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**APPLICATION OF GROUP
CONTRIBUTION ANALYSIS TO THE
HAVRILIAK-NEGAMI MODEL**

J.P. Szabo — W.M. Davis

**Defence
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APPLICATION OF GROUP CONTRIBUTION ANALYSIS TO THE HAVRILIAK-NEGAMI MODEL

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Approved by: R.M. Morchat
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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 9 structural groups which were studied here. The derived group coefficients were sometimes negative or outside of acceptable bounds, a problem which may be addressed in future work by a careful selection of the monomers and structural groups included in the analysis.

Résumé

L'analyse CGA a déjà été appliquée à de nombreuses propriétés physiques des polymères. Dans cette communication, l'analyse CGA a, pour la première fois, été appliquée au module complexe, variant avec la fréquence, des matières polymériques, qui peut être décrit en termes de l'équation d'Havriliak-Negami (H-N). Nous avons évalué cette approche sur une ensemble de polyuréthanes pour lequel les paramètres H-N ont été déterminés de façon unique. On a montré que le comportement mécanique dynamique des polymères peut être décrit en termes de relations additives des groupes, du moins pour les 14 polyuréthanes et les 9 groupes structuraux qui ont été étudiés. Les coefficients des groupes dérivés étaient parfois négatifs ou se trouvaient à l'extérieur de limites acceptables; il s'agit là d'un problème que l'on pourra aborder lors de travaux ultérieurs en choisissant avec soin les monomères et les groupes structuraux inclus dans l'analyse.

Application of Group Contribution Analysis to the Havriliak-Negami Model

J.P. Szabo and W.M. Davis

EXECUTIVE SUMMARY

Background

The behaviour of the complex Young's or shear modulus of a polymer as a function of frequency may be described by a unique set of 5 Havriliak-Negami (H-N) parameters. These parameters correspond to the rubbery and glassy moduli, and the height, width, and asymmetry of the loss modulus peak. The purpose of this study was to explore the possibility of applying group contribution analysis to the H-N parameters, as a method of predicting the dynamic mechanical properties of polymers from their chemical structure. This work was part of a TTCP collaborative effort to model the dynamic mechanical properties of polymers.

Principal Results

For a set of 14 polyurethanes containing 9 structural groups, it has been shown that the H-N parameters and the resulting dynamic mechanical properties may be described in terms of group additive relations. The derived group coefficients were sometimes outside of acceptable bounds, a problem which may be addressed in future work by a careful selection of the monomers and structural groups included in the analysis.

Significance of the Results

The results of this study suggest that it may be possible to predict the dynamic mechanical behaviour of polymers from their chemical structure through the use of group additive techniques. This would enable the optimization of polymers employed as vibroacoustic materials in such applications as engine mounts, anechoic coatings, decoupling materials, and structural damping.

Future Plans

The techniques outlined in this study will be tested on a set of polyurethanes that are being synthesized for the TTCP Operating Assignment MAT-6-O9, Polymers for Noise Reduction in Military Platforms. This new polymer dataset contains five structural groups which are well represented in the polymer set, and which an error analysis has shown will result in accurate group coefficients. Future work will also include utilizing topological structure descriptors for the polymers, and applying statistical methods such as cross-validation and partial least squares to the problem.

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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_∞), 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 *et al* have 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 a widely used method 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 [5,6,7,8]. Porter has shown [6] that physical properties calculated using group contributions can be used with success to determine many other properties using 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_∞ is the upper limit of the modulus at high frequency, α is related to the width of the loss peak, β controls the asymmetry of the loss peak, and τ is the relaxation time. In equation 1, $\omega = 2\pi f$ is the angular frequency, and

$i^2 = -1$. 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

Group Contribution Analysis owes its earliest form to 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]:

$$T_g = \frac{\sum_i s_i T_{gi}}{\sum_i s_i} \quad [2]$$

where T_{gi} 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.

4. Polymer Dataset

A set of 14 polyurethanes for which the H-N parameters had been previously calculated was studied in this paper. 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 (BDO13), 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.

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 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:

$$\alpha = WF \cdot A \quad [4]$$

$$\beta = WF \cdot B \quad [5]$$

$$\log(\tau) = WF \cdot C \quad [6]$$

$$\log(G_0) = WF \cdot D \quad [7]$$

$$\log(G_\infty) = WF \cdot E \quad [8]$$

These five matrix equations were then solved using least square 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 coefficient vectors A, B, C, D, and E for the nine groups that comprise the polymer dataset used. These parameters are listed in Table 3. Note that the derived group coefficients for urethane are all zero. This is due to the fact 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. If we combined the urethane and phenyl groups into a single group and repeated the analysis, the weighting function would no longer be "rank deficient" and there would be no zero coefficients. A closer examination of Table 3 shows that many of the derived group coefficients are negative or outside of acceptable bounds. For example, all the coefficients in columns A and B should have values between 0 and 1, since they represent structural group contributions to the H-N parameters α and β , which vary between 0 and 1. This problem may be attributed to the relative ratios of the structural groups in the polymer set, which Fedderly *et al* [10] have shown must contribute to a "well conditioned" weighting function matrix. The problem may be overcome by careful selection of the structural groups and polymers in the dataset being analyzed, and by carrying out an error analysis similar to that presented in Reference 10, to ensure that each group is well represented.

Once the group contribution parameters were determined, the H-N parameters were calculated using equations 4-8 and compared to the experimental values [4]. These comparisons are shown in Figures 1-5. In general, the calculated and experimental values are in excellent agreement over a wide range of values for the H-N parameters. For example, there is excellent agreement of the experimental and calculated relaxation time τ over the range 10^{-10} s to 10^0 s (Figure 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 Figures 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.

Figures 8-12 show plots of the storage modulus and the loss factor for five selected polyurethanes from our dataset. In all 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 Figures 8-12 have master curves that vary significantly from each other in terms of loss peak position, height, breadth and shape.

This work has shown the plausibility of applying group contribution analysis 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. Topology based structure descriptors, such as connectivity indices [8], may be more suited than group contribution methods to modelling new groups that are not included in the training set of data. An additional concern is the specificity of the group contribution analysis. The regression coefficients derived in this study may be used for similar types of polyurethanes, but should not be used to predict the dynamic mechanical behaviour of any polymer including the structural groups examined. A training set of data containing structural groups from many polymers would provide a better starting point for deriving group coefficients that may be more universally applied. Finally, there is no provision to incorporate the effects of phase mixing and thermal history into the group contribution analysis.

