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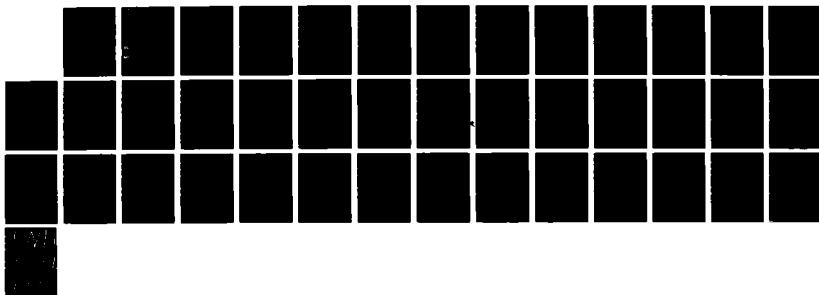   HOMOPOLYMERS STATI..(U) LEHIGH UNIV BETHLEHEM PA
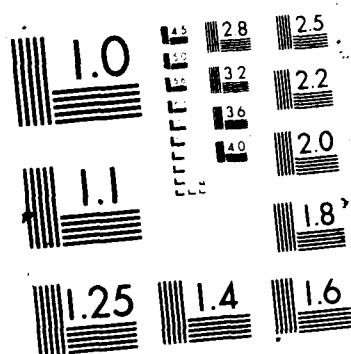   M C CHANG ET AL. 1987 N00014-84-K-0508

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AD-A185 904

GROUP CONTRIBUTION ANALYSIS OF THE DAMPING

BEHAVIOR OF HOMOPOLYMERS, STATISTICAL COPOLYMERS,

AND INTERPENETRATING POLYMER NETWORKS

BASED ON ACRYLIC, VINYL, AND STYRENIC MERS

M. C. O. Chang, D. A. Thomas*, and L. H. Sperling

Polymer Science and Engineering Program

Department of Chemical Engineering

Materials Research Center #32

Lehigh University, Bethlehem, Pennsylvania 18015

*Department of Materials Science and Engineering

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ABSTRACT

The integral of the loss modulus versus temperature plots in the vicinity of the glass transition temperature (loss area, LA) was characterized for various homopolymers, statistical copolymers and interpenetrating polymer networks, (IPN's) based on acrylics, vinyls, and styrenic mers. The quantity LA was found to be a molecular characteristic, governed by the structure of the individual mers. The LA of both IPN's and statistical copolymers obeys an additive relation of the component polymers. A group contribution analysis for LA was developed, in which each moiety contributes a specific value to LA. A table derived via this group contribution analysis permits the prediction of LA values. The results show that backbone motions and the moieties attached directly to the backbone contribute the most to the damping peak, and that long side chains act as diluents.

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INTRODUCTION

When polymers undergo vibration near their glass transition temperature, T_g, some of the mechanical energy is absorbed as heat, i.e., as increased thermal motion. The fraction of energy absorbed reaches a maximum near the frequency and temperature defining T_g. The loss modulus, E", measures the conversion of mechanical energy to molecular motion (1).

The glass transition results from large-scale conformational motion of the polymer chain backbone, such rearrangements involving a mechanism of hindered rotation around the main chain. Hence, all moieties making up the polymer mer contribute to the glass transition. The main chain motions also satisfy the de Gennes (2) reptation model, where the chains move back and forth in snake-like motions.

Several papers have examined some facets of the areas of interest to the present work (3-14). Among these papers, Kawaguchi (3) found that the area under the tan δ-temperature peak of the γ-relaxation was linearly proportional to the number of methylene units in a series of nylons. Wada, et al. (4) correlated the notched Izod impact strength of various polymers to

the area under the tan δ vs. temperature curves. Read, et al. (5) used areas under the loss modulus vs. reciprocal temperature (at constant frequency) to obtain the average activation energy for the relaxation processes. Heijboer (6) proposed the use of areas under a shear loss modulus vs. 1/T plot to measure the "strength of relaxation". Oberst (7) suggested that the area under the loss modulus vs. temperature plots divided by the glassy storage modulus is approximately constant for amorphous polymers.

Interpenetrating polymer networks, IPN's, are a combination of two polymers in network form (15). Usually, at least one is synthesized and/or crosslinked in the immediate presence of the other. Because the introduction of crosslinks in IPN's restricts the domain size and enhances the degree of mixing, some IPN's exhibit a microheterogeneous domain morphology. Such materials have broad glass transitions, which are potentially useful in sound and vibration damping because they damp well over broad temperature ranges (15-29).

