

Characterization of the Area Under Loss Modulus and $\tan \delta$ -Temperature Curves: Acrylic Polymers and Their Sequential Interpenetrating Polymer Networks

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Synopsis

Areas under the *linear* $\tan \delta$ -temperature (tA) and *linear* loss modulus-temperature (LA) curves of the polyacrylate and polymethacrylate homologous series and their interpenetrating polymer networks (IPNs) were investigated. For poly(methyl acrylate), LA values are independent of crosslinking level through 25%, but tA decreases. With increasing side group length, on the other hand, tA remains nearly independent of side group length for both homologous series, having values near 50 and 65 (units of K) for the acrylate and methacrylate series, respectively. However, LA decreases steeply with increasing side group length. A phenomenological treatment of areas is presented in order to explain tA and LA behavior semiquantitatively. Both tA and LA exhibit areas characteristic of the structure of the particular polymers. The homopolymer LA areas are additive in determining the area under the corresponding curve for the IPN. This suggested a group contribution analysis for LA , where each moiety contributes specific values to the area.

INTRODUCTION

The fundamental nature of damping in polymers stems from the onset of coordinated chain motion associated with relaxation processes, especially, the glass transition. These motions can be used to convert mechanical energy into heat. As temperature or frequency is varied, the loss modulus E'' and the loss tangent, $\tan \delta$, exhibit peaks, where damping reaches a maximum. Consequently, polymers constitute useful noise and vibration damping materials near their glass transition temperature, T_g .¹⁻⁴ This paper will consider the temperature variation of the E'' and $\tan \delta$, holding frequency constant.

A need exists to obtain a better understanding of the damping process, especially, for a temperature range of relaxation processes. In this paper, the areas under the *linear* $\tan \delta$ -temperature (loss tangent area = tA) and *linear* E'' -temperature (loss area = LA) curves are characterized in order to develop relationships between the extent of damping and molecular architecture. Several papers in the past have examined some facet of the areas of interest to

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the present work.⁵⁻²⁵ Among these papers, Kawaguchi⁵ found that the area under the $\tan \delta$ -temperature peak (in γ -relaxation) was linearly proportional to the number n of methylene units in a series of nylons. Wada and Kasahara⁸ correlated the notched Izod impact strength of various plastics to the area under $\tan \delta$ -temperature curves. Read and Williams⁶ used areas under loss modulus against reciprocal temperature at constant frequency to obtain the average activation energy for the relaxation processes. Heijboer¹¹ proposed the use of area under a G'' (shear loss modulus)- $1/T$ plot to measure the "strength of activation."

Viscoelastic polymeric materials are capable of attenuating the amplitude of vibrating mechanical systems and thereby reducing noise and vibration.²⁶ However, in almost all homopolymers efficient damping occurs over only about 30°C around the glass transition.²⁷ One way of attaining a broader damping range involves the use of interpenetrating polymer networks (IPNs).^{28,29} An IPN may be defined as a combination of two polymers in network form, at least one of which is synthesized and/or crosslinked in the immediate presence of the other.³⁰ Because the introduction of crosslinks into both polymers restricts the domain size and enhances the mutual miscibility, IPN combinations broaden the damping temperature range of these polymers.

THEORY

A simple understanding of the areas under the linear loss modulus-temperature and linear $\tan \delta$ -temperature curves can be derived via a phenomenological treatment. Two quantities are defined: LA, the area under the linear E'' - T curve, and tA, the area under the linear $\tan \delta$ - T curve. The derivation is sketched in the Appendix. The results are shown as follows:

$$LA = \int_{T_G}^{T_R} E'' dT \cong (E'_G - E'_R) \frac{R}{(E_a)_{\text{avg}}} \frac{\pi}{2} T_g^2 \quad (1)$$

where E'_G and E'_R represent the storage moduli in the glassy and rubbery states, respectively, T_G and T_R are glassy and rubbery temperatures just below and just above the glass transition, $(E_a)_{\text{avg}}$ is the average activation energy of the relaxation process, and the R is the gas constant. Similar relations hold for tA:

$$tA = \int_{T_G}^{T_R} \tan \delta dT \cong (\ln E'_G - \ln E'_R) \frac{R}{(E_a)_{\text{avg}}} \frac{\pi}{2} T_g^2 \quad (2)$$

In both eq. (1) and (2), the integral should be done above the background level (see Fig. 1). Equations (1) and (2) convert earlier equations having frequency as a variable to ones having temperature as a variable, such as for use with Rheovibron data. The temperature ranges covered to obtain the values of LA and tA were governed by the drop off of E'' and $\tan \delta$ both below T_g , and the onset of the plateau region above T_g .

