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**TITLE**  
Group contribution analysis applied to the Havriliak-Negami model for polyurethanes

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# Group contribution analysis applied to the Havriliak–Negami model for polyurethanes

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Received 3 June 1999, received in revised form 5 August 1999, accepted 6 August 1999

## Abstract

Group contribution analysis (GCA) has been applied to many of the physical properties of polymers in the past. In this paper, GCA has been applied for the first time to the frequency dependent complex modulus of polymeric materials, which may be described in terms of the Havriliak–Negami (H–N) equation. This approach has been tested on a set of polyurethanes for which the H–N parameters have been uniquely determined. It has been shown that the dynamic mechanical behaviour of polymers may be described in terms of group additive relationships, at least for the 14 polyurethanes and nine structural groups which were studied here. © 2000 Elsevier Science Ltd. All rights reserved.

**Keywords:** Group contribution analysis, Complex modulus, Havriliak–Negami model, Viscoelasticity

## 1. Introduction

The frequency dependent complex modulus ( $G^*(\omega)$ ) of a polymer has several commonly observed characteristics: a rubbery plateau ( $G_0$ ) at low frequencies, a glassy plateau at high frequencies ( $G_\infty$ ), and a rapidly changing modulus in the vicinity of the glass transition. The glass transition region is also characterized by a peak in the loss modulus ( $G''$ ) and a peak in the loss tangent,  $\tan \delta = G''/G'$ . There have been several analytical models for this behaviour suggested in the literature with the most important expressions being the single relaxation time model of Cole and Cole [1], the Davidson–Cole method [2] which includes asymmetric frequency behaviour, and finally the Havriliak–Negami (H–N) model [3] which includes aspects of the previous two models. Hartmann has shown that the H–N model can accurately describe the dynamic mechanical behaviour of polymers, including the height, width, position, and shape of the  $\tan \delta$  peak [4].

Group contribution techniques are widely used methods in polymer modelling. These techniques are used to fit experimental data to parameters specific to the polymer's chemical structure. In this way, the derived parameters can be used to predict properties of new polymeric structures that include the parameterized chemical groups. It has been shown that these methods can be used with success on such

properties as the glass transition temperature, density, and volume as well as many other physical properties [5–8]. Porter [6] has shown that physical properties calculated using group contributions can be used with success to determine many other properties using his so-called Group Interaction Modelling methods.

It is the goal of this study to apply group contribution techniques to the H–N parameters in order to determine if the parameters are group additive. We have chosen a set of polyurethanes which are of interest as sound damping materials and for which the H–N parameters have been previously determined [4].

## 2. The Havriliak–Negami model

This model is a generalization of the single relaxation time model that combines both the broadening of the Cole–Cole [1] model and the asymmetry of the Davidson–Cole [2] model, as proposed by Havriliak and Negami [3] in the following equation for the complex shear modulus:

$$G^*(\omega) = \frac{G_0 - G_\infty}{[1 + (i\omega\tau)^\alpha]^\beta} + G_\infty \quad (1)$$

where the five H–N parameters can be related to the shape of the master curve:  $G_0$  is the lower limit of the modulus at low frequency,  $G_\infty$  is the upper limit of the modulus at high

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Table 1

Number of structural groups per monomer unit for the polymer studied (ptmg, poly(tetramethylene)glycol, mdi, 4,4'-diphenylmethane diisocyanate, h12mdi, 4,4'-dicyclohexylmethane diisocyanate, bdo, 1,4-butanediol, 13bdo, 1,3-butanediol, dmpd, 2,2-dimethyl-1,3-propanediol, empd, 2-ethyl-2-methyl-1,3-propanediol, bepd, 2-butyl-2-ethyl-1,3-propanediol, depd, 2,2-diethyl-1,3-propanediol)

Monomer	MW	-CH <sub>2</sub> - 14	-O- 16	Phenyl 76	Cyclohexane 82	Urethane 59	DMPD 43	EMPD 57	BEPD 99	DEPD 71
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 1,3bdo	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
Ptmg650/3h12mdi/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

frequency,  $\omega = 2\pi f$  is the angular frequency,  $\alpha$  is related to the width of the curve,  $\beta$  controls the asymmetry of the curve and  $\tau$  is the relaxation time. This study will try to determine if these five H-N parameters are additive and explore their relationship to the chemical structure of the polymer.

