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TITLE
Synthesis and characterization of a series of thermoplastic polyurethanes

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Synthesis and Characterization of a Series of Thermoplastic Polyurethanes

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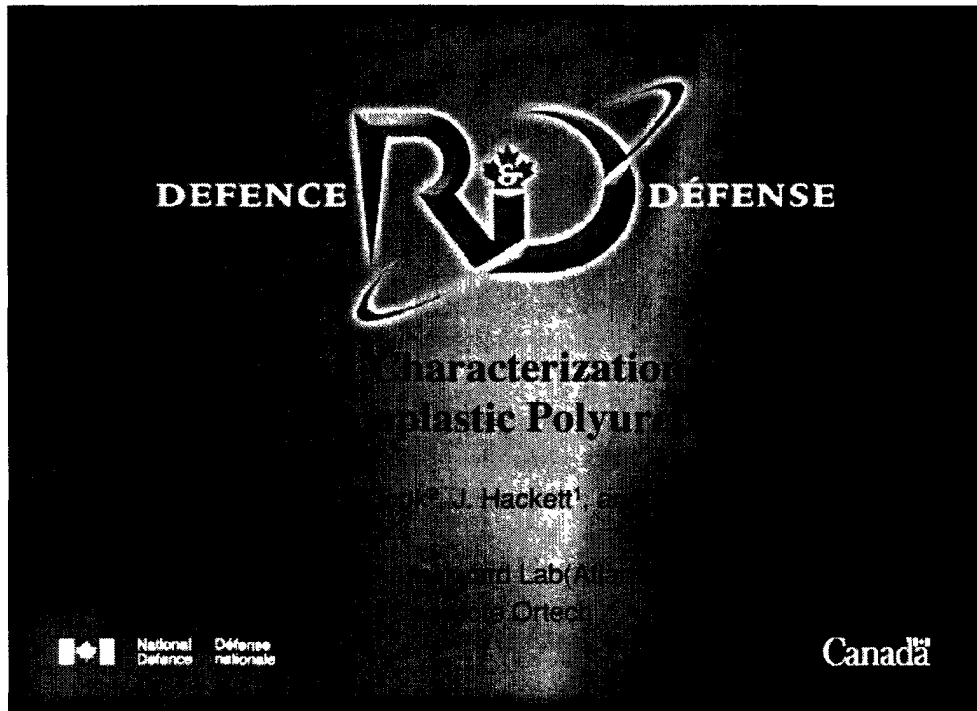
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Abstract

The use of Group Contribution Analysis (GCA) and Group Interaction Modelling (GIM) to model the dynamic mechanical properties of polymers is the subject of an ongoing TTCP (The Technical Cooperation Panel) study. This paper describes the synthesis of 20 phase mixed thermoplastic polyurethanes for the TTCP modelling study, and the characterization of these polymers by dynamic mechanical thermal analysis (DMTA). The polyurethane formulations were synthesized from 4,4'-methylenebis(phenyl isocyanate) or 1,6-diisocyanatohexane, and glycol, polyglycol, or glycol/polyglycol mixtures. The standard "one-shot" batch reaction method was initially tried for several of the formulations, but a number of problems were identified. These included bubble formation in the samples, high exotherms, and fast reaction times. As a result, a solution polymerization/ solution casting method was developed, using N,N-dimethylformamide as a solvent. This approach has several advantages including control of the reaction temperature and rate and the absence of bubble formation in the samples. All 20 of the formulations were successfully prepared in solution, and 15 of the formulations were successfully solvent cast into 1 mm thick film samples for DMTA testing. The dynamic mechanical properties of the solvent cast samples were determined over a range of temperatures and frequencies, and time-temperature superposition was used to produce DMTA master curves. The dependence of the dynamic mechanical properties of on chemical structure is discussed in terms of qualitative factors, such as soft segment molecular weight, and quantitative group contributions.