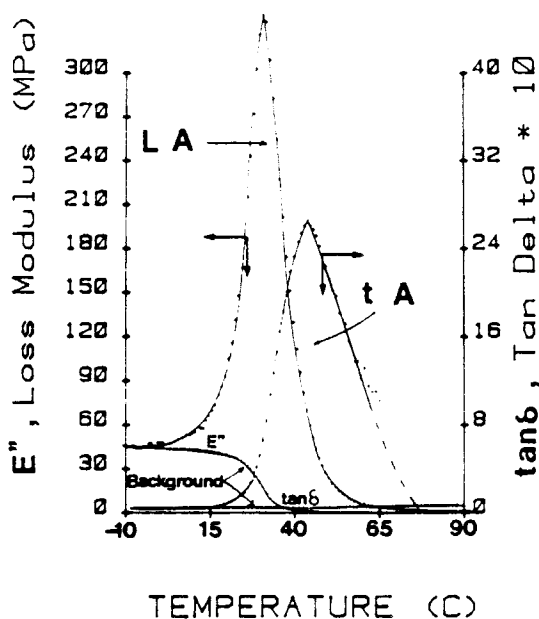


Fig. 1. *Linear* loss modulus and *linear* loss tangent versus temperature curves for poly(methyl acrylate) (1 mol % TEGDM); curves in the lower portion are background for E'' and $\tan \delta$. The upper portion of the $\tan \delta$ curve lacks data points because the sample buckled. The curve was assumed to be symmetrical.

EXPERIMENTAL

Synthesis

A series of crosslinked acrylic and methacrylic homologous series homopolymers, polystyrene, and sequential IPNs was synthesized in bulk by a UV photopolymerization technique³¹ (see Table I). Except for polystyrene being crosslinked by divinyl benzene, tetraethylene glycol dimethacrylate (TEGDM) was used as the crosslinking agent for other polymers. All monomers were dried and freed from inhibitor by a column chromatographic technique using neutral alumina. To each 100 g of monomer, 0.4 g benzoin was added as a UV photoinitiator. Other chemicals were used as received. Atactic polypropylene with the trade name A-FAX 250 was used as supplied by the Hilmont Co.

For the homopolymer synthesis, a mixture of monomer, crosslinker and benzoin was poured into a glass mold fitted with an EPDM rubber cord gasket and exposed to UV light for 72 h. The homopolymers and subsequent IPNs were dried under vacuum at 60°C until constant weight. Conversions were usually more than 95%. The IPNs were prepared by swelling polymer network I in a mixture of monomer II, crosslinker, and benzoin, and polymerizing *in situ*. Most of the IPNs made were near a 50/50 composition.

Dynamic Mechanical Spectroscopy

An Autovibron dynamic viscoelastometer (Rheovibron DDV-III-C type; Toyo Baldwin Co., Ltd.) coupled with a computer and a plotter (assembled by Imass, Inc.) was used to obtain E' , E'' , and $\tan \delta$. The heating rate was