### 3. Group contribution techniques

The Group Contribution Analysis (GCA) techniques used in this paper are derived from the work of Van Krevelen [7] and has been extended and modified by Bicerano [8] and others. The general form of this method is illustrated in the equation below to calculate

the glass transition temperature ( $T_g$ ) [7]:

$$T_g = \frac{\sum_i s_i T_{g_i}}{\sum_i s_i} \quad (2)$$

where  $T_{g_i}$  is the specific contribution to the glass transition temperature of a given structural group  $i$  and  $s_i$  is the weight factor associated with a given structural group. The GCA method assumes that a specific property of a polymer is a result of the contributions from each of the polymers constituent chemical groups. In this way, a specific property can be calculated given the parameters of the polymer's chemical groups

Table 2

Experimental H-N parameters, taken from Ref [4]

	$\alpha$	$\beta$	$\log(\tau/s)$	$\log(G_0/Pa)$	$\log(G_\infty/Pa)$
Ptmg2000/3mdi/2dmpd	0.571	0.036	-6.78	6.331	9.269
Ptmg2000/3mdi/3dmpd	0.533	0.027	-5.80	6.193	9.553
Ptmg2000/6mdi/4dmpd	0.617	0.026	-2.76	6.369	9.376
Ptmg1000/3mdi/2dmpd	0.614	0.070	-3.10	6.375	9.068
Ptmg1000/3mdi/2depd	0.661	0.053	-3.52	6.173	9.151
Ptmg2000/3mdi/2depd	0.556	0.031	-6.80	6.283	9.379
Ptmg1000/3mdi/2 1,3bdo	0.638	0.030	-3.83	6.301	9.328
Ptmg1000/3mdi/2empd	0.680	0.057	-2.53	6.363	9.041
Ptmg2000/3mdi/2empd	0.535	0.066	-7.02	6.246	9.211
Ptmg1000/3mdi/2bepd	0.724	0.094	-2.51	6.351	8.914
Ptmg2000/3mdi/2bepd	0.640	0.073	-6.53	6.364	9.014
Ptmg650/3h12mdi/114bdo	0.494	0.136	-0.77	6.701	8.908
Ptmg1000/3mdi/114bdo	0.261	0.117	-8.11	7.104	9.225
Ptmg1430/3mdi/114bdo	0.295	0.378	-10.31	7.042	9.023

Table 3  
Least squares coefficients for each structural group and group contribution parameter

	A	B	C	D	E
-CH <sub>2</sub> -	-26.42	14.28	-690.70	85.11	-103.65
-O-	94.26	-49.53	2262.50	-232.66	462.30
Phenyl	12.46	-5.79	308.40	-1.41	88.22
Cyclohexane	12.36	-5.79	329.50	-4.82	82.80
Urethane	0.00	0.00	0.00	0.00	0.00
DMPD	-9.94	5.18	-205.60	33.73	-36.71
EMPD	-5.85	3.95	-127.40	28.77	-26.92
BEPD	-2.27	2.60	-71.40	23.87	-10.97
DEPD	-4.63	2.92	-123.50	22.18	-12.40

#### 4. Polymer dataset

In this paper, a set of 14 polyurethanes for which the H–N parameters had been previously calculated, were studied. This polymer dataset including the corrections to the original literature article [4,5] is shown in Table 1, while the experimental H–N parameters at 25°C are listed in Table 2. The narrow focus of this study is due to the lack of good H–N data for other polymers.

The polymers used in this study were synthesized in two stages [4]. Prepolymers were prepared from poly(tetramethylene ether) glycol (PTMG) having nominal molecular weights of 650, 1000, 1430 and 2000, and either 4,4'-diphenylmethane diisocyanate (MDI) or 4,4'-dicyclohexylmethane diisocyanate (H12MDI). These prepolymers were then chain extended with either 1,4-butanediol (BDO), 1,3-butanediol (1,3BDO), 2,2-dimethyl-1,3-propanediol (DMPD), 2-ethyl-2-methyl-1,3-propanediol (EMPD), 2-butyl-2-ethyl-1,3-propanediol (BEPD) or 2,2-diethyl-1,3-propanediol (DEPD). For the purpose of the calculations the idealized structures were used.

