

Correlation Between Some Solution and Mechanical Properties of Poly(vinyl Chloride) and Chlorinated Poly(vinyl Chloride)

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Synopsis

Correlations have been found between solubility parameters and some mechanical properties of a series of vinyl polymers containing 56.6–69.9% chlorine when tested below their glass transition temperature. It is shown that stress at yield increases similarly with chlorine content and with the volume occupied by a monomer unit in the polymer. Using the Reiner-Weissenberg theory of the dynamic strength of materials as a criterion and a rheological model based on a pair of Maxwell bodies in parallel with a Hooke spring, the amount of dissipated and conserved work to yield point was calculated. A parameter, defined as the ratio of work to cohesive energy density, describes the efficiency of the system. The overall efficiency of the system, based on work to break, and proportional efficiency, based on work to yield point, are affected by chlorine content and strain rate. In addition, a potential energy parameter is defined which describes the cohesive energy per volume occupied by monomer unit of the polymer. This parameter is proportional to the total work to break as well as to the ratio of the residual work after yield to total work at all strain rates tested. The major portion of work is conserved up to yield; only a small portion is dissipated. From the yield point to break, after the onset of viscous flow, the major part of this work is dissipated.

INTRODUCTION

The application of "the volume occupied by the monomer" concept in characterizing the solubility parameter of poly(vinyl chloride) (PVC) and chlorinated PVC (CPVC) is extended to interpret tensile yield properties and work obtained from a series of polymers containing 56.6–69.9% chlorine. For temperatures below the glass transition temperature, various workers¹⁻³ attribute the yielding of rigid, glassy polymers to a free-volume increase. According to this approach, the stress is sufficient to transform the glass to a liquid state; yielding is ascribable to a free-volume increase arising from the applied strain and the attainment of an energy level to overcome the energy barriers to segmental molecular motion. Robertson⁴ suggests that yielding involves deformation of the polymer molecules and distortions of their shapes. It can be implied that the behavior at yield stress of a glassy polymer would depend on geometric factors including number and bulkiness of substituent groups. For unplasticized PVC, molecular weight and molecular weight distribution appear not to be very important

factors in delineating stress-strain properties.⁵ In addition, Crugnola, Zoppie, and Moraglio⁶ found a yield stress of approximately 575 kg/cm² for three PVC samples, two suspension and one emulsion, with number-average molecular weights of 69,600, 40,300, and 75,000, respectively.

One of the authors⁷ studied the solubility parameter δ of PVC and of a series of chlorinated PVC (CPVC) samples and found that a maximum occurred at a chlorine content of approximately 63%. The square of the solubility parameter, δ^2 , is equal to a quantity E/V , the "cohesive energy density," where E is the cohesive energy and V , the molal volume. A number of workers^{8,9} have pointed out the dependence of cohesive energy density (CED) and T_g on structural factors and the increase of T_g with CED.

It was considered of interest to compare solubility parameters with mechanical properties. Correlations were sought between: (1) the volume occupied by a monomer unit and the yield stress in the polymer (geometric factors); (2) the potential energy and the mechanical energy (work) to the yield point; (3) the potential energy and the mechanical energy from yield to break; and (4) the potential energy and the total work at break. In addition, the data were analyzed on the basis of the Reiner-Weissenberg¹⁰ criterion, which implies that a body fails after it has absorbed an amount of elastic energy that is a constant for a given material.

THEORETICAL BACKGROUND

The deviatoric stress work W_s acting on a body in time t is given¹¹ by the equation

$$W_s = \int_0^t \xi_{\alpha\beta} \dot{\epsilon}_{\alpha\beta} dt \quad \alpha, \beta = 1, 2, 3 \quad (1)$$

where $\xi_{\alpha\beta}$ is the stress deviator tensor and $\dot{\epsilon}_{\alpha\beta}$, the deviator of strain rate tensor. If it is assumed that the rheological behavior of a body can be represented by that of a row of n Kelvin bodies,⁹ then,

