

Evaluation of the Area under Linear Loss Modulus-Temperature Curves

J. J. FAY,¹ D. A. THOMAS,² and L. H. SPERLING^{3*}

¹Department of Chemistry, ²Department of Materials Science and Engineering, and ³Departments of Materials Science and Engineering and Chemical Engineering, Materials Research Center, Center for Polymer Science and Engineering, Whitaker Laboratory #5, Lehigh University, Bethlehem, Pennsylvania 18015

SYNOPSIS

The area under the linear loss modulus-temperature curves, LA, has been shown to be related to the chemical composition of the material. In addition, it can be significantly affected by morphology in multicomponent polymer systems. To characterize LA quantitatively, base-line corrections for instrumental contributions to LA were evaluated by several different methods and the results compared. In some instances, the calculation method affects only the LA magnitude, while general trends are unchanged; whereas in others, qualitative differences also become important. Not all of the methods described can be utilized universally. However, a straight-line-type of base line, similar to that which is used in infrared spectroscopy and differential scanning calorimetry, provides a widely applicable means of quantifying the loss area.

INTRODUCTION

Dynamic mechanical spectroscopy (DMS) is a useful analytical tool that is used to characterize the dynamic mechanical properties of polymers. The specific information that can be obtained by this method includes the storage modulus, E' , the loss modulus, E'' , and $\tan \delta$, as a function of both temperature and frequency. The DMS experiment typically involves the application of small amplitude cyclical strains to the polymeric sample with concomitant measurement of the sample stress response. The mechanical energy imparted to the sample either is stored elastically, which yields the storage modulus, or is dissipated as heat through increased molecular motion, which is the loss modulus. $\tan \delta$, which is the ratio of E''/E' , is also the tangent of the phase angle between the sinusoidal strain and the resultant sinusoidal stress of the sample. In DMS instrumentation such as the Rheovibron,[†] the strain level is on the order of 0.03–

0.05%, in order to ensure linear viscoelastic response. The information thus obtained can be utilized to evaluate many materials' properties. In the glass transition region of linear polymers, the storage modulus usually decreases by three to four orders of magnitude over a temperature range of 20–30°C. Also, in the glass transition region, E'' and $\tan \delta$ go through maxima. The quantities E'' and $\tan \delta$ can be utilized in mechanical damping applications to reduce mechanical vibrations and noise emission.^{1,2} Recently, there has been an increase in the interest in polymers for sound and vibration damping.³ In this paper, several methods are used to quantify the area under the linear loss modulus-temperature curves and are compared with previous LA determination methods.

Many analytical techniques, such as NMR, GC, GPC, and IR, incorporate the determination of areas under absorption or resonance peaks as a part of the analysis. The determination of the area is an inherent part of the experiment, as is the case with GPC where the molecular weight distribution depends on the area under the GPC absorbance (UV) versus retention time curve. Alternatively, area determination may be used on a secondary basis to provide additional information. In IR spectroscopy, a straight base line is drawn connecting the points

* To whom correspondence should be addressed.

† Autovibron Dynamic Viscoelastometer, IMASS, Inc., Hingham, MA.

of minimum absorbance on either side of the absorbance of interest to determine relative concentrations of chemical moieties for the determination of chemical compositions. One specific application is the determination of copolymer composition by IR.^{4,5} In H_1 -NMR, the area under each resonance peak is proportional to the number of hydrogens generating the peak. With proper phasing of the NMR signal, it is possible to obtain a straight NMR base line, which then enables integration of the NMR spectrum to provide additional information about the relative number of hydrogens corresponding to specific peaks.⁶ Whereas blanks can be run in these techniques to obtain instrumental background, dynamic mechanical spectrometers cannot be run without a sample in order to determine instrumental background.

Whereas the preceding techniques utilize the area under the various experimental curves on a regular basis, evaluation of the area under the linear loss modulus curves obtained by dynamic mechanical spectroscopy has received relatively little attention. There have been a few cases in which the area under the loss modulus curves has been related to the activation energy of the loss transition.^{7,8} However, much of this work was aimed at deriving expressions for the areas as a function of reciprocal temperature at fixed frequency and the exact description of the area calculation, especially the integration limits, are not fully described.