Outline

- Background and Objectives
- Polyurethane Synthesis
- Characterization
- Qualitative trends
- Quantitative analysis
- Summary



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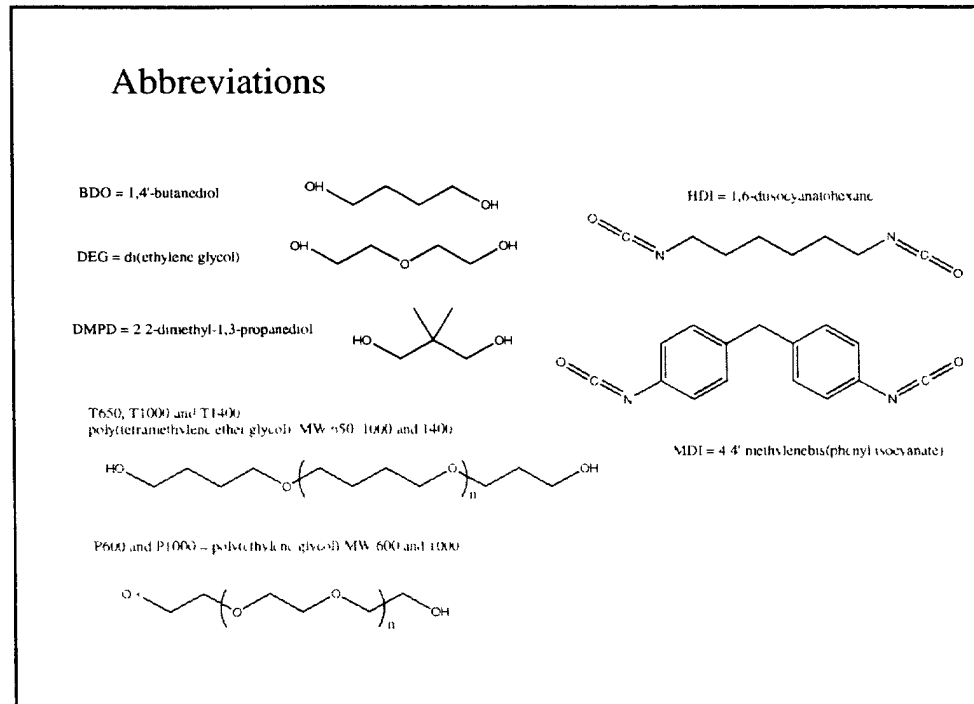
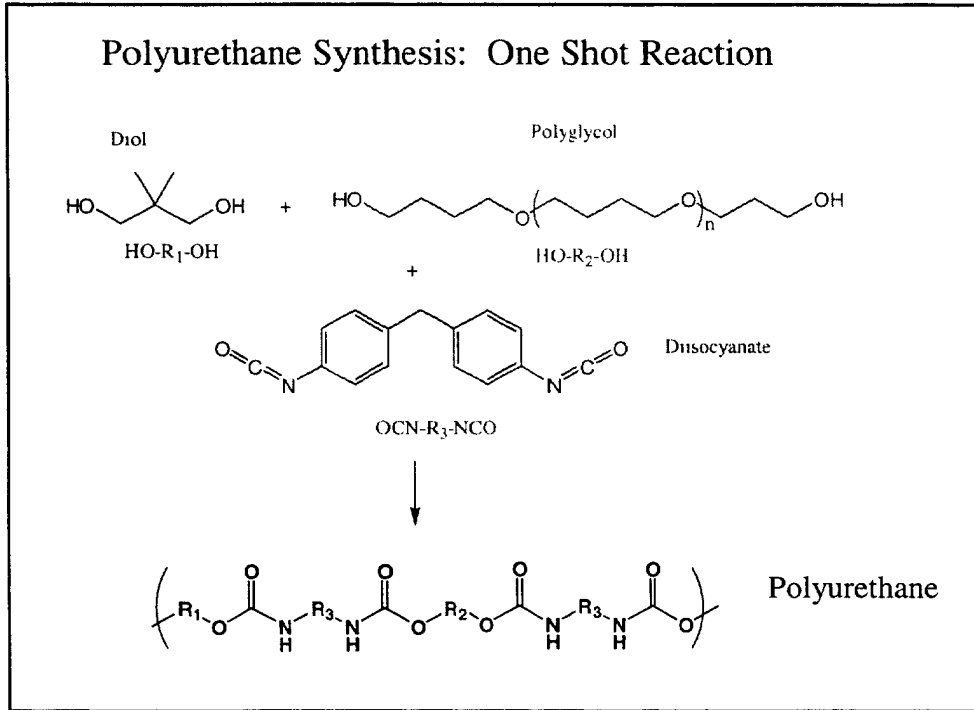
Polymer Modelling