TABLE I
Homopolymer and IPN Compositions

Polyacrylate series	PMA; PEA; PnPa; PnBA; PnHA (all crosslinked by 4 mol % TEGDM); PEA (2 mol % TEGDM); PEA (1 mol % TEGDM)
Polymethacrylate series	PMMA; PEMA; PnPMA; PnBMA, PnHMA; PnOMA (all crosslinked by 4 mol % TEGDM; PMMA (1 mol % TEGDM); PEMA (1 mol % TEGDM)
Poly(methyl acrylate)	PMA with different crosslink level: 1, 2, 3, 4, 5, 10, 15, 20, and 25 mol % TEGDM
Polystyrene	4 mol % divinyl benzene
Polypropylene	Actactic, without crosslinker
IPN-1	54/46* PMA/PMA (1 mol % TEGDM/1 mol % TEGDM)
IPN-2	57/43 PEA/PEA (1 mol % TEGDM/1 mol % TEGDM)
IPN-3	48/52 PEA/PEA (2 mol % TEGDM/2 mol % TEGDM)
IPN-4	48/52 PMA/PMMA (1 mol % TEGDM/4 mol % TEGDM)
IPN-5	58/42 PMA/PMMA (1 mol % TEGDM/1 mol % TEGDM)
IPN-6	56/44 PMA/PEMA (1 mol % TEGDM/4 mol % TEGDM)
IPN-7	55/45 PMA/PEMA (1 mol % TEGDM/1 mol % TEGDM)
IPN-8	72/28 PEA/PMMA (2 mol % TEGDM/4 mol % TEGDM)
IPN-9	63/37 PEA/PMMA (1 mol % TEGDM/1 mol % TEGDM)
IPN-10	56/44 PEA/PEMA (1 mol % TEGDM/1 mol % TEGDM)
Acronyms	
PMA	Poly(methyl acrylate)
PEA	Poly(ethyl acrylate)
PnPA	Poly(<i>n</i> -propyl acrylate)
PnBA	Poly(<i>n</i> -butyl acrylate)
PnHA	Poly(<i>n</i> -hexyl acrylate)
PMMA	Poly(methyl methacrylate)
PEMA	Poly(ethyl methacrylate)
PnPMA	Poly(<i>n</i> -propyl methacrylate)
PnBMA	Poly(<i>n</i> -butyl methacrylate)
PnHMA	Poly(<i>n</i> -hexyl methacrylate)
PnOMA	Poly(<i>n</i> -octyl methacrylate)
TEGDM	Tetraethylene glycol dimethacrylate

*Weight ratio.

approximately 1°C/min, and the frequency was set at 110 Hz, the best frequency for operating the Rheovibron. However, for measuring the activation energy of the polyacrylate homologous series, dynamic mechanical spectroscopy was made at a number of frequencies, i.e., 3.5, 11, 35, and 110 Hz.

In order to calculate LA and tA, all of the classical semilogarithmic plots of loss modulus and $\tan \delta$ were turned into the corresponding linear plots. Background instrumental loss was measured using a standard aluminum plate. The background was subtracted from the observed data. An aluminum plate has very low damping and its $\tan \delta$ is around 10^{-4} at room temperature.²⁶ The background loss of this Rheovibron system was about $\tan \delta = 0.03$.

RESULTS

Homopolymers

The experimental results are shown in Figures 1–6. The dynamic mechanical spectroscopy of poly(methyl acrylate) (PMA) (1 mol % TEGDM) is shown

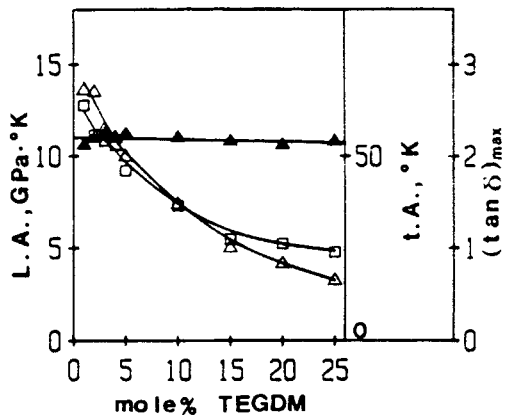


Fig. 2. LA (▲) and tA (□) poly(methyl acrylate) with different crosslink levels. Values of $(\tan \delta)_{\max}$ (△) are also shown.

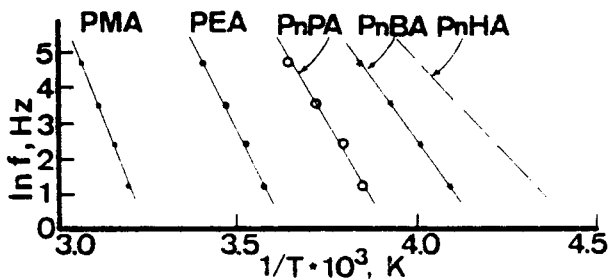


Fig. 3. The Arrhenius plot for the polyacrylate series to determine the apparent activation energy.