Sperling and Thomas (16-19) investigated broad-temperature damping materials using latex IPN's made from acrylic polymers. Klempner and coworkers (28) studied the cross-polyurethane-inter-cross-epoxy

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IPN foams. In an impedance tube absorption method, they found that those IPN foams showed superior sound absorption at all frequencies compared to pure polyurethane foams. Hourston and McCluskey (22) made a cross-poly(vinyl isobutyl ether)-inter-cross-poly(methyl acrylate) sequential IPN, noting one broad loss modulus peak ranging from -20 to +20 $^{\circ}$C.

Foster, et al. (20) prepared a cross-poly(n-butyl acrylate)-inter-cross-poly(n-butyl methacrylate) 50/50 sequential IPN filled by 6 vol-% graphite. They found that graphite increased the absolute value of tan δ and the integral of E"-temperature curve. The IPN subject has been recently reviewed (15, 30-31).

To obtain a better understanding of the glass transition, Fradkin, et al. (32) characterized the integral of the E" vs. temperature (areas under the linear loss modulus vs. temperature curves). During an investigation of acrylic/methacrylic IPN's, they found that the areas were invarient for a given composition, independent of decrosslinking or subsequent annealing. This result strongly suggested that the areas were determined by the structures of the individual chains, i.e., they are molecular characteristics. By using various acrylic and methacrylic polymers, Chang, et al. (33) found that the integral of the E"-temperature plots (loss area, LA) for various IPN's obey an

additive relation. Chang, et al. (33) used the
additivity concept to develop a group contribution
analysis for LA, where each moiety contributes
specific values to the area.

In this paper, the integral of the loss modulus
vs. temperature curve is characterized to develop a
relationship between the extent of damping and the
contribution from each group from a broad range of
acrylic, vinyl, and styrenic polymers. For completion,
values from Reference 33 are included in this paper.

THEORY

Physical quantities for which group contribution
methods have been applied are molar volume, cohesive
energy, solubility parameter, glass transition
temperature, heat of fusion, entropy of fusion, molar
heat capacity, molar parachor, and others (34).
Fedors (35) proposed a system of group contribution to
the molar volume of polymers at 298 K ($V_{(298)}$). Bunn
(36) applied the group contribution analysis to the
cohesive energy of polymers (E_{coh}). According to
Hildebrand's thermodynamics, Small (37) and Hoy (38)
demonstrated that the combination $(E_{coh} V_{(298)})^{1/2} =$
F, the molar attraction constant, is a useful additive

quantity. Via the molar attraction constant of each moiety in the mer, the solubility parameter of polymers can be predicted, widely used for the estimation of polymer-solvent interaction. Several authors (34, 39-41) have also proposed group contribution analysis for glass transition properties. According to the Fox equation relating the glass transition and composition of compolymers, the moieties in the mer provide weighted additive contributions to T_g. This concept was widely used by the several authors above in their own group contribution analysis.

By examining the area under the glass transition, a quantitative analysis of group contributions can also be made. The group contribution analysis for LA is based on the assumption that the structural groups in the repeating units provide a weight fraction additive contribution to the total loss area. The basic equation for the group contribution analysis of LA is (33),

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

where M_i is the molecular weight of the ith group in

the repeating unit, M is the molecular weight of the whole mer, G_i is the molar loss constant for the ith group, $(LA)_i$ is the loss area contributed by the ith group, and n represents the number of moieties in the mer. Equation (1) provides a predictive method for LA values via the structure of the polymer.

The area under an infrared curve provides a quantitative measure of the concentrations of the moiety causing the particular absorption. Infrared spectroscopy and dynamic mechanical spectroscopy have a good deal in common; both measure aspects of molecular relaxation (42). Dynamic mechanical spectroscopy involves interactions of a periodic mechanical force field with the structural units of the material, resulting in formation of specific peaks in which the interactions show resonance. On the other hand, the infrared absorption peaks result from moieties interacting with electromagnetic radiation.

The vibration frequencies of these two spectra are different, note that dynamic mechanical spectroscopy in the sonic region. Polymers investigated by both methods show a longitudinal displacement of long chain motion, following the de Gennes reptation model (2). In infrared spectroscopy, all the contributions from moieties can be resolved. However, in the dynamic mechanical spectroscopy of the

glass transition region, all the moieties of the polymer molecule are combined into a nonresolved resonance peak. Both phenomena, in their own ways are subject to the laws of quantum mechanics. Infrared spectroscopy carried out at one frequency as a function of temperature, and dynamic mechanical spectrospcopy as a function of frequency at one temperature are less often reported because of the lack of range and instrumental difficulties.