Several semi-empirical methods have been developed:

- **Group Contribution Analysis** (van Krevelen).. Physical properties of polymer determined by sum of contributions from structural groups.
- **Connectivity Index Method** (Jozef Bicerano). Each polymer has a set of 4 indices related to its topology that may be used to derive a wide variety of physical properties.
- **Group Interaction Modelling** (David Porter). Mean field method uses 6 input parameters for each structural sub-unit: $(L, N, M, \theta_1, V_w, E_{coh})$. Relies on above two methods for calculation of V_w and E_{coh} .

Damping Properties

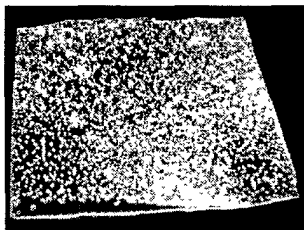
- The damping properties of polymers are a critical aspect of acoustic signature control on naval ships and submarines.
- TTCP Assignment: Objective is to study methods (GIM, GCA) for predicting the dynamic mechanical properties of polymers from their chemical structures.
- Can we predict the height, width, shape, and position of damping peak from structural considerations only?
- As part of this project, a series of thermoplastic polyurethanes have been synthesized and characterized. Limited number of structural sub-groups (5).



Molar Ratios of Reactants for PU Formulations

	DIOL			POLYGLYCOL					DIISOCYANATE	
	BDO	DEG	DMPD	T650	T1000	T1400	P600	P1000	HDI	HDI
1	1								1	
1R	1								1	
2	1		1							2
3			0.5		1				1.5	
4			5		1				6	
5			1			1			2	
6			5			1			6	
7		1	1							2
8			0.5				1		1.5	
8R			0.5				1		1.5	
9			1					1	2	
9R			1					1	2	
10			5					1	6	
11			5					1		6
13		1							1	
13R		1							1	
14			5	1					6	
16					1				1	
16R					1				1	
17			3		1				4	
18			3		1					4

One Shot Synthesis (No Solvent)

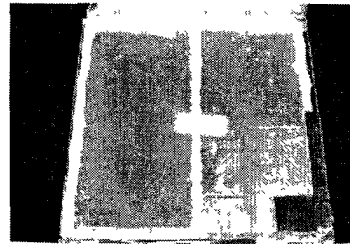


- heat reactants separately to ~ 45-55°C, and degas
- mix well under nitrogen, then degas
- pour reaction mixture into mold and allow to cure at 60–100°C
- Conventional method was unsuitable for many of the formulations.

- Problems with bubble formation in sheet samples.
- For high urethane samples (no polyether diol) problems with **high exotherms, fast reactions**, solubility of isocyanate, and brittleness.
- For HDI samples, concerns about HDI volatility.
- DMPD solubility/ volatility

Solution Polymerization/ Casting

- A solution polymerization/ casting method was developed using dimethylformamide (DMF) as solvent.
- Problems with high exotherms, rapid reaction times, and bubbles were avoided
- 16 out of 21 formulations were successfully cast into 1-2 mm thick films.
- 5 formulations did not form satisfactory samples for dynamic mechanical characterization (cracked during film formation).