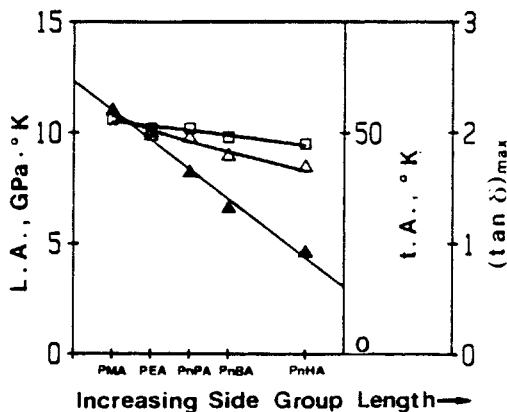


Fig. 4. LA (▲) and tA (□) for the polyacrylate homologous series: (△) $(\tan \delta)_{\max}$.

in Figure 1, illustrating the appearance of the linear loss modulus and $\tan \delta$ terms. For homopolymers, both E'' and $\tan \delta$ show sharp, well-defined peaks. Also shown are the areas to be subtracted for background.

The LA and tA values of PMA for increasing crosslinker levels are shown in Figure 2. Interestingly, LA retains substantially the same value up to very high crosslink levels. Also shown in Figure 2 are the values of $(\tan \delta)_{\max}$, the

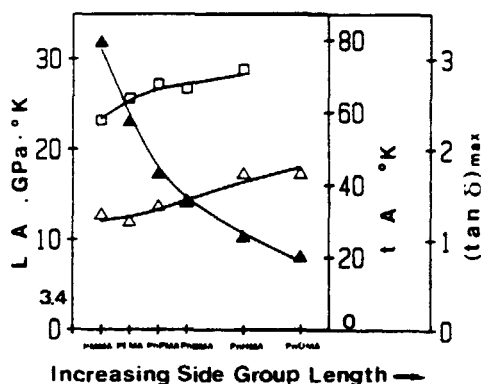


Fig. 5. LA (▲) and tA (□) for the polymethacrylate homologous series: (---) asymptotic LA value for backbone; (Δ) $(\tan \delta)_{\max}$.

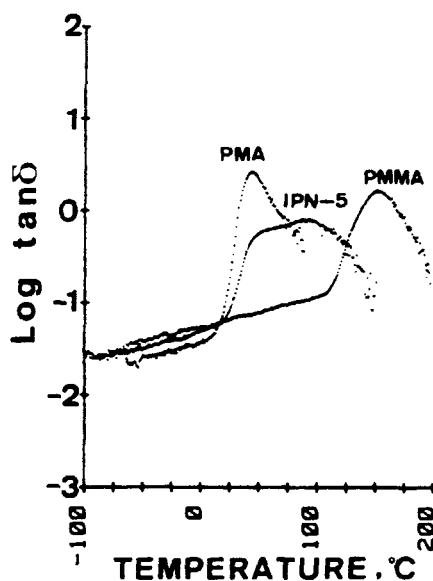


Fig. 6. Loss tangent of PMA and PMMA homopolymer, and PMA/PMMA 58/42 IPN. One mole percent TEGDM as crosslinker is present in each polymer.

peak height of $\tan \delta$. While Figure 2 presents mol % of crosslinker stoichiometrically, Flory-Rehner swelling and Young's modulus experiments confirmed actual crosslinking levels up to 15 mol % TEGDM. Above that value, reduced swelling was observed.

Values for the polyacrylate and polymethacrylate homologous series at 4% crosslinker are shown in Table II. The values of the apparent activation energy of the polyacrylate series are derived from a plot of $\ln f$ vs. $1/T$ at $(\tan \delta)_{\max}$ (see Fig. 3). These results agree fairly well with the values derived from dielectric data³² also listed in Table II.

Using eq. (1), the LA value of PMA (4 mol % TEGDM) calculated from the activation energy and glass transition temperature (Table II) is 14.5 GPa K in comparison with 11.0 GPa K from the observed data. Agreement between calculated and observed values is only fair due to the semiquantitative nature

TABLE II
 Damping Characteristics of Acrylic Polymers (4% Crosslinker Level)