In the development of the group contribution analysis of the loss area by Chang et al.,^{9,10} the area under the loss modulus versus temperature curve was determined in order to relate the damping obtained for a polymeric material with its specific chemical composition. To do this, the classical semilogarithmic plot, log modulus versus temperature, was converted into a linear plot to facilitate the determination of the area. It became apparent, however, that some type of background correction was necessary to define the area under the curve. Although background or base-line determination in GPC, IR, NMR, etc., are dependent upon a stable base line or zero absorption level, the loss modulus data do not lend themselves to straightforward integration. For many polymers, E'' is usually on the order of 30–60 MPa in the glassy region, whereas above the glass transition, the loss modulus approaches zero MPa at some $T > T_g$. Therefore, while the high-temperature integration limit is easily defined, where E'' approaches zero MPa, such is not the case for the low-temperature limit, where E'' retains some finite value. Therefore, some assumptions were proposed in order to define the loss area and

develop reliable calculation methods. A critical review of this and other LA calculation methods will also be presented.

EXPERIMENTAL

Dynamic Mechanical Spectroscopy

An Autovibron Dynamic Viscoelastometer (Rheovibron DDV-III-C; Toyo-Baldwin Co.) coupled with a computer and plotter (assembled by Imass, Inc.) was used to obtain the storage modulus, E' , loss modulus, E'' , and $\tan \delta$ at a heating rate of approximately $1^\circ\text{C}/\text{min}$ and a frequency of 110 Hz. The classical logarithmic loss moduli were converted to the corresponding linear plots by a computer program in order to calculate the loss area, LA, by the various methods.

Materials

Several acrylic, styrenic, vinyl, and polybutadiene polymers and IPNs were used in this paper. The synthesis of these materials is described elsewhere.¹¹

DESCRIPTION OF CALCULATION METHODS

Chang et al.^{9,10} developed a relationship between LA and the individual moieties for a number of poly-

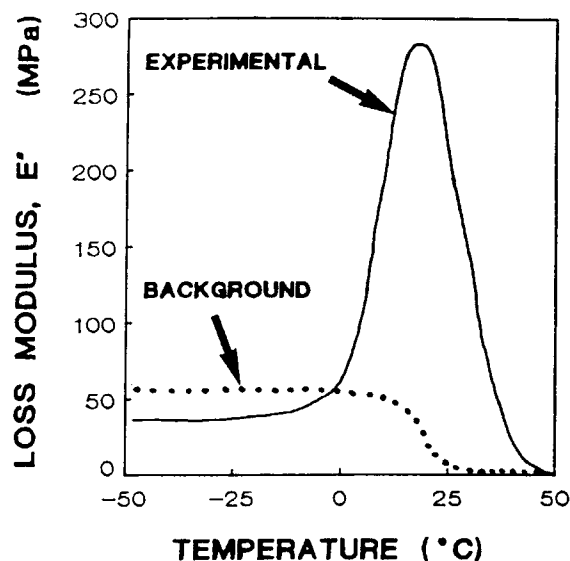


Figure 1 Schematic illustration of the E'' background correction for the case when the experimental $\tan \delta$ is less than the value of $\tan \delta$ used to obtain the base-line correction.

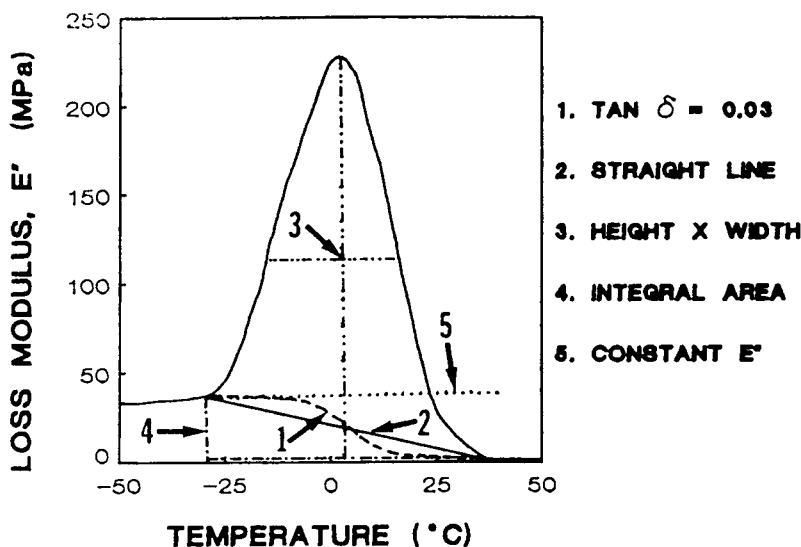


Figure 2 Schematic diagram illustrating five different methods of calculating the loss area, LA. Types 1 and 2 yield approximately equivalent areas.

