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CLASSIFICATION	SYSTEM NUMBER
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TITLE

Dynamic Mechanical Property Prediction by Group Contribution Analysis

System Number:

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Dynamic Mechanical Property Prediction by Group Contribution Analysis

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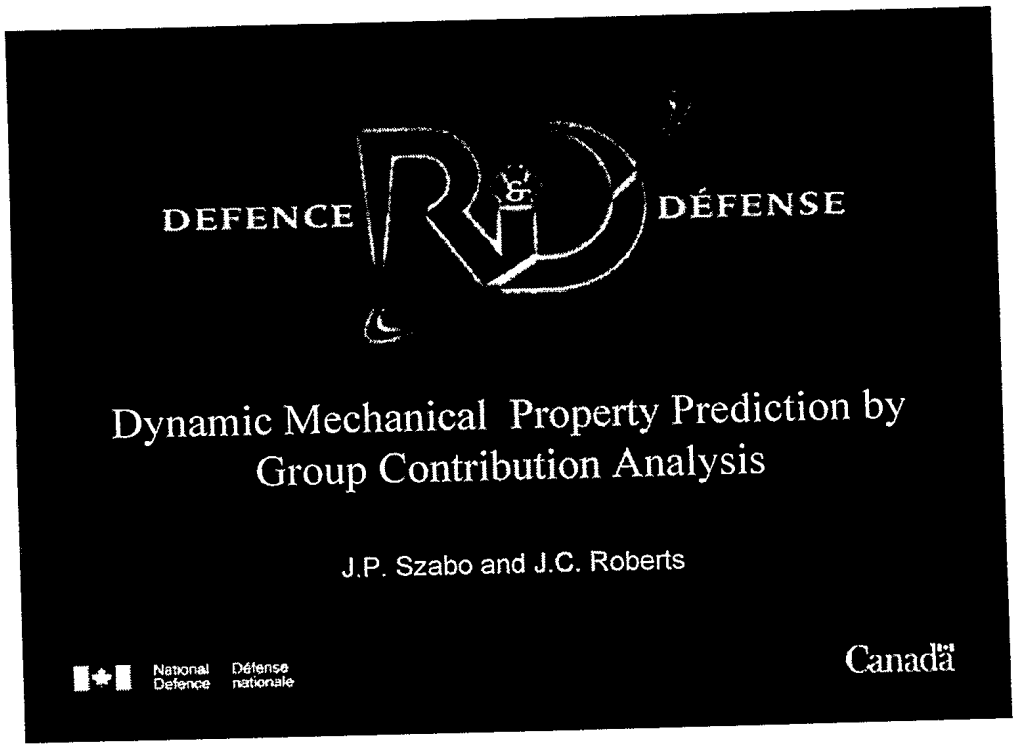
ABSTRACT