$$W_s = \sum_{i=1}^n \mu_i \epsilon_i^2 + 2 \sum_{i=1}^n \eta_i \int_0^t \dot{\epsilon}_i^2 dt \quad (2)$$

where μ_i , η_i are material parameters, modulus and viscosity coefficient, respectively. The first part of eq. (2) is the accumulated work, $W_c = \sum_{i=1}^n \mu_i \epsilon_i^2$, or that part of the mechanical energy going into the breaking of the material. The second term is the dissipated work, $W_a = 2 \sum_{i=1}^n \eta_i \int_0^t \dot{\epsilon}_i^2 dt$, or the amount of the mechanical energy given up through heating of the sample.

On the other hand, for n Maxwell bodies,⁹ eq. (3) is obtained for the total work, W_s , after summarizing all the constituent parts of energy:

$$W_s = \sum_{i=1}^n \left[\frac{S_i^2}{4\mu_i} + \frac{1}{2\eta_i} \int_0^t S_i^2 dt \right] \quad (3)$$

Equation (3) consists of two parts, one of which describes accumulated work, W_c , and the other, dissipated work, W_d :

$$W_c = \sum_{i=1}^n \frac{S_i^2}{4\mu_i} \quad (3a)$$

$$W_d = \sum_{i=1}^n \frac{1}{2\eta_i} \int_0^t S_i^2 dt. \quad (3b)$$

For the case when $S_i = 0$ at $t = 0$, and at a constant rate of deformation with $\dot{\epsilon} = \dot{\epsilon}_c$, the value W_s can be obtained as follows:

$$W_s = 2\dot{\epsilon}_c^2 \sum_{i=1}^n \left\{ \eta_i t - \frac{\eta_i^2}{\mu_i} \left[1 - \exp\left(-\frac{\mu_i}{\eta_i} t\right) \right] \right\} \quad (4)$$

and

$$W_c = \dot{\epsilon}_c^2 \sum_{i=1}^n \frac{\eta_i^2}{\mu_i} \left[1 - \exp\left(-\frac{\mu_i}{\eta_i} t\right) \right]^2 \quad (4a)$$

$$W_d = 2\dot{\epsilon}_c^2 \sum_{i=1}^n \frac{\eta_i^2}{\mu_i} \left\{ \frac{\mu_i}{\eta_i} t - \frac{1}{2} \left[1 - \exp\left(-\frac{\mu_i}{\eta_i} t\right) \right]^2 - \left[1 - \exp\left(-\frac{\mu_i}{\eta_i} t\right) \right] \right\}. \quad (4b)$$

In the studies reported here, a rheological model was selected based on a pair of Maxwell bodies in parallel with a Hooke spring. In this instance, eqs. (4a) and (4b) for the value of work to yield point become

$$W_s = 2\dot{\epsilon}_c^2 \left\{ \eta_1 t - \eta_1 \tau_1 \left[1 - \exp\left(-\frac{t}{\tau_1}\right) \right] + \eta_2 t - \eta_2 \tau_2 \left[1 - \exp\left(-\frac{t}{\tau_2}\right) \right] + \epsilon^2 \mu_0 \right\} \quad (5)$$

$$W_d = 2\dot{\epsilon}_c^2 \left\{ \eta_1 t - \frac{1}{2} \left[1 - \exp\left(-\frac{t}{\tau_1}\right) \right]^2 - \left[1 - \exp\left(-\frac{t}{\tau_1}\right) \right] + \eta_2 t - \frac{1}{2} \left[1 - \exp\left(-\frac{t}{\tau_2}\right) \right]^2 - \left[1 - \exp\left(-\frac{t}{\tau_2}\right) \right] \right\} \quad (5a)$$

$$W_c = W_s - W_d \quad (5b)$$

where $\tau = \eta/\mu$.

