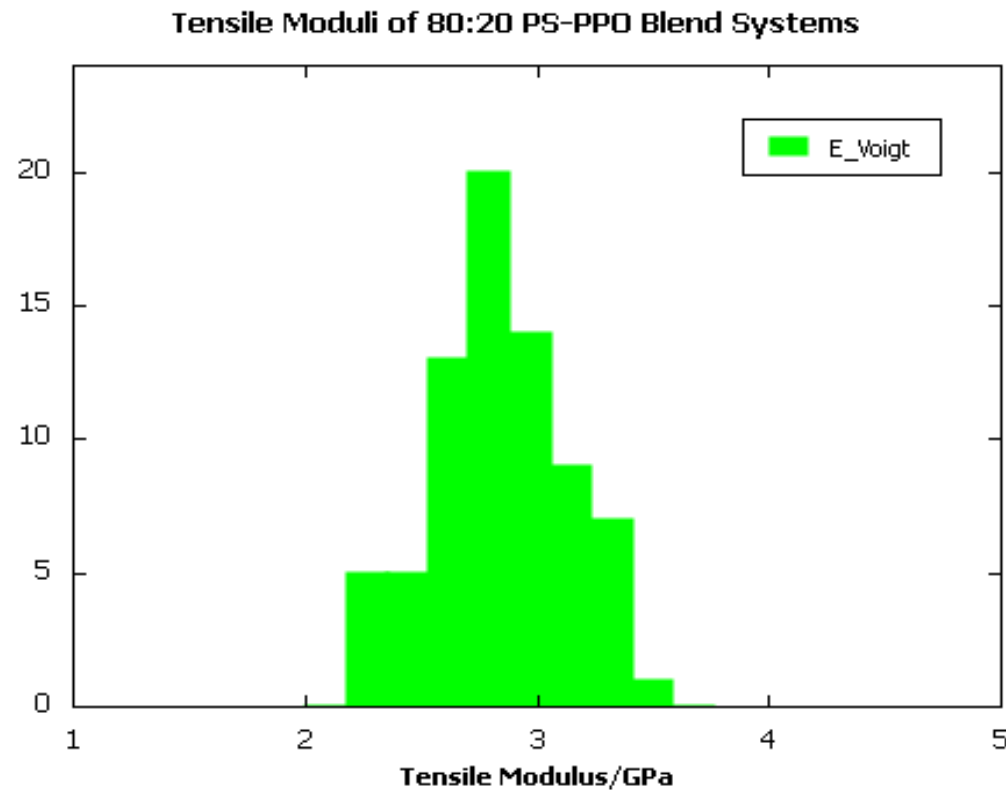
Analysis – Bounds Estimates

- Suter & Eichinger testing of the H-W approach: Note that <u>the typically narrow H-W range and its midpoint are consistently closer to the moduli of the 'real' parent polystyrene than the so-called 'Hill' average</u> (midway between Reuss and Voigt extreme bounds).

Table 1
Bounds and self-consistent means for sets of eleven structures derived from C_{PS} for atactic polystyrene

Model system		G (GPa)	B (GPa)	E (GPa)	ν
"Parent" material		1.2	5.0	3.4	0.38
Random noise,[a] $\Delta = 1$ GPa (non-symmetric Cs, one is non-positive definite)	Reuss/Voigt bounds	0.86/1.28	4.73/4.99	2.44/3.54	0.38/0.41
	Hill–Walpole average	1.12	4.88	3.13	0.39
	Hill–Walpole bounds	1.12/1.16	4.87/4.90	3.11/3.21	0.39/0.39
Random noise,[b] $\Delta = 1$ GPa (symmetric Cs, five are non-positive definite)	Reuss/Voigt bounds	0.86/1.28	4.73/4.99	2.44/3.54	0.38/0.41
	Hill–Walpole average	1.12	4.88	3.13	0.39
	Hill–Walpole bounds	1.12/1.16	4.87/4.90	3.11/3.21	0.39/0.39
Random noise,[a] $\Delta = 2.5$ GPa (non-symmetric Cs, seven are non-positive definite)	Reuss/Voigt bounds	0.76/1.33	5.01/5.09	2.17/3.66	0.38/0.43
	Hill–Walpole average		Did not converge		
	Hill–Walpole bounds	1.10/2.82	2.65/5.14	3.08/7.16	0.26/0.40
Evenly spaced B and G,[c] spanning $B = 0.6$–1.8 GPa and $G = 2.5$–7.5 GPa	Reuss/Voigt bounds	1.07/1.20	4.45/5.00	2.97/3.33	0.39/0.39
	Hill–Walpole average	1.14	4.60	3.17	0.39
	Hill–Walpole bounds	1.12/1.16	4.54/4.65	3.11/3.21	0.39/0.39

[a] The stiffness matrix of aPS and 10 matrices derived from it by adding "random noise" from a uniform distribution with maximum amplitude Δ to the individual elements. Negative matrix elements were replaced by their absolute values.
[b] As in previous footnote, but the matrices have been made symmetric ($C_{ij} = C_{ji}$).
[c] The matrices were computed from Eqs. (11) and (12), B and G assuming the values (2.5, 0.60), (3.0, 0.72), (3.5, 0.84), (4.0, 0.96), (4.5, 1.08), (5.0, 1.20), (5.5, 1.32), (6.0, 1.44), (6.5, 1.56), (7.0, 1.68), (7.5, 1.80), respectively.

- Automatic calculation of Hill-Walpole bounds is implemented in Materials Design's MedeA$^{®}$ Flowcharts software environment.

Analysis – Bounds Estimates

- **Conclusion**: 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.

Selected Examples – Systems Studied

Illustrative systems discussed here are as follows:

- **PS-PPO** - the compatible glassy blend system polystyrene – poly(2,6-dimethyl-1,4-phenylene oxide)
.
- **Epoxy thermoset architecture effects** - 2, 3, or 4 functional resins cured with 4,4'-diamino-diphenyl sulfone (DDS).

- **Composites** - crosslinked epoxy – primer - hydroxylated silica interfacial systems (preliminary).

