Dielectric and Dynamic Mechanical Measurements of Poly(4-methyl Pentene-1)

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Synopsis

The α-relaxation process of poly(4-methyl pentene-1) was studied by dielectric and dynamic mechanical means. The complex dielectric constant was determined at nine discrete frequencies from 100 to 10,000 Hz and over a temperature range of -50–$90°C$. The complex dynamic mechanical Young's modulus was determined over the audiofrequency range of 10–22,000 Hz and a temperature range of 21–76°C, from which a master curve was constructed. The relaxation process was studied by comparing the activation energies and width of the dispersion curves. The results of a logarithmic frequency vs. reciprocal temperature plot of the loss peak maxima show that both the dielectric and mechanical curves are roughly linear but have different slopes. From the slopes the activation energies were determined. For the dielectric data an activation energy of 39 kcal/mol was obtained, whereas for the mechanical data a value of 106 kcal/mol was found. The width of the dispersion curves was determined by using a Cole–Cole empirical fit. The width of the dielectric dispersion curve is narrower by as much as a factor of 3 than the mechanical dispersion curve. It is concluded that the energy to cause the large scale molecular motion involved in the α-relaxation is lower when excited by an alternating electric field than by an alternating stress field. Also the number of repeat units involved is smaller in the dielectric case than in the mechanical case.

INTRODUCTION

The α-relaxation process in poly(4-methyl pentene-1) (PMP) was investigated by dielectric and dynamic mechanical means, where the α-relaxation is the glass transition, even though this polymer has a melting point. PMP is of interest because it has a lower density than any other commercially available polymer; thus it represents one extreme case in our general study of relating physical properties of polymers to their molecular structure. Dielectric[1] and dynamic mechanical[2,3] studies have been done on PMP. In this paper the complex dielectric constant and Young's modulus are determined in the audiofrequency range over a temperature region where the relaxation occurs. The relaxation process was studied by comparing the activation energies and the width of the dispersion curves.

BACKGROUND

Activation Energy

The activation energy ΔH can be determined by the frequency shift method and the area under the curve method. In the frequency method two activation energies can be determined from frequency–temperature dependence of either the imaginary part of the complex quantity or loss factor

peak maxima, by assuming the temperature dependence takes on the Arrhenius form $\ln(f/f_0) = (\Delta H/R) [1/T_0 - 1/T]$.

Using the dielectric case as an illustration, the frequency maxima are obtained from plots of the imaginary part of the complex dielectric constant ϵ'' or loss factor tan δ vs. frequency at constant temperature. The loss factor is tan $\delta = (\epsilon''/\epsilon')$, where ϵ' is the real part. When the relaxation process is modeled by a single relaxation time, the activation energies determined by using ϵ'' or tan δ data are equal.

Two more activation energies can also be determined from the area under the loss curve,[4] either from ϵ'' or tan δ vs. $1/T$ at constant frequency. Then the activation energies are

$$\Delta H = (\epsilon_R - \epsilon_U) R\pi/[2 \int_0^\infty \epsilon'' \, d(1/T)] \tag{1}$$

and

$$\Delta H = (\epsilon_R - \epsilon_U) R\pi/[2 \int_0^\infty \tan \delta \, d(1/T)] \tag{2}$$

where ϵ_R and ϵ_U are the relaxed and unrelaxed real part of dielectric constant, respectively, at temperature T and R is the universal gas constant. These same methods can be used with mechanical data.

Complex Plane

Complex plane analysis is used to determine the width of the relaxation process by constructing an isotherm plot either for dielectric or mechanical data, in which the imaginary part of the complex quantity is plotted against the real part and each point corresponding to one frequency. Then the plotted data are fitted with an empirical function. A well-known function is that due to Cole and Cole,[5]

$$[\epsilon' - (\epsilon_R - \epsilon_U)/2]^2 + [\epsilon'' + (\epsilon_R - \epsilon_U) \cot(\overline{\beta}\pi/2)/2]^2$$
$$= [(\epsilon_R - \epsilon_U)\csc(\overline{\beta}\pi/2)/2]^2 \tag{3}$$

where $\overline{\beta}$ is related to the width of the dispersion curve. For example, if $\overline{\beta} = 1$, then the dispersion can be characterized by a single relaxation time model. This models predicts that in a stress–relaxation experiment the initial stress will relax exponentially to zero with a relaxation time constant τ. For polymers $\overline{\beta} = 1$ has not been observed, usually $0 < \overline{\beta} < 1$. Thus the relaxation curve of polymers are formed from the superposition of many single relaxation time curves, which is known as a distribution of relaxation times.