Sample	LA (GPa K)		tA (K)		$(\tan \delta)_{\max}$	E_a (kcal/mol)		T_g (from E''_{\max})	T_g (from $\tan \delta_{\max}$)
	Theoret	Obs	Theoret	Obs		Lit	Obs	(K)	(K)
PMA	14.5	11.0	36.3	53.0	2.20	51.7	53.0	311	324
PEA	12.8	10.0	35.9	51.0	1.97	44.0	41.8	279	294
PnPA	10.7	8.2	37.7	51.0	1.95	28.4	33.0	256	275
PnBA	8.7	6.6	37.3	49.0	1.79	—	29.0	243	260
PnHA	7.8	4.6	38.6	47.5	1.69	—	21.8	227	250
PMMA	—	31.8	—	58.0	1.27	—	—	400	424
PEMA	—	23.0	—	64.0	1.19	—	—	365	395
PnPMA	—	17.2	—	68.0	1.36	—	—	343	371
PnBMA	—	14.2	—	66.7	1.40	—	—	333	354
PnHMA	—	10.2	—	72.0	1.72	—	—	296	327
PnOMA	—	8.0	—	—	1.72	—	—	280	311
PS	—	9.7	—	74.4	2.49	—	—	394	408
α -PP	—	6.1	—	—	—	—	—	270	276

of eq. (1) (see the Appendix³³) and the difference between the average activation energy and activation energy measured by the kinetic shift method. In the polyacrylate series (Fig. 4), the tA values remain substantially constant with increasing length of side chain. On the other hand, as the length of the side group increases, LA decrease more rapidly. The loss tangent peak values are also shown for comparison.

LA and tA values of polymethacrylate series are shown in Figure 5. At a frequency of 110 Hz, the α and β combined relaxations overlap, making the evaluation of the α -relaxation portion of tA difficult. However, LA shows a marked decrease with lengthening side groups.

Interpenetrating Polymer Networks

Sperling et al.^{1,28,34,35} investigated the damping behavior of methacrylic/acrylic latex IPNs in the 1970s. These IPNs exhibit semimiscibility, i.e., they are partly miscible with different portions of the material displaying different compositions. This results in a broad glass transition spanning the entire range between the transition temperatures of the originating homopolymers. It was thought that the transition breadth was maximized when the composition domains were just large enough to contribute independently to the areas under the loss modulus and $\tan \delta$ -temperature curves. Of course, if the IPN is completely immiscible, two separate transitions will be observed, each at the temperature of its respective homopolymer. The intensity of each transition would be expected to be proportional to that polymer's mass fraction.

At the time, it was thought that the IPN structure developed a synergism of some type in damping behavior, but its nature was not understood completely. Questions that remained included the exact mechanisms of broadening of the glass transition, and the chemistry controlling the areas under the curves. It is partly through that train of thought that the present experiments were undertaken.

Figure 6 shows values of $\tan \delta$ for the poly[*cross*-(methyl acrylate)]-*inter*-poly[*cross*-methyl methacrylate)], PMA/PMMA, 58/42 IPN. For this material, the temperature range of $\tan \delta > 0.5$ is about 80°C, in comparison with 40 and 55°C for PMA and PMMA, respectively, and the IPN transition spans much of the range between the two homopolymers. In a parallel investigation, Matsuo et al.³⁶ studied the dynamic mechanical spectroscopy of styrene-butadiene block copolymers, with the same feed of styrene/butadiene mole ratio, but different block lengths, sequences, and number of blocks. Of course, the limit for short block lengths result in partial miscibility, similar to the IPN case. They found that the areas under the loss modulus-temperature curves were nearly the same for the same feed ratio.

As a major point of the preceding investigation on acrylic/methacrylic IPNs,³⁷ the areas under the *linear* loss modulus-temperature curves were shown to be invariant for a given composition, even independent of annealing or subsequent decrosslinking. This result strongly suggested that the areas were determined by the structures of the individual chains; i.e., they were molecular characteristics.

The bulk sequential IPNs of the present study are the analog of the latex IPNs used earlier. The bulk sequential IPNs are potentially useful for damping materials in their own right, and are easier to study on such instruments as the Rheovibron. The quantities LA and tA were determined via Rheovibron at 110 Hz.

Figure 7 shows that LA obeys the simple mixing rule within experimental error, i.e.,

$$(LA)_{IPN} = w_I(LA)_I + w_{II}(LA)_{II} \quad (3)$$

where w_I and w_{II} are the weight fraction of components I and II, respectively.