Additionally, assessment of force field quality for the organic systems has been conducted by performing basic PVT studies for the following small molecules:

- Ethyl benzene
- Diphenyl ether
- Selected amines

The following slides illustrate typical forcefield validation study results…

Typical Simulation Protocols

For <u>small molecule</u> PVT behavior (used mostly for forcefield validation):

- System size 100-200 molecules.

- Initial preparation of a single disordered configuration using MedeA's Amorphous Materials Builder.

- Initial equilibration using LAMMPS minimization, followed by 100-200 ps each of NVT and NPT dynamics. 9.5 Angstrom cutoffs applied to nonbonded interactions.

- Production runs consisting of 200-500ps NPT dynamics to determine density at a series of temperatures, with nonbonded interactions computed using the accurate particle-particle particle-mesh (PPPM) approach.

- <u>A</u>ll simulations performed using the **PCFF+** force field - a refined version of the classII PCFF force field included in the LAMMPS distribution, which is continuously enhanced at Materials Design.

Small Molecule PVT Results

Liquid density as a function of temperature was calculated for ethyl benzene (structurally almost identical to the repeat unit of polystyrene; 323K error is ~-0.7%)
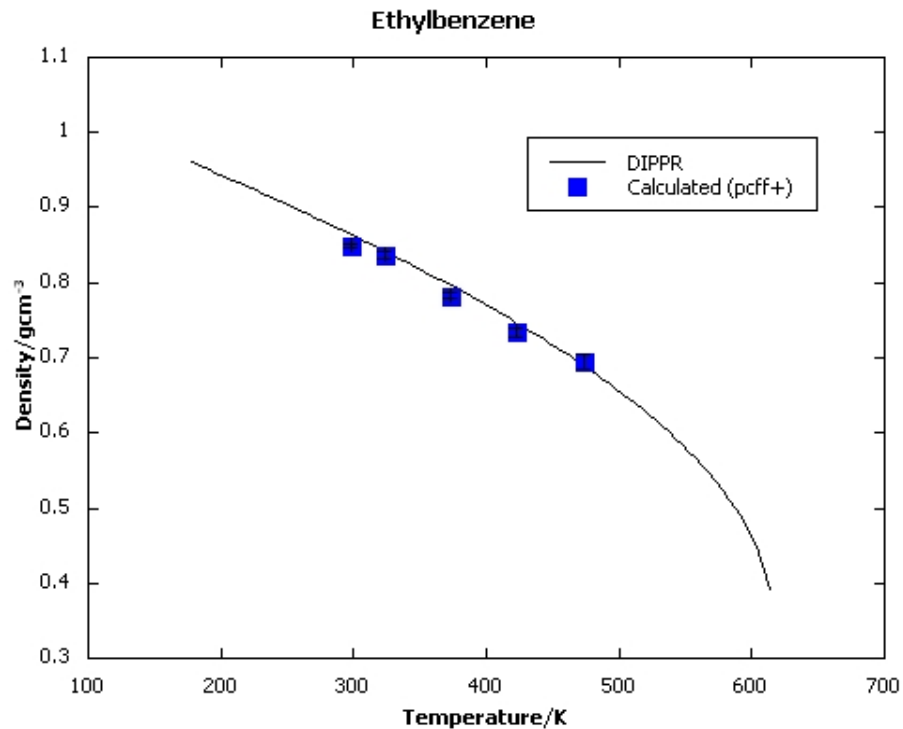

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Small Molecule PVT Results

Liquid density as a function of temperature was calculated for diphenyl ether (structurally similar to the repeat unit of PPO)
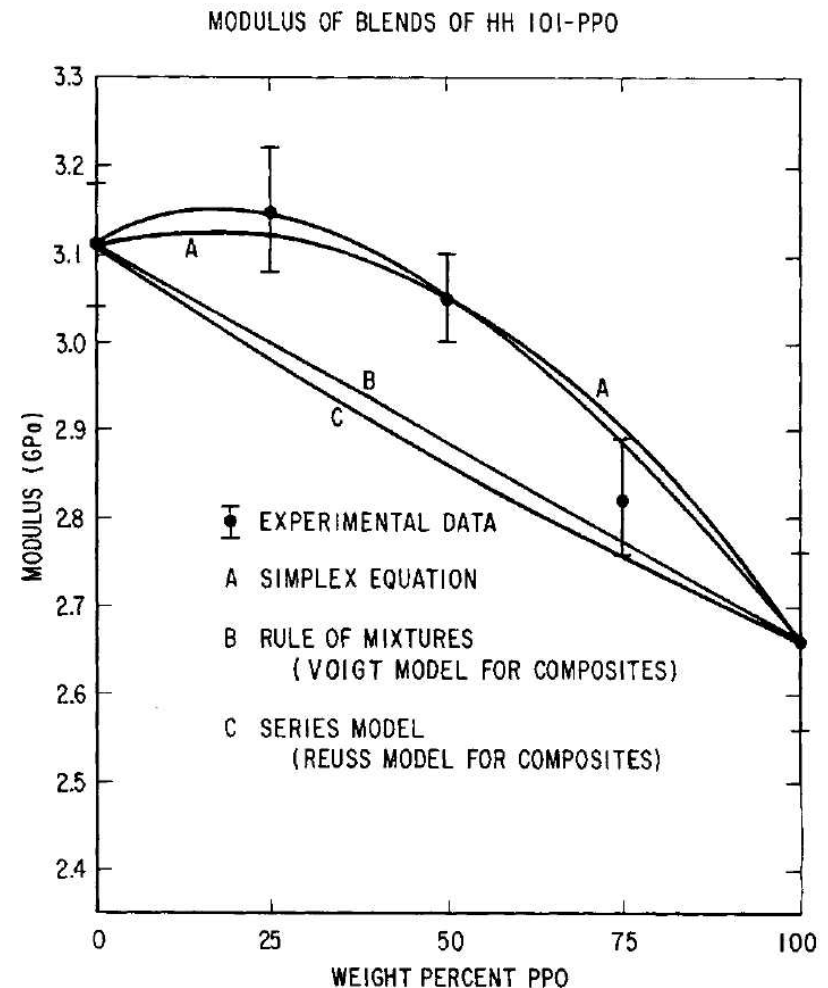
Diphenyl Ether