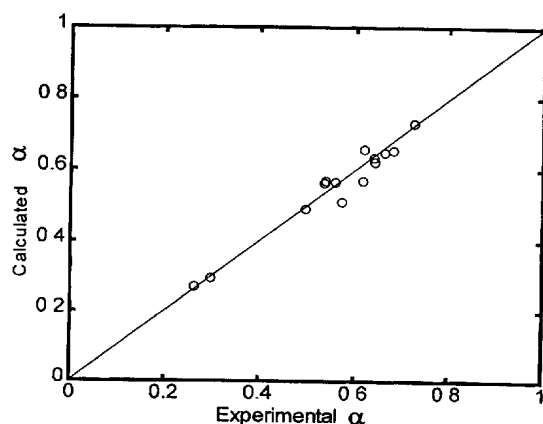


Fig. 1. Comparison of experimental and calculated  $\alpha$  using Eq. (4), the weighting factors from Table 1, and the group contribution vector  $A$  from Table 3.

#### 5. Method

The five H–N parameters were fit to five independent group additive parameters using the weight function given by the equation

$$WF_{k,j} = N_{k,j} \frac{M_j}{M_k} \quad (3)$$

where  $M_j$  is the molecular weight of the structural group of interest,  $M_k$  is the molecular weight of the monomer unit, and  $N_{k,j}$  is the number of times the specific group  $j$  appears in the monomer. The structural groups for this set of polymers were taken to be methylene, ether oxygen, phenyl, cyclohexyl, urethane (OCONH), and the substituted methylenes dimethyl, ethylmethyl, butyl ethyl, and diethyl (see Table 1) as these groups were present in the 14 polyurethanes studied and this approach is consistent with previous studies [5,7]. The parameters for 1,3-butanediol assume that the pendant methyl group is equivalent to a pendant hydrogen for simplification purposes. The five H–N parameters were then taken as a function of five independent variables  $A$ ,  $B$ ,  $C$ ,  $D$  and  $E$ . These variables are related to the H–N parameters according to the following five equations:

$$\alpha = WF \times A \quad (4)$$

$$\beta = WF \times B \quad (5)$$

$$\log(\tau) = WF \times C \quad (6)$$

$$\log(G_0) = WF \times D \quad (7)$$

$$\log(G_\infty) = WF \times E \quad (8)$$

These five simultaneous matrix equations were then solved using least squares methods for vectors  $A$ ,  $B$ ,  $C$ ,  $D$ , and  $E$  which satisfy the above equations. The equations were solved using MATLAB [9].

#### 6. Results and discussion

The method described above was used to derive the group contribution coefficients  $A$ ,  $B$ ,  $C$ ,  $D$ , and  $E$  for the nine groups that comprise the polymer dataset used. These parameters are listed in Table 3. The most obvious point of discussion in the table is the fact that the urethane parameters are all zero using the least squares method. This is due to the fact that the weight function matrix is over-determined and that the urethane and phenyl groups are essentially invariant to each other, that is, they occur in the same ratio in all the polymers in this dataset with the exception of one. In essence, two mathematically equivalent groups are being treated as separate variables.

Once the group contribution parameters were determined, the H–N parameters were calculated using Eqs. (4)–(8) and compared to the experimental values [4]. These comparisons are shown in Figs. 1–5. In general, the calculated and

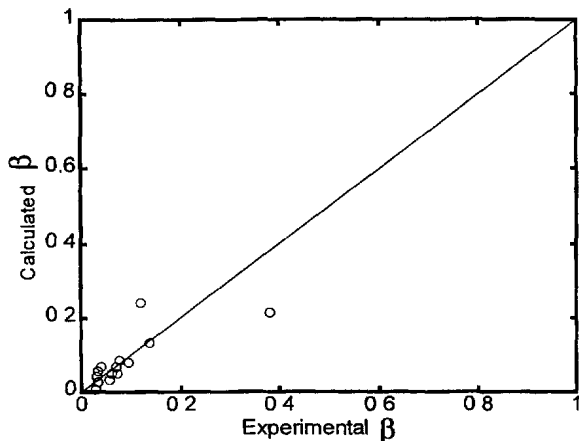


Fig 2 Comparison of experimental and calculated  $\beta$  using Eq (5), the weighting factors from Table 1, and the group contribution vector  $B$  from Table 3