EXPERIMENTAL

Dielectric Measurements

The dielectric apparatus consists of a capacitance measuring assembly (GenRad Model 1620) and a three-terminal sample holder (Balsburgh Model

LD-3). The sample holder is placed in a refrigerator-oven. Measurements are made between $-50°C$ and $90°C$. Three measuring methods,[6] contacting electrodes, air-gap, and two fluid method are examined. Data analysis shows that the two-fluid method is the most accurate, where the accuracy is about 1%. The capacitance and dissipation factor are measured at nine frequencies: 100, 120, 200, 400, 500, 1000, 2000, 5000, and 10,000 Hz. From these two measured quantities the dielectric constant and loss factor are determined.

Dynamic Mechanical Measurements

The apparatus has been previously described.[7] Briefly describing the apparatus a strip of polymer is excited into resonance by a noise source. Accelerometers are used to measure the mechanical noise input and the response of the polymer. The signals from the accelerometers are then processed by a fast Fourier spectrum analyzer. The analyzer displays the processed signals as amplitude and phase of the acceleration ratio over the audiofrequency range of 10 to 22,000 Hz. The amplitude and frequency at resonance are used to determine the Young's modulus and loss factor. Measurements are performed over a temperature range of $21–76°C$. A family of modulus and loss factor curves is generated over the audiofrequency range and at constant temperature. The data are then processed in one of two ways: as a frequency plot or a temperature plot. In a frequency plot, modulus and loss factor curves are mechanically shifted until they partially overlap in a well-known procedure called time–temperature superposition. The final result is a constant temperature plot over a wider frequency than actually measured. To obtain a temperature plot, the following procedure is used: Frequency plots are generated at several different reference temperatures. For a given frequency, modulus and loss factor are determined by interpolation and then plotted vs. temperature.

Material

The polymer used in this work is a commercial product obtained from Westlake Plastics Co., Lenni, PA, with a reported molecular weight of 400,000. Its measured density at room temperature is 0.835 g/cm^3. Also its measured glass transition temperature T_g and melting point temperature are $28°C$ and $232°C$, respectively. The latter two measurements were done on a differential scanning calorimeter.

RESULTS AND DISCUSSION

Dielectric Properties

The loss factor vs. temperature curves are presented in Figure 1 for the three frequencies: 200, 1000, and 5000 Hz. The peak maxima represent the α-relaxation shifting with frequency. The peak maximum temperatures T_M shift to high temperature as the frequency is increased: For instance, at 200 Hz, T_M is approximately 57°C; at 1000 Hz, T_M is 69°C; and finally, at 5000 Hz, T_M is 78°C. These results are similar to Romanovskaya et al.[1] The imaginary part of the dielectric constant ϵ'' is plotted versus frequency in
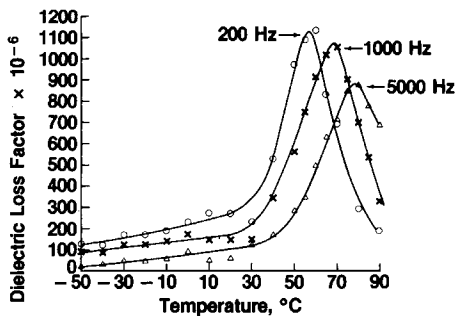
Fig. 1. Dielectric loss factor vs. temperature of PMP at three frequencies 200, 1000, and 5000 Hz.

Figure 2. The peak maxima decrease in size and shift to high frequency with increasing temperature. This data are not superimposible. It has been observed [8] that the assumption of time–temperature superposition is invalid when applied to dielectric data.