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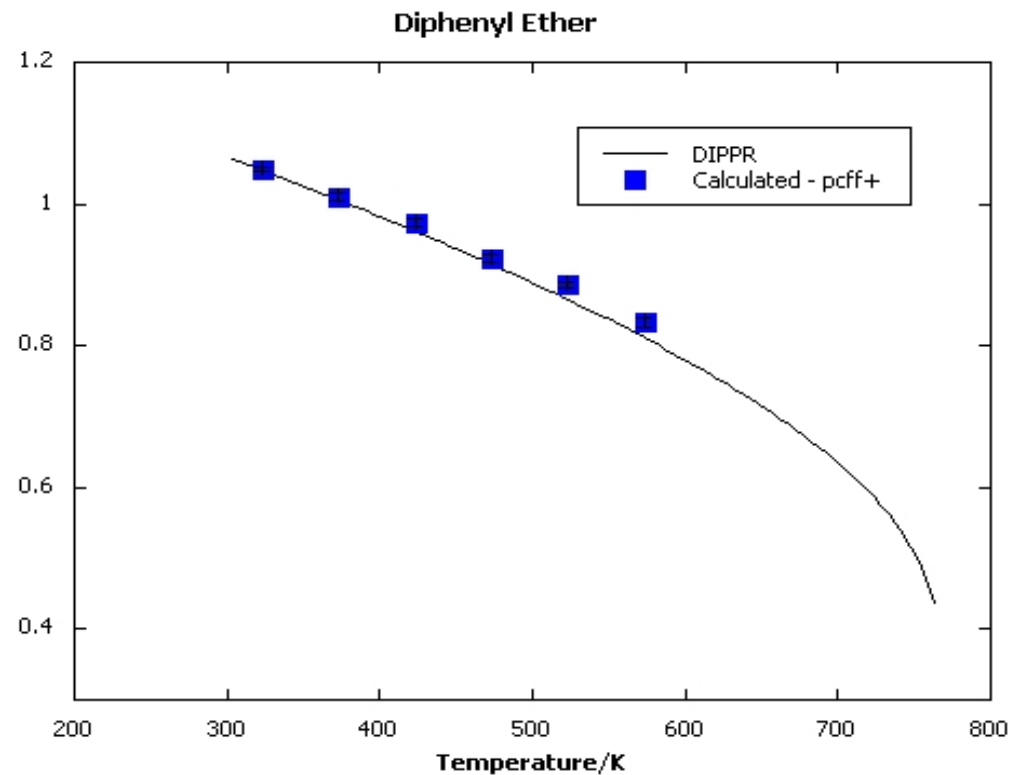
Small Molecule PVT Results

- For thermosets (and primer in composite studies) – PCFF+ includes recently-improved parameters for secondary and tertiary amine groups found in many epoxies.

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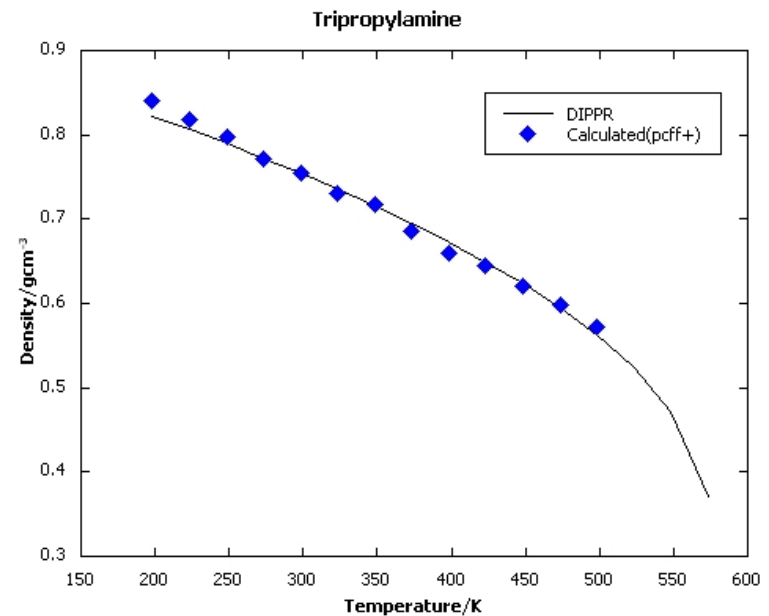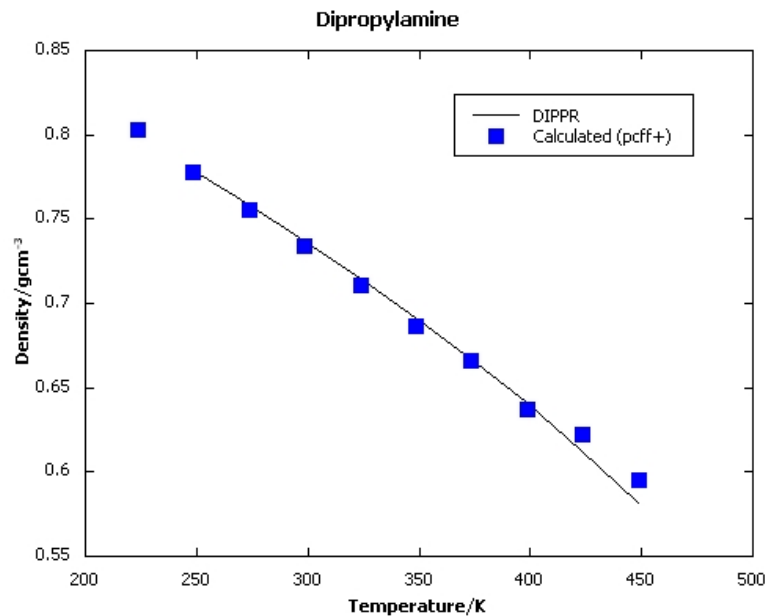
Examples – PS-PPO Blends

- The polystyrene-poly(2,6-dimethyl-1,4-phenylene oxide) compatible blend system, PS-PPO, has been shown experimentally to exhibit interesting behavior in which the extreme modulus values differ by less than 20% across the composition range (see, Kleiner et al., Polym. Eng. Sci. (1979)).

