Effect of K-Value on the Tensile Yield Properties of Poly(vinyl Chloride)

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Synopsis

Tensile measurements were made on milled compression molded test specimens of PVC of different K values from strain rates of 0.0001–0.1 s^{-1} and temperatures of -40 to 25°C. The dependence of yield stress on temperature and strain rate was treated in terms of the Ree–Eyring model as proposed by Roetling for poly(methyl methacrylate) and Bauwens-Crowet et al. for poly(vinyl chloride). The data reduction was achieved using sophisticated and unbiased statistical techniques that not only provided parameter estimates but their confidence intervals. The yield stress parameters for the alpha and beta processes were found to be independent of K value and within experimental error the same as those reported by Bauwens-Crowet et al. The activation energy for the beta process from these yield stress studies (15.1 ± 0.3 kcal) is within experimental error the same as that determined from viscoelastic measurements (14.1 ± 1.2 kcal) reported by the authors. This observation supports the contention that beta process in the viscoelastic and yield stress measurments are closely related mechanisms.

INTRODUCTION

An impact mechanism study involves the construction of a failure envelope which is made by plotting the yield and fracture stresses as a function of strain rate and temperature. Under those conditions where the yield stress is lower than fracture stress, a considerable amount of energy is dissipated and the material is considered to be tough. When the yield stress exceeds the fracture stress, yielding does not occur; hence the energy expended is much lower and the material is considered to be brittle. The temperature and strain rate combination at which the fracture and yield stresses are equal is called the brittle to ductile transition.

Tensile yield studies are made by determining the yield stress at a variety of strain rates and temperatures. Attempts to fit the experimental data of acrylics in terms of a single (Ree–Eyring) jumping process by Roetling[1-3] failed. However, Roetling was able to represent his data if he assumed two processes. He found for poly(methyl methacrylate) and poly(ethyl methacrylate) that the slower process had an activation energy similar to the viscoelastic and dielectric alpha process while the faster one had an activation energy similar to the viscoelastic and dielectric beta process. On the basis of these correlations, the nomenclature has been extended to all tensile yield studies of polymers.

Bauwens-Crowet et al.[4] extended these measurements to poly(vinyl chloride), i.e., PVC. He also found that the yield stress behavior of poly(vinyl chloride) could be represented by two processes. The activation energies for the slower and faster processes were similar once again to the viscoelastic and

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dielectric alpha and beta processes, respectively. Recent low temperature viscoelastic studies by the authors[5] reaffirmed the correlation between the activation energy of the viscoelastic beta and the activation energy reported for the faster tensile yield process in PVC.[4] These observations suggest that the high strain rate or low temperatures behavior of PVC is determined by the beta relaxation process. In turn this process may be thought to influence impact behavior of neat and modified PVC. However, in the studies cited above, any influence of compositional factors on the parameters of the alpha or beta processes was not studied. In this work we make similar tensile yield measurements on PVC test specimens of differing K value (molecular weight). In addition we shall use sophisticated statistical techniques to estimate parameters and their confidence limits.

METHODS

Materials and Test Specimens

The compositions for the test specimens in this study are given in Table I. These compositions were first milled at 177°C for 3.5 min, compression-molded into 9 × 12 × 0.125 in. flat plates at 177°C and then cooled to 66°C. Test specimens, 0.375 × 3.0 × 0.125 in. were cut from the plaque with the long dimension parallel to the mill direction. All testing was done in an Instron testing machine equipped with an environmental chamber. Measurements were made over a strain rate range of 0.0001–0.1 s^{-1} (seven rates) and at temperatures of −40, −25, 0, and 23°C. Single measurements were made at each condition except at the reference condition. The reference condition is considered to be a replication study for these tensile measurements. These results are given in Table II.