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 9 structural units which make up these polymers. The derived group coefficients were sometimes negative or outside of acceptable bounds, a problem which may be addressed in future work by a careful selection of the monomers and structural groups included in the analysis. 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.

8. Acknowledgments

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

Table 1. Number of structural groups per monomer unit for the polymer studied.

Monomer	MW	-CH ₂ -		-O-		phenyl		cyclohexane		urethane		DMPD		EMPD		BEPD		DEPD	
		14	16	76	82	59	43	56	98	70									
ptmg2000/3mdi/2dmpd	2999	119	27	6	0	6	2	0	0	0	0	0	0	0	0	0	0	0	0
ptmg2000/4mdi/3dmpd	3354	122	27	8	0	8	3	0	0	0	0	0	0	0	0	0	0	0	0
ptmg2000/6mdi/5dmpd	4065	128	27	12	0	12	5	0	0	0	0	0	0	0	0	0	0	0	0
ptmg1000/3mdi/2dmpd	1989	63	13	6	0	6	2	0	0	0	0	0	0	0	0	0	0	0	0
ptmg1000/3mdi/2depd	2043	63	13	6	0	6	0	0	0	0	0	0	0	0	0	0	0	0	2
ptmg2000/3mdi/2depd	3053	119	27	6	0	6	0	0	0	0	0	0	0	0	0	0	0	0	2
ptmg1000/3mdi/2bdo13	1931	65	13	6	0	6	0	0	0	0	0	0	0	0	0	0	0	0	0
ptmg1000/3mdi/2empd	2015	63	13	6	0	6	0	0	0	0	0	2	0	0	0	0	0	0	0
ptmg2000/3mdi/2empd	3025	119	27	6	0	6	0	0	0	0	0	2	0	0	0	0	0	0	0
ptmg1000/3mdi/2bepd	2099	63	13	6	0	6	0	0	0	0	0	0	0	0	0	2	0	0	0
ptmg2000/3mdi/2bepd	3109	119	27	6	0	6	0	0	0	0	0	0	0	0	0	2	0	0	0
ptmg650/3h12mdi/2bdo	1635	47	8	0	6	6	0	0	0	0	0	0	0	0	0	0	0	0	0
ptmg1000/3mdi/2bdo	1959	67	13	6	0	6	0	0	0	0	0	0	0	0	0	0	0	0	0
ptmg1430/3mdi/2bdo	2392	91	19	6	0	6	0	0	0	0	0	0	0	0	0	0	0	0	0

ptmg=poly(tetramethylene ether) glycol
 mdi=4,4'-diphenylmethane diisocyanate
 h12mdi=4,4'-dicyclohexylmethane diisocyanate
 bdo=1,4-butanediol
 bdo13=1,3-butanediol
 dmpd=2,2-dimethyl-1,3-propanediol
 depd=2,2-diethyl-1,3-propanediol
 empd=2-ethyl-2-methyl-1,3-propanediol
 bepdpd=2-butyl-2-ethyl-1,3-propanediol

Table 2. Experimental H-N parameters, taken from Reference 4.

	α	β	$\log(\tau/s)$	$\log(G_0/pa)$	$\log(G_\infty / Pa)$
ptmg2000/3mdi/2dmpd	0.571	0.036	-6.78	6.331	9.269
ptmg2000/4mdi/3dmpd	0.533	0.027	-5.80	6.193	9.553
ptmg2000/6mdi/5dmpd	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/2bdo	0.494	0.136	-0.77	6.701	8.908
ptmg1000/3mdi/2bdo	0.261	0.117	-8.11	7.104	9.225
ptmg1430/3mdi/2bdo	0.295	0.378	-10.31	7.042	9.023

Table 3. Least square coefficients for each structural group and group contribution parameter.

	A	B	C	D	E
-CH2-	-24.9	15.1	-330.9	64.8	-8
-O-	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

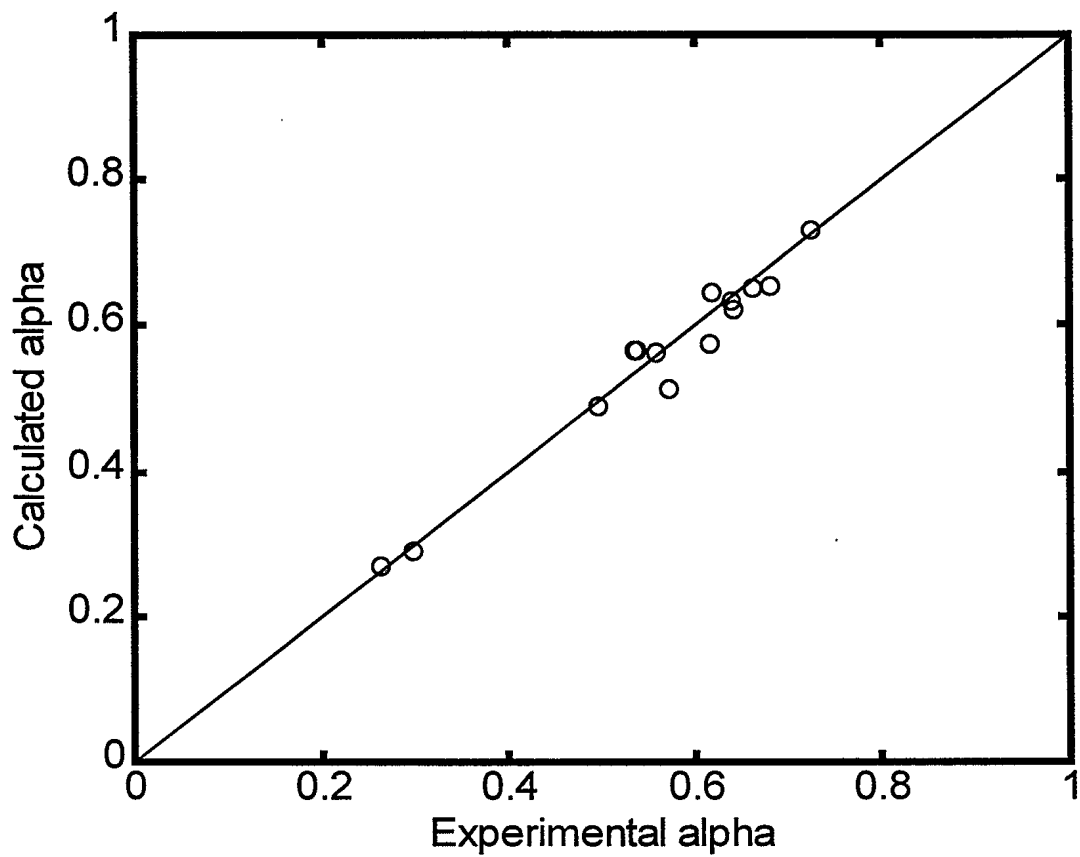


Figure 1. Comparison of experimental and calculated α using Equation 4, the weighting factors from Table 1, and the group contribution vector A from Table 3.