mers. They introduced a background correction, attributed to instrumental errors in the Rheovibron to the loss modulus. Aluminum generally has low damping, with $\tan \delta$ on the order of 10^{-3} – 10^{-4} . A standard piece of aluminum was evaluated in the Rheovibron as a means of determining instrumental error, which resulted in a background value of 0.03 for $\tan \delta$. It was then assumed that all samples evaluated in the Rheovibron would have the same background loss tangent, $\tan \delta = 0.03$. Then, using this number, a correction to estimate the background loss modulus was defined by

$$E''(T)_{\text{background}} = E'(T)_{\text{EXPTL}} \times 0.03 \quad (1)$$

Applying this relationship, a curve is obtained as a function of temperature that was used as a background and was subtracted from the experimental E'' curve.

However, application of the above correction factor only yields a suitable base line when the experimental value for $\tan \delta$ in the glassy state is approximately 0.03. Otherwise, the background correction and the experimental E'' curves do not superimpose and a low-temperature integration limit is not properly defined. In addition to this problem, the interpretation of this correction suggests that the ratio $E''/E' = 0.03$ would have to be constant for all polymeric materials just below the glass transition in order for the base line to function properly. Although this is certainly not the case, the background was a first attempt to compensate for sys-

tematic instrumental error in the experimental values.

For example, if the background correction of $\tan \delta = 0.03$ is used, for a polystyrene sample with $E' = 2.85 \times 10^{10}$ dynes/cm², $E''_{\text{background}}$ would then be

$$E''_{\text{background}} = 0.03 \times 2.85 \times 10^{10} \text{ dynes/cm}^2 \\ = 8.55 \times 10^8 \text{ dynes/cm}^2 \quad (2)$$

As mentioned previously, the value of 0.03 for $\tan \delta$ may be somewhat different than that obtained for various polymeric materials. Experimental variations in $\tan \delta$ produces dramatic shifts in the background. Schematically, Figure 1 shows an example of the application of this base-line approach when

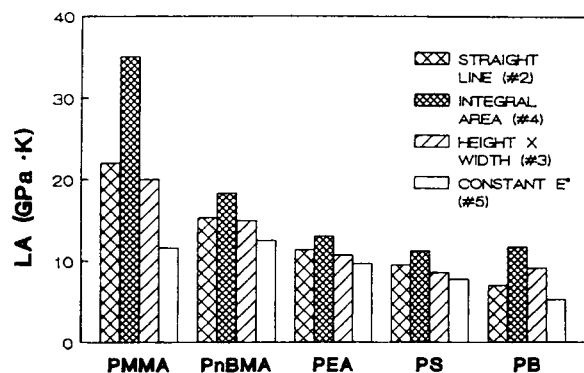


Figure 3 Comparison of the homopolymer LAs by four different LA calculation methods.

the correction factor, $\tan \delta = 0.03$, is larger than the experimental $\tan \delta$ value in the glassy region. Comparatively, should the experimental $\tan \delta$ be greater than the correction factor, then the correction curve will be below the experimental curve and the two curves will not intercept in the temperature region below T_g . This figure demonstrates the limitations of the method. An interesting side point relates to the correction of E'' in the glassy state. Clearly, E'' remains finite, but may be significantly smaller after background correction.

Figure 2 illustrates several alternative methods to determine LAs. The critical point for initiating background corrections is the point where the second derivative of the curve is at a maximum. A straight line (curve 2) may be drawn from that point (about -25°C in Fig. 2) to the point at which E'' approaches 0 MPa. This straight line yields approximately the same area as does the sigmoidally shaped $\tan \delta = 0.03$ correction curve when the latter superimposes on the experimental E'' data. The straight-line alternative has a distinct advantage in that it is not subject to the problems associated with the $\tan \delta$ correction factor base line as described above. This straight-line approach was utilized in the preceding paper¹¹ to calculate LAs.