When one attempts to resolve the $(LA)_i$ contributions, a series of simultaneous equations results, with one more unknown than equations. The extra unknown is the backbone structure common to all the materials in this investigation, $-CH_2-CH-$. The family of equations have the general form,

$$LA_p = w_b * (LA)_b + \sum w_i * (LA)_i \qquad (2)$$

where LA_p is the LA value for the polymer in question, the subscript b represents the backbone, and the subscript i all other moieties in the polymer.

The quantity $(LA)_b$ can be determined in two ways: (1) By trial and error, until consistent values are obtained throughout the family of polymers, or (2) By study of polymers with long aliphatic side groups. Then substantially the whole polymer consists of $-CH_2-$

groups. Both methods are employed below. After the backbone value is determined, the remaining moieties can be systematically evaluated.

EXPERIMENTAL

Synthesis

All monomers were dried and freed from inhibitor by a column chromatographic technique using neutral alumina (43). A series of crosslinked homopolymers, statistical copolymers, sequential IPN's, and polymer blends were synthesized in bulk by a U.V. photopolymerization technique (43). Except for polystyrene being crosslinked by divinyl benzene, tetraethylene glycol dimethacrylate (TEGDM) was used as the crosslinking agent. Tables I to III show the polymers studied. For the homopolymer or statistical copolymer synthesis, mixtures of monomer(s), crosslinker, and benzoin was poured into a glass mold fitted with an EPDM rubber cord gasket and exposed to U.V. light for 72 hours.

The IPN's (33) were prepared by swelling polymer

network I in a mixture of monomer II, crosslinker, and benzoin, and polymerized <u>in situ</u> to make sequential IPN's. By a similiar method, poly(vinyl methyl ether)/polystyrene blend was prepared by dissolving poly(vinyl methyl ether) in styrene and benzoin mixture, then polymerized. The resulting samples were dried in a vacuum oven until constant weight was reached to assure the removal of unreacted monomer. The compositions of statistical copolymers and polymer blends were investigated by Mattson Sirius 100 Fourier transform infrared spectrometer using 0.6 wt-% THF-solutions.

Commercial polymers used herein include poly(vinyl chloride), poly(vinyl acetate), a vinyl acetate-vinyl alcohol copolymer, and a styrene-acrylonitrile copolymer (Polysciences Company). These polymers were dissolved in suitable solvents, precipitated by nonsolvents, dried in a vacuum oven, then molded in a hot-press for Rheovibron measurements.

<u>Dynamic</u> <u>Mechanical</u> <u>Spectroscopy</u>

An Autovibron Dynamic Viscoelastomer (Rheovibron DDV-III-C type, Toyo Baldwin Co. Ltd.) coupled with a computer and a plotter (assembled by Imass, Inc.) was

used to obtain the storage modulus, E', loss modulus, E'', and the loss tangent, $\tan\delta$ ($=E''/E'$). The heating rate was approximately 1 °C/min, and the frequency was set at 110 Hz.

In order to calculate LA, all of the classical semi-logarithmic plots of loss modulus vs. temperature were replotted with the corresponding linear axes. An aluminum plate was used to obtain the background $\tan\delta$. Its $\tan\delta$ is around 10^{-4} at room temperature. The background loss of this Rheovibron system was about $\tan\delta = 0.03$, which was subtracted as shown in Figure 1. The background loss modulus, calculated from $0.03 * E'$ of the polymer, decreases near T_g, as shown.

Because the value of complex modulus (or storage modulus) can affect the loss modulus value, the Rheovibron was also calibrated by the aluminum plate. After calibration, the storage modulus of a polystyrene sample at 25 °C (110 Hz) was found to be $2.85 * 10^{10}$ dyne/cm^2 in comparison with the values of 2.3 to $3.3 * 10^{10}$ dyne/cm^2 (44) by ASTM test method D638.

RESULTS

All samples were cut to appropriate dimension,
and their loss moduli determined as a function of
temperature on the Rheovibron. Figure 1 shows the
linear loss modulus vs. temperature plot for
cross-poly(methyl acrylate)-_inter_-_cross_-poly(ethyl
methacrylate), PMA/PEMA, 55/45 IPN. (In the classical
logarithmic loss modulus vs. temperature plot, this
IPN shows a relative broad curve instead of a sharp
peak shown in Figure 1.)