- As such this system is ideal for testing the accuracy and precision of atomistic simulations…

MODULUS OF BLENDS OF HH 101-PPO

- ● EXPERIMENTAL DATA
- A SIMPLEX EQUATION
- B RULE OF MIXTURES
  (VOIGT MODEL FOR COMPOSITES)
- C SERIES MODEL
  (REUSS MODEL FOR COMPOSITES)

MODULUS (GPa)

WEIGHT PERCENT PPO

Typical Simulation Protocols

For elastic constants of <u>polymer glasses</u>:

- Typical systems contain ~2500-5000 atoms, with either a single polymer chain or several shorter chains (e.g. 5, in the case of PS-PPO blends).

- Building, equilibration, elastic constant calculation and analysis is performed using batches of 50-100 configurations, managed using a single MedeA® Flowcharts protocol with the following stages:
  - Create 'nstruct' independent amorphous configurations
  - For Each Structure:
    - Apply initial equilibration stage, using atom based cutoffs and employing NPT dynamics to compress to target density.
    - Second NVT equilibration stage, using PPPM 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/Å is reached.
    - Minimize undeformed and 12 deformed structures (strain=.001) to gradient of .000001 kcal/mol/Å to extract Cij from $\Delta\sigma i/\Delta\varepsilon j$
    - Apply Hill-Walpole bounds analysis

Simulation Protocols (cont'd)

Some additional details of elastic constants simulations:

- For the PS-PPO 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
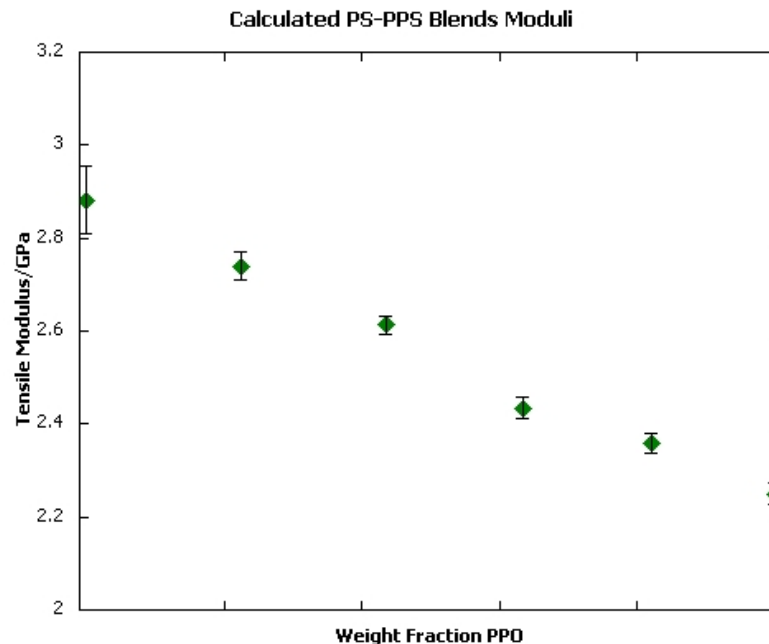   - the density as measured during the experimental tensile modulus studies.

PS-PPO Blends Results

PS-PPO: Calculated Tensile Moduli

PS-PPO tensile moduli with Hill-Walpole bounds – initial results for mixtures with densities corresponding to the density of the oligomers actually used in the simulations:

Points to note:
- Bounds represented by upper and lower extremes of error bars
- Uncertainties from H-W are comparable with (or smaller) than experiment **-small differences of a few percent can be resolved!!!**
- Percent decrease in modulus ~21% compared with ~15% experiment

Note however that the Kleiner data refer to much higher molecular weight polymers (PS is highly polydisperse with DPn ~900, DPw~2700, and PPO has DPn ~140, DPw~285), compared with the DP=30 oligomers used in the simulations. Accordingly, simulations have also been performed using the actual densities measured by Kleiner et al.
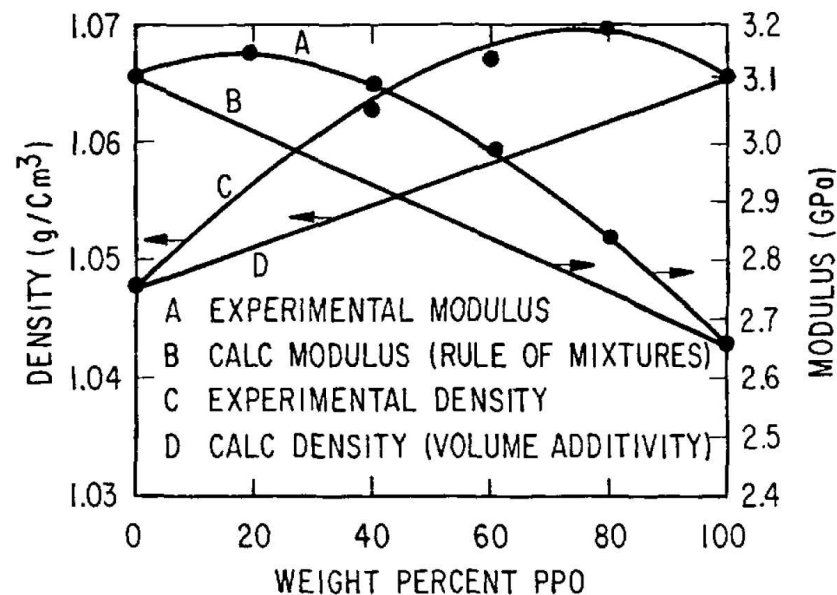
Fig. 3 *Dependence of modulus and density upon composition.*

Notes:

- PS density (30-mers) = 1.0334; Kleiner et al. = 1.048
- PPO density (30-mers) = 1.06; Kleiner et al. = 1.066

PS-PPO: Calculation vs Experiment

Comparison with experimental data after performing additional calculations **using Kleiner et al. PS and PPO densities (higher MW), and using actual oligomer densities**