The activation energies determined by the four methods are presented in Table I. The activation energies are in good agreement, where the average value is about 39 kcal/mol. Both the shift method and area method give reasonable results. However, the shift method can provide additional insight in the temperature dependence of ΔH by showing a nonlinear curve in the Arrhenius plot, whereas the area method just gives an average ΔH over a temperature range of interest.

Arrhenius plots of dielectric measurements made by Romanovskaya et al.[1] and of this work are plotted together in Figure 3 with other data which will be discussed later. The activation energy calculated from Romanovskaya et al. is about 29 kcal/mol. Romanovskaya et al. also concluded that the peak maximum represented the α-relaxation.

Typical Cole–Cole fits to the dielectric data are shown in Figure 4 at 60°C, 70°C, and 80°C. The empirical fits to the data are done by choosing the "best" values of $\bar{\beta}$, ϵ_R, and ϵ_U to minimize the sum of the squares of the error. These three parameters are presented in Table II as a function of temperature. The results seem to indicate that $\bar{\beta}$ increases with tempera-
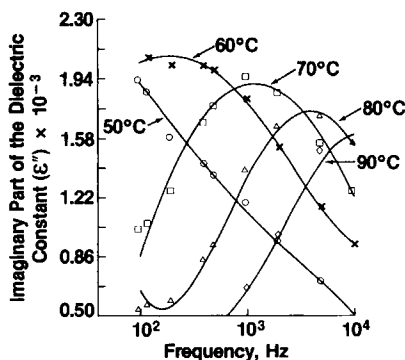

Fig. 2. Imaginary part of the dielectric constant vs. frequency of PMP at four temperatures 60°C, 70°C, 80°C, and 90°C.

TABLE I
Activation Energies Determined by Four Methods for the α-Relaxation
by Dielectric Measurements

	Activation energy (kcal/mol)
Shift method	
ln f (tan δ peak maximum) vs. $1/T$	36
ln f (ϵ'' peak maximum) vs. $1/T$	35
Area Method	
tan δ vs. $1/T$	43
ϵ'' vs. $1/T$	42

ture, which means the width of the dispersion curves is broad at low temperatures and narrow at high temperatures. The two parameters ϵ_R and ϵ_U decreased with temperature as one would expect.

Mechanical Properties

Young's modulus and loss factor versus frequency are presented in Figure 5 at 65°C with WLF[9] (Williams, Landel, and Ferry) shift constants of $c_1{}^g = 20.7$ and $c_2{}^g = 37$ at T_g. Penn[10] reported $c_1{}^g$ and $c_2{}^g$ of 17.3 and 40.3, which were determined from compliance frequency data. The peak in the loss factor curve represents the α-relaxation at a frequency of 4.5×10^4 Hz. In Figure 6, Young's modulus and loss factor are plotted against temperature for a constant frequency of 200 Hz. This constant frequency plot is compared with Kvacheva et al.[2] The α-relaxation temperature of Kvacheva et al. is 51°C compared to 50°C of this work. An Arrhenius plot is shown in Figure 3 which includes data from Choy et al.,[3] Woodward et al.,[11] Kvacheva, and Griffith and Ranby.[12] Most data from the literature are consistent with this work except for two data points of Choy et al. The plotted data are roughly linear, so an average ΔH is calculated. The activation energies determined by four methods are tabulated in Table III. They are in excellent agreement where the average value is about 106 kcal/mol. Kvacheva et al. obtained a value of 95 kcal/mol. Choy noted a low value of 60 kcal/mol. But activation
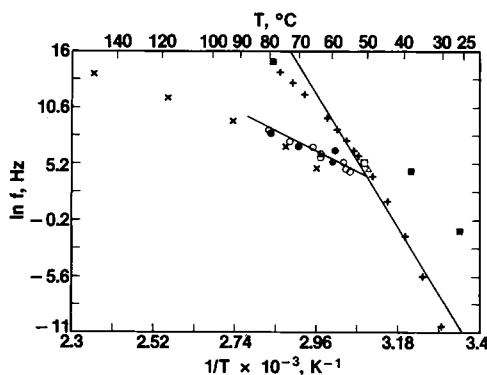