Due to the highly crystalline nature of
polyethylene and arguments concerning its glass
transition (45), it was quite difficult to estimate
the LA value of the backbone of "amorphous" linear
polyethylene, or rather $-CH_2-\overset{|}{C}H-$, the basis for
vinyl, acrylic, and styrenic polymers. Starting with
the LA's of the polyacrylate homologous series (33), a
series of simultaneous equations were written
containing one more unknown (the LA of backbone) than
equations, i.e.,

$$(LA)_{ac} = w_b*(LA)_b + w_{ester\ s.g.}*(LA)_{ester\ s.g.} \qquad (3)$$

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where, $(LA)_{ac}$, $(LA)_{ester\ s.g.}$, and $(LA)_b$ are the LA

values of polyacrylate polymers, ester side group, and

backbone, respectively, and w_b and $w_{ester\ s.g.}$ are the

weight fractions of backbone and ester side group,

respectively. The backbone value was estimated by

trial and error until a constant increment of LA of

the methylene group was obtained and to obtain the

best overall fit, see Figure 2. Thus an $(LA)_b$ of 3.4

GPa K was obtained.

Using another method, it is 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 LA for $-CH_2-CH_2-$

group. Figure 3 shows LA's of polymethacrylate series

versus no. of carbons of the ester side groups, a

similar value of 3.4 Gpa K was obtained for the

backbone. Figure 2 also showed the extrapolated LA

value for ester moiety of acrylate polymers. Once the

backbone value was determined, all of the other

moieties could be determined by application of

equation (2), where the number of unknowns equalled

the number of equations.

Table IV summarizes loss areas, $(LA)_i$ and molar

loss constants, G_i, for a number of moieties derived

from group contribution analysis. The values shown in

Table IV are reproducible to within $\pm 8\%$.

The Additive Mixing Rule

As a corollary to equation (1), an additive mixing urle can be written,

$$LA = w_I * (LA)_I + w_{II} * (LA)_{II} \qquad (4)$$

where w_I and w_{II} are the weight fractions of components I and II in IPN's, statistical copolymers, etc. A plot was made of the calculated LA's from equation (4) vs. the experimental values, Figure 4, for the statistical copolymers and IPN's available. Figure 4 shows that LA obeys the simple additive mixing rule, equation (4), within experimental error for both IPN's and statistical copolymers. For example, the linear loss modulus-temperature plot of cross-poly(n-butyl methacrylate)-inter-cross-polystyrene and the corresponding statistical copolymer with nearly 50/50 compositions are shown as Figure 5. Although the shape of the curves for those two polymers are different, their LA's are the same within experimental error. This suggests that the integral of the loss modulus vs. temperature curve in the vicinity of glass transition is a molecular characteristic, governed by the structure of the polymers.

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A schematic diagram for LA behavior of polymer mixtures is shown as Figure 6. In this figure, several polymer mixtures are made from the same polymer pair but by different combining methods, forming systems from low to high miscibility. These are : (a) totally immiscible; (b) with limited miscibility; (c) microheterogeneous systems; and (d) statistical copolymers or miscible systems. Although the miscibility of these four systems is different, the total ability of each to convert mechanical energy into coordinated molecular motion is the same, i.e., they have the same LA value. The loss area depends on the nature of each moiety, independent of enviroments of the moieties.

Equation (1) shows that LA depends only on the polymer's structure. If more than one type of mer exists in the system, the logic can be extended to include all possibilities, whether the mers are in the same chains or different chains.

A Sample Calculation

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From equations (1) and (4), the group
contribution analysis can be utilized to determine LA
for unknown systems. This analysis has the predictive
ability for damping. For example, the LA value for a
PS/PMA 33/67 statistical copolymer (S-9), from
equations (1) and (4), and Table IV can be calculated:

$$\text{L.A.} = 0.33 * \frac{91.8 + 916}{104.2} + 0.67 * \frac{91.8 + 936 - 42.0 * 1}{86.1} \tag{5}$$

$$\text{L.A.} = 10.9 \tag{6}$$

The observed LA for S-9 is 11.2; the error is about
3%.

Moieties situated at different positions on the
mer have different LA values. In particular, both
chlorine and nitrile were studied in two positions,
both on the backbone and off. The smaller value for
chlorine attached to the backbone may be a consequence
of poly(vinyl chloride)'s large beta peak.