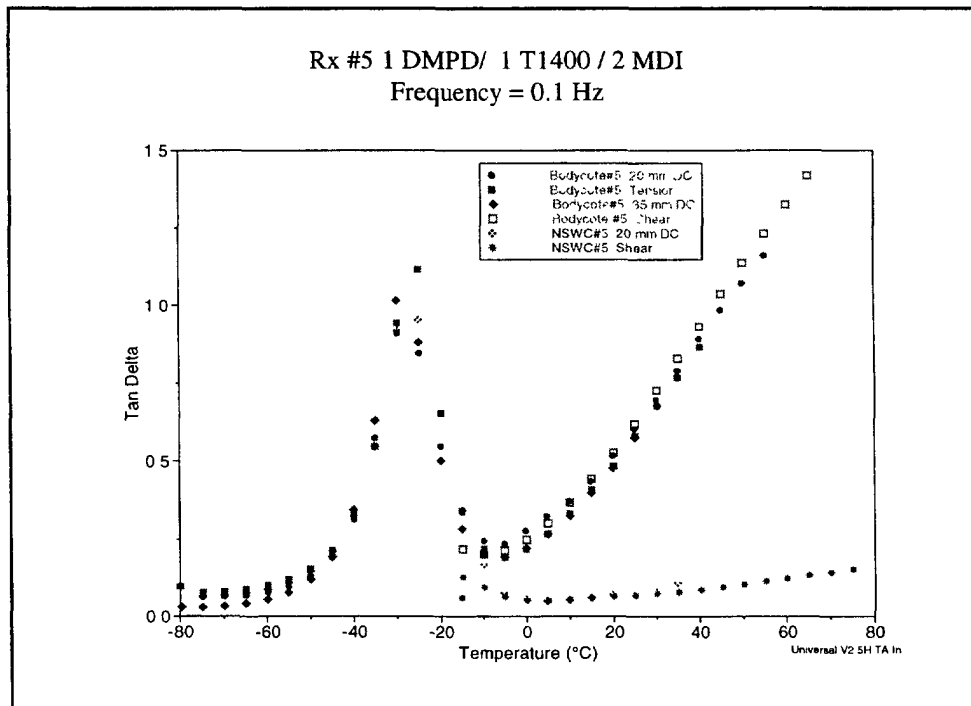
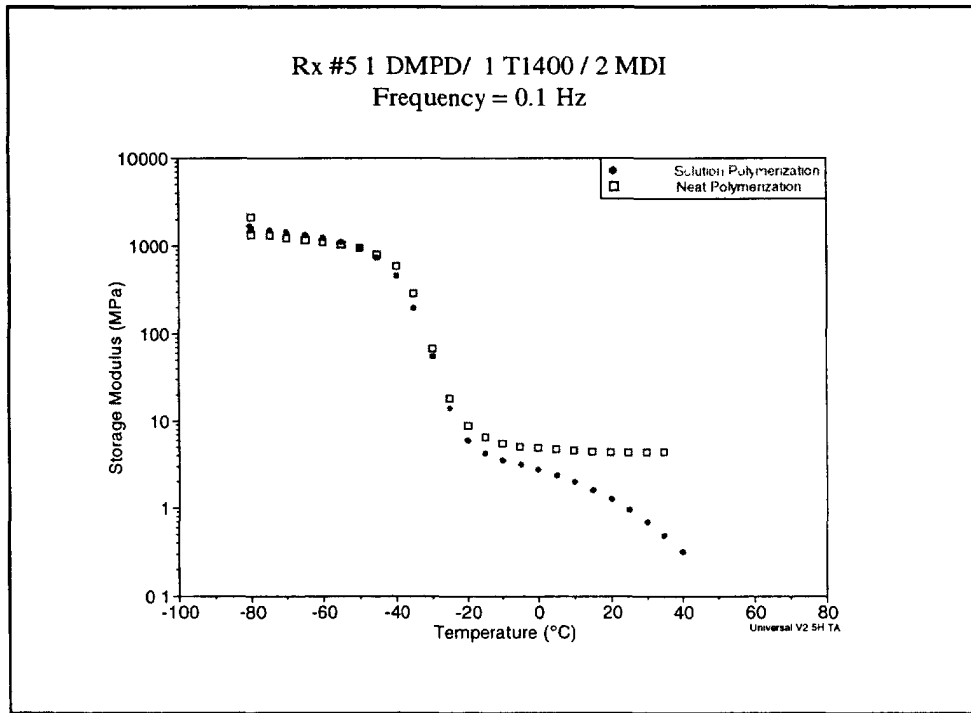
Characterization