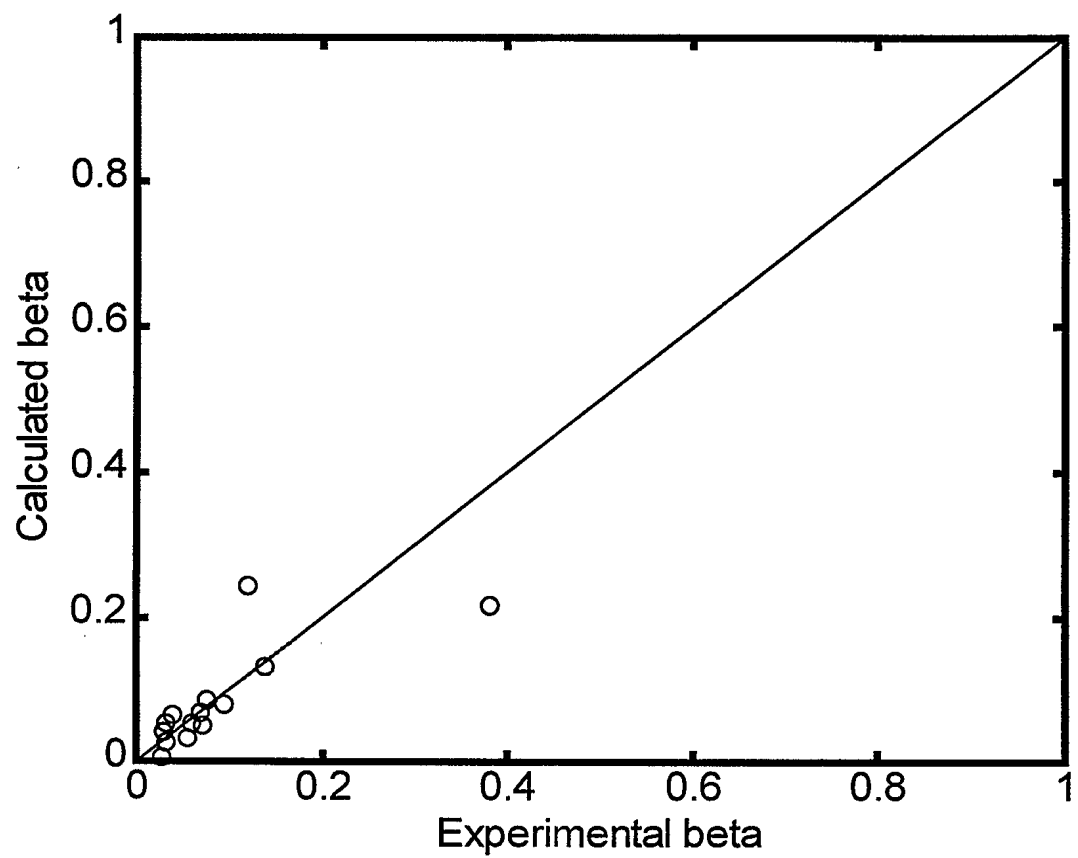


Figure 2. Comparison of experimental and calculated β using Equation 5, the weighting factors from Table 1, and the group contribution vector B from Table 3.