TABLE I
Compositions of the Compression-Molded Plaques

Sample no.	Stabilizer level[a]	Lubricant level[b]	Processing aid level[c]	PVC level	K value
1	2.0	0.5/0.2	1.5	100[d]	69
2	2.0	0.5/0.2	1.5	100[e]	61
3	2.0	0.5/0.2	1.5	100[f]	55
4	2.0	0.5/0.2	1.5	100[g]	58

[a] The stabilizer used in this study is a methyl tin compound manufactured by Morton Thiokol under the trade name TM181.

[b] The first lubricant is a glycerol monostearate compound manufactured by Glycol, Inc under the code name of Aldo MS. The second lubricant is a calcium salt of partially saponifiedmontan wax manufactured by Hoechst under the code name of OP Wax.

[c] The acrylic processing aid used in this work was manufactured by Rohm and Haas Co. under the name of K-120N.

[d] The PVC used here was manufactured by B. F. Goodrich under the code name GEON 103EPF76.

[e] Manufactured by B. F. Goodrich under the trade name GEON 85.

[f] Manufactured by B. F. Goodrich under the trade name GEON 110 × 334.

[g] Manufactured by Firestone under the trade name of FPC 9445.

TABLE II
Tensile Properties of PVC at Reference Conditions
23°C and Strain Rate of 1.0 in./in.[a]

K value	Initial modulus ($\times 10^{-3}$ psi)	Yield stress (psi)	Yield elong. (%)
55	93/11	8700/200	12.4/.5
58	88/9	8790/260	11.9/.6
61	89/9	8730/260	13.0/.9
69	90/7	8720/240	13.4/.7

[a] Data are listed as mean/standard deviation of 10 tests.

Numerical Analysis

Experimental data were assembled and analyzed in an SAS[6] data set. SAS is a user-friendly, versatile statistical and graphics software package. All statistical results described here were derived with the aid of SAS.

RESULTS AND DISCUSSION

Results of Yield Stress Regression

A plot of the lhs of eq. (1), i.e. σ_0/T with the logarithm of strain rate, i.e., $\ln(\dot{\epsilon})$ is given in Figure 1 for the different temperatures and *K* values. The symbols represent the different *K* values while the temperatures are listed in the figure.

Roetling[1-3] and Bauwens-Crowet et al.[4] extended the Ree–Eyring theory to the specific case of two processes contributing to the tensile yield stress σ_0 and found the expression to be

$$\frac{\sigma_0}{T} = A_\alpha\left[\ln 2C_\alpha\dot{\epsilon} + (Q_\alpha/RT)\right] + A_\beta \sinh^{-1}\left[C_\beta\dot{\epsilon}\exp(Q_\beta/RT)\right] \qquad (1)$$

with $\dot{\epsilon}$ = strain rate, R = gas constant, and T = absolute temperature. Significance of the parameters for eq. (1) is given in Ref. 4. The subscripts alpha and beta signify the alpha and beta processes.

Initial attempts to regress the tensile yield data by allowing C_α and C_β to be variables of the regression along with the parameters A_α, Q_α, A_β, and Q_β using SAS's PROC NLIN failed. The failure was traced to the observation that these two parameters form a very shallow minimum and that any value in the range of the exponent is a suitable choice. This problem was resolved by using a stepwise procedure to the regression. In this technique values for the two *C*'s were fixed to the values listed in Ref. 4, while allowing the other four parameters to be variables of the regression. Once the four sensitive parameters were determined, they were fixed and the two *C*'s were allowed to vary. The results of this stepwise regression are given in Table III for the four