Fig. 3. Plot of logarithmic frequency vs. reciprocal temperature for both dielectric and mechanical data for PMP. Dielectric: ($\times$) Romanovskeya; ($\bigcirc$) Lee tan δ; ($\bullet$) Lee ϵ''. Mechanical: ($\blacksquare$) Choy; ($+$) Lee E''; ($\odot$) Woodward; ($\square$) Kvacheva; ($\triangle$) Griffith.
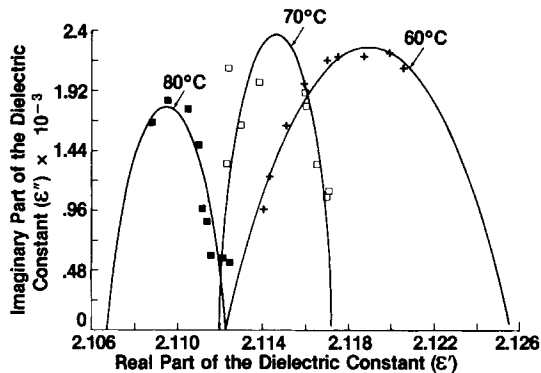
LEE AND HILTZ

Fig. 4.   Imaginary part vs. real part of the dielectric constant for three temperatures 60°C, 70°C, and 80°C for PMP.

energy calculations are known for large differences among experiments, as much as a factor of 2. Choy et al., Woodward et al., Kvacheva et al., and Griffith and Ranby also noted that the relaxation was the α-relaxation.

A Cole–Cole plot is presented in Figure 7 where the $\bar{\beta}$ parameter is 0.3, indicating a broad distribution of relaxation times. The distribution of relaxation times was found to be independent of temperature.

Von Koppelmann[13] has made a similar comparison for poly(vinyl chloride). He found that the activation energy and relaxation time determined from dielectric and mechanical data are identical for the α-relaxation; thus the molecular motions are the same in both cases. This same conclusion cannot be drawn for PMP. PMP does not have a dipole on every repeat unit like PVC. Any dielectric response of PMP is probably due to impurities or oxidation in the polymer chain, which may not be on every repeat unit, but possibly on every two or three repeat units. These numbers are obtained based on the activation energy differences. Thus for PMP the molecular motion are the same, but the number of repeat units in motion when stimulated dielectrically is fewer than excited mechanically.

CONCLUSIONS

Based on the dielectric results the following conclusions are made:

1. The loss peak maximum represents the α-relaxation.

TABLE II
Temperature Dependence of $\bar{\beta}$ Parameters, Relaxed and Unrelaxed Dielectric Constants ϵ_R and ϵ_U, Respectively

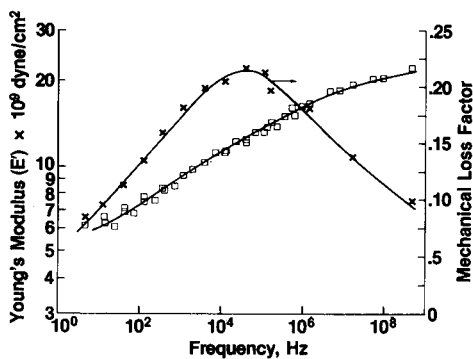| T (°C)	$\bar{\beta}$	ϵ_R	ϵ_U
40	0.5	2.129	2.122
50	0.5	2.126	2.117
60	0.4	2.126	2.112
65	0.8	2.117	2.111
70	0.9	2.118	2.112
75	0.7	2.111	2.104
80	0.7	2.113	2.107

Fig. 5. Master curves of the Young's modulus and loss factor at 65°C for PMP.
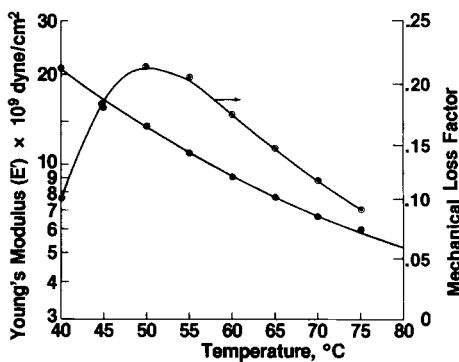

Fig. 6. Young's modulus and loss factor vs. temperature at 200 Hz for PMP.