A third approach, which does not rely on the integration of the area under the curve, is the use of the maximum value of the loss modulus and the width of the transition at one-half the maximum loss modulus value (item 3, Fig. 2). This height \times width at half-max method of calculating the LA has some distinct advantages; however, it also has limitations. The major drawback of this method is the assumption that the shape of the loss modulus curve approximates an isosceles triangle. This is

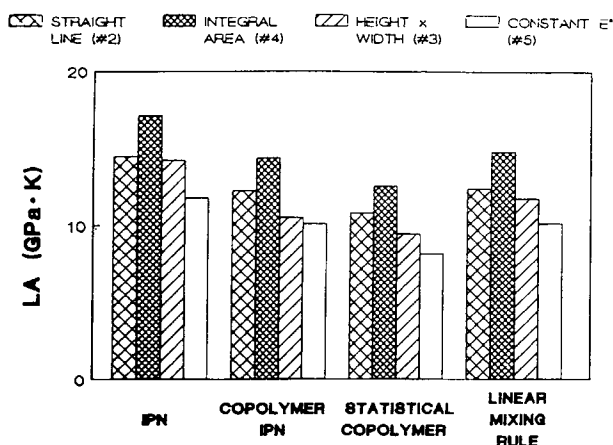


Figure 4 Comparison of LAs of the 50/50 *n*BMA/S samples by the various LA calculation methods.

usually not the case, especially as the loss peak broadens due to phase separation. As the shape deviates from an isosceles triangle, so too does the accuracy of the assumption. Obviously, this method cannot be invoked in cases when there are two maxima in the loss modulus curve. Additionally, when a shoulder is present in the curve, slight changes in the position and the height of the shoulder can yield significant variability in the calculated area, since in these cases the assumption of an isosceles triangle is not adhered to. Additionally, no background correction is made. However, this method can be used to compare similar-shaped curves with reasonable results. An advantage of this method is that the height of the loss modulus transition and the temperature width at one-half the loss modulus maximum value can be determined unambiguously from the experimental data for symmetrically shaped loss modulus curves.

A fourth approach involves the integration of the area under the loss modulus curve over defined temperature limits. In this case, the only adjustable parameter is the lower integration temperature (line 4, Fig. 2). This limit may be held constant for a series of materials in order to obtain more reasonable comparisons. Alternatively, the lower temperature limit may be arbitrarily set by some other convention to standardize the LA calculation. This method evolves from integration of the loss modulus curve over temperature limits, which is incorporated into derivations relating the loss modulus area and the loss modulus activation energy.^{7,8} However, in these equations, specified integration limits are not defined.

Lastly, a line may be drawn at a constant value for E'' , where the value of E'' is assigned the value at the beginning of the transition (line 5, Fig. 2). The intersection of this line with the E' curve above T_g will define the LA. This would then only consider the loss modulus area above the background (or glassy) loss modulus of the sample.

RESULTS AND DISCUSSION

Using the above-described base-line types and the height \times width at half-max approach, LAs can then be evaluated for various samples to demonstrate differences and limitations in the calculated LAs imposed by the selected method of evaluation. Figure 2 illustrates the four different methods used to calculate LA in the following comparison. Since the $\tan \delta = 0.03$ correction and the straight-line base line yield approximately equal areas, the straight-

line method will be used exclusively for comparison purposes.

The LAs of the five homopolymers evaluated in the preceding paper¹¹ are calculated using the four different methods described above. The results are shown in Figure 3. In general, for these samples, the LA trends are not significantly affected by the evaluation method. In Figure 4, the LA of the three different sample preparations with overall composition of 50/50 *n*-butyl methacrylate/styrene¹¹ are evaluated by the different LA methods. Again, the same general LA trends are obtained without regard to the specific LA calculation method.

Table I summarizes the LA calculations for the polybutadiene/polystyrene (PB/PS) IPNs and the PB/PS-latex mechanical blends.¹¹ For these samples, the evaluation method results in very significant differences in the calculated LAs. Now, limitations inherent in the different methods become more apparent. Referring back to Figure 2, the integral base line includes all the area under the loss modulus curve in the vicinity of the glass transition. Comparatively, the straight line and the constant E'' base-line types both exclude portions of the "damping area" that fall below the base line. As a result, as the width of the transition increases, the excluded area under the base line increases. Deviations in the height \times width at half-max approach are directly related to the variance of the shape of

the curve from the assumed isosceles triangle, as well as to the effects of transition broadening. From these data, as the concentration of PS increases, the LA tends to follow the group contribution analysis or shows LA values significantly larger than the group contribution prediction. However, the integral method results in IPN loss areas that are significantly higher than either of the two homopolymers at all compositions, irrespective of cross-link density. As compared with the shapes of the loss modulus curves for the homopolymers summarized in Figure 3, which are generally symmetrical, single peak E'' curves, the PB/PS samples exhibit two transitions, although not necessarily yielding two loss maxima and have, for the most part, significantly broader transition regions.