EXPERIMENTAL

The tensile stress-strain curves were obtained with the aid of an Instron tensile testing machine, and pressed samples of four polymers were prepared as follows: A mixture comprising 100 parts polymer and 8 parts stabilizers, Chemische Werke, Munich (5 parts tribasic lead sulfate V220 Mc; 2 parts

barium-cadmium ester BC8, and 1 part dibasic lead stearate Pb 51S) was dry blended in a sigma-type mixer for 15 min at 75°C. The blends were fluxed in a Brabender Plastograph equipped with a Roller Mixer, Type 30 (capacity 30 cc) operating at 20 rpm 2 min past the flux point. In each case, the bath temperature was set at 220°C, and the stock temperature was 195°–198°C. The compounds were then molded at 205°C into the shaped specimens (ASTM D 1708-66) by preheating for 2 min without pressure, pressing for 50 sec, and cooling to 150°C in the press under pressure to provide samples of uniform (0.19 ± 0.01 cm) thickness. The specimens were kept in an environment of 23°C and 50% R.H. a minimum of 48 hr prior to testing. The tests were conducted at 23°C and 50% R.H. at three strain rates: 3.74×10^{-4} , $-\times 10^{-3}$, and $-\times 10^{-2}$ cm cm⁻¹ sec⁻¹. Strain rate was based on displacement of the cross head moving at speeds of 0.05, 0.5, and 5.0 cm/min, respectively.

RESULTS

Summaries of the solution and mechanical properties of PVC and CPVC are given in Tables I and II. The value of V_p is the total volume occupied by an average monomer unit of the polymer at 23°C and is based on the measured density of the polymers. The value of CED ($\delta^2 = E/V_p$) is based on solubility parameter studies⁷ and is a measure of the amount of energy required to separate polymer chains (or, more precisely, segments of chains) from each other. The "effective volume," V_c , was calculated as the sum of the volumes occupied by spheres, with the radius r equal to the cova-

TABLE I
Summary of Solution Properties of PVC and CPVC^a

Chlorine, wt-%	Total volume occupied by one monomer unit of polymer at 23°C (V_p), cm ³ × 10 ²³	Cohesive energy density (δ^2)		ϕ	Potential energy parameter ($\delta^2\phi$), ergs/cm ³ × 10 ⁻¹⁰
		cal/cm ³	ergs/cm ³ × 10 ⁻⁹		
56.6	7.66	94.5	4.03	9.40	3.79
64.6	8.65	97.1	4.15	9.05	3.76
65.9	8.83	95.1	4.08	8.96	3.66
69.9	9.81	89.6	3.82	8.87	3.39

^a Data taken from Krozer;⁷ cohesive energy density,

$$\delta^2 = \frac{E}{V_p} = E \left/ \frac{\text{MW (monomer unit)}}{6.023 \times 10^{23} \times \rho_{\text{polymer}}} \right.;$$

$$\phi = \frac{V_p = \text{total volume occupied by an average monomer unit in polymer}}{V_c = \text{effective volume occupied by an average monomer unit in polymer}}$$

TABLE II
Summary of Mechanical Properties of PVC and CPVC^a at 23°C

Chlorine, ^b wt-%	Yield point data				Work, ^d (ergs/cm ³) 10 × 10 ⁻⁶			Efficiency (W/δ ²), %			Residual energy parameter [(W _b - W _d)/ W _b], %	
	Strain rate (ε̇), ^c cm/cm-sec	Stress, (S _{yp}), kg/cm ²	Strain (ε _{yp}), %	To yield point	To break	W/δ ²			W _c /δ ²			
						W _b /δ ²	W _s /δ ²	W _c /δ ²	W _d /δ ²	W _c /δ ²		W _d /δ ²
56.6	3.74 × 10 ⁻⁴	478	6.06	189	1638	40.7	4.69	4.66	0.03			88.5
	3.74 × 10 ⁻³	521	6.30	227	1500	37.2	5.06	4.86	0.20			84.8
	3.74 × 10 ⁻²	546	6.63	231	930	25.6	5.73	5.10	0.63			75.1
64.6	3.74 × 10 ⁻⁴	564	7.70	285	1250	30.3	6.86	6.84	0.02			77.2
	3.74 × 10 ⁻³	624	8.50	358	1338	32.4	8.64	8.56	0.08			73.3
65.9	3.74 × 10 ⁻²	676	8.61	382	988	23.9	9.42	9.38	0.04			61.4
	3.74 × 10 ⁻⁴	613	8.00	343	1023	24.0	8.40	8.34	0.06			66.5
	3.74 × 10 ⁻³	685	8.93	413	1060	24.6	10.11	10.0	0.11			60.9
69.9	3.74 × 10 ⁻²	729	9.19	402	1070	24.6	15.3	14.62	0.68			62.4
	3.74 × 10 ⁻⁴	653	6.27	227	316	11.2	4.19	4.19	0.00			28.2
	3.74 × 10 ⁻³	720	7.85	262	292	7.6	7.02	6.90	0.12			10.3
	3.74 × 10 ⁻²	789	8.53	377	593	15.5	10.0	7.80	2.2			36.4