PS-PPO Blend Moduli Calculated vs Experiment
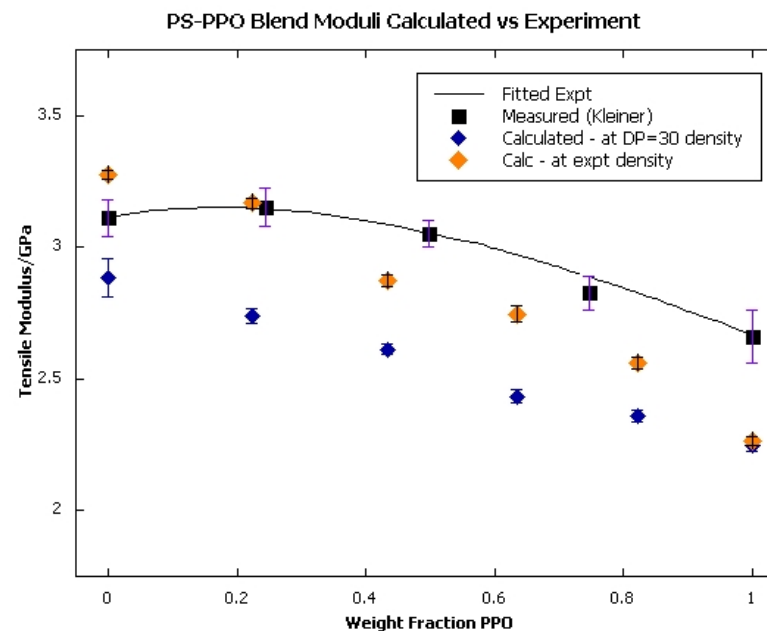
Remarks:

- Measurable density effect in pure PS; less for pure PPO

- It should also be remarked that experimental PPO moduli from other sources range from ~2.14-2.62 GPa, which *does* include the simulated range (it would be good to resolve this discrepancy!)
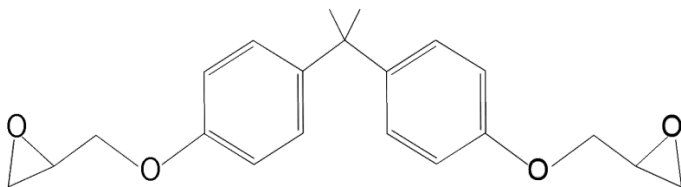
Epoxy Thermosets

Epoxy Thermoset Architecture Studies

- Experimental data for thermosets formed using crosslinkers with different architecture show a fairly significant reactant functionality effect on mechanical properties

- In earlier studies, we examined elastic constants of bulk resins with different architectures, cured with 4,4' diaminodiphenylsulfone (DDS) architecture;:
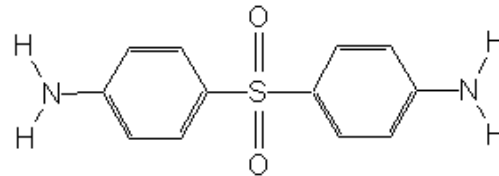
- Typically 50-100 thermoset models were examined for resins of 3 types:

- 'Type RB2' : Diglycidyl ether of bisphenol A (DGEBA)

- 'Type RB3' : Triglycidyl p-amino phenol (TGAP)

- 'Type RB4' : Tetraglycidyl diaminodiphenylmethane (TGDDM)
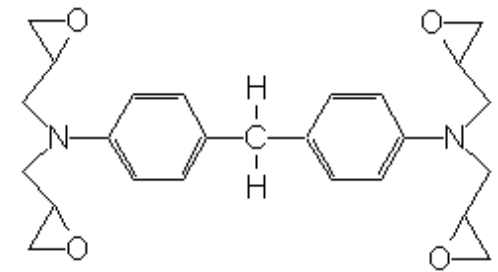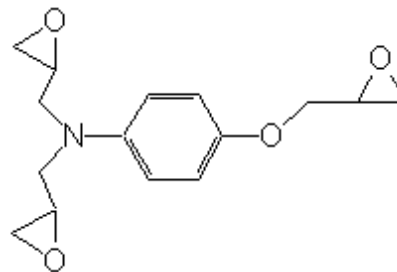
Epoxy Thermoset Model Building

- Thermoset models have been constructed using the MedeA® Thermoset Builder, which is capable of generating realistic models with respectably high degree of conversion – typically 85%-95% reaction. Note that the building procedure also constantly monitors internal strain, and produces additional useful information such as the gel point.
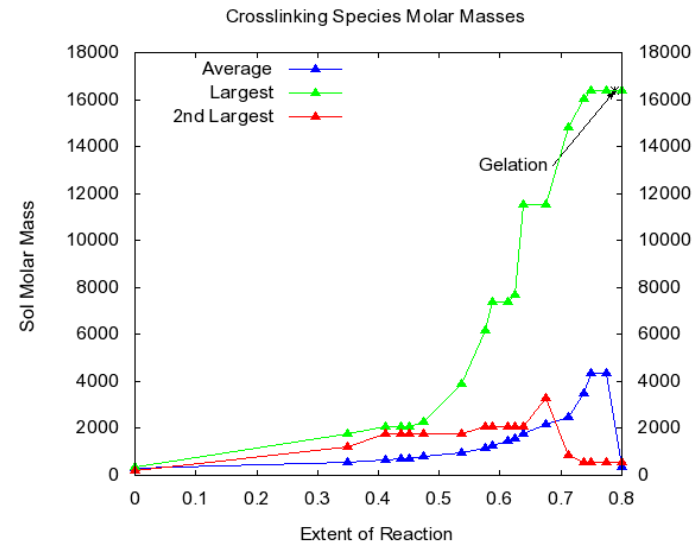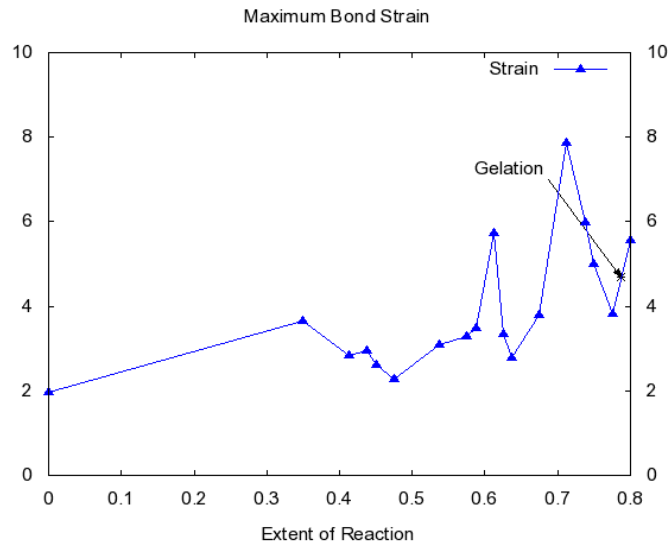
Batches of 50-100 independently-generated are then subjected to equilibration using constant temperature (NVT) and constant pressure (NPT) molecular dynamics, and can then be subjected to elastic constant calculation with bounds analysis.