Vibroacoustic materials play a key role in signature control of military platforms, and their performance is related to the frequency dependence of the modulus and loss factor of the polymers from which they are fabricated. The height, width, and position (fmax) of the loss factor peak varies from polymer to polymer, as does the rubbery and glassy plateau moduli. This paper presents work in progress on a TTCP operating assignment whose goal is to extend and validate models which relate a polymer's dynamic mechanical properties to its chemical structure. The complex modulus of polymeric materials may be described by the Havriliak-Negami (HN) equation. Group contribution analysis (GCA) was used to derive contributions to the five parameters of the HN equation for a set of polyurethanes. Use of the calculated contributions gave HN parameters which show good agreement with experimental values when used on the training set, but had high error when tested on other polymers. Redefining the groups used for GCA show significantly improved results. The use of a new training set of polymers and the use of different structure descriptors is also discussed.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J.P. Szabo and J.C. Roberts
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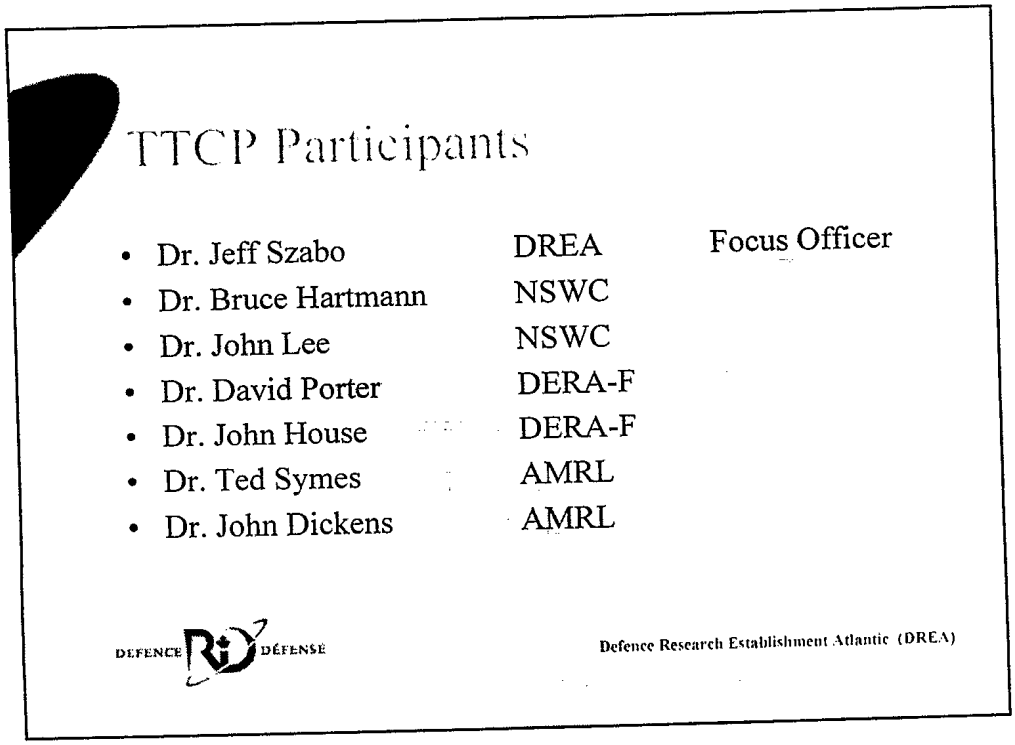
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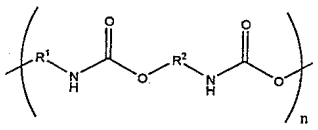
TTCP-MAT-TP-6-09

- The goal is to develop methods to predict the dynamic mechanical properties of polymers from their chemical structures.

Chemical Structure → Polymer Properties → System Performance



$E^*(\omega,t)$

$G^*(\omega,t)$

Vibration Isolators

Decoupling Tiles

Anechoic Tiles

Structural Damping

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Assignment Tasks

- Preliminary modelling using data from the literature
  - Group Interaction Modelling (GIM)
  - [illegible]
- Synthesis, characterization, and modelling of 20 phase mixed polyurethanes.
- Effect of static load on dynamic mechanical properties
- Phase morphology effects (blends, block copolymers)

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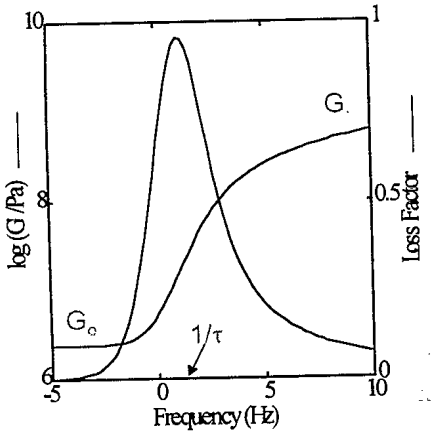
Dynamic Mechanical Properties



$$G^* = G' + i\,G''$$

$$\tan\delta = G''/G'$$

Structure controls:

- Limiting moduli G_o, G_∞
- Peak height, width β
- Peak shape α
- Peak position $1/\tau$

$$G^* = \frac{G_o - G_\infty}{\left[1 + (i\omega\tau)^\alpha\right]^\beta} + G_\infty$$

Havriliak - Negami Eqn

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Group Contribution Analysis

- Based on the assumption that each chemical group contributes a certain amount to a given property, eg density

$$\rho = \sum_j W_j \rho_j$$

- Can GCA be applied to HN parameters: α, β, τ, G_o, G_∞ ?