- Specimens were characterized by
 - gel permeation chromatography
 - elemental analysis
 - infrared spectroscopy
 - differential scanning calorimetry
 - **dynamic mechanical analysis:**

$$E^* = E' + iE''$$

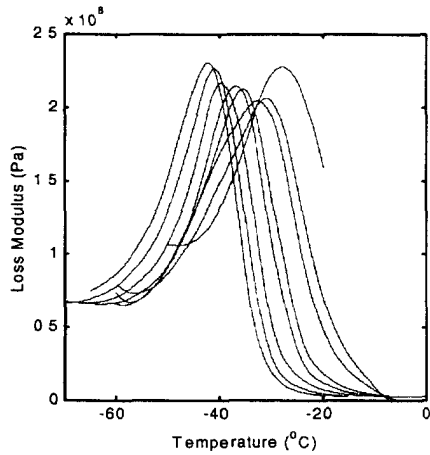
$$\tan \delta = \frac{E''}{E'}$$

E^*	complex modulus
E'	storage modulus
E''	loss modulus
$\tan \delta$	loss factor



Master Curves

Rx #3 1 T1000 / 0.5 DMPD / 1.5 MDI



Step 1

Multiple frequency DMTA

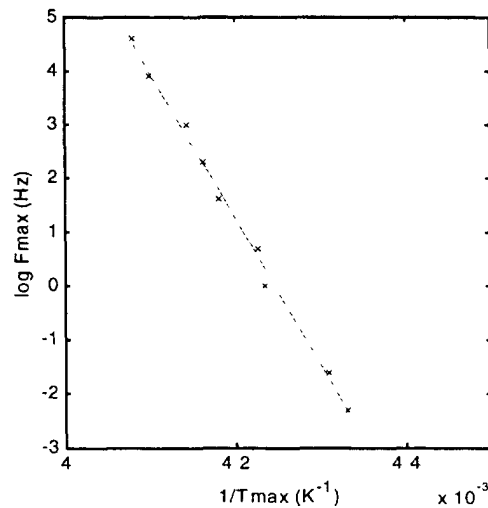
Step 2

Identify loss modulus peaks for each frequency:

$$T_{\max}(f)$$

Rx #3 1 T1000 / 0.5 DMPD / 1.5 MDI

Arrhenius Plot



Step 3

Fit peak data to Arrhenius relationship:

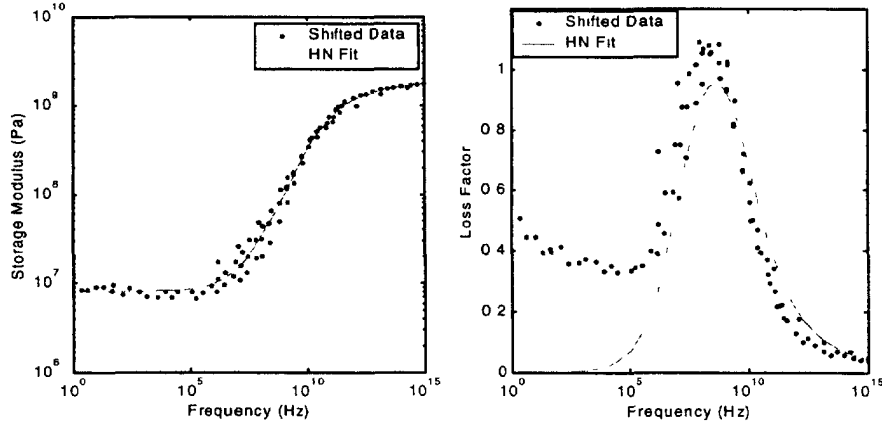
$$f = A \exp(-E_a/RT_{\max})$$

Determine E_a from plot of $\log f$ versus $1/T_{\max}$.