Bulk Thermosets – Mechanical Properties

• Application of Hill-Walpole analysis yields narrow bounds, and correctly predicts resin 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$\pm$.027[b]
RA_4+RB_4	TGDDM	5.18-5.19	5.103$\pm$.033[c]

a. Extents of reaction relatively broad **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)

Bulk Thermosets – Mechanical Properties

• In recent work (ongoing), we have also investigated the effect on tensile moduli of varying the relative probability of reaction of primary and secondary amine groups during the crosslinked model building process. Results for TGDDM are shown below:

Ratio $2^y/1^y$ Amine Reactivity	Type	Resin	Calculated Bounds (GPa)
1.0	RA_4+RB_4	TGDDM	5.18-5.19
0.4	RA_4+RB_4	TGDDM	4.73-4.77
0.1	RA_4+RB_4	TGDDM	4.80-4.82

Note that other properties such as gel points also appear to be affected to only a small extent (complete results to be presented at annual meeting of the AIChE, Minneapolis, Oct 31, 2017).

Composites

Composites

- Studies of small strain elastic constants have recently been performed for **multicomponent systems** consisting of inorganic filler surfaces covalently bonded to silane primer and crosslinked with epoxy resin.

- Preliminary results based on small sample sizes are summarized in the following slides…

Epoxy-Oxide Interfacial System Studies

In general, interfacial composite systems of interest contain:

• Various epoxies (amine, anhydride-cured; epoxy-phenol-novolac, etc.)
• Oxides (SiO_2, Al_2O_3, TiO_2, etc.)
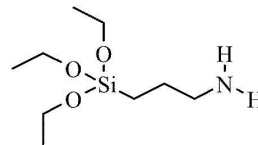• Primers ('coupling agents'/'adhesion promoters')

Specifically, in this study, we focused on tensile stiffness coefficient calculation for systems containing:

• DGEBA epoxy crosslinked with 4,4' diaminodiphenylsulfone
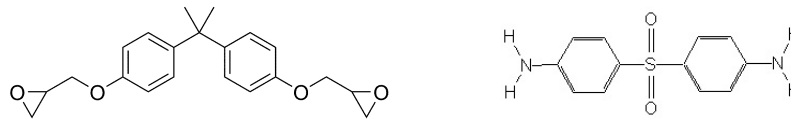
• SiO_2 (as hydroxylated α-Quartz)
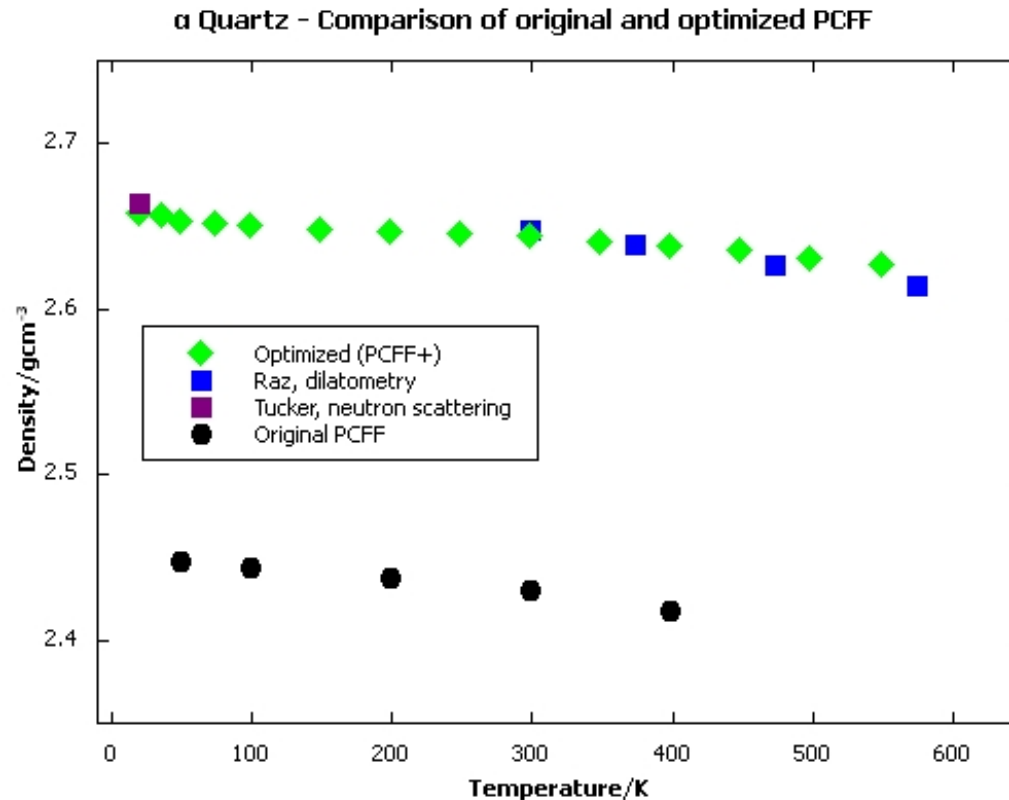
• γ-aminopropyltriethoxysilane

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Force Field: 298K α-Quartz Properties

Method	298K Density (g/cm^3)	Bulk Modulus (GPa)	Young's Modulus (GPa)	Shear Modulus (GPa)
Original PCFF[1]	2.45	97	203	88
Revised **PCFF+**	2.64	39	82	35
Expt.	2.65	36-38	73-96	31-41

- Note 1: Original parameters for SiO_2 from Hill and Sauer (1994)

- Note 2: Forcefield optimization using VASP DFT energies and forces yields an improved model showing good agreement with crystal density and experimental mechanical properties (mechanical properties were not included in the fitting)

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Force Field:
Temperature Dependence of α-Quartz Density


α Quartz - Comparison of original and optimized PCFF

- Refining the SiO_2 parameterization successfully reproduces quartz density over temperature range of interest in SiO_2-Thermoset composite studies (using LAMMPS NPT dynamics simulation).