The inversion of position yields approximately
the same damping properties, however, see -COO- and
-OCO-. The LA carboxylic acid value derived from
poly(acrylic acid) is similiar to the LA value of
-COO- extrapolated from LA's of polyacrylate
homologous series, see Figure 2. It seems that the

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structural group or moiety is the smallest unit in LA
analysis and complex side groups consisting of several
moieties have unique LA values. From Table IV,
generally, polar side groups not attached to the
backbone contribute more damping capability compared
with nonpolar side groups. Hydrocarbon side groups,
e.g., isobutyl, cyclohexyl, methylene, and benzyl only
give small positive or even negative contributions to
LA's. Large side chains appear to act as a diluent.
The backbone and groups immediately attached to it
constitute the main damping capability.

It should be noted that the value of the complex
modulus (or storage modulus) can affect the loss
modulus value, i.e., $E^*\sin\delta = E"$ (or, $E'\tan\delta = E"$).
Hence, the modulus of the dynamic mechanical
measurement must be calibrated to obtain an accurate
LA value. The LA's shown in Table IV were collected in
the condition of storage modulus of a polystyrene
sample equal to $2.85 * 10^{10}$ dyne/cm^2 ($25\,^{\circ}$C, 110 Hz),
see "Experimental".

The LA's were calculated for some homopolymers
and multicomponent polymers of various workers (7, 19,
20, 21, 25, 29, 46-47) by the present group
contribution analysis method. The background loss
which original workers did not apply was neglected.
Loss curves of homopolymers were made to be

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symmetrically centered around the glass transition. LA's of polymethacrylate polymers (including the β-relaxation) were from the preceding work (33). After the calculations, the conclusion can be drawn that most of the data agree with the present work within $\pm$15 % error, if the modulus is calibrated before calculating LA's, see Table V. The correction factor in Table V is the factor used by us to multiply the storage modulus (or loss modulus) of the various workers in order to calculate the LA's by using Table IV.

The values shown in Table IV are useful in understanding the molecular motion of a polymer chain. If one starts with the de Gennes reptation concept (2), it is obvious that the main chain moves in a back and forth motions. However, long side chains and groups attached to them behave independently. While the main chain motions appear in the glass transition region, side groups motions appear elsewhere, as beta peaks, etc. Most importantly, the notion of the loss modulus for polymers is put on a quantitative basis.

While the experimental data in this paper are quantitatively described by the group contribution method, two additional factors need to be borne in mind:

1. The LA's may depend on the mer surroundings to some extent. Polar solvents, hydrogen-bond forming surroundings, etc. may introduce noticeable effects, as they do in infrared spectroscopy.

2. Morphological features may be important in phase separated materials. The introduction of crystalline regions will reduce the amorphous portions of the polymer, reducing LA accordingly.

CONCLUSIONS

The area under the loss modulus-temperature curve in the vicinity of the glass transition, LA, is molecular characteristic, which is quantitatively determined by the molecular structure of the polymer material. LA's of both IPN's and statistical copolymers obey an additive equation for component mers. A group contribution analysis was developed which provides a method for predicting LA values via the architecture of the polymers. This analysis may help to select polymers with specified damping

characteristics and provides a quantitative basis for developing new theories of molecular motion near the glass transition temperature.

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Table Captions

Table I.   Homopolymers.

Table II.   Statistical copolymer compositions.

Table III. IPN and polymer blend compositions.

Table IV.   Group contribution to LA.

Table V.   Correction factor for LA's.

.

Table I. Homopolymers

| Sample	Polymers	TEGDM
H-1	poly(methyl acrylate)	1 to 25 mole-%
H-2	poly(ethyl acrylate)	4 mole-%
H-3	poly(n-propyl acrylate)	4 mole-%
H-4	poly(n-butyl acrylate)	4 mole-%
H-5	poly(n-hexyl acrylate)	4 mole-%
H-6	poly(methyl methacrylate)	4 mole-%
H-7	poly(ethyl methacrylate)	4 mole-%
H-8	poly(n-propyl methacrylat)	4 mole-%
H-9	poly(n-butyl methacrylate)	4 mole-%
H-10	poly(n-hexyl methacrylate)	4 mole-%
H-11	poly(n-octyl methacrylate)	4 mole-%
H-12	poly(cyclohexyl acrylate)	4 mole-%
H-13	poly(isobutyl acrylate)	1 mole-%
H-14	poly(2-cyanoethyl acrylate)	1 mole-%
H-15	poly(2-chloroethyl acrylate)	1 mole-%
H-16	poly(benzyl acrylate)	1 mole-%
H-17	poly(acrylic acid)	1 mole-%
H-18	polystyrene	4 mole-% DVB
H-19	polypropylene	none
H-20	poly(vinyl chloride)	none
H-21	poly(vinyl acetate)	none