Step 4 Calculate shift factors using $\log a_T = -\frac{E_a}{R} \left[\frac{1}{T_r} - \frac{1}{T} \right]$

Step 5 Fit master curves to Havriliak-Negami model

Rx #3 1 T1000 / 0.5 DMPD / 1.5 MDI $T_r = 298$ K



Properties Determined

$$E^* = \frac{E_0 - E_\infty}{[1 + (i\omega\tau)^\alpha]^\beta} + E_\infty$$

Havriliak - Negami Eqn

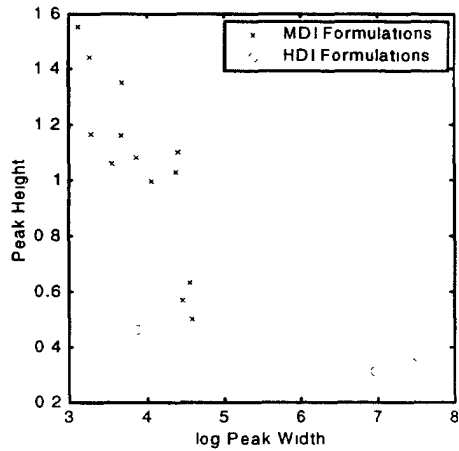
For 16 formulations studied by DMTA, determined:

- Arrhenius activation energy E_a
- 5 HN parameters at reference temperature $T = 298$ K
- Height, width, and position of loss factor peak in temperature and frequency domains

No data for 5 of the formulations: 1, 1R, 2, 13, 13R

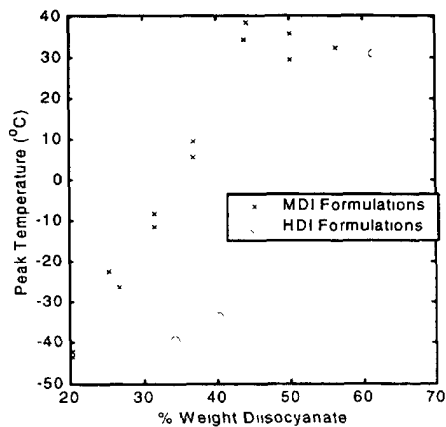
Observations

Height-Width Limitations



- Peak height inversely related to peak width in both frequency and temperature domains
- Dependence different for MDI and HDI based formulations
- Consistent with HN equation

Effect of Hard Segment Content



- The temperature of the loss factor peak proportional to %weight of diisocyanate in Rx
- MDI and HDI formulations results were different

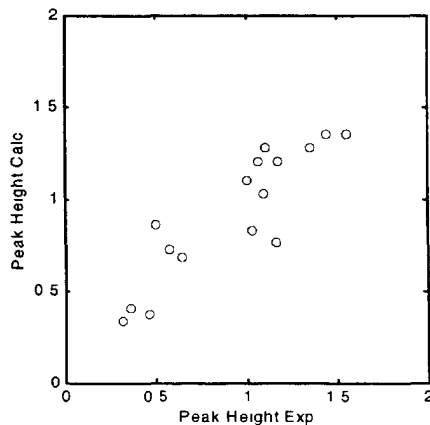
Modelling Damping Properties

- Group Interaction Modelling (GIM)
 - Approach looks promising for dynamic mechanical property prediction.
 - Results published in internal DERA report.
- Group Contribution Analysis (GCA)
 - van Krevelen method used
 - Results of this study with data for 16 polyurethanes are inconclusive
 - May not be large enough set of polymers



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GCA: Small Groups



- Used least squares approach to find group coefficients for 5 small groups in table.
- Derived coefficients were able to explain experimental data reasonably well, BUT
- Negative value for dimethyl propane height coefficient does not make physical sense
- Analysis done with larger groups gave slightly better results

	Group Contributions		
	Height	Width	log(fmax)
Methylene	0.379	5.389	13.533
Ether Oxygen	3.413	-2.446	40.662
Dimethyl Propane	-9.298	9.142	75.982
Phenyl	1.976	0.586	-23.349
Urethane	1.806	8.737	-31.635

Summary and Conclusions

- Solution polymerization/ casting avoided problems with high exotherms and bubble formation.
- 16 out of 21 formulations were successfully cast and characterized by dynamic mechanical analysis.
- Loss peak height inversely correlated with loss peak width
- Loss peak position related to hard segment concentration.
- Group contribution analysis results were inconclusive so far. This analysis is not yet complete - 5 more samples to be made, characterized, and included in analysis.



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