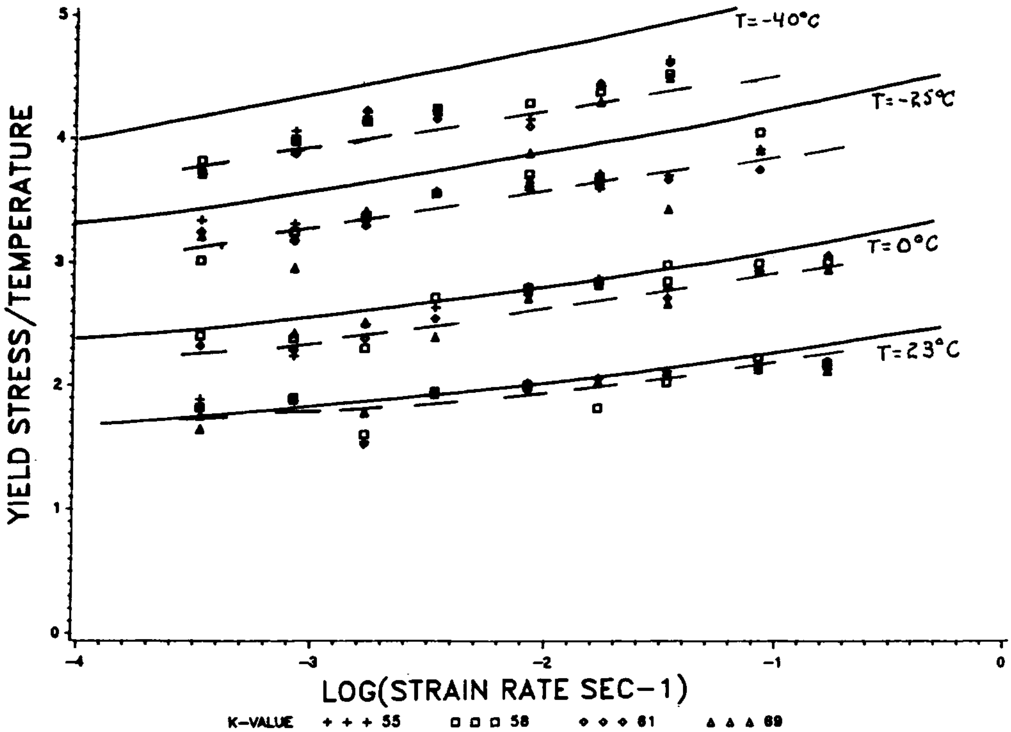

Fig. 1. The yield stress, expressed as kg/sq cm K is plotted against log(strain rate) with strain rate expressed in s^{-1}. Symbols representing the different K values are given in the figure, while temperatures are in °C near the end of the lines. The solid lines were estimated from eq. (1) and the parameters given in Ref. 4 while the long dashed lines are the calculated results of this study using the pooled parameters in Table III and eq. (1).

TABLE III
Parameter Estimates and Their Confidence Intervals[a]

Parameter	Ref. 4	All data	$K = 69$	$K = 61$	$K = 58$	$K = 55$
			Alpha process			
$A\ (\times 10^4)$	7	5.2/.3	4.9/.7	5.1/0.5	5.3/.8	5.1/0.6
Q (kcal/m)	70.5	75.5/1.0	75.9/3.3	76.0/2.1	75.0/3.2	74.9/2.4
$C\ (\times 10^{38})$	1	3.2/2.1	7.3/8.4	0.76/0.71	1.4/1.5	2.2/2.7
			Beta process			
$A\ (\times 10^4)$	10.1	8.6/.9	8.5/2.5	9.0/1.7	7.8/3.0	8.9/1.9
Q (kcal)	14	15.1/.3	15.8/1.1	15.1/.6	15.0/1.1	15.8/.8
$C\ (\times 10^{-10})$	4.26	2.5/2.1	0.9/0.7	3.5/2.2	7.5/5.8	2.8/2.2
No. of observations	—	130	32	31	32	32
Reg. S.S.*	—	1290/1291	316/318	311/311	325/332	328/329
Res. S.S.*	—	1.7/1.7	0.8/0.5	0.4/0.4	1.0/0.4	0.5/0.4
Skewness	—	−0.83	−1.12	−0.46	−0.77	−0.47
Kurtosis	—	0.72	0.64	0.38	0.02	0.57

[a] Note that all units are the same as those in Ref. 1 and that all parameter estimates are followed by their std. error of estimates. The / separates the two sums of square estimates, i.e., S.S./S.S. The first S.S. is the result of the four parameters to be variables of the regression with the other two parameters, i.e., C_α and C_β fixed at the Ref. 4 values. The second estimate comes from fixing the four parameters at the regression results and then allowing C_α and C_β to vary.