In Figure 8, all the observed loss tangent areas of IPNs are below the simple mixing rule:

$$(tA)_{IPN} = w_I(tA)_I + w_{II}(tA)_{II} \quad (4)$$

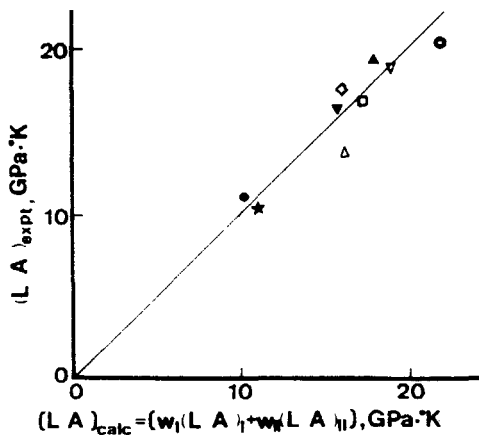


Fig. 7. Test of additivity of the homopolymer LA's in predicting corresponding IPN areas [see eq. (3)]: (★) IPN-1; (○) IPN-2; (●) IPN-3; (◊) IPN-4; (▽) IPN-5; (△) IPN-6; (□) IPN-7; (◇) IPN-8; (▲) IPN-9; (▼) IPN-10.

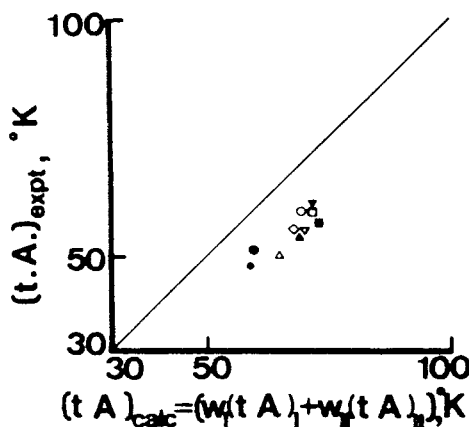


Fig. 8. Test of additivity of the homopolymer tA's in predicting the corresponding IPN areas [see eq. (4)]: (\square) IPN-1; (\circ) IPN-2; (\bullet) IPN-3; (Δ) IPN-4; (∇) IPN-5; (\diamond) IPN-6; (\blacksquare) IPN-7; (\bullet) IPN-8; (\blacktriangle) IPN-9; (\blacktriangledown) IPN-10.

The reason for this important difference lies in the nature of the functions involved. The quantity E'' is a simple function, while $\tan \delta = E''/E'$, i.e., depends on two quantities. Since the quantity $1/E'$ is not expected to obey additivity, especially in the transition region, the relationship breaks down.

Group Contribution Analysis

Dynamic mechanical spectroscopy is one kind of relaxation spectroscopy;³⁸ others are dielectric spectroscopy, infrared spectroscopy, optical spectroscopy, NMR spectroscopy, etc. Dynamic mechanical spectroscopy involves interactions of a periodic mechanical force field with the structural units of the material which results in formation of specific peaks in which the interactions show resonance. From these resonance peaks (especially secondary relaxations), the rotation,³² wagging motion,³⁹ chair-to-chair transformation,⁴⁰ or crankshaft motion⁴¹ from specific groups can be understood.

The glass transition results from large-scale conformational rearrangements of the polymer chain backbone, such rearrangements occurring by a mechanism of hindered rotation around the main chain. Hence, all the groups in the polymer molecule contribute to the glass transition. By examining the area under the glass transition, a quantitative analysis of group contributions can be made. The group contribution analysis for LA is based on the assumption that the structural groups in the repeating units provide an additive contribution to the total loss area. This analysis has been treated in a similar way for group contributions to the solubility parameter, molar volume, heat of fusion, entropy of fusion, glass-transition temperature, cohesive energy, molar attraction constant, parachor, and others.⁴²⁻⁴⁴

Figure 9 develops the basic idea of group contribution analysis for dynamic mechanical spectroscopy ($E''-T$ plot). From Figure 7, it seems that the weight fraction obtains the best additivity. The weight fraction providing the weighting coefficient,

$$LA = \sum_{i=1}^n \frac{(LA)_i M_i}{M} = \sum_{i=1}^n \frac{G_i}{M} \quad (5)$$

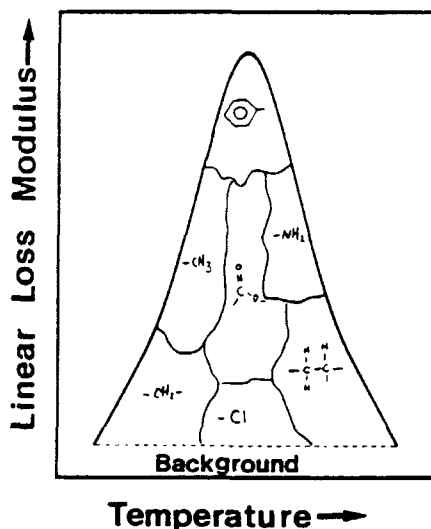


Fig. 9. The basic idea of group contributions analysis for dynamic mechanical spectroscopy ($E''-T$ plot).

where M_i is the molecular weight of the i th group in the repeating unit, M is molecular weight of the mer, and G_i is the molar loss constant for the i th group, and $(LA)_i$ is the loss area contributed by the i th group, and n represents the number of groups or moieties in the mer.