When the polybutadiene/poly(methyl methacrylate) (PB/PMMA) IPNs are examined in a similar manner (Fig. 5), there is a very significant difference between them and the corresponding PB/PS IPNs. Whereas the PB/PS IPNs showed considerably higher LAs than did the component homopolymers using the integral LA approach, the PB/PMMA IPNs have LAs only slightly higher than the LA for the PB homopolymer and tend to exhibit LA values much less than those predicted by the group contribution analysis. This is also true for the other LA calculation methods, except for the 79/21 PB/PMMA compositions, which show slightly higher

Table I Comparison of Calculated LAs by Different Methods for PB/PS Samples

Sample	LA (GPa K)			
	Straight Line	Integral Area	H \times W	E'' Constant
PB homopolymer	7.0	11.7	9.1	5.3
PS homopolymer	9.5	11.2	8.6	7.8
75/25 IPN (1.0% Dicap)	5.1	12.9	9.3	3.5
75/25 IPN (0.25% Dicap)	9.4	12.6	9.1	7.7
50/50 IPN (1.0% Dicap)	8.0	15.2	9.4	4.1
50/50 IPN (0.25% Dicap)	8.8	15.3	9.8	7.4
25/75 IPN (0.25% Dicap)	12.2	15.3	NA	9.0
75/25 PB PS-latex	5.1	6.6	5.8	4.3
50/50 PB PS-latex	8.1	12.8	8.8	6.4

NA, not applicable; two distinct E'' maxima.

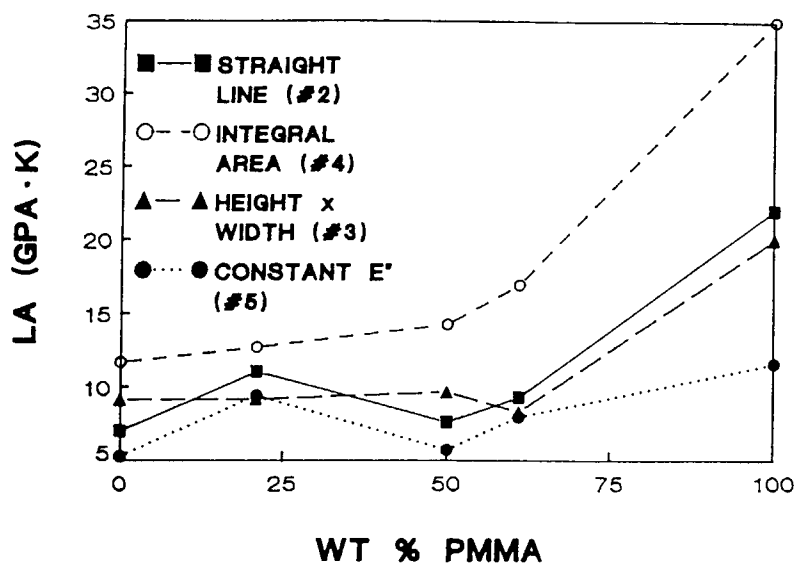


Figure 5 Comparison of PB/PMMA IPN LAs as a function of composition and LA calculation method.

than predicted LAs. This difference in the LA behavior as a function of composition, where PB/PS IPNs follow the group contribution prediction or show larger LAs than predicted and where PB/PMMA tend to show LAs significantly lower than the group contribution values, was attributed to the decreased mixing in the PB/PMMA system as a result of lower miscibility relative to the PB/PS system.