individual K values, for pooling of all the K values to form a single data set, and finally for the results in Ref. 4. In addition to the six parameters, their confidence intervals are also listed in Table III, along with regression sums of squares, the residual sums of squares, and the model coefficient of variation. The statistical results, i.e., regression sums of squares (Reg. S.S. in Table III) and residual sums of squares (Res. S.S. in Table III) separated by a / gives the results for the first and second steps in the regression. Parameter estimates and their confidence intervals are also separated by a / in Table III. In some cases, i.e., the result for the alpha process, $C_\alpha \times 10^{38} = 2.2/2.7$ means that the fitted value is 2.2 and the confidence interval is 2.7, i.e., the low limit is -0.3 and the upper limit is 5.4. This confidence interval should be interpreted to mean that 0 is in the confidence range and a negative value has no physical meaning. In other words, the physically significant confidence interval is 0–5.4.

Results of fitting the data in by the pooled set of parameters given in Table III are represented by the dashed lines in Figure 1. The solid lines in that figure were calculated from the parameters in Ref. 4 for the experimental condition given in Figure 1, i.e., strain rate and temperature.

There are a number of important results that should be mentioned. First, the model coefficient of variation is similar in size to the standard deviation obtained from the replication study, suggesting that the model, i.e., eq. (1) represents the data within the accuracy of the tensile measurement. Next, the parameters for the four individual K values are within their own 95% confidence limits and within the 95% confidence limits of the pooled model, suggesting that these parameters do not depend on K value. The model sum of squares for the pooled data (Reg. S.S. = 1290/1291 in Table III) is a little larger than it is for the sum of the four individual K values, i.e.,

$$[(316 + 311 + 325 + 328)/(318 + 311 + 332 + 329)] = 1280/1290$$

taken from Table III. On the other hand, the residual sum of squares are somewhat smaller for the pooled model (Res. S.S. = 1.7/1.7 in Table III) than they are for the sum of the residual sums of squares for the individual models (2.7/1.7 in Table III). These results suggest that K value (i.e., molecular weight) does not effect the tensile yield stress behavior within the limits of experimental error and the range of conditions studied in this work.

The parameters for the present study listed in Table III are within three standard errors of parameter estimates of those in Ref. 4, also listed in Table III. Unfortunately, no parameter estimates were given in Ref. 4, although it may be reasonable to assume that their parameter estimates are similar to those of the present study. For this reason we may assume that the parameters in Table III for the two studies are the same within experimental error.

Skewness and kurtosis quantities[6] which define the nature of the residual distribution are also given in Table III. A frequency (distribution) plot of the residuals is given in Figure 2 for the pooled case. We see that the distribution of residuals is independent of K value, supporting the results in the previous paragraph. The residuals are not normally distributed about zero, which is verified by the skewness and kurtosis terms.