- Slightly low CTE of calculated data at highest temperatures may be caused by neglect of cubic and quartic terms in forcefield parameter fitting?
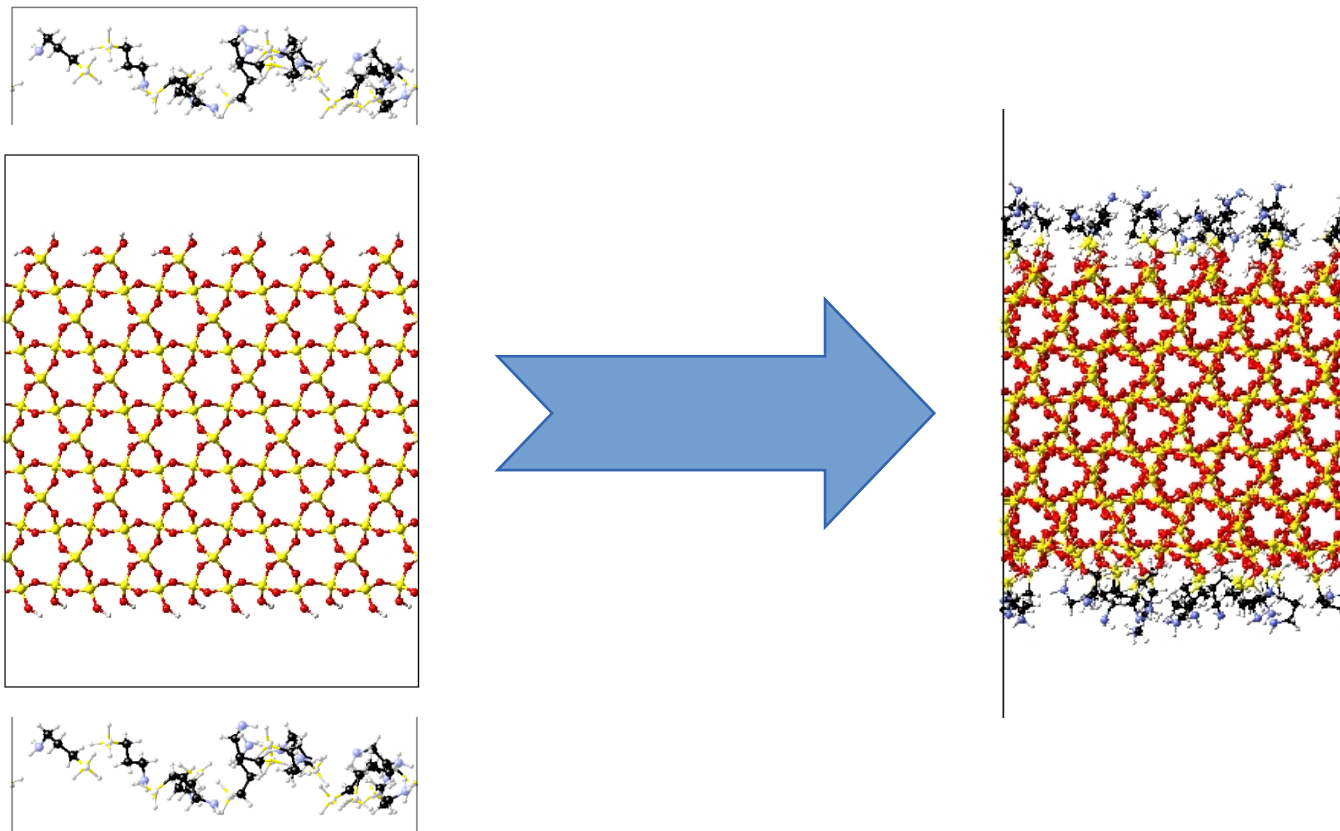
Epoxy-SiO$_2$ Interfaces – Model Building

