

A Numerical Prediction of Peak Area in Loss Factor for Polymers

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SYNOPSIS

We tried to correlate the polymer constitutes with the peak areas under $\tan \delta$ -temperature curves, which are abbreviated as TA (loss tangent area) hereafter. TAs for homopolymers were obtained as the summation of ratio of contributions for functional groups in addition to the constant. TAs for semicrystalline polymers decreased with increase of the degree of crystallinity. Therefore, TAs for semicrystalline polymers were estimated from the ratio of the contribution of functional groups and crystallinity. TAs for copolymers were obtained by adopting the idea of mole ratio. Thus, the predicted values were fairly good in agreement with the measured ones for almost all kinds of linear polymers adapted in this study.

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INTRODUCTION

Factors of low noise and low vibration have become very important for industrial products,¹⁻³ though these factors were not noticed in the past. As one of the methods of controlling noise and vibration, the materials resulting in energy loss are attached to steel plates. These materials belong to polymers and are usually called damping ones. The composite of steel plates with polymers are known as the laminated or sandwich steel plates.^{4,5}

We can evaluate the damping properties of the polymers by loss factor η , or $\tan \delta$. The loss factor is expressed in the form

$$\eta = \frac{\text{loss energy}}{\text{vibration energy}} = \frac{\text{loss modulus } E''}{\text{storage modulus } E'}$$

A large number of data on viscoelasticity have been measured and reported in various forms. However, we cannot find any method to predict the extent of damping so far. Therefore, it is eagerly awaited to be able to predict the chemical structure of polymers having a large loss factor and an ap-

propriate temperature showing the maximum loss factor.

Although Bicerano⁶ tried to predict many properties of polymers, only viscoelasticity was not carried out. Chang et al.⁷⁻¹¹ tried to correlate chemical structure with the loss modulus for several copolymers. However, the loss modulus does not directly reflect damping properties. Therefore, loss factor-temperature curves were collected and arranged for a number of polymers found in the literature. We tried to develop a numerically predictable method for the peak area under the loss factor ($\tan \delta$)-temperature curves, which are abbreviated as TA hereafter.

THE MULTIPLE REGRESSION ANALYSIS

The multiple regression analysis is one of the statistical methods for describing the characteristic of the subject as a function of many factors.¹² This method is used to describe analyses of data that are multivariate in the sense that numerous observations or variables are obtained for each individual or unit. This method was applied to correlate TA with the number of functional groups such as methyl and ester groups. The basic equation for linear multiple regression analysis is

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$$Y = a_0 + \sum_{i=1}^n a_i X_i \quad (1)$$

where Y is a criterion variable, namely, TA, and $X \cdots X_p$ explanatory variables, namely, the number of functional groups. a_0 is a constant, and a_1, a_2, \dots, a_p are the regression coefficients, which mean the rate of contribution of each functional group to TA. For carrying out the calculation, all functional groups must be classified so as to give the most appropriate relationship between TA and functional groups by the method of trial and error.

DATA TREATMENT

Measurement of Peak Area

In the first step, the suitable polymers for this study must be chosen. Treatment such as heat treatment or cold drawing are not suitable. Hashimoto and Kunugi reported that the dynamic viscoelasticity of nylon 6 varied with the cold drawing or heat treatment.^{13,14} Jacobs and Jenckel mentioned that the dynamic viscoelasticity of polyurethane was easily influenced by the solvent content absorbed.¹⁵ Thus, the loss factor-temperature curves vary in various ways. Furthermore, TAs of semicrystalline polymers are influenced by the degree of crystallinity. Therefore, amorphous phases were taken up for the first step. Semicrystalline polymers and copolymers were discussed separately from amorphous phases.