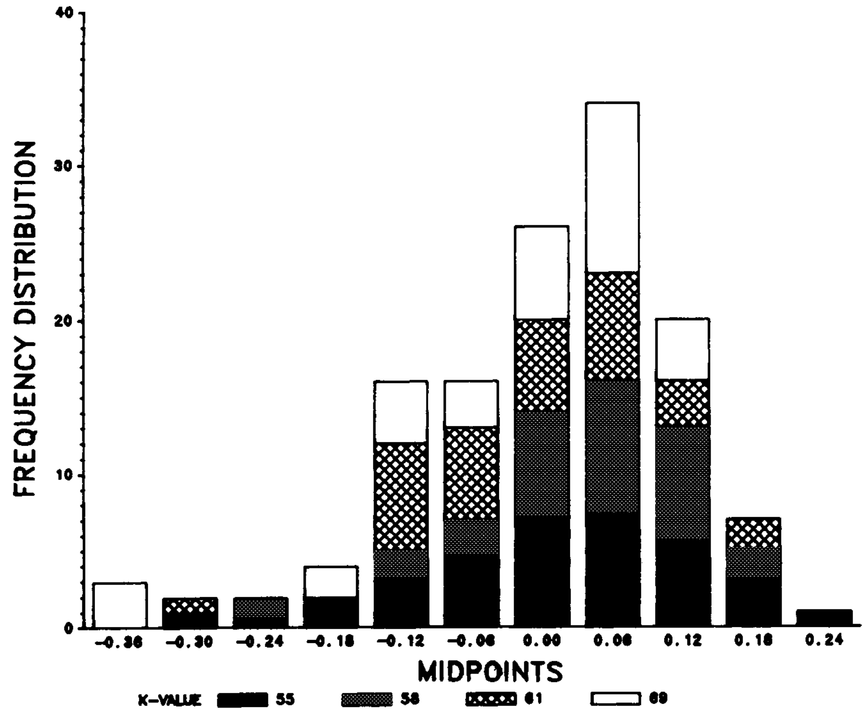

Fig. 2. A frequency distribution, i.e., number of observations in a residual range is plotted against the midpoint of the range. The different *K* values are given in the figure.

Room Temperature Behavior

It is instructive to plot the predicted yield stress over a wide strain rate range at room temperature 23°C. Such a plot is given in Figure 3. It is readily apparent in that figure that in strain rate range of 10^{-4}–10^{-1} s^{-1} the beta process does not make any significant contribution to the total yield (impeding) stress. At about 0.1 s^{-1} the beta process begins to make a significant contribution to the total yield stress and in effect doubles the slope of the total yield stress against strain rate line. If the impact region is assumed to be in the range of 10^3–10^6 s^{-1}, then the beta process contribution to the yield stress is about 25–35% in this region.

Other Tensile Parameters

In addition to the yield stresses, several other tensile parameters were determined, i.e., initial modulus, elongation at yield, break stress, and ultimate elongation. These quantities were examined using SAS's PROC STEPWISE and assuming linear responses in temperature (°C), log(strain rate), and *K* value. Yield stress is included in the study and these results are summarized in Table IV. Also listed in Table IV is the model coefficient of variation. Again we see that *K* value plays little or no role in the tensile properties of PVC determined under these conditions.