TABLE III
Activation Energies Determined by Four Methods for the α-Relaxation by Dynamic
Mechanical Means

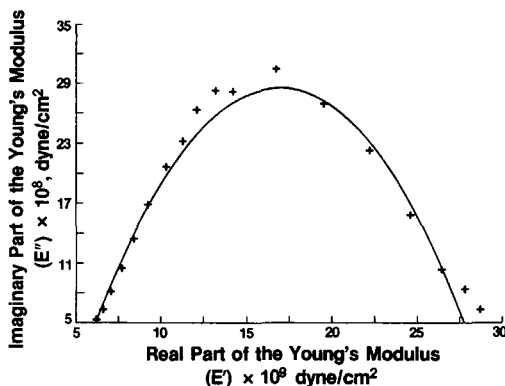|	Activation energy (kcal/mol)
Shift method	
ln f (tan δ peak maximum) vs. $1/T$	113
ln f (E'' peak maximum) vs. $1/T$	106
Area method	
tan δ vs. $1/T$	106
E'' vs. $1/T$	99

Fig. 7.   Imaginary part vs. real part of the Young's modulus for PMP. $\bar{\beta} = .3$.

2. The activation energy of this relaxation is approximately 39 kcal/mol.

3. The width of the distribution of relaxation times decreased with temperature; i.e., $\bar{\beta} = 0.5$ at 40°C and $\bar{\beta} = 0.9$ at 70°C.

Based on the mechanical results the following conclusions are made:

1. The loss peak maximum also represents the α-relaxation.
2. The average activation energy of this relaxation is 106 kcal/mol.
3. The width of dispersion $\bar{\beta}$ is about 0.3.

It is concluded that the energy to cause the large scale molecular motion involved in the α-relaxation is lower when excited by an alternating electric field than by an alternating stress field. Also the number of polymer repeat units involved is smaller in the dielectric case than in the mechanical case.

References

1. O. S. Romanovskaya, M. P. Eidel'nant, V. P. Shuvayev, A. M. Lobanov, B. I. Sazhin, V. A. Duvakin, and N. V. Shueninova, *Plast. Massy,* **7,** 36 (1978).

2. L. A. Kvacheva, A. I. Kirvonsov, B. Y. Mar'yasin, and I. I. Perepevhko, *Sov. Phys. Acoust.,* **23,** 371 (1977).

3. C. L. Choy, W. K. Luk, and F. C. Chen, *Polymer,* **22,** 543 (1981).

4. M. E. Read and G. Williams, *Trans. Faraday Soc.,* **57,** 1979 (1961).

5. K. S. Cole and R. H. Cole, *J. Chem. Phys.,* **9,** 341 (1941).

6. Application Note from GenRad, "Impedence Measurements, Dielectric Loss and Permittivity Measurements with GenRad Precision Capacitance Bridges," EID 11.

7. W. M. Madigosky and G. F. Lee, *J. Acoust. Soc. Am.,* **73,** 1374 (1983).

8. N. G. McCrum, B. E. Read, and G. Williams, *Anelastic and Dielectric Effects in Polymers Solids,* Wiley, New York, 1967.

9. J. D. Ferry, *Viscoelastic Properties of Polymers,* Wiley, New York, 1961.

10. R. W. Penn, *J. Polym. Sci.,* **4,** 559 (1966).

11. A. E. Woodward, J. A. Saver, and R. A. Wall, *J. Polym. Sci.,* **50,** 112 (1961).

12. J. H. Griffith and B. G. Ranby, *J. Polym. Sci.,* **44,** 369 (1960).

13. J. Von Koppelmann, *Kolloid Z.,* **189,** 1 (1963).