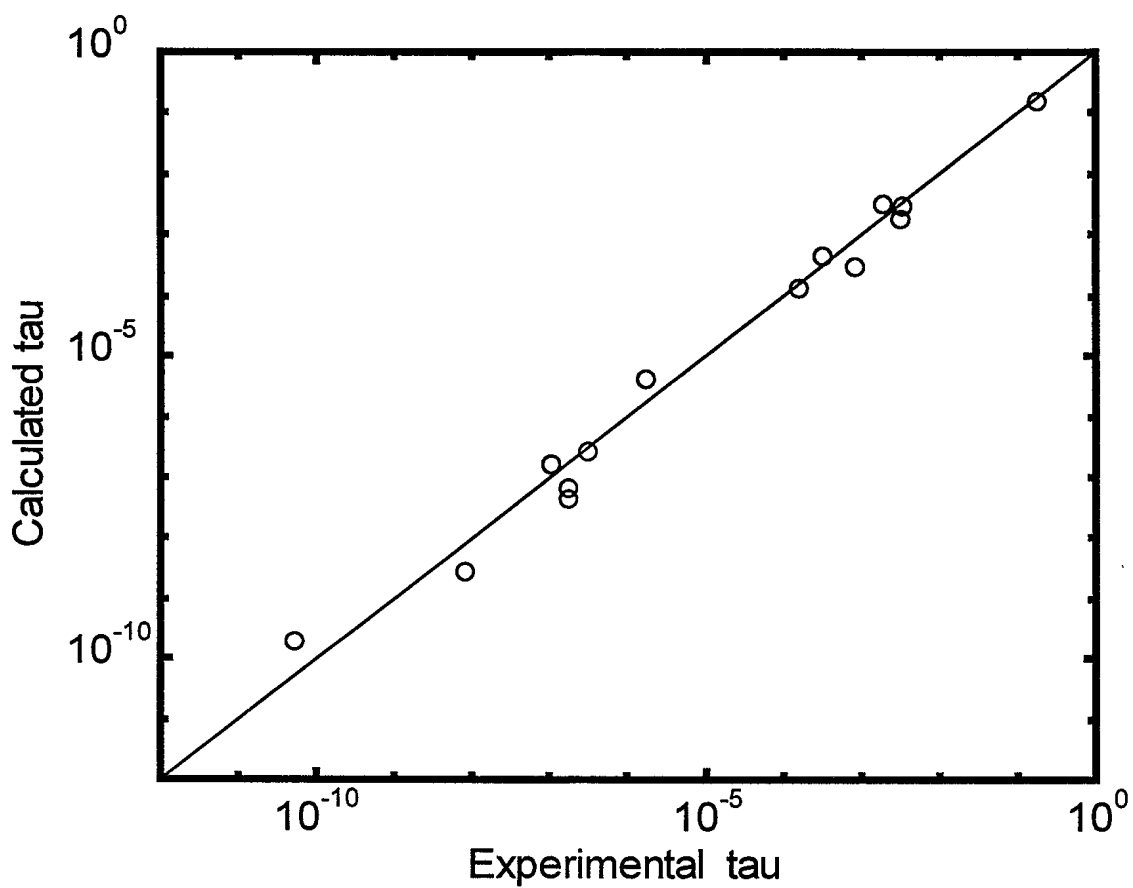


Figure 3 Comparison of experimental and calculated τ using Equation 7, the weighting factors from Table 1, and the group contribution vector D from Table 3.

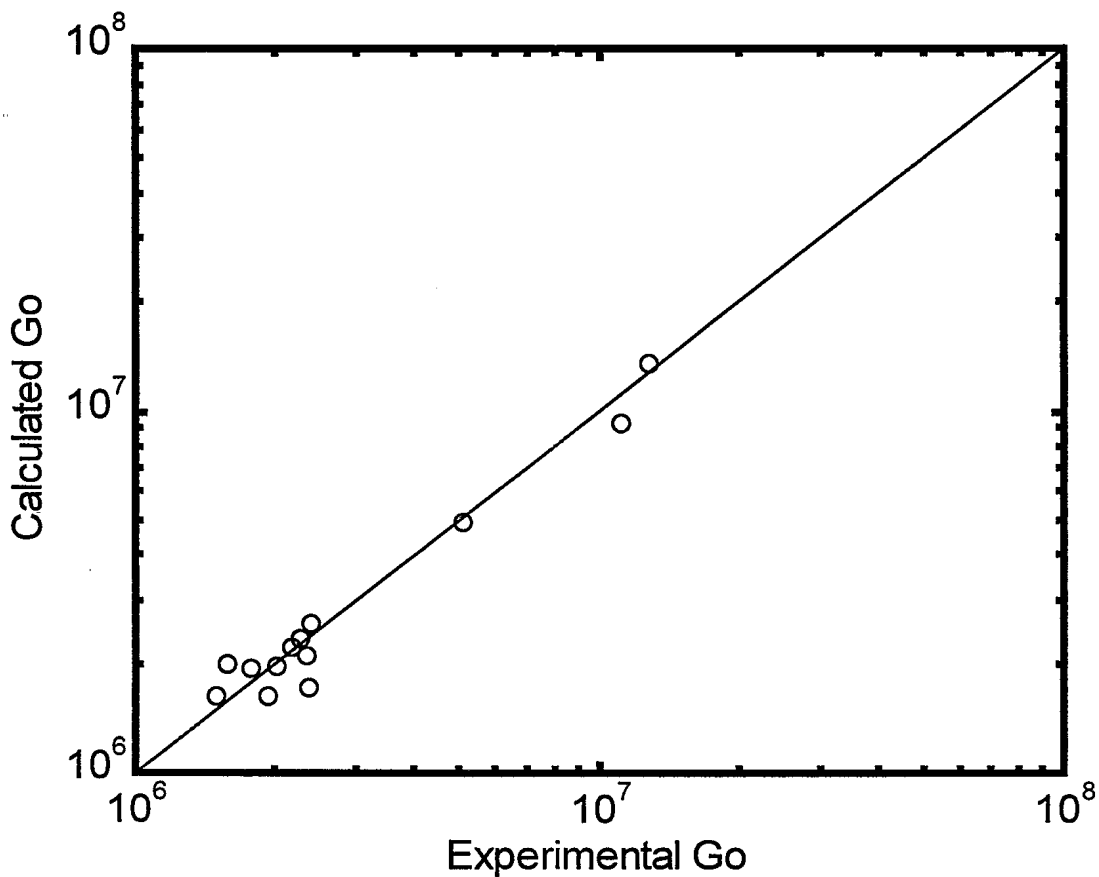


Figure 4. Comparison of experimental and calculated G_0 using Equation 7, the weighting factors from Table 1, and the group contribution vector D from Table 3.