^a ASTM D 1708-66 microtensile specimens.

^b Commercial sample Frutarom Electrochemical Industries, Haifa, PVC Epivyl 46; CPVC samples were prepared in the laboratory.

^c Instron tensile testing machine model TTGM.

^d Work (area under stress-strain curve, obtained by planimetry) was obtained by dividing the values by the cross-sectional area of the sample and, by an additional division, by the gauge length 2.220 cm.

lent radii of the atoms in an average monomer unit of the polymer. It should be pointed out that, below T_g , the free volume of amorphous polymers is approximately $1/40$ of the total volume.⁹ Our estimate is about $1/10$. We consider this satisfactory since our interest is in the value $\phi = (V_p/V_c)$, the ratio of the total volume to effective volume as an indication of the extent of packing and shape of the molecules. The value $\delta^2\phi = E/V_c$ is a parameter related to the potential energy of the system and to the effective volume of the polymer molecule. The significant difference between V_c and V_p is that, while V_c reflects only the bulkiness of the atoms in the polymer molecule, V_p is related to both the bulkiness factor and free volume. Values of yield stress and strain, as well as work to yield point and to break, are the averages of at least four results; reproducibility was approximately 10%. Work was calculated by graphic integration of the stress-strain curves.

In these studies, attention was directed to total work to yield point, W_s , and work to break, W_b . In order to evaluate the contributions of the accumulated work, W_c , and dissipated work, W_d , to the total work to yield point, W_s , a model was selected based on a pair of Maxwell bodies in parallel with a Hooke spring. Two relaxation times, 200 and 10 sec, were assumed to be based, in part, on the order of magnitude reported for the mechanical relaxation of PVC¹² and, on trial and error calculations, to provide reasonable agreement with experimental data obtained on the four polymers. Since our interest was to gain information on the portion of the accumulated work and of the dissipated work to the total work to the yield point, and we do not attach physical significance to the relaxation times used in this study, we consider the result obtained using these assumed values satisfactory.

DISCUSSION

Figure 1 shows that correspondence exists between tensile yield stress at 23°C and both total volume occupied by a monomer unit and chlorine content. The abscissa indicates both chlorine content and values of V_p . The scale of V_p was adjusted so that the values corresponding to V_p and chlorine contents of 56.6 and 64.6% were coincident. The results show that the tensile yield stress at 23°C of PVC and CPVC with chlorine contents between 56.6 and 69.9% varies likewise with chlorine content and/or with the total volume occupied by a monomer unit in the polymer molecule. The data show that the yield stress exhibited by an amorphous, chlorine-substituted hydrocarbon polymer increases with increasing substitution by chlorine. These results indicate that the observed increase in yield stress arises, in the main, from stereochemical factors related to the configuration of the polymer chain.