1) Took a number of polymers with known $G^*(\omega)$, solved for HN parameters **"Training Data"**

2) Broke down monomer structures into groups, e.g. $-CH_2-$, -O-, phenyl, urethane,...

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3) Calculated weighting factors for each group i and polymer j:

$$W_{i,j} = N_{i,j} \frac{M_{i,j}}{M_j}$$

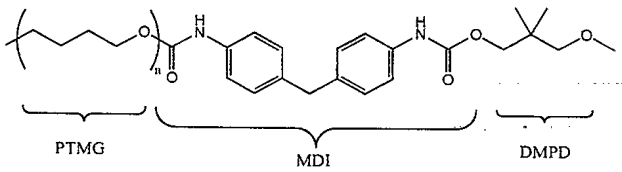
4) Solved for coefficients A, B, C, D, E which satisfy matrix equations:

$$\alpha = W\,A \qquad \log(\tau) = W\,C$$
$$\beta = W\,B \qquad \log(G_o) = W\,D$$
$$\log(G_\infty) = W\,E$$

Can now use coefficients to calculate dynamic mechanical properties of other polymers with same groups

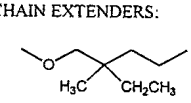
Polyurethane Structures

GENERAL POLYURETHANE:

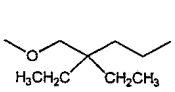


PTMG MDI DMPD

CHAIN EXTENDERS:



EMPD



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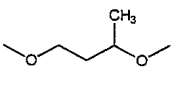
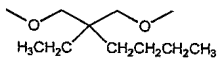
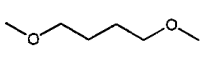


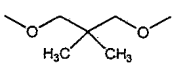
1,3 BDO



BEPD



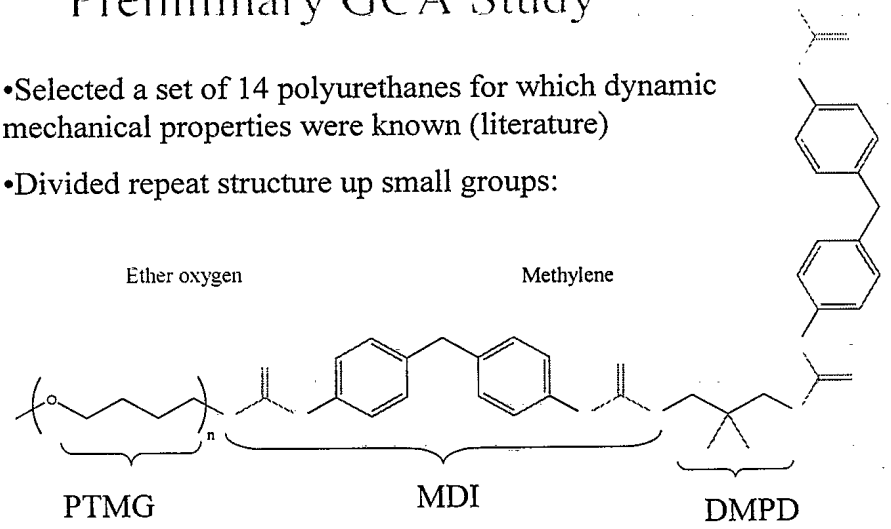
BDO



DMPD

Preliminary GCA Study

- Selected a set of 14 polyurethanes for which dynamic mechanical properties were known (literature)
- Divided repeat structure up small groups:



Number of Groups per Monomer (N)

Monomer	MW	Methylene 14.027	Oxygen 15.999	Phenyl 76.098	cyclohexane 82.146	urethane 59.025	DMPD 42.081	EMPD 56.108	BEPD 98.189	DEPD 70.135
ptmg2000/3mdi/2dmpd	2995	119	27	6	0	6	2	0	0	0
ptmg2000/4mdi/3dmpd	3350	122	27	8	0	8	3	0	0	0
ptmg2000/6mdi/5dmpd	3958	128	27	12	0	12	5	0	0	0
ptmg1000/3mdi/2dmpd	1987	63	13	6	0	6	2	0	0	0
ptmg1000/3mdi/2depd	2043	63	13	6	0	6	0	0	0	2
ptmg2000/3mdi/2depd	3051	119	27	6	0	6	0	0	0	2
ptmg1000/3mdi/2 13bdo	1959	65	13	6	0	6	0	0	0	0
ptmg1000/3mdi/2empd	2015	63	13	6	0	6	0	2	0	0
ptmg2000/3mdi/2empd	3023	119	27	6	0	6	0	2	0	0
ptmg1000/3mdi/2bepd	2099	63	13	6	0	6	0	0	2	0
ptmg2000/3mdi/2bepd	3107	119	27	6	0	6	0	0	2	0
ptmg650/3 h12mdi/2bdo	1546	47	8	0	6	6	0	0	0	0
ptmg1000/3mdi/2bdo	1870	67	13	6	0	6	0	0	0	0
ptmg1430/3mdi/2bdo	2303	91	19	6	0	6	0	0	0	0