Loss factor, decline ratio, logarithmic decline ratio, and $\tan \delta$ -temperature curves were taken from various literature. The loss factor and $\tan \delta$ -temperature curves can be utilized directly to measure TA. However, the decline ratio and logarithmic decline ratio must be converted to $\tan \delta$ by using the following correlation:

$$\Lambda = \ln \Delta \quad (2)$$

$$\tan \delta = \frac{\Lambda}{\pi} \left(1 + \frac{\Lambda}{4\pi^2} \right) \quad (3)$$

where Δ is the decline ratio, and Λ , the logarithmic decline ratio.

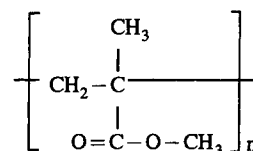
When the storage modulus E' and the loss modulus E'' are known, $\tan \delta$ can be calculated by eq. (4):

$$\tan \delta = \frac{E''}{E'} \quad (4)$$

Thus, TAs were obtained from the $\tan \delta$ -temperature curves, after correction of the background by drawing an appropriate base line for each curve, as shown in Figure 1, where the dimension of TA is the absolute temperature K.

Data Filing

For a fundamental definition of functional groups, van Krevelen^{16,17} reported the group contribution techniques for correlating polymer properties and chemical structure. A similar idea was adopted in this study. A criterion variable is TA for polymers. Explanatory variables are the number of functional groups that can be classified into the backbone (first cluster), the side groups attached to backbone (side chains) (second cluster), and the side group not attached to backbone (third cluster) in the polymeric repeat unit. An example is shown for poly(methyl methacrylate):



In this case, the value of the criterion variable is 38.12 K,¹⁸ and the explanatory variable can be classified into

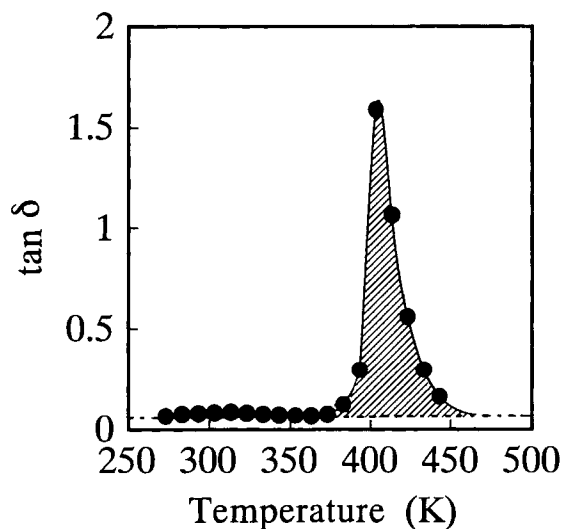
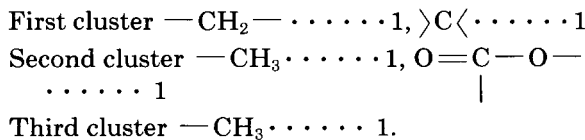


Figure 1 $\tan \delta$ vs. temperature curve for poly(methyl methacrylate).¹⁸ The part expressed by the oblique line is counted as the TA.

Table I Contribution of Functional Groups

Classification ^a	No.	Functional Group	S _i (K)
First cluster	1		-536.090
	2		-248.323
	3		-101.543
	4		61.366
	5		16.900
	6		-146.566
	7		-123.032
	8		344.806
Second cluster	9		113.440
	10		150.153
	11		277.349
	12		266.853
	13		255.275
	14		256.453
	15		253.273
	16	(backbone) 	67.847
Third cluster	17	(backbone) 	35.618
	18		222.385
	19		227.870
	20		233.375
	21		238.295
	22		188.354
Const		108.343	

^a First cluster: backbone; second cluster: side group attached directly to backbone; third cluster: side group not attached to backbone.