In order to characterize the systems under investigation, a model was selected based on a pair of Maxwell bodies in parallel with a Hooke spring. The rheological model is shown in Figure 2, and the calculated values for η and μ are given in Table III. In these calculations, two relaxation times

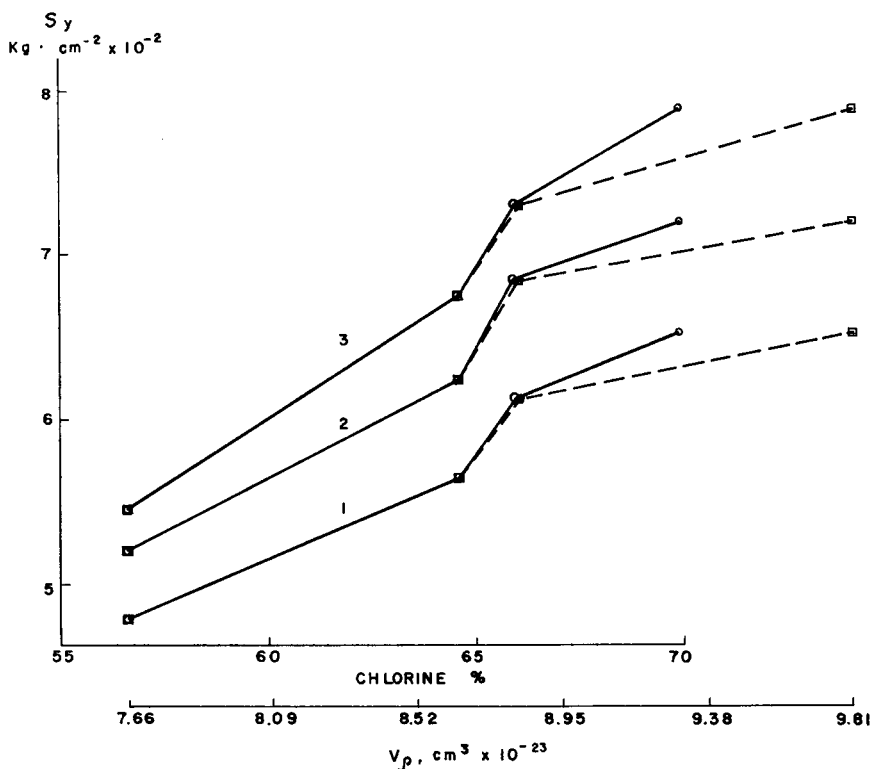


Fig. 1. Correspondence of chlorine content and V_p on tensile yield stress at 23°C: (—) chlorine content; (---) V_p ; numbers 1, 2, and 3 refer to strain rate ($\dot{\epsilon}$ in sec^{-1}) 3.74×10^{-4} , $- \times 10^{-3}$, $- \times 10^{-2}$. V_p data taken from Krozer.⁷

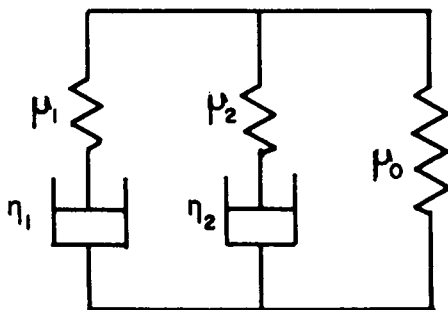


Fig. 2. Rheological model.

were assumed, $\tau_1 = 200$ sec and $\tau_2 = 10$ sec. Based on these values, solution of the rheological eqs. (5) and (5a) provided the values for η and μ shown in Table III. The data show that satisfactory agreement was obtained between the observed and calculated values for the total work to yield point, W_s .