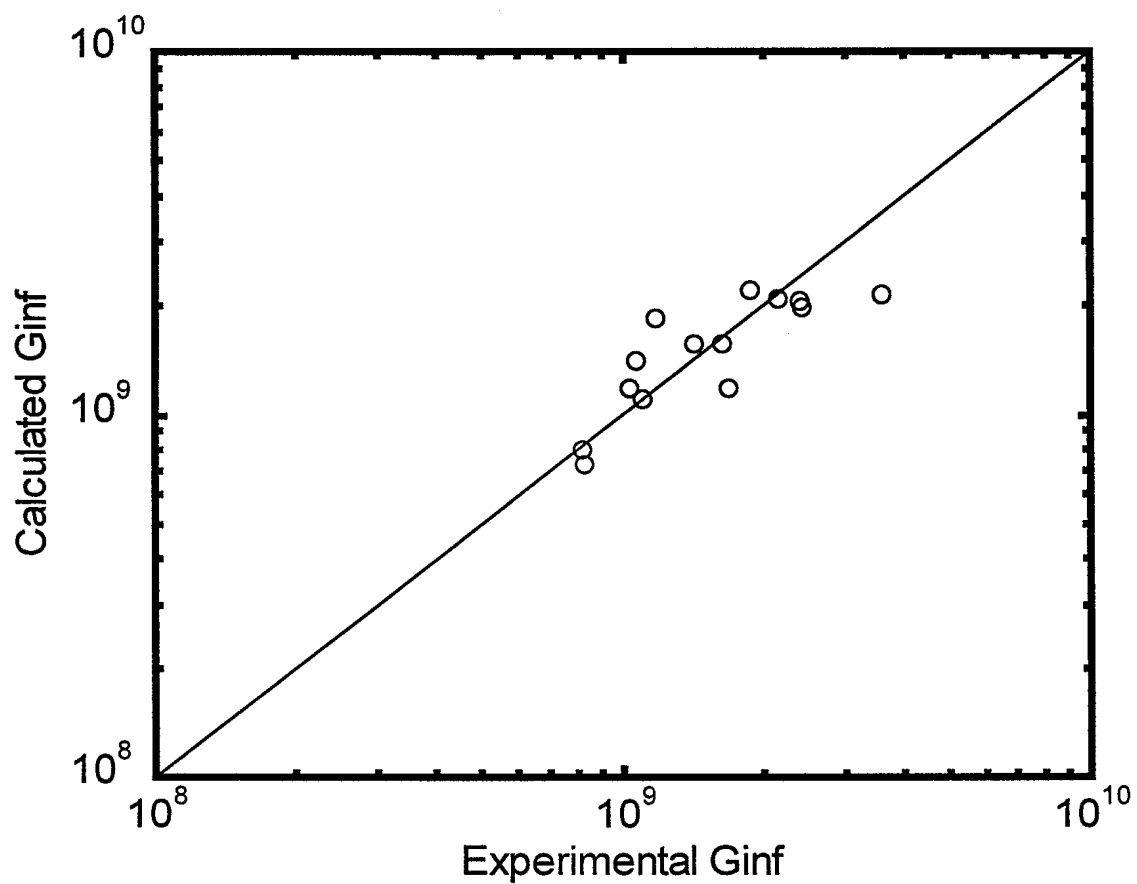


Figure 5. Comparison of experimental and calculated G_{∞} using Equation 8, the weighting factors from Table 1, and the group contribution vector E from Table 3.

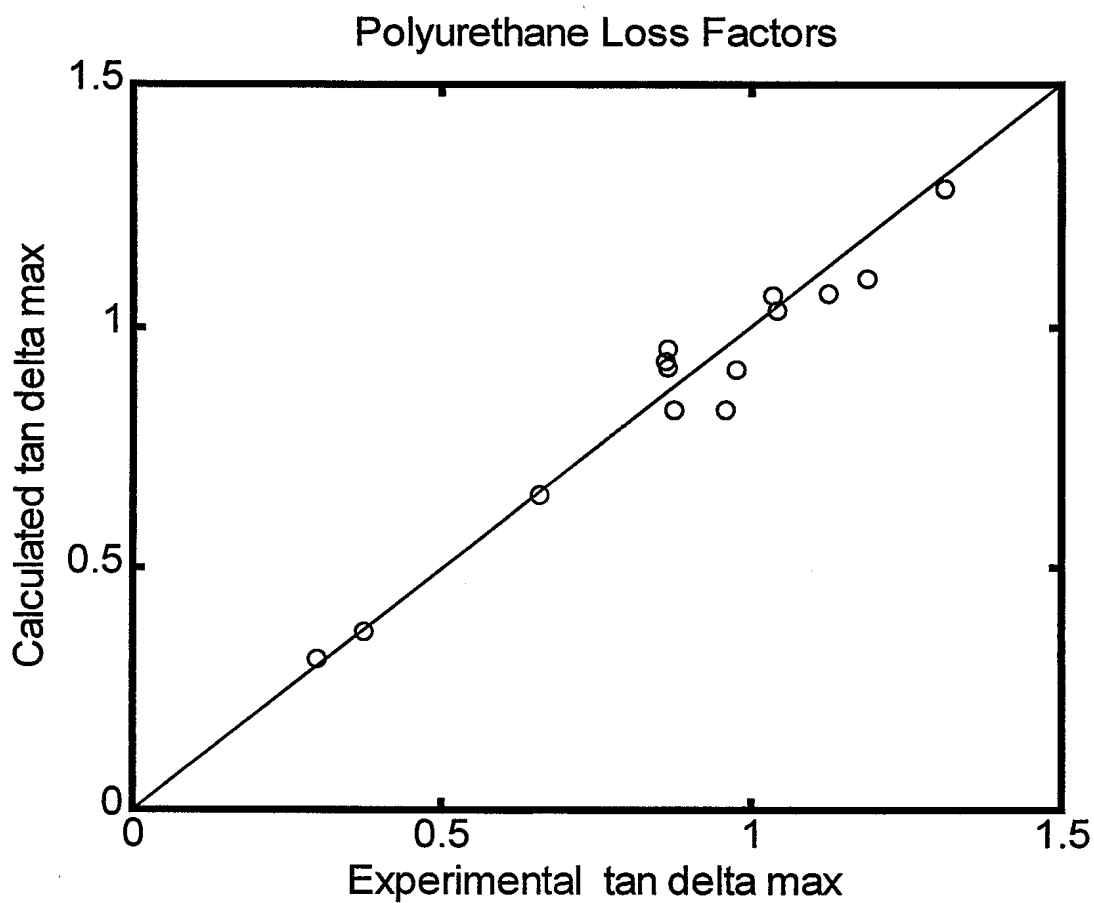


Figure 6. Comparison of experimental and calculated $\tan \delta_{\max}$ calculated from the weighting factors in Table 1, the group contribution vectors in Table 3, and equations 1-7.