In other words, the contribution to the criterion variable was attained by the mol fraction of functional groups. These values are filed according to the multiple regression equation as follows:

$$\begin{aligned}
 (TA) \quad Y = a_0 + a_1 X_1 + a_2 X_2 + a_3 X_3 + a_4 X_4 + \dots \\
 38.12 \quad \quad \quad 1 \quad \quad 0 \quad \quad 1 \quad \quad 0
 \end{aligned}$$

$$\begin{aligned}
 &+ a_{11} X_{11} + a_{12} X_{12} + \dots + a_{15} X_{15} + a_{16} X_{16} + a_{17} X_{17} \\
 &\quad \quad \quad 1 \quad \quad 0 \quad \quad \quad \quad \quad \quad 0 \quad \quad 1 \quad \quad 0 \\
 &+ a_{18} X_{18} + a_{19} X_{19} + \dots + a_{22} X_{22} \\
 &\quad \quad \quad 1 \quad \quad 0 \quad \quad \quad \quad \quad \quad 0
 \end{aligned}$$

RESULTS AND DISCUSSION

Homopolymers

A number of trials to correlate TA and functional groups were carried out by classifying functional groups in various ways. The classification of functional groups and the summary of the rate of contribution are shown in Table I. The final statistical results are shown in Table II. The standard deviation of errors is about 0.87 (K). This value is satisfiable for practical application.

TAs can be obtained for various homopolymers by the following equation:

$$TA = 108.343 + \sum S_i N_i \quad (5)$$

Here, S_i is the ratio of the contribution based on the mol fraction for the i-th functional group and N_i represents the number of each functional group in the polymeric repeat unit. The calculated values of TA are shown in Table III. The comparison of the experimental results (TA_e) with calculated ones (TA_c) is shown in Figure 2. Almost all predicted values fell on the 45° line, and the result proves that the predicted ones agree well with the experimental ones.

Semicrystalline Polymers

For semicrystalline polymers, the value of TA generally decreased when the degree of crystallinity increased. The relations of TA with the degree of crys-

Table II Average and Standard Deviation of Residual

Number of data: n	25
Average (K):	
$X = 1/n \times \sum Y - Y' $	0.401 (K)
Standard deviation (K):	
$\sigma = \{1/(n - 1) \times \sum (Y - Y' - X)^2\}^{1/2}$	0.868 (K)

n: no. of samples; Y: experimental TA; Y': predicted TA.

Table III Experimental and Calculated TAs for Homopolymers

Polymers	TA (K)		
	Experimental	Calculated	Error ^a (%)
Polyethylene	6.800 ¹⁹	6.800	0.000
Polypropylene	32.820 ²⁰	35.826	9.159
Poly(vinyl chloride)	28.220 ²¹	25.330	-10.241
Poly(vinylidene chloride)	2.970 ²²	4.415	48.653
Poly(vinyl fluoride)	13.750 ²²	13.752	0.015
Polychlorotrifluoroethylene	68.840 ²²	68.839	-0.001
Poly(ethylene terephthalate)	9.110 ²³	9.110	0.000
Polystyrene	11.750 ²⁴	11.750	0.000
Polyacrylonitrile	14.930 ²⁵	14.930	0.000
Nylon 6	6.800 ²⁶	6.800	0.000
Polycarbonate	11.230 ²²	11.230	0.000
Poly(<i>cis</i> -1,4-isoprene)	36.040 ²⁷	36.040	0.000
Poly(isobutylene)	26.970 ²⁸	25.408	-5.792
Polybutadiene	55.410 ^b	55.410	0.000
Poly(methyl methacrylate)	38.120 ¹⁸	38.291	0.449
Poly(ethyl methacrylate)	43.790 ¹⁸	43.776	-0.032
Poly(propyl methacrylate)	49.490 ¹⁸	49.281	-0.422
Poly(butyl methacrylate)	54.030 ¹⁸	54.201	0.316
6,4-Polyurethane	9.410 ²⁶	9.411	0.011
Poly(cyclohexyl methacrylate)	4.260 ²⁹	4.260	0.000
Poly(vinyl acetate)	16.480 ¹⁹	16.480	0.000
Poly(methyl acrylate)	48.880 ^b	48.709	-0.350
Poly(ethyl acrylate)	54.180 ^b	54.194	0.026
Poly(propyl acrylate)	59.490 ^b	59.699	0.351
Poly(butyl acrylate)	64.790 ^b	64.619	-0.264