Table II. Statistical Copolymer Compositions

Sample	Polymers	Weight ratio[*]	TEGDM
S-1	PMA/PMMA	25/75	1 wt-%
S-2	PMA/PMMA	50/50	1 wt-%
S-3	PMA/PMMA	75/25	1 wt-%
S-4	PnBMA/PS	79/21	none
S-5	PnBMA/PS	57/43	none
S-6	PnBMA/PS	28/72	none
S-7	PMA/PS	83/17	none
S-8	PMA/PS	58/42	none
S-9	PMA/PS	33/67	none
S-10	vinyl acetate/ vinyl alcohol	87/13	none
S-11	styrene/ acrylonitrile	82/18	none

[*] Samples S-4 to S-11 were characterized by FTIR. In all cases, agreement with monomer feed compositions was ± 10%.

Table III. IPN and Polymer Blend Compositions

Sample	Polymers	weight ratio	TEGDM
Interpenetrating Polymer Networks			
IPN-1	PMA/PMA	54/46	1 mole-%/1 mole-%
IPN-2	PEA/PEA	57/43	1 mole-%/1 mole-%
IPN-3	PEA/PEA	48/52	2 mole-%/2 mole-%
IPN-4	PMA/PMMA	48/52	1 mole-%/4 mole-%
IPN-5	PMA/PMMA	58/42	1 mole-%/1 mole-%
IPN-6	PMA/PEMA	56/44	1 mole-%/4 mole-%
IPN-7	PMA/PEMA	55/45	1 mole-%/1 mole-%
IPN-8	PEA/PMMA	72/28	2 mole-%/4 mole-%
IPN-9	PEA/PMMA	63/37	1 mole-%/1 mole-%
IPN-10	PEA/PEMA	56/44	1 mole-%/1 mole-%
IPN-11	PnBMA/PS	34/66	1 mole-%/1 mole-%
IPN-12	PnBMA/PS	57/43	1 mole-%/1 mole-%
IPN-13	PnBMA/PS	79/21	1 mole-%/1 mole-%
Polymer Blends			
B-1	PVME/PS	46/54	none

Table IV. Group Contribution to LA

Group	Group location	$(LA)_i$ Gpa K	G_i (Gpa K)(g/mole)
H H -C-C- H	1	3.4	91.8
O -C-O-( )-H	2	20.8	936
O -O-C-( )-H	2	20.1	905
O -C-OH	2	20.8	936
⬡ (benzene)	2	11.9	916
$-CH_3$	2	11.0	165
$-OCH_3$	2	21.7	674
$-C{\equiv}N$	2	23.2	603
-O-H	2	4.7	80
-Cl	2	9.2	327
⬡ (cyclohexane)	3	3.5	287
⬡ (benzene)	3	2.2	166
CH_3 $-CH_2-CH-CH_3$	3	-1.7	-98
-CH-	3,4	0.5	7
$-CH_2-$	3	-3.0	-42
$-C{\equiv}N$	3	14.5	377
-Cl	3	15.7	556

1. Backbone.
2. Side group attached to backbone directly.
3. Side group not attached to backbone.
4. Value derived from isobutyl side group.

Table V. Correction Factor for LA's

Group	Ref.	Polymers[a]	Storage modulus, Gpa[a,b]	Corr. factor[c,d]
Foster, et al.	20	PnBA, PnBMA, and IPN's based on acrylic polymers	3.05 (PnBMA, glassy state)	1.0
Widmaier, et al.	21	PS, PnBA, and IPN's based on PS/PnBA	2.75 (PS, room temperature)	ca. 1.0
Hourston, et al.	25	IPN's based on acrylic polymers	for example, 3.0, (cross-PiBA-inter-cross-PEMA 50/50 IPN, glassy state)	ca. 1.0
Oberst	7	Poly(vinyl acetate)	2.5 (PVA, glassy state)	ca. 1.0
Hermant, et al.	29	PMMA	3.3 (PMMA, room temperature)	1.1
Lorenz, et al.	19	IPN's based on acrylic polymers	for example, 1.6 (cross-poly(EMA-stat-EA)-inter-cross-poly(nBA-stat-EA) (21-stat-9)/(49-stat-21) IPN glassy state)	1.8
Gillham, et al.	46	PMMA	4.2 (PMMA, room temperature)	0.9
Weiss, et al.	47	PS	1.0 (PS, room temperature)	2.85

a. PnBA : poly(n-butyl acrylate); PnBMA : poly(n-butyl methacrylate); iBA : isobutyl acrylate; EA : ethyl acrylate.