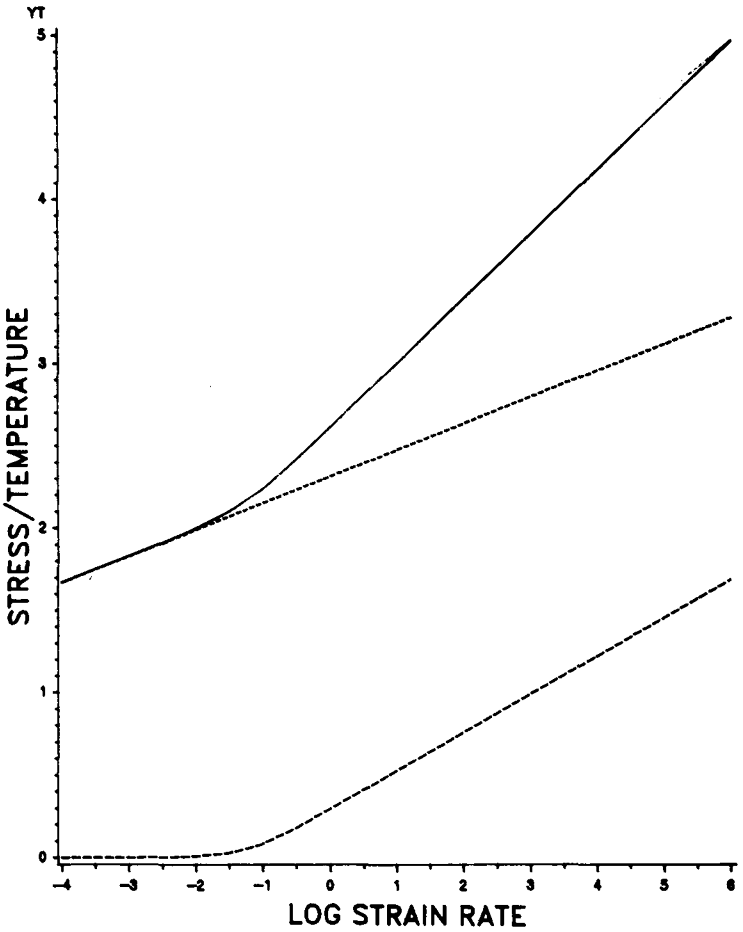

Fig. 3. The yield stress (kg/sq cm K), is plotted over a very large strain rate range. The solid line represents the total stress, the short dashed line represents the alpha process contribution, and the long dashed line the beta process contribution. Temperature in the calculation is set at 23°C.

TABLE IV

Statistical Results of Correlating Tensile Properties with Experimental Conditions

Tensile property	Temp (°C)	log(starting rate) (in./in.)	*K* value	Total R^2	Coeff. of var. (%)
Yield stress	0.81	0.13	0.001	0.94	5
Break stress	0.70	0.18	—	0.88	11
Tensile modulus	0.41	0.17	—	0.60	10
Yield elongation	0.43	0.05	—	0.48	11
Break elongation	0.27	0.02	0.02	0.40	27

TABLE V
Statistics Summary for the Dependence of Initial Modulus with Strain Rate for Various Temperatures

	Temperature (°C)			
Parameters	23	0	−25	−40
Intercept	217/8	248/12	259/8	316/10
Slope	6.5/1.5	5.9/2.2	6.2/1.6	6.3/1.9
R^2	0.37	0.16	0.28	0.58
Root MSE	17.5	27.3	20.7	21
Coefficient of variation	9.5%	12%	9.0%	8.3%
Shift factor	—	4.8	1.7	8.7
Cumulative shift factor	0	4.8	6.5	15.2

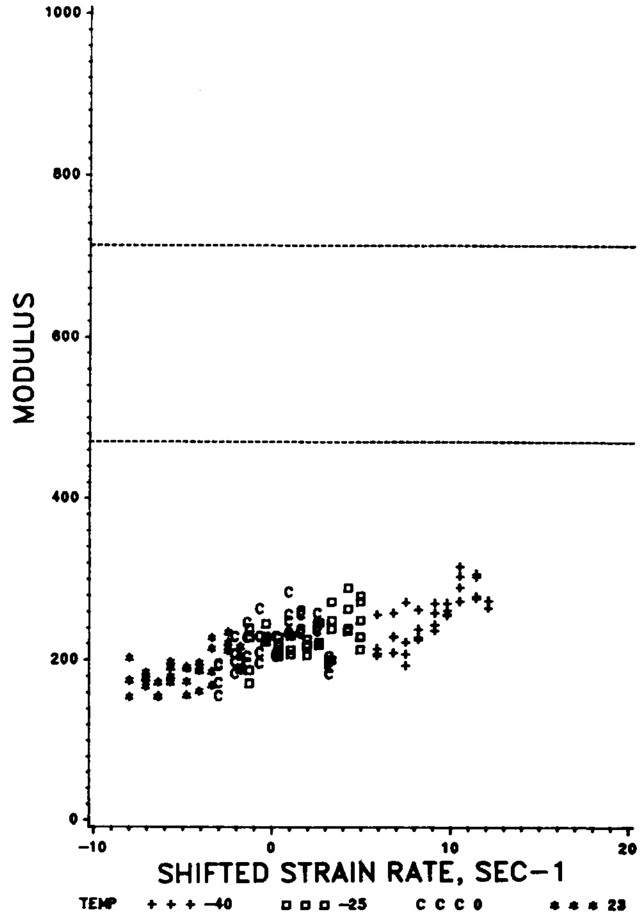

Fig. 4. The tensile modulus, represented in lb/sq in. is plotted against log(strain rate) in s^{-1}. The various temperatures are listed in the legend. The two dashed lines represent the instantaneous (upper line) and equilibrium (lower) moduli of the beta process estimated from Ref. 6. Temperature for estimation and shifting is 23°C. Temperature (°C): (+) −40; (□) −25; (C) 0; (*) 23.