Average of error 1.690

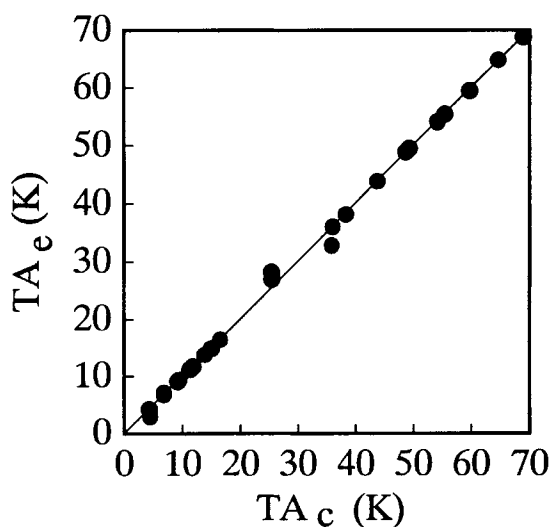
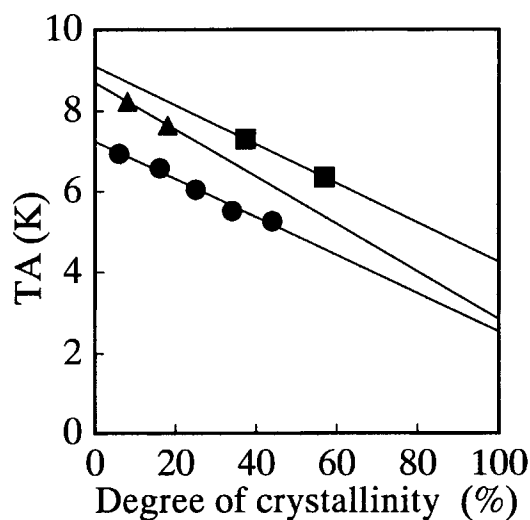
^a $(TA_{\text{calcd}} - TA_{\text{exptl}})/TA_{\text{exptl}} \times 100$.^b Obtained in our laboratory.**Figure 2** Correlation between experimental and calculated TAs for homopolymers.**Figure 3** TAs for semicrystalline polymers: (●) nylon 6²⁶; (▲) 6,4-polyurethane²⁶; (■) poly(ethylene terephthalate).²³

Table IV TAs Obtained for the Crystalline Phase (S_c) and Amorphous Phase (S_a) in Homopolymers

Crystalline Polymers	S_c (K) ^a	S_a (K) ^b
Nylon 6	2.69	7.25
6,4-Polyurethane	2.91	8.70
Poly(ethylene terephthalate)	4.26	9.23

^a Obtained from Figure 3.^b Obtained from Table I.

tallinity are shown in Figure 3 for nylon 6,²⁶ 6,4-polyurethane,²⁶ and poly(ethylene terephthalate).²³ Thus, it is clear that the TAs of semicrystalline polymers are influenced considerably by the degree of crystalline polymers expressed as

$$S_s = rS_c + (1 - r)S_a \quad (6)$$

where S_s is the TA of a semicrystalline polymer; S_c , that of the crystalline phase; S_a , that of the amorphous phase; and r , the degree of crystallinity ($0 \leq r \leq 1$). Probably, r must be expressed based on the mol fraction. However, there is no big difference in the density between crystalline and amorphous parts. Therefore, we can adopt the r value that was obtained by the usual methods such as X-ray diffraction.

Therefore, S_s can be expressed as a liner function for r as shown in eq. (7). The values of S_a and S_c

can be obtained from Figure 3 for several polymers. Furthermore, the values of S_a can be obtained from calculation of eq. (5), namely, the idea that the mol fraction can be applicable for the side groups:

$$S_s = S_a + (S_c - S_a)r \quad (7)$$

S_a and S_c obtained thus are summarized in Table IV. Additionally, S_c must be known in advance for each semicrystalline polymer, when we apply eq. (6) to the polymers other than those shown in Table IV.