TABLE III
Rheological Constants and Work to Yield Point for PVC and CPVC

Chlorine, wt-%	Strain rate ($\dot{\epsilon}$), cm/cm-sec	t_s^a sec	η_1^b , poises $\times 10^{-10}$	η_2^b , poises $\times 10^{-10}$	μ_0 (dynes/ cm ²) $\times 10^{-10}$	W_{s^c} (ergs/cm ³) $\times 10^{-8}$		W_c	W_d
						Observed	Found ^c		
56.6	3.74×10^{-4}	162	4.42	3.00	5.10	1.89	1.89	1.88	0.01
	3.74×10^{-3}	22.86				2.27	2.04	1.96	0.08
64.6	3.74×10^{-2}	2.10				2.31	2.31	2.06	0.25
	3.74×10^{-4}	206	5.00	1.00	4.80	2.85	2.85	2.84	0.01
65.9	3.74×10^{-3}	22.8				3.58	3.59	3.56	0.03
	3.74×10^{-2}	2.3				3.82	3.91	3.48	0.43
69.9	3.74×10^{-4}	214	10.0	1.00	5.00	3.43	3.43	3.41	0.02
	3.74×10^{-3}	24				4.13	4.13	4.08	0.05
69.9	3.74×10^{-2}	2.5				4.02	6.24	5.96	0.28
	3.74×10^{-4}	168	1.38	1.29	4.10	2.27	1.61	1.60	0.01
69.9	3.74×10^{-3}	23.1				2.62	2.68	2.64	0.04
	3.74×10^{-2}	2.3				3.77	3.82	2.99	0.83

^a $t_s = \Delta l / \dot{\epsilon}$.

^b $\tau = \eta / \mu$; $\tau_1 = 200$ sec; $\tau_2 = 10$ sec.

^c Equations (5).

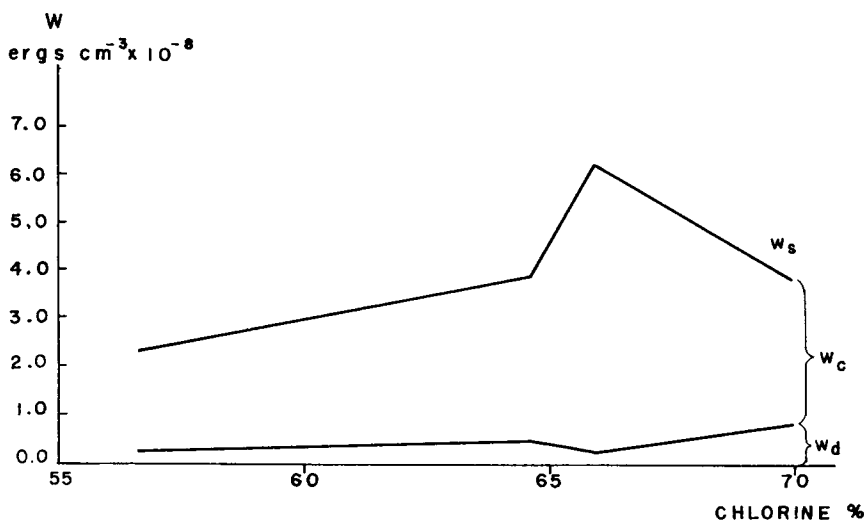


Fig. 3. Distribution of mechanical energy, accumulated and dissipated, to yield point with chlorine content at a strain rate of $3.74 \times 10^{-2} \text{ sec}^{-1}$. Values for dissipated work, W_d , conserved work, W_c , and total work, W_s , were calculated by using the eqs. 9. Observed and calculated values for W_s are given in Table III.

The total work to yield point was studied further (Table III). Figure 3 shows that from a phenomenologic point of view, the major portion of the work appeared as accumulated work, W_c . The percentage of accumulated work varied, at the highest strain rate, between 89% for PVC and CPVC, 64.6% Cl, to 78% for CPVC, 69.9% Cl; at the lowest and intermediate strain rates, between 98% and 99% for all the samples. The largest proportion of dissipated work, W_d , was evidenced by all samples at the higher strain rates, and, based on the limited data, appears to increase with increasing chlorine content.

Table II summarizes the dependance of the ratio W/δ^2 on the chlorine content at the three strain rates. The cohesive energy density, δ^2 , is energy required to overcome intermolecular forces. We consider that the cohesive energy density describes the ultimate potential energy, since, for thermo-plastic polymers, primary valence bonds are involved only to a limited extent in tensile rupture. The ratio of work to cohesive energy density is taken, then, as a measure of efficiency. The ratio W_d/δ^2 is taken as a measure of overall efficiency, while W_c/δ^2 is efficiency to yield point.