In light of the different evaluation methods that have been considered, which method then is best for calculating the LA? In many cases, the same general trends were observed for a particular series of samples. However, the magnitude of the loss area is very dependent on the method used, which affects the total energy dissipation measured during the experiment. Limitations imposed by the different determination methods become more apparent with the various shapes of the loss modulus-temperature curves that are obtained experimentally. The height times the width at half-max method provides a rough approximation for single peak, symmetric E'' transitions, yet is poor when two peaks or shoulders are present. Thus, this method cannot be universally applied with good results. The straight-line method and the constant E'' base lines are more quantitative and overcome some of the shortcomings of the previously mentioned type. However, both of these methods neglect area contributions in those regions that are under the base line in the vicinity of the E'' transition. There is not, however, any fundamental reason at this time to exclude these regions from

the damping contribution of the material; it is an artifact of the base-line method. The straight-line method is therefore probably more reasonable than is the constant E'' base line. Comparatively, the integral method includes the area under the loss modulus versus temperature curves over a well-defined temperature range without neglecting any area directly beneath the E'' transition. The main difference between the straight-line area and the integrated area is the area that lies below the straight-line baseline. The net result is that for broad transitions the straight-line base line excludes larger areas than are excluded for narrow transitions. Thus, while the straight-line base line and the integral area provide different absolute values for LA, both may be used to determine LA.

Further developments are necessary to decide which is a more accurate representation of the loss area and which provides a better correlation with physical properties, or if a still more appropriate base line might be developed. It should be noted that other analytical techniques such as differential scanning calorimetry utilize various base-line types, depending upon the application, in the evaluation or integration of transition areas with corresponding qualitative and quantitative differences in the results. It is quite possible that different base-line types might also be employed in evaluating dynamic mechanical data depending upon the particular application.

While the preceding discussion focused on the loss modulus α -transition, the area under other

transitions such as the β and γ can also be quantified. Although these secondary transitions are not of as much importance as is the α -transition for damping, might there be a correlation between the area under these secondary transitions and physical properties such as impact strength, fracture toughness, and fatigue resistance?

Quantification of the area under $\tan \delta$ -temperature curves also requires the introduction of some type of base line or integration over temperature ranges as is required to quantify LA. Continued and improved quantitative analysis of the areas under dynamic mechanical data curves is a field where research may yield additional information and theories regarding the dynamic mechanical behavior of polymeric materials. Fundamental explanations regarding the effects of geometry and structural factors such as morphology, phase continuity, fillers and voids, and chemical composition on damping behavior and other physical properties may be accessible through quantitative analysis of dynamic mechanical data.

CONCLUSIONS

The method used to calculate the loss areas has a significant effect on the magnitude of the LA obtained for a particular material. The straight-line type of base line provides quantitative LA evaluation while also compensating for instrumental errors. The integration of the loss modulus curve over temperature limits may also be used to determine LA. Further research is needed to more accurately define the loss area and to determine which base-line type provides a better correlation with physical properties

or if a still more appropriate base line might be developed.

The authors wish to thank the Office of Naval Research for financial support and the Plastics Institute of America for a supplemental fellowship to J. J. F.

REFERENCES

1. A. Thurman and R. K. Miller, *Fundamentals of Noise Control Engineering*, Fairmont Press, Atlanta, GA, 1986.
2. D. I. G. Jones, in *Damping Applications for Vibration Control*, P. J. Torvik, Ed., American Society of Mechanical Engineers, New York, 1980.
3. R. D. Corsaro and L. H. Sperling, Eds., *Sound and Vibration Damping with Polymers*, ACS Symp. Ser. 424, American Chemical Society, Washington, DC, 1990.
4. E. A. Collins, J. Bares, and F. W. Billmeyer, *Experiments in Polymer Science*, Wiley, New York, 1973.
5. J. F. Rabek, *Experimental Methods in Polymer Chemistry*, Wiley, New York, 1980.
6. D. L. Pavia, G. M. Lampman, and G. S. Kriz, *Introduction to Spectroscopy*, Saunders College, Philadelphia, 1979.
7. B. E. Read and G. Williams, *Trans. Faraday Soc.*, **57**, 1979 (1961).
8. G. Adam and F. H. Muller, *Z. Electrochem.*, **66**, 844 (1962).
9. M. C. O. Chang, D. A. Thomas, and L. H. Sperling, *J. Appl. Polym. Sci.*, **34**, 409 (1987).
10. M. C. O. Chang, D. A. Thomas, and L. H. Sperling, *J. Polym. Sci. Polym. Phys.*, **26**, 1627 (1988).
11. J. J. Fay, C. J. Murphy, D. A. Thomas, and L. H. Sperling, *Polym. Eng. Sci.*, to appear.

Received October 16, 1990

Accepted January 2, 1991