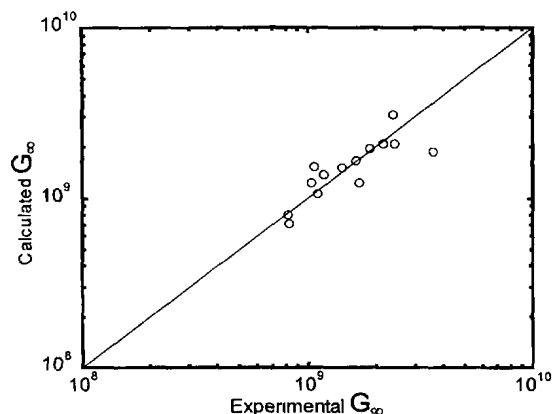


Fig 5 Comparison of experimental and calculated  $G_{\infty}$  using Eq (8), the weighting factors from Table 1, and the group contribution vector  $E$  from Table 3

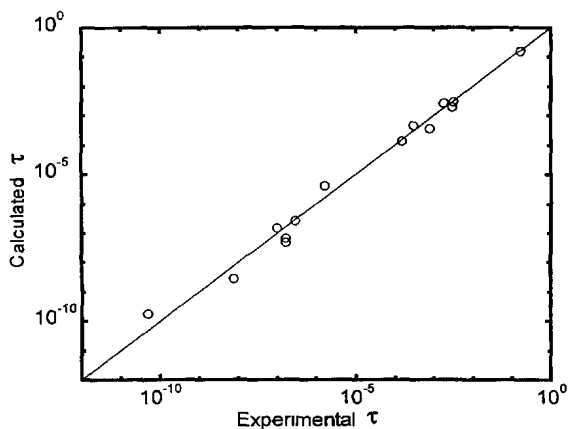


Fig 3 Comparison of experimental and calculated  $\tau$  using Eq (6), the weighting factors from Table 1, and the group contribution vector  $C$  from Table 3

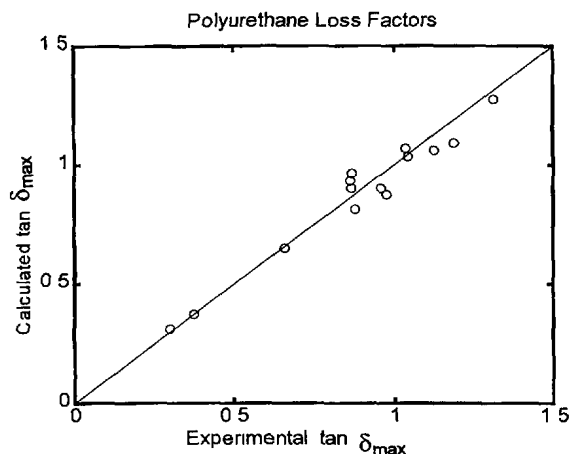


Fig 6 Comparison of experimental and calculated  $\tan \delta_{\max}$  calculated from the weighting factors in Table 1, and the group contribution vectors in Table 3, and Eqs (1)–(7)

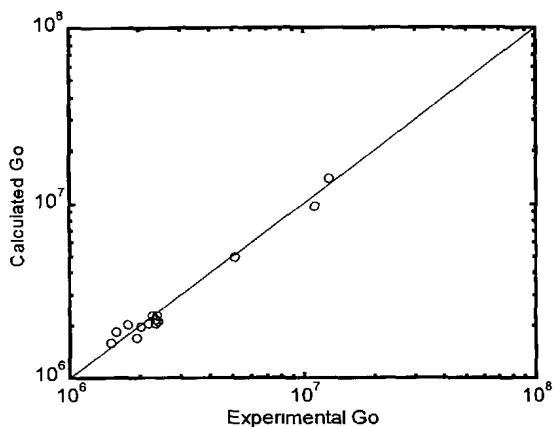


Fig 4 Comparison of experimental and calculated  $G_0$  using Eq (7), the weighting factors from Table 1, and the group contribution vector  $D$  from Table 3