b. Storage modulus measured by different groups. According to Tobolsky (48), Young's modulus of amorphous polymer is proportional to δ^2 (δ,

Table V. Correction Factor for LA's (continued)

solubility parameter), because most amorphous polymers have the δ values from 16 to 20 $(J/cm^3)^{1/2}$, their glassy modulus are nearly the same, i.e., 3.0 GPa. The storage modulus at the glassy state for amorphous astate can also be roughly estimated by Tobolsky's relation, i.e., $E'_{PVA}/E'_{PS}=0.95$, $E'_{PVC}/E'_{PS}=1.17$, $E'_{PMMA}/E'_{PS}=1.34$, etc.

c. A factor can be multiplied by the loss modulus to calculate LA's.

d. Although each worker may use different frequencies for running dynamic mechanical spectroscopy, it has been explained by the equation (1) of Ref. 33 that frequency carries unimportant effect on LA value.

FIGURE CAPTIONS

Fig. 1   <u>Linear</u> loss modulus versus temperature plot

for a PMA/PEMA 55/45 IPN. The background

correction for E" is also shown.

Fig. 2   LA's of the ester group of the polyacrylate

homologous series versus the weight fraction

of methylene moiety in the ester side group.

Also shown is the extropolated LA value of the

ester group.

Fig. 3   LA's of the polymethacrylate homologous series

versus number of methylene groups in the ester

side group. The asymptotic value is assumed to

be the LA of backbone.

Fig. 4   Test of additivity of the homopolymer LA's in

predicting the corresponding IPN and

statistical copolymer LA's.

Fig. 5   Comparison of an IPN and a statistical

copolymer based on poly(n-butyl

methacrylate)/polystyrene with nearly 50/50

compositions.

Fig. 6   Schematic diagram for loss modulus vs.