Tensile Modulus

It is useful to treat the initial tensile modulus by the method of reduced variables, using room temperature as the reference temperature. The initial tensile modulus in this study was estimated at strains less than 0.7%. The entire data set was pooled, since the modulus was found to be independent of *K* value in the previous section. The logarithm of the modulus was assumed to be a linear function of log(strain rate) and SAS was used to estimate the regression parameters. The regression parameters are given in Table V. The shift factor reported in Table V was estimated as the distance between two successive straight lines assuming the lines to be parallel (the slopes appear to be constant in Table V). The total or cumulative shift factor at each temperature was calculated as the sum of shift factors starting at room temperature, which was set to zero.

A plot of the tensile modulus with shifted log (strain rate) is given in Figure 4. The two horizontal dashed lines in Figure 4 represent the equilibrium, M_0, and instantaneous M_∞, tensile modulus estimated from the beta process parameters in Ref. 5. The parameters in Ref. 5 were determined from shear compliance measurements at a series of frequencies, temperatures, and a strain of 0.1%. Two of the parameters in Ref. 5, J_0 and J_∞, represent the equilibrium (zero frequency) and instantaneous (infinite frequency) shear compliance for the beta process. These quantities are expected to be related to the equilibrium and instantaneous tensile modulus[7] provided that the Poisson ratio is known; for present purposes, the ratio was set to 0.5. We see from these results that the initial tensile modulus is not determined by the beta process. On the other hand, significant contributions from the alpha process to the modulus is expected in this experimental range.

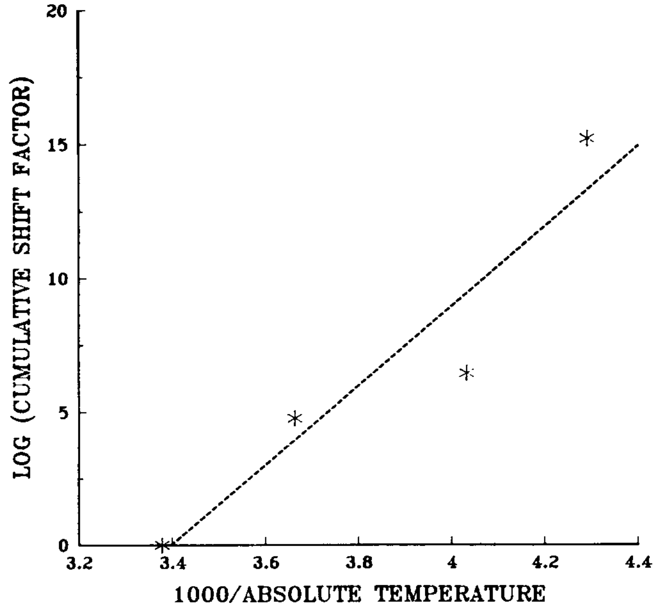

Fig. 5. An Arrheneous rate plot of the shift factor with reciprocal temperature absolute. The slope of the line is 57.7 kcal.

A plot of the cumulative shift factor with reciprocal temperature absolute is given in Fig. 5. The slope of this line expressed as an activation energy is 28 ± 7 kcal/mol, a value intermediate to the alpha and beta processes given in Table III.

CONCLUSIONS

The agreement between the parameters of this study listed in Table III using unbiased statistical methods and those of Ref. 4 also listed in Table III are within experimental error. In addition we have found the tensile yield properties to be independent of the PVC *K* value, hence molecular weight, at least in the range studied. Perhaps the most important result is that the activation energies for the beta process cited in Refs. 4 and 5 and the present study are the same within experimental error. This result suggests that the beta processes in viscoelastic and tensile yield studies are either closely related or one in the same process. This result is satisfying because it suggests that no new process need to be postulated to describe yielding phenomena. It also suggests the importance for understanding the underlying molecular origins of this process and how various conditions, including the addition of impact modifiers, alters these parameters.

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