Results: Group Contributions

Contributions to HN Parameters:

Group	alpha	beta	log(tau)	log(Go)	log(Ginf)
Methylene	-24.9	15.1	-330.9	64.8	-8
Ether Oxygen	89	-52.4	1093.4	-199.2	70.9
phenyl	11.8	-6.1	146.6	-12	23.1
cyclohexane	11.8	-6.1	156.1	-12.7	21.8
urethane	0	0	0	0	0
DMPD	-9	5.5	-102.2	28	2.4
EMPD	-5.4	4.2	-65.2	21.4	-0.1
BEPD	-2	2.8	-36.4	15.5	2
DEPD	-4.2	3.1	-61.5	16.8	4

- Note urethane coefficients are zero
- Note strange values for some coefficients

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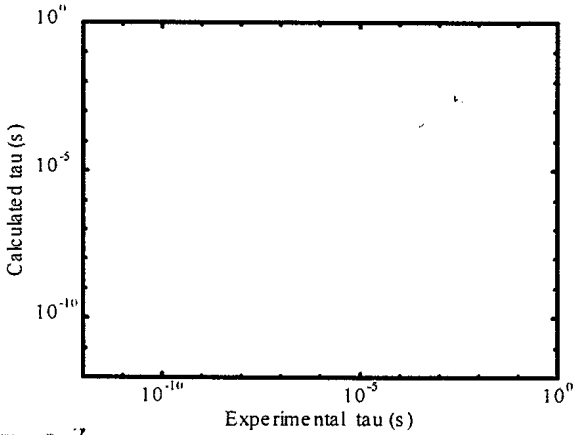
Results: Training Set



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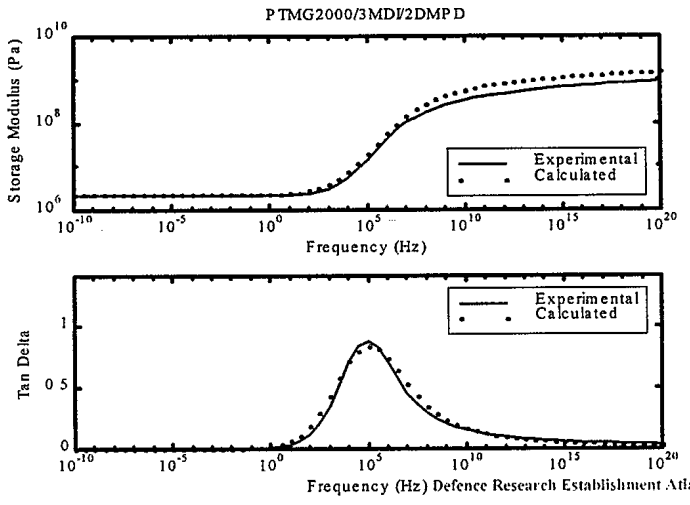
Polymer in Training Data Set