temperature behavior of polymer I/polymer II

with different miscibility, (a) totally

immiscible polymer pairs, (b) polymer blends
with limited miscibility, (c)
microheterogeneous system, (d) miscible
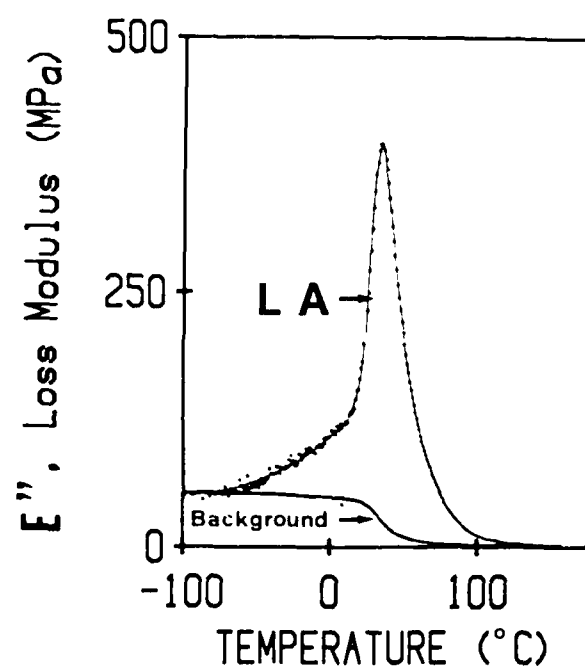system. The weight fraction of each component
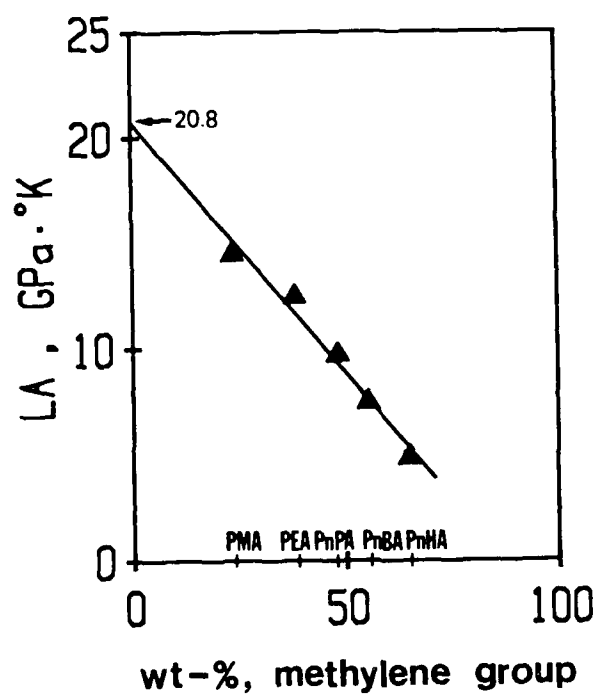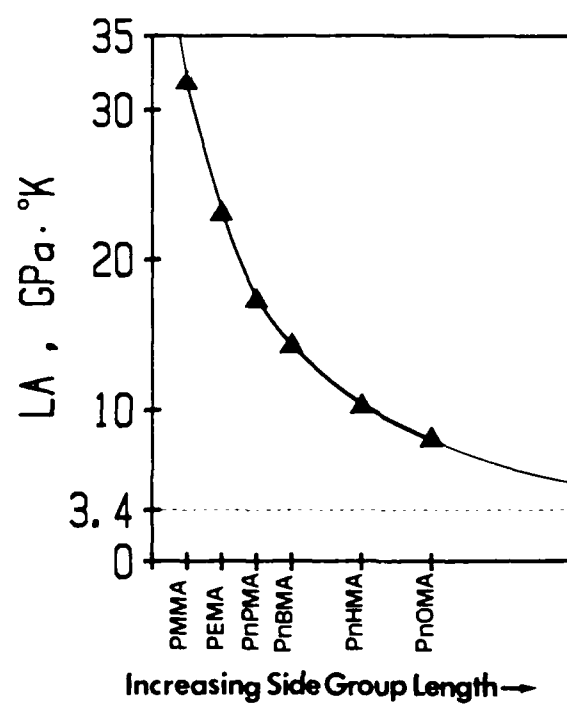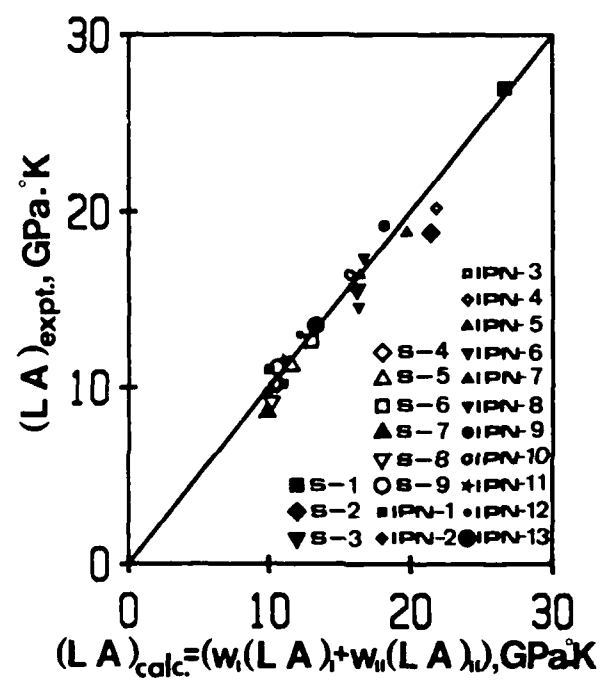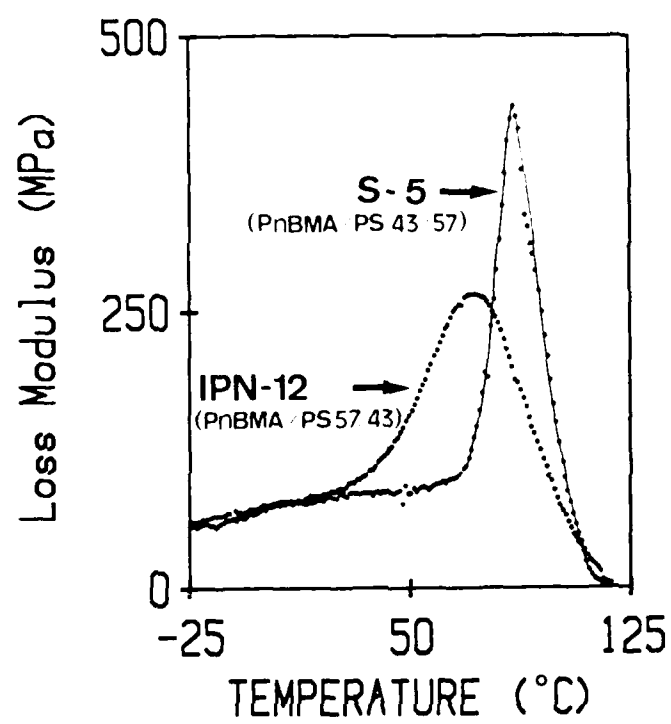is 50% for all these systems.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig 5

Fig. 6

END

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