Figure 4 shows that greatest overall efficiency is exhibited by PVC and that CPVC, 69.9% Cl, is the least efficient system. At the lowest strain rate, W_d/δ^2 decreases rapidly with increasing chlorine content from 40.65% for PVC to 11.20% for CPVC, 69.9% Cl. At the highest strain rate, the value of W_d/δ^2 decreases only slightly with increasing chlorine content, except for CPVC, 69.9% Cl, which decreases to 15.5% from approximately 25%. To the yield point, the major difference between PVC and CPVC is

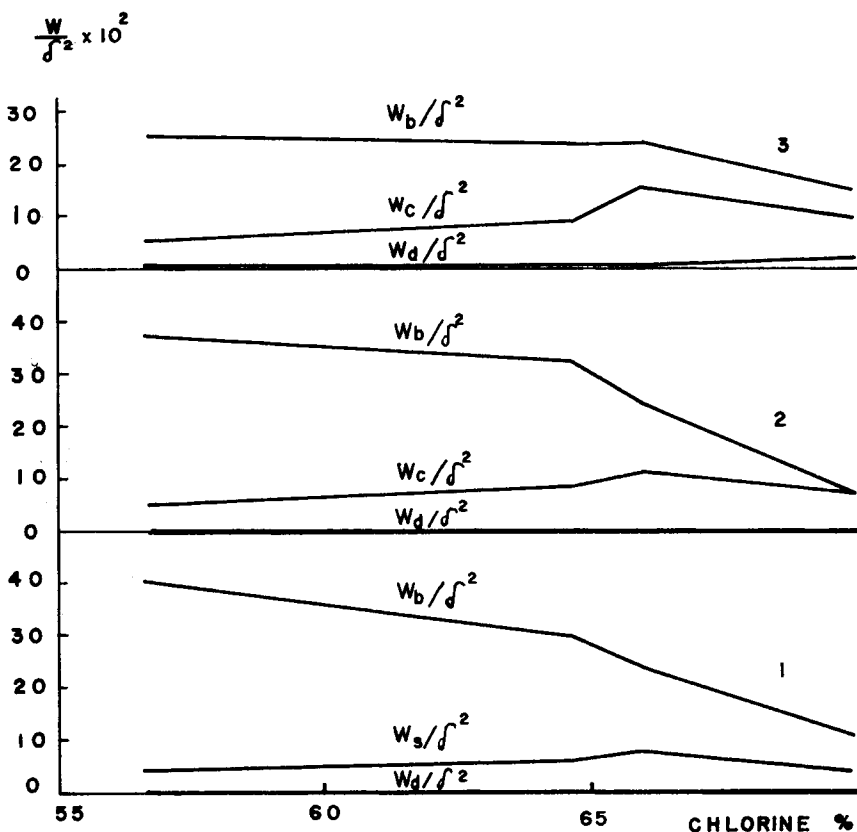


Fig. 4. Effect of chlorine content and strain rate on W/δ^2 : Numbers 1, 2, and 3 refer to strain rate as given in Fig. 1; values for W_b , work to break, W_a , dissipated work, and W_c , conserved work, are from Tables II and III; δ^2 is the cohesive energy density. The ratio W/δ^2 is a parameter reflecting the efficiency of the system.

found in W_c/δ^2 both in terms of absolute values and its proportion of overall efficiency (Table II). The results show that, except for CPVC, 69.9% Cl, W_c/δ^2 increases, and efficiency decreases, with increasing chlorine content and strain rate. Using the values obtained on PVC as figures of merit, at the lowest strain rates, for CPVC, 64.46% Cl, W_s/δ^2 increases by 48%, while it increases by 79% for CPVC, 65.9% Cl. At the higher strain rates, larger differences are observed.