Due to the highly crystalline nature of polyethylene and arguments concerning its glass transition,⁴⁵ it is quite difficult to predict the LA values of the backbone of "amorphous" linear polyethylene, the basis for vinyl and acrylic polymers. For a preliminary calculation, it was assumed that with lengthening the side group in polymethacrylate series, the α - and β -relaxations will be diminished in magnitude to an asymptotic value of 3.4 GPa K

TABLE III
Group Contributions to LA

Group	$(LA)_i$ (GPa K)	G_i (GPa K) (g/mole)
$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C} - \text{C}- \\ \\ \text{H} \end{array}$	3.4	91.8
$\begin{array}{c} \text{O} \\ // \\ -\text{C} \\ \backslash \\ \text{O}- \end{array}$	20.8	936
$-\text{C}_6\text{H}_5$	11.9	916
$-\text{CH}_3^a$	11.0	165
$-\text{CH}_2-^b$	-3.0	-42.0

^aMethacrylate methyl.

^bMethylene group in the side chain.

(Fig. 5, dotted line) for $-\text{CH}_2-\text{CH}-$. Then all the remaining group contributions can be deduced via subtraction procedures.

Table III shows loss areas (LA)_{*i*} and molar loss constants G_i of several groups which were derived from the LA values of polyacrylate polymers, polystyrene, and atactic polypropylene.

DISCUSSION

Often, the damping at the glass transition is examined at constant temperature through a range of frequencies.^{33,46} This paper presents experimental data measuring the damping over a range of temperatures at constant frequency. Experimentally, the background corrected absolute area of the linear loss modulus and tan δ vs. temperature is obtained, and shown to vary systematically with crosslink density and composition through the homologous series of acrylates and methacrylates.

As illustrated in Figure 2, the LA values remain substantially constant, independent of crosslinker level. In part, this can be explained by eq. (1). As the crosslinker level increases, both T_g and E_a increase slightly. While values of both are determined by the polymer's molecular architecture, in eq. (1) they compensate significantly. The dominant factor is the glassy storage modulus, which remains substantially constant. The rubbery storage modulus, being some 1000 times smaller, has little influence, although it increases with crosslink level according to the theory of rubber elasticity.

On the other hand, tA is seen to decrease significantly with increasing crosslinking level in Figure 2. This may be caused, in part, by the logarithmic form of the two storage moduli in eq. (2), in which form the rubbery storage modulus presents values of the same order of magnitude as the glassy storage modulus.

In the acrylate series (Fig. 4), with increasing side group length, both T_g and activation energy decrease, again, in part from eq. (2). The compensation of those factors results in the substantially constant tA values.

In the characteristic areas of polymethacrylates, the longer the alkyl-side group of polymethacrylates, the lower the activation energy of α - and β -relaxations.³² Also, the lower glass-transition and secondary relaxation temperatures³² lead to the trend of increasing tA values. In this series, the α - and β -relaxations stem from main-chain and side-group motions, respectively.³² For each of these polymers, with the merging of α - and β -relaxations, it seems that the apparent α -mechanism values were considerably influenced by β -process. As the length of the side-group increases, neighboring chains are pushed further apart, thus decreasing the hindrance to the backbone motions. The rotational motion of the side-group enhances the effect of "internal plasticization", which may affect the tA behavior in this series (Fig. 5).

While continuum mechanics provides useful equations for understanding the areas under the E'' and tan δ -temperature curves, the detailed experiments required to obtain E_a , T_g , and the various moduli also provide experimental values for LA and tA. Thus, they have, in fact, little predictive value. Also, while the various parameters are obviously sensitive to molecular characteristics, this is not reflected in the continuum mechanics approach [eqs. (1) and (2)].