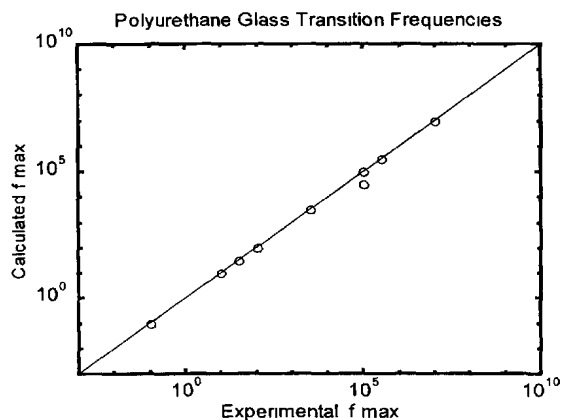


Fig 7 Comparison of experimental and calculated  $f_{\max}$  calculated from the weighting factors in Table 1, and the group contribution vectors in Table 3, and Eqs (1)–(7)

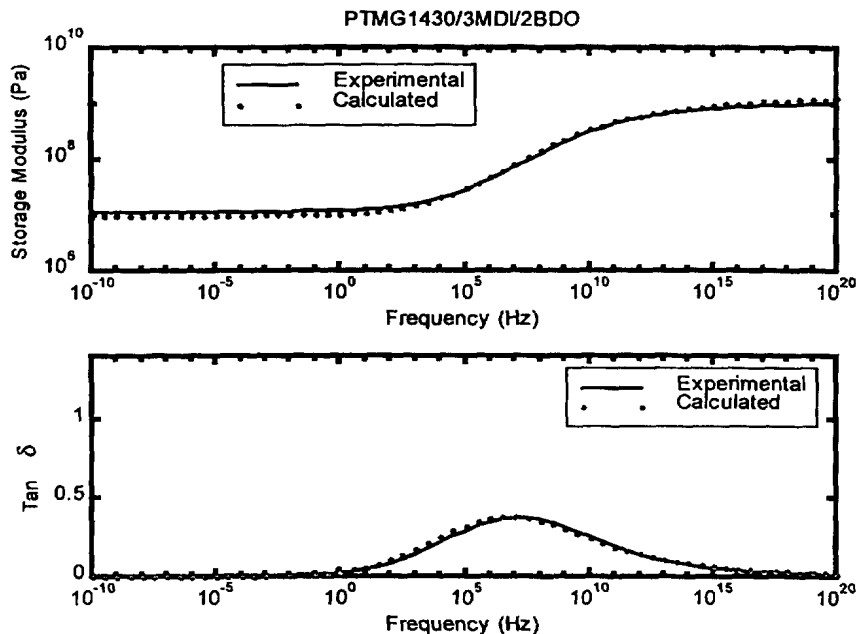


Fig 8 Experimental and calculated shear storage modulus and loss factor curves for PTMG1430/3MDI/2BDO at 25°C

experimental values are in excellent agreement over a wide range of values for the H–N parameters. For example, there is an excellent agreement of the experimental and calculated relaxation time  $\tau$  over the range  $10^{-10}$ – $10^0$  s (Fig. 3). The results to this point have shown that the H–N parameters may be treated as group additive. The discussion below presents results on the actual complex modulus master curves for these 14 polymers.

The positions ( $f_{max}$ ) and heights ( $\tan \delta_{max}$ ) of the loss factor peaks are shown in Figs. 6 and 7 for the 14 polymers in this study. Once again, the calculated values are in excellent agreement with experiment over the large range of values. The agreement is particularly striking for  $f_{max}$  which has values that range over 10 orders of magnitude.

Figs 8–12 show plots of the storage modulus and the loss factor for five selected polyurethanes from our dataset. In all