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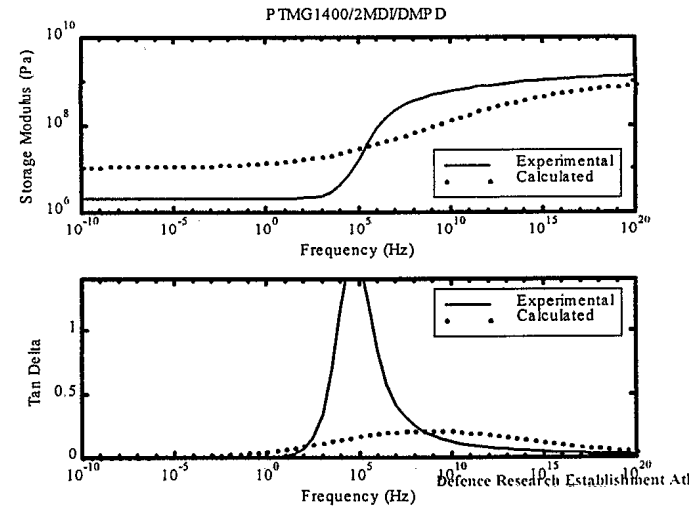

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Comments: Preliminary Analysis

- The calculated HN parameters and G*(ω) correlated very highly with the experimental values for polymers in the training data set.
- For polymers outside of data set, poor predictions

Basic problem:

- The effect of each group is not separable from all other groups (e.g. urethane and phenyl).
- Requires a correct selection of polymers and groups
- Poorly conditioned W matrix will propagate errors

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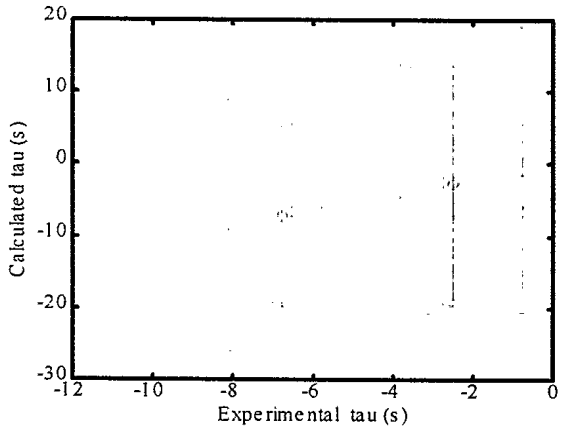
Error Propagation -Small Groups



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Possible Solutions

1) Synthesize a set of polymers that contain a small number of groups, designed with low propagation error in W matrix.

   This should be completed by Fall 1999:

   20 polyurethanes containing 5 groups

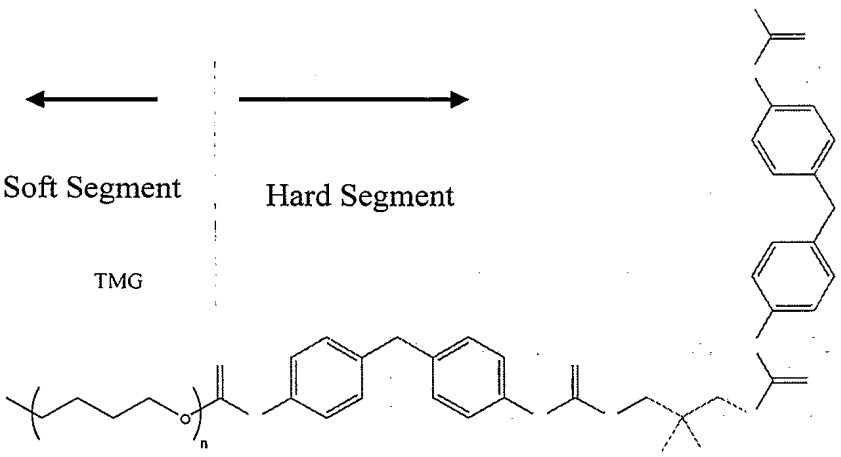
2) Using existing polyurethane dataset from literature, represent structures in terms of larger groups such as tetamethylene glycol or MDI segments.

Larger Groups

Soft Segment

Hard Segment

TMG



Results from Large Group Analysis

Group	alpha	beta	log(tau)	log(Go)	log(Ginf)
TMG	0.37	0.10	-15.09	6.26	9.5
MDI	1.11	0.23	10.78	6.63	5.3
HDI	-0.21	-1.16	3.00	5.44	24.1
DMPD	1.57	-0.05	22.47	5.39	5.3
DEPD	0.30	-0.94	-0.51	4.52	20.9
EMPD	0.29	-0.89	5.96	5.43	21.0
BEPD	0.97	-0.40	4.79	6.03	16.2
BDO	-5.19	1.36	-70.87	16.27	26.5
1,3 BDO	-0.16	-1.59	-6.57	4.76	29.6