As a result, a new method of analysis is introduced, based on the group contribution theory (Table III). This method was developed in analogy with the concepts used by Small⁴³ and Hoy⁴⁴ in their development of tables useful for predicting solubility parameters. Table III should be considered as a first step in the eventual development of a much larger assembly of G_i and $(LA)_i$ values to form a more comprehensive, and hence much more useful table.

Of course, the group contribution analysis method potentially has great predictive value. As an example, poly(ethyl acrylate), mer molecular weight of 100 g/mol, will be used. From Eq. (5) and Table III,

$$LA = (91.8 + 936 - 42.0 \times 2)/100 \quad (6)$$

$$LA = 9.4 \quad (7)$$

Since the experimental value of LA for poly(ethyl acrylate) was 10.0 (Table II), the error introduced was about 6%. With additional quantities added to Table III, it may be possible to select polymers with either high or low damping, as required.

CONCLUSIONS

While $(\tan \delta)_{\max}$ or $\log E''$ provide a measure of damping inherent in the polymers at a temperature or frequency of interest, for the evaluation of damping through a temperature range, tA and LA provide useful terms. The quantity LA expresses a measure of mechanical energy converted to heat per unit volume of material. LA is a polymer characteristic, depending on the chain structure itself but not on crosslinking level as measured herein (Fig. 2). The quantity LA obeys the simple linear mixing rule in the sequential IPNs, but tA does not.

Perhaps the most important finding in this research program is that LA depends only on the chain's chemical structure. On IPN formation, the LA obeys an additive relation. A group contribution analysis was developed which could provide an opportunity for predicting LA values via the structure of polymers.

APPENDIX

In the following, the phenomenological mechanical theory rearranged in a form suitable for plotting linear loss modulus and $\tan \delta$ vs. temperature. Storage modulus E' is a function of T and the angular frequency $\omega = 2\pi f$; therefore,

$$\left(\frac{\partial E'}{\partial T} \right)_{\omega} = - \left(\frac{\partial E'}{\partial \ln \omega} \right)_T \left(\frac{\partial \ln \omega}{\partial T} \right)_{E'} \quad (8)$$

Then^{27,33}

$$- \frac{2}{\pi} \frac{1}{R} \int_{T_G}^{T_R} \frac{E''}{T^2} E_a dT \cong - \frac{2}{\pi} \frac{1}{R} \int_{T_G}^{T_R} \frac{E''}{T^2} (E_a)_{\text{avg}} dT \cong \int_{T_G}^{T_R} dE' \quad (9)$$

where $(E_a)_{\text{avg}}$ is the activation energy during the relaxation process (tempera-

ture range between T_G and T_R). For a not-so-wide temperature range of relaxation processes, it is reasonable to replace T with T_g in eq. (9):

$$\int_{T_G}^{T_R} E'' dT \cong (E'_G - E'_R) \frac{R}{(E_a)_{\text{avg}}} \frac{\pi}{2} T_g^2 \quad (10)$$

In almost the same manner as above,

$$\int_{T_G}^{T_R} \tan \delta dT \cong (\ln E'_G - \ln E'_R) \frac{R}{(E_a)_{\text{avg}}} \frac{\pi}{2} T_g^2 \quad (11)$$

Hence, comparing with eq. (1) and (2),

$$\frac{\text{LA}}{\text{tA}} \cong \frac{E'_G - E'_R}{\ln E'_G - \ln E'_R} \quad (12)$$

Equation (12) strongly suggests that the ratio of LA to tA should be a constant for polymers with a given crosslink density, for then E'_R is constant and $E'_g \cong 3 \times 10^9$ Pa for virtually all polymers just below T_g . Part of the variation in this ratio in the polymers characterized in this paper are due to variations in E'_R , but part of it remains unexplained. The quantity E_a as used above assumes an average activation relaxation energy, rather than a more realistic distribution of relaxation activation energies.

It must be noted that in eq. (1) and (2), if LA and tA are divided by the corresponding modulus terms,

$$[\text{LA}] = \frac{\text{LA}}{E'_G - E'_R} \quad (13)$$

$$[\text{tA}] = \frac{\text{tA}}{\ln E'_G - \ln E'_R} \quad (14)$$

then both [LA] and [tA] are approximately equal to

$$\frac{R}{(E_a)_{\text{avg}}} \frac{\pi}{2} T_g^2 \quad (15)$$

Thus, there are unexpected algebraic relationships between [LA] and [tA].

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