α Quartz (100) + Primer + Unreacted epoxy
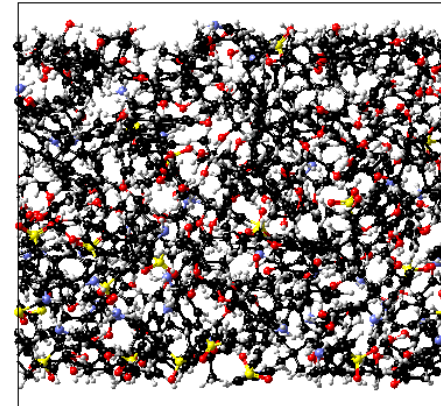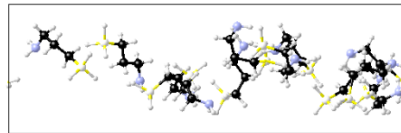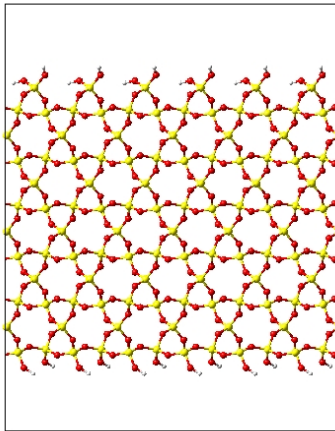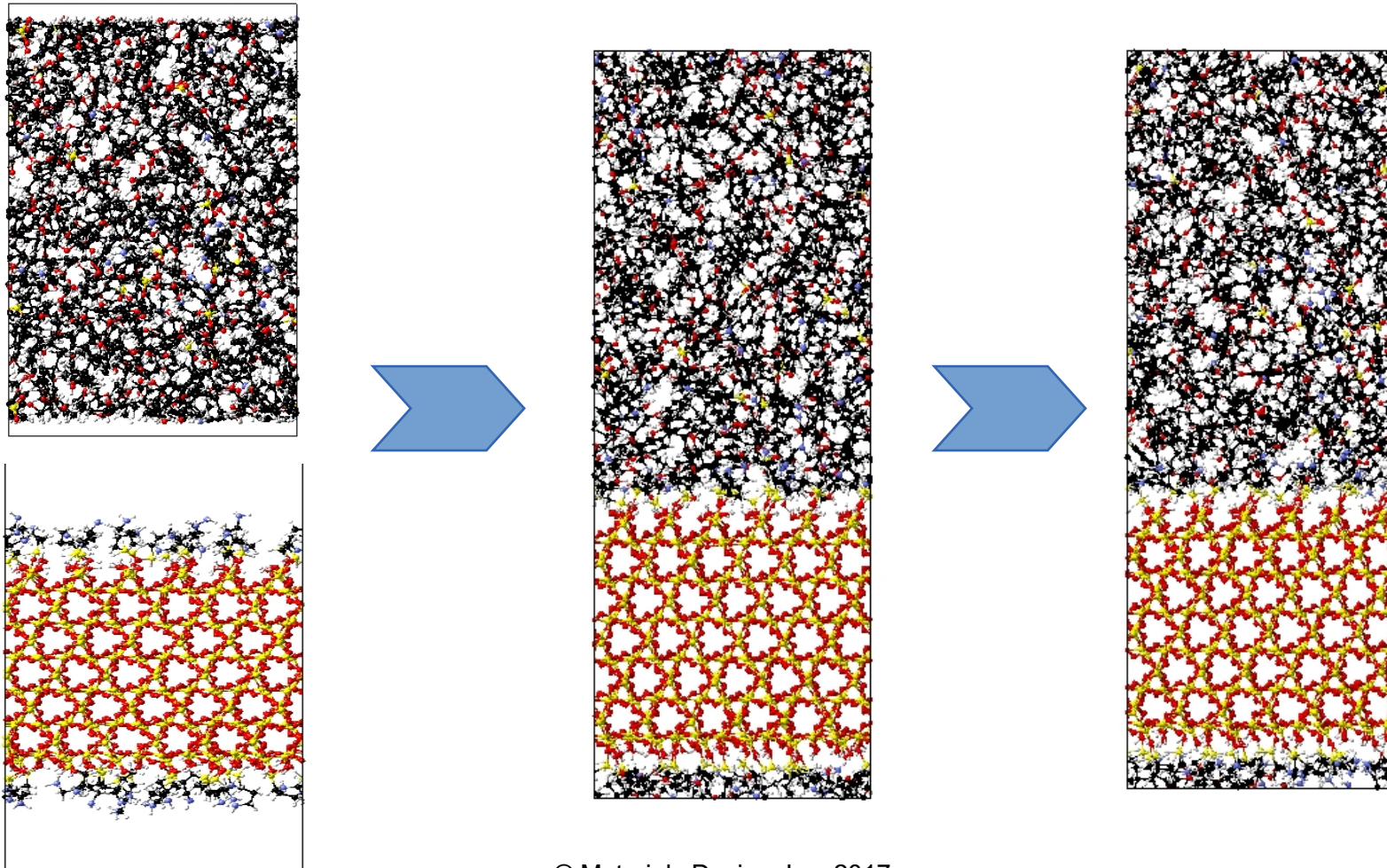
Epoxy-SiO$_2$ Interfaces – Model Building

$\gamma-$APS-coated (crystalline) silica (covalently bonded)

Epoxy-SiO$_2$ Interfaces – Model Building

Primed SiO$_2$+unreacted epoxy, crosslinking and equilibration

Epoxy-SiO$_2$ Interfaces – Mechanical Properties

Following equilibration, epoxy-SiO$_2$ systems were subjected to elastic constant calculations, as previously applied to bulk systems.

- Without primer

- Including primer with 12.5%, 25% and 50% of surface hydroxyls covalently bonded to primer, and exact stoichiometric balance of epoxide:amine groups present

- Compared C$_{33}$ (perpendicular to interface) stiffness coefficients for pure epoxy and various silica-containing primed composites**…**

Epoxy-SiO$_2$ Interfaces – Mechanical Properties

Stiffness coefficient C$_{33}$ (normal to the interface) for SiO$_2$ - epoxy composite layer systems with various levels of primer coverage:

Primed surface sites (%)	C$_{33}$ (GPa)
0	7.2
12.5	7.8
25	8.8
50	5.0
Reference: Bulk Cured Resin	5.97 +/-0.29

Preliminary results suggest **intermediate** primer coverage may produce optimal enhancement in small strain mechanical behavior (larger sample size studies are still required)

Summary & Conclusions

- Sampling a modest number of independent configurations of polymer glasses, combined with analysis using the Hill-Walpole method (as described by Suter and Eichinger), yields reproducible predictions of elastic constants with bounds comparable with experimental uncertainties

- Careful parameterization of force field nonbonded interactions, mostly using experimental PVT and heat of vaporization data for molecular liquids, also leads to prediction of elastic constants of glassy polymers comparable with experiment.

- For the PS-PPO system, while the overall change in tensile moduli with blend composition is reproduced reasonably well, the experimentally observed synergistic/antplasticisation effect leading to a maximum in the modulus-composition plot is weak or non-existent. This absence of a maximum persists even when the experimentally-measured blend densities are used in the simulations, and requires further investigation.

- The effect of varying epoxy resin chemical functionality in thermosets cured with DDS, is well-reproduced.

- Extension of simulations to more complex systems including interfaces between resin and inorganic filler is relatively straightforward and potentially useful in optimizing the properties of filled composites.

Thoughts on Future Work…

As is always the case in an active research environment, a number of areas for possible software development and basic research are desirable, as follows:

- Software enhancements:
  - Additional force field parameter developments to enable handling of inorganic materials of interest in the area of composites (metal oxides, Boron Nitride, etc.)

- Additional mechanical property and related work to:
  - Quantify the effect of density on computed moduli.
  - Study the excess volume in blend systems and its relationship to synergistic effects on the mechanical properties of miscible blend systems.
  - Investigate effective methods for making precise predictions of <u>large</u> strain deformation behavior.

Additional Information

The MedeA® simulation environment used in these studies features a diverse range of methods suitable for studying properties of material, including:

In addition to the LAMMPS simulation program used here, MedeA features comprehensive access to the VASP electronic structure program, in addition to the widely used Gaussian and MOPAC packages. Fluid phase equilibria simulations can be performed using the GIBBS Monte Carlo program, and mesoscale simulations using the UNCLE universal cluster expansion method.

A series of webinars illustrating materials applications using the above scientific methods can be accessed via the following link:

http://www.materialsdesign.com/webinars

Acknowledgements