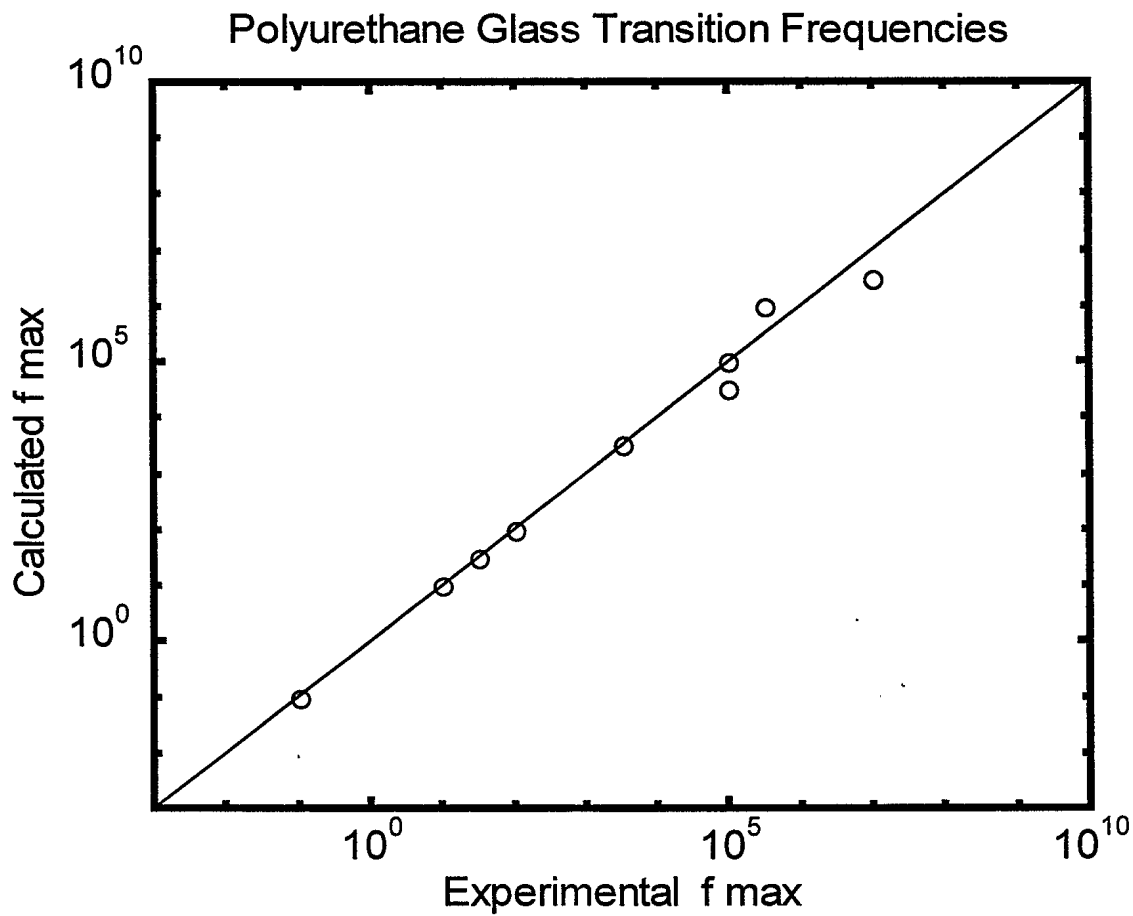


Figure 7. Comparison of experimental and calculated f_{max} calculated from the weighting factors in Table 1, the group contribution vectors in Table 3, and equations 1-7.

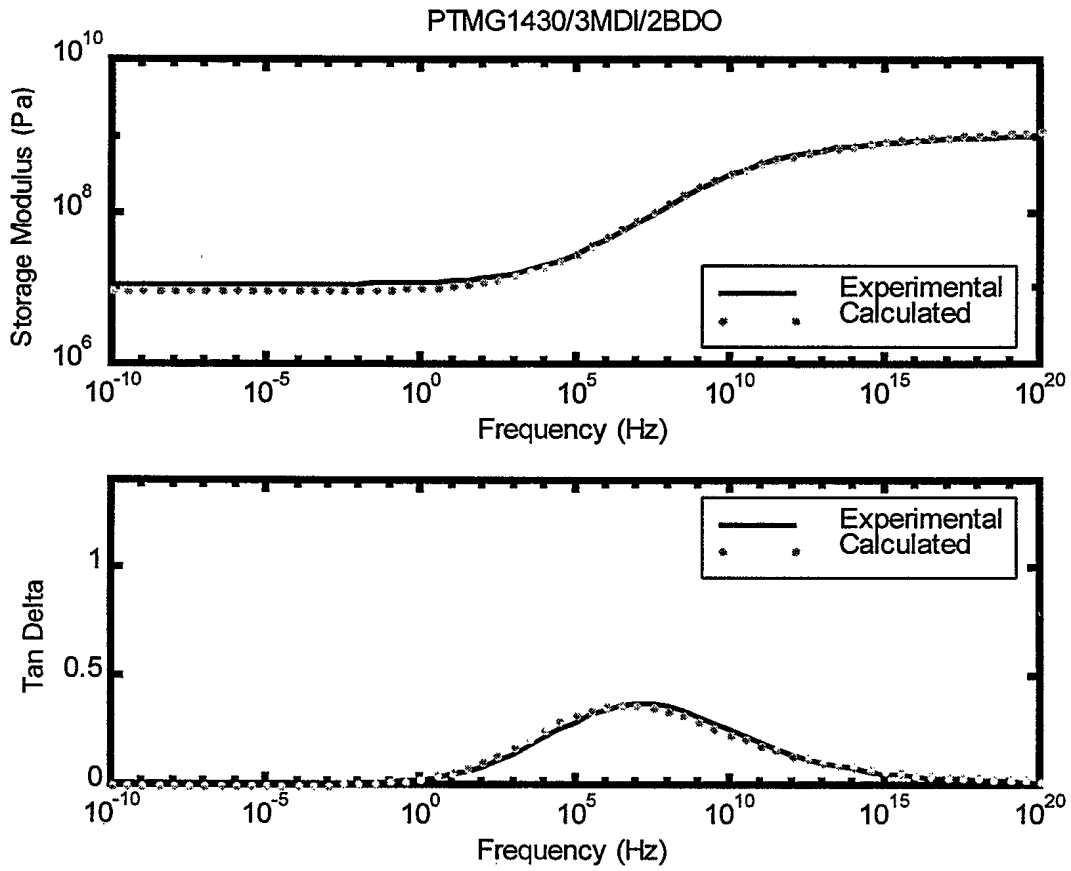


Figure 8. Experimental and calculated shear storage modulus and loss factor curves for PTMG1430/3MDI/2BDO at 25°C.