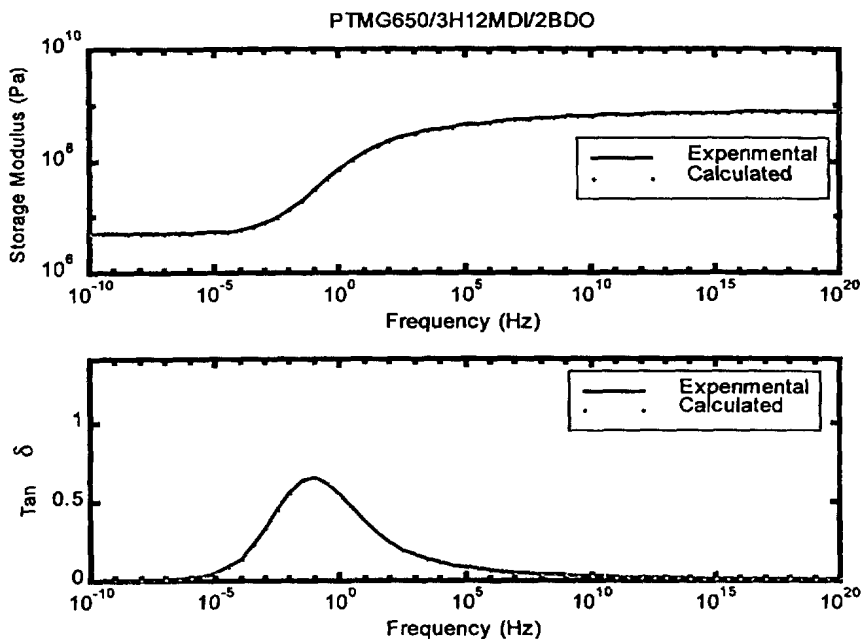


Fig 9 Experimental and calculated shear storage modulus and loss factor curves for PTMG650/3H12MDI/2BDO at 25°C

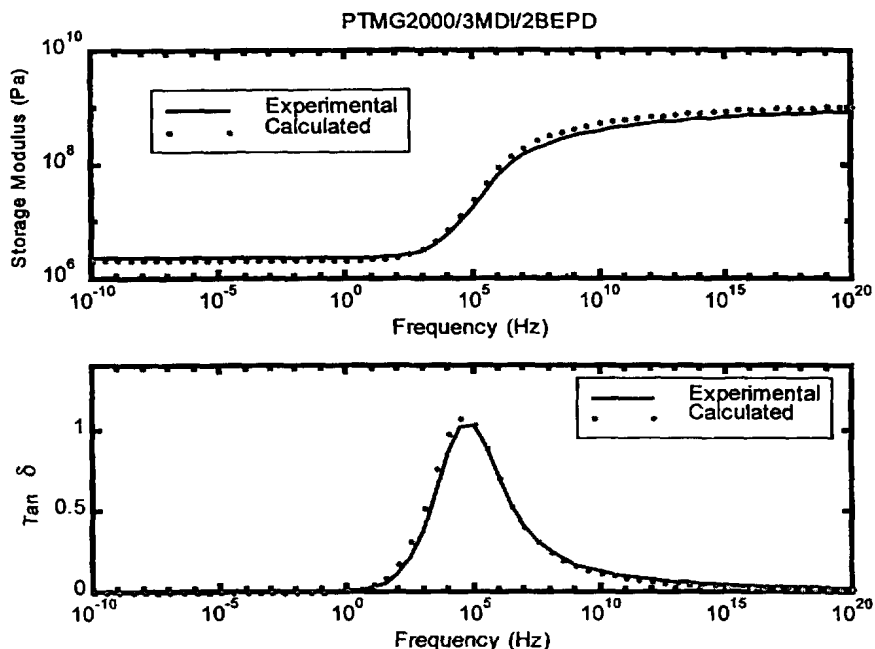


Fig 10 Experimental and calculated shear storage modulus and loss factor curves for PTMG2000/3MDI/2BEPD at 25°C

cases, the deviation of the curves calculated using group contribution techniques from the experimental curves is negligible. Note that the five polyurethanes that are shown in Figs. 8–12 have master curves that vary significantly from each other in terms of peak position, height, breadth and shape. The remaining nine calculated polyurethane master curves show similar agreement when compared to experiment

This work has shown the plausibility of applying GCA to predict the dynamic mechanical properties of polymers. However, there are several possible limitations to this method that need to be addressed. Perhaps the most obvious concern for this method is the need to determine the parameters for each new group introduced into the analysis, which requires good experimental data on several polymers containing this group. An additional concern is the