Copolymers

The TAs of copolymers are expected to depend on the mol fraction. However, when the copolymers have two peaks for the $\tan \delta$ -temperature curve, these cases were removed in this study. Therefore, the copolymers having only one peak were adopted. To express the ratio of two comonomers in a copolymer, mol, weight, and volume fractions can be considered. However, only the mol fraction led to a sufficient result in the correlation of TA between copolymer and homopolymers. The basic equation for calculating the TA of a copolymer is

$$S_p = X_A S_A + (1 - X_A) S_B \quad (8)$$

where S_p is the TA of a copolymer, and S_A and S_B are the TAs of corresponding homopolymers. The

Table V Experimental and Calculated TAs for Copolymers

Polymers	Mol Fraction X_A	TA (K)		
		Experimental	Calculated	Error ^a (%)
A: Poly(isobutylene) B: Poly(cis-1,4-isoprene)	0.980	27.150 ²⁸	25.621	-5.632
A: Polybutadiene B: Polyacrylonitrile	0.740	44.884 ^b	44.885	0.002
A: Nylon 6 B: Poly(vinyl acetate)	0.812	8.788 ²⁵	8.620	-1.912
A: Polyethylene B: Poly(vinyl acetate)	0.179	14.311 ¹⁹	14.747	3.047
	0.474	12.965 ¹⁹	11.892	-8.276
	0.570	9.604 ¹⁹	10.962	14.140
A: Polyacrylonitrile B: Nylon-6	0.217	7.622 ²⁵	8.564	0.124
	0.402	10.577 ²⁵	10.068	-4.812
A: Poly(methyl methacrylate) B: Poly(butyl acrylate)	0.460	53.690 ^b	54.668	1.822
	0.770	44.750 ^b	46.506	3.924

^a $(TA_{\text{calc}} - TA_{\text{expt}})/TA_{\text{expt}} \times 100$.^b Obtained in our laboratory.

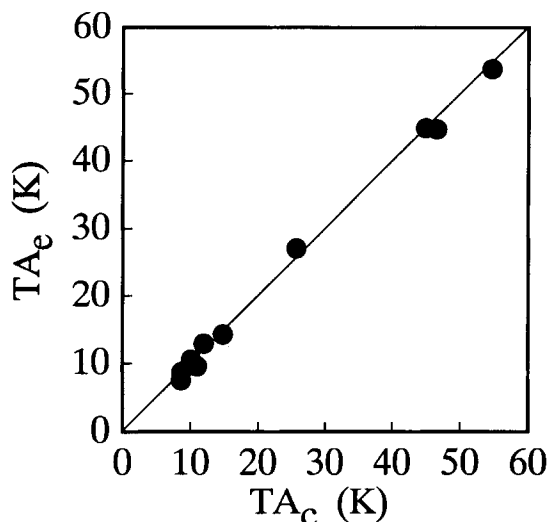


Figure 4 Correlation between experimental and calculated TAs for copolymers.

values of S_A and S_B can be obtained from the values shown in Table I. X_A is the mol fraction for the A monomer. The calculated values of TA are shown in Table V. Comparison of the experimental result (TA_e) with predicted one (TA_c) is shown in Figure 4. Most values fell on the 45° line, and this result proves that the predicted values agree well with the experimental ones.

CONCLUSIONS

The contribution of functional groups to the peak areas under $\tan \delta$ -temperature curves was examined by means of multiple regression analysis. From the above calculations, the following results were obtained:

1. The peak areas under $\tan \delta$ -temperature curves can be predicted from chemical structure of polymers for amorphous homopolymers by assuming additivity in the mol function.
2. The peak areas of semicrystalline polymers can be estimated from the degree of crystallinity and the chemical structure.
3. The peak areas of copolymers can be given by the sum of the product of each peak area of corresponding homopolymers and the mol fraction.

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