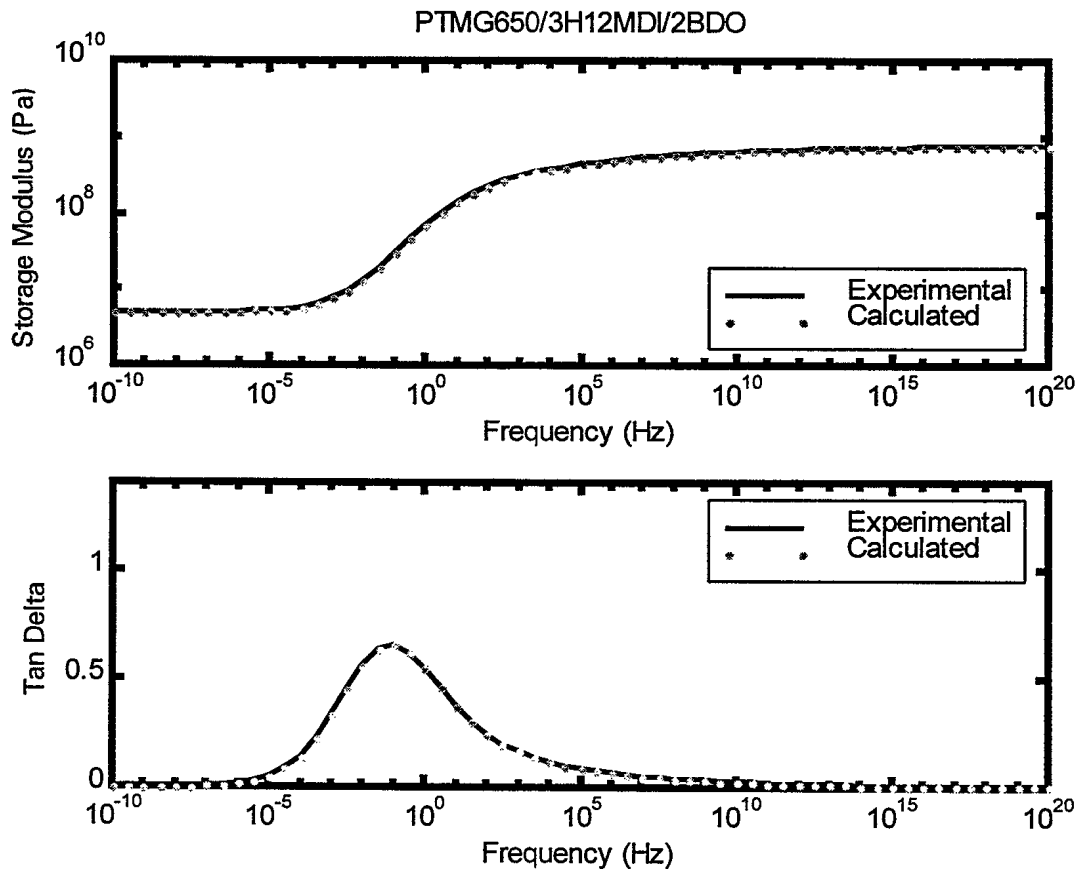


Figure 9. Experimental and calculated shear storage modulus and loss factor curves for PTMG650/3H12MDI/2BDO at 25°C.

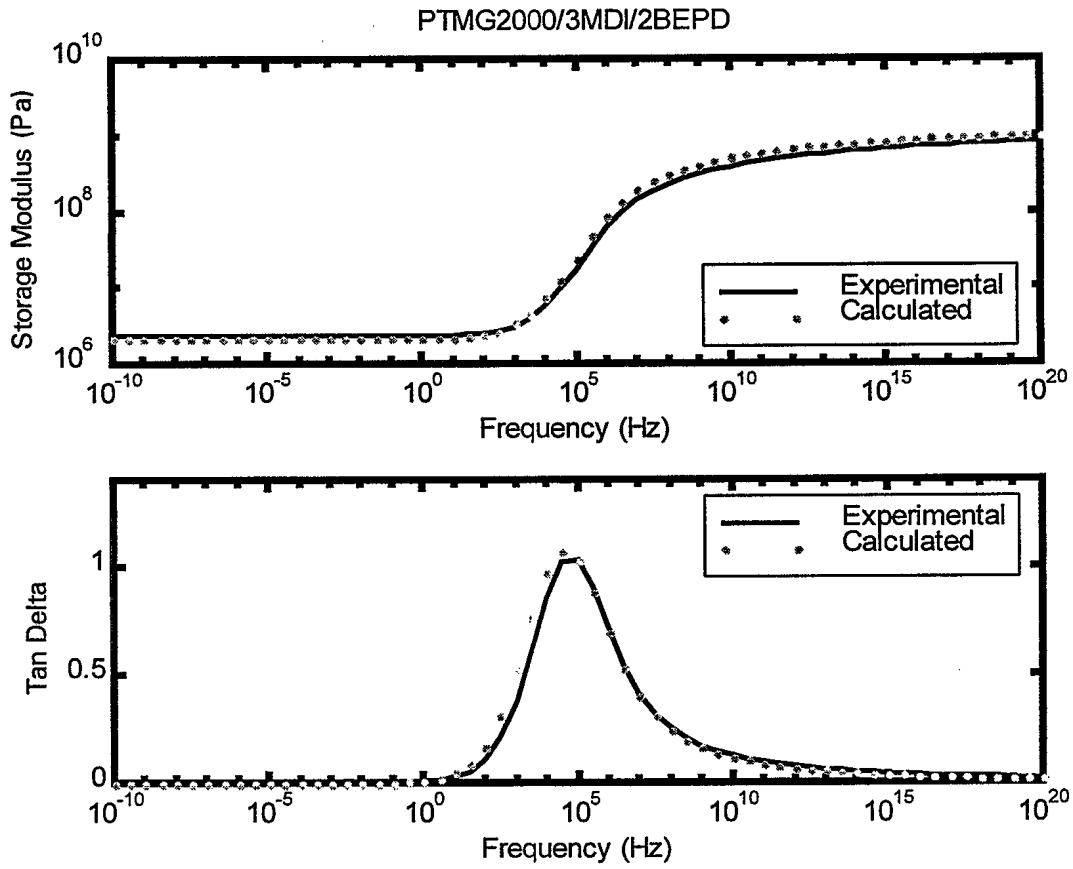


Figure 10. Experimental and calculated shear storage modulus and loss factor curves for PTMG2000/3MDI/2BEPD at 25°C.