- Correlations between the experimental HN parameters for the data set and those calculated using the values above:

log(Go)	log(Ginf)	log(Tau)	alpha	beta
0.989	0.820	1.000	0.991	0.764

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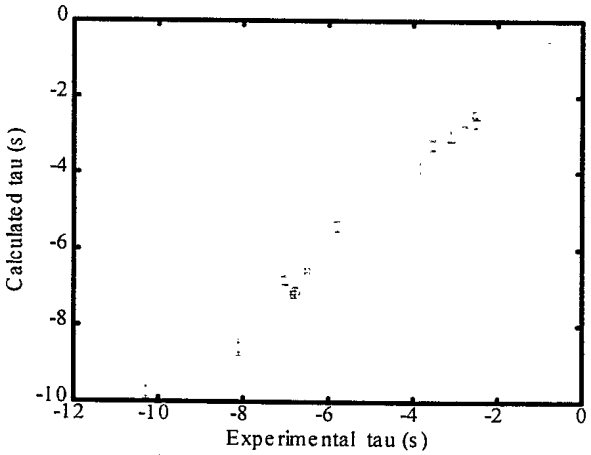
Error Propagation: Large Groups



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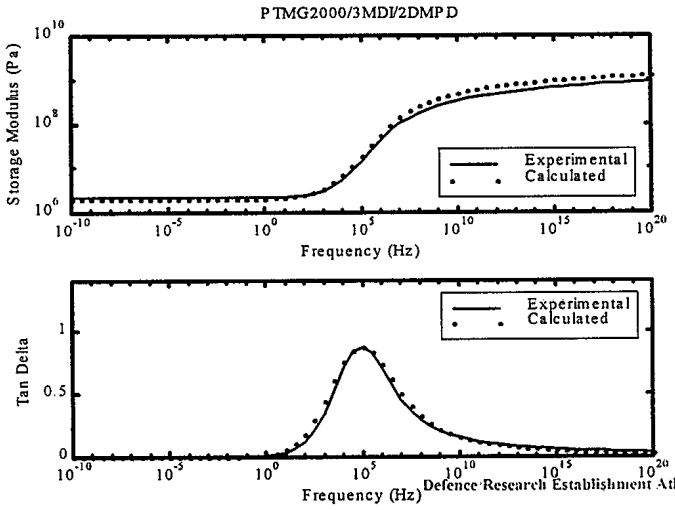
Training Set Polymer: Large Groups



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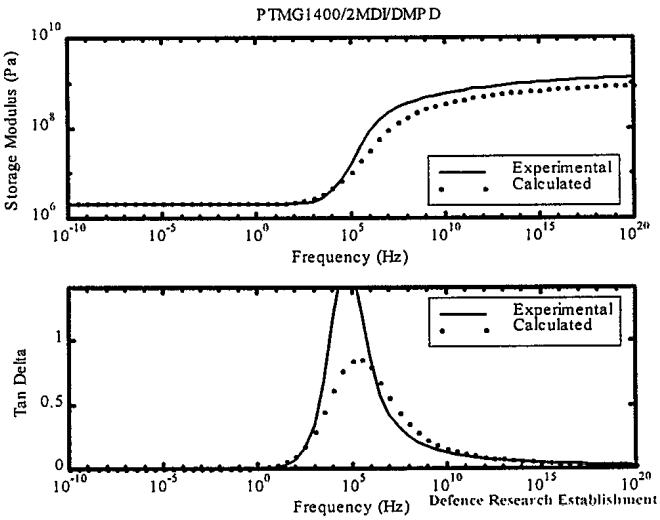

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Summary

- Prediction of dynamic mechanical properties with GCA has been explored in this work using data from literature
- Calculation of HN parameter contributions using the original set of groups and GCA gave good agreement with experimental parameters, but not for polymers outside the training data set.
- Redefining the groups used to describe the polymers gave improved results, but not to the degree desired.
- New polymers being synthesized and characterized should provide a better basis for evaluation of this method.

Future Work

- Re-evaluation of GCA using newly synthesized polymer set
- Exploration of topological structure descriptors
  - Connectivity index method
  - Distance matrix approach
- Static load effects
- Blends