Figure 5 shows the mutual dependence between the potential energy parameter, $\delta^2\phi$, and work to break for the four polymers studied at the three strain rates. At the lowest strain rate, a point is shown also for poly(methyl methacrylate) taken from data reported by Maxwell and Harrington.¹³ We used the energy-to-break results of polymer tested at 30°C at a rate of straining of 0.001 sec⁻¹ and a value for solubility parameter, δ , of 9.4 (cal/cm³)^{1/2} as an average of reported values.¹⁴ The value of ϕ was calculated as 10.05. The data show that the available amount of work to break

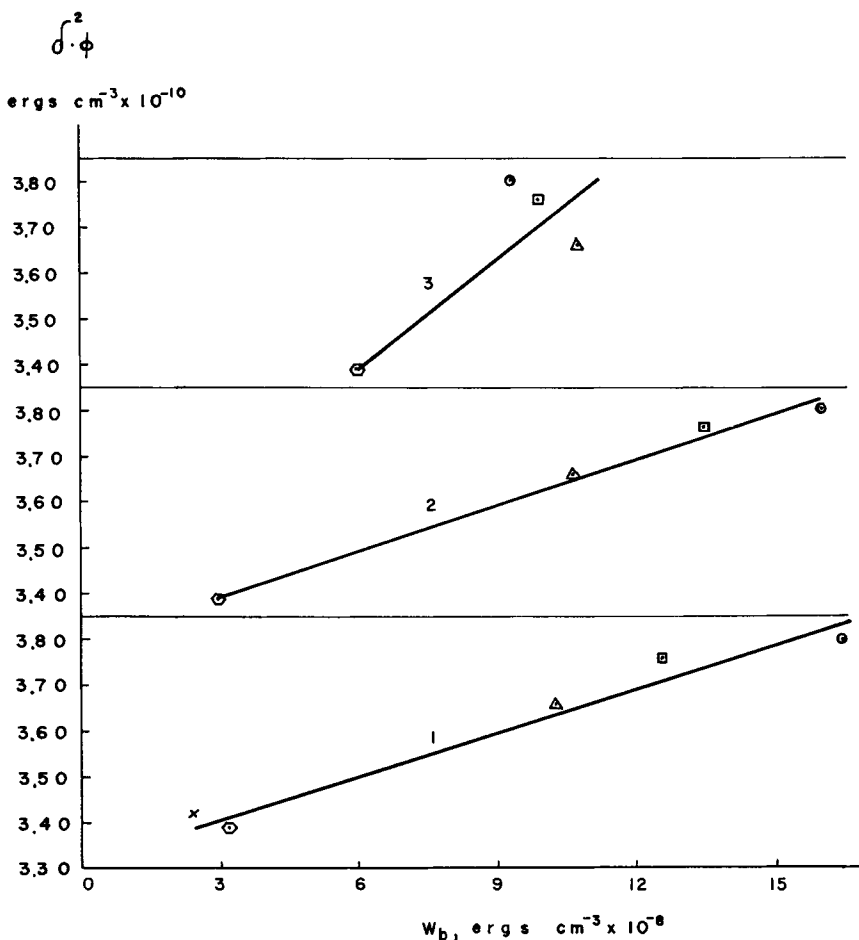


Fig. 5. Plot of potential energy parameter, $\delta^2\phi$, vs. work to break at 23°C with strain rate and polymer type; ϕ is the ratio of the total volume to the effective volume occupied by an average monomer unit; $\delta^2\phi$ is a parameter reflecting the potential energy of the system and is considered to be dependent only on the bulkiness of the substituents on the polymer chains; x -value of W_b for PMMA taken from data of Maxwell and Harrington¹² at 30°C and strain rate of $1 \times 10^{-3} \text{ sec}^{-1}$; numbers 1, 2, and 3 refer to strain rate ($\dot{\epsilon}$) as given in Fig. 1; (○) PVC; (□) CPVC, 64.6% Cl; (△) CPVC, 65.9% Cl; (○) CPVC, 69.9% Cl.

is linearly related to the potential energy parameter of the system. In the case of the lower strain rates, 3.74×10^{-4} and $3.74 \times 10^{-3} \text{ sec}^{-1}$, good agreement was obtained. At the highest strain rate, scatter was observed, although the trend is still evident. It may be that, at high strain rates, retardation phenomena may play an overriding role.

Figure 6 shows the correlation between the potential energy parameter, $\delta^2\phi