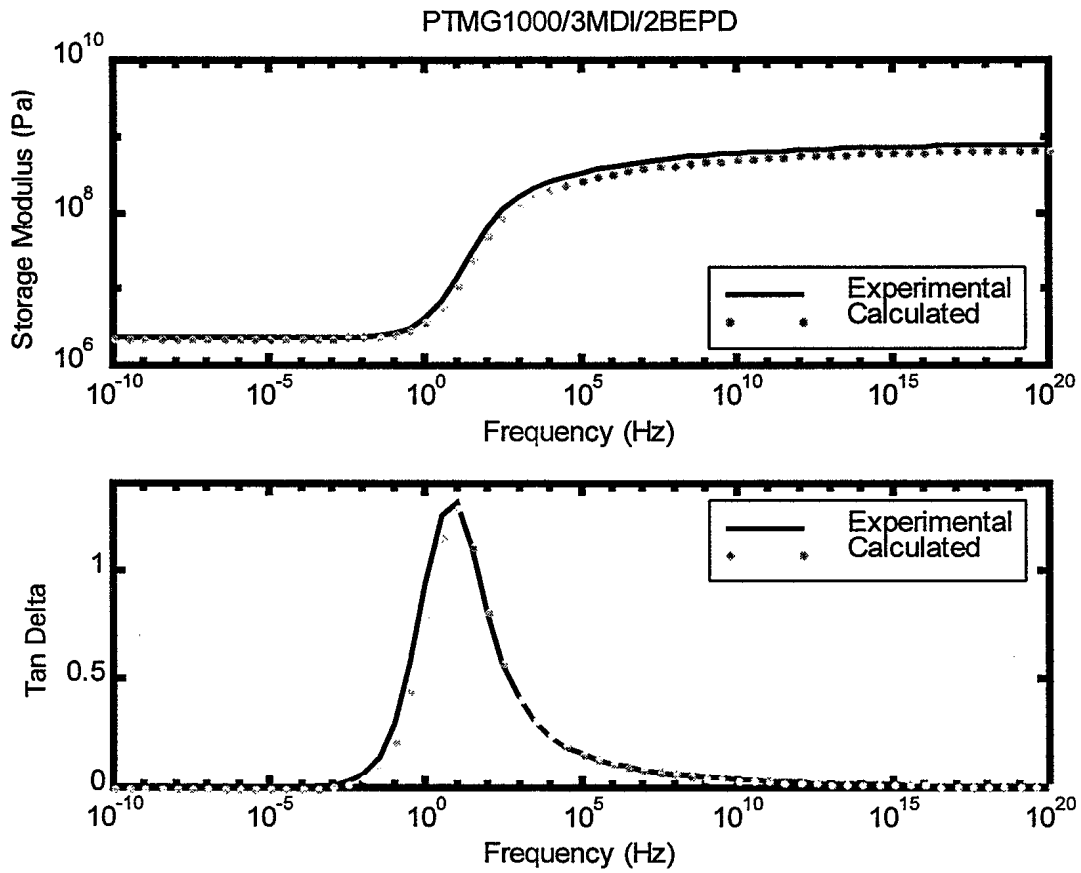


Figure 11. Experimental and calculated shear storage modulus and loss factor curves for PTMG1000/3MDI/2BEPD at 25°C.

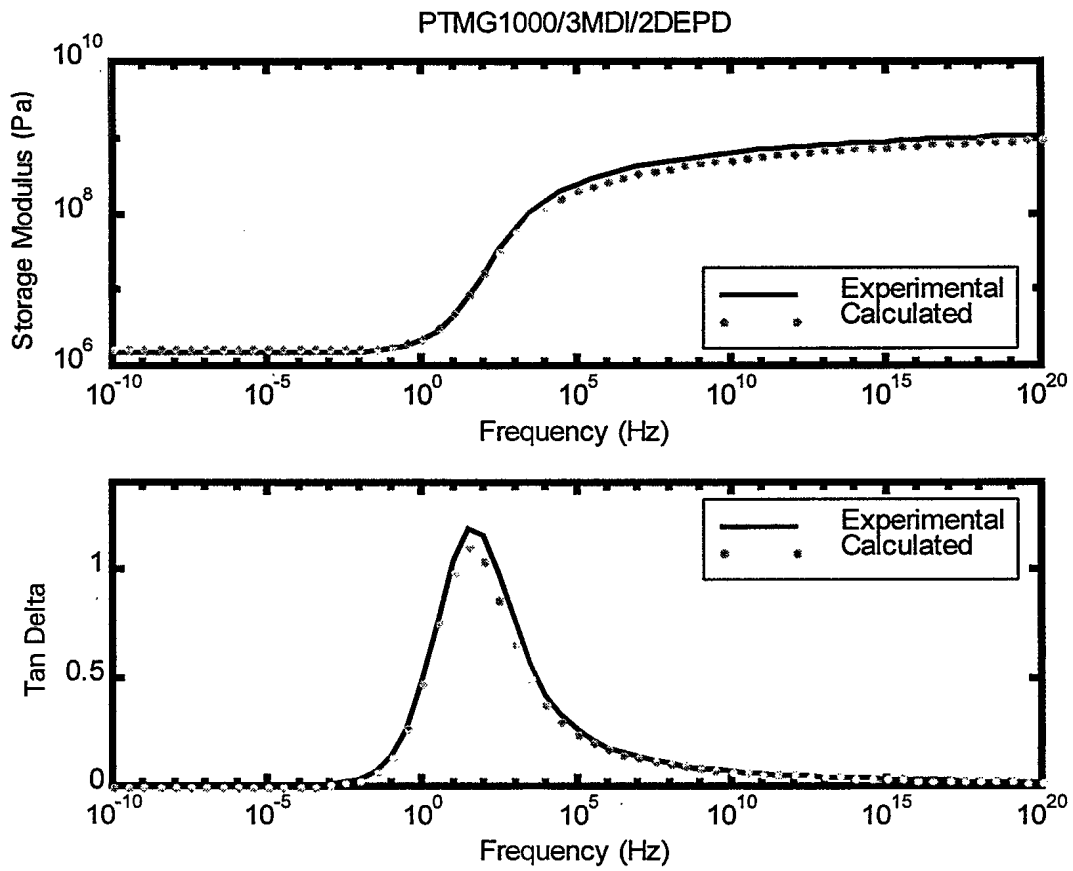


Figure 12. Experimental and calculated shear storage modulus and loss factor curves for PTMG1000/3MDI/2DEPD at 25°C.

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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 9 structural groups which were studied here. The derived group coefficients were sometimes negative or outside of acceptable bounds, a problem which may be addressed in future work by a careful selection of the monomers and structural groups included in the analysis.

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