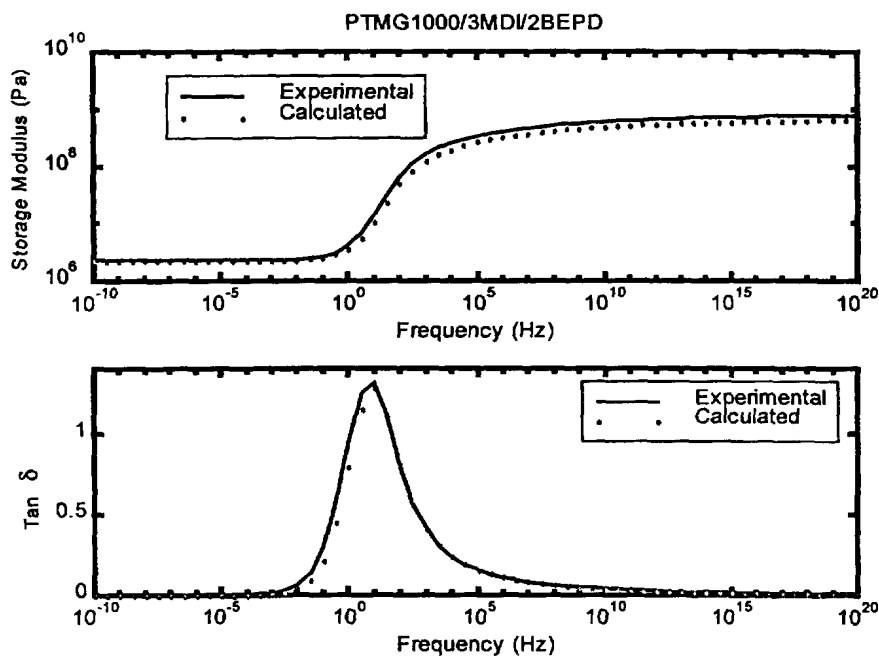


Fig 11 Experimental and calculated shear storage modulus and loss factor curves for PTMG1000/3MDI/2BEPD at 25°C



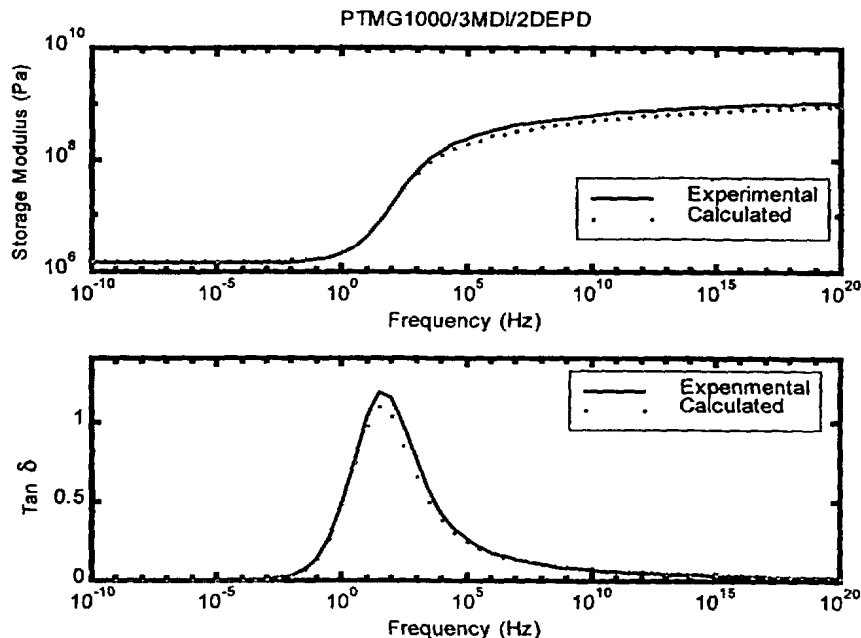


Fig. 12. Experimental and calculated shear storage modulus and loss factor curves for PTMG1000/3MDI/2DEPD at 25°C.

specificity of the GCA. It is not clear if the parameters derived in this study will work for polymers other than this specific class of polyurethanes. As well, there is no provision to incorporate the effects of phase mixing and thermal history into the GCA.

## 7. Conclusions

This study has shown that the five parameters of the Havriliak–Negami viscoelastic model are group additive for a specific group of 14 polyurethane polymers and nine structural units which make up these polymers. The group additive nature of the H–N parameters makes it possible to predict the dynamic mechanical behaviour of polyurethanes incorporating these groups. Because this study was limited in scope, further work is required before it is known what the limitations of this method are, and if it may be extended to a wider range of polymers.

## Acknowledgements

The authors would like to thank Drs B. Hartmann and J.D. Lee of the Naval Surface Warfare Center for stimulating discussions. W.M.D. thanks the Natural Sciences and Engineering Research Council of Canada (NSERC) for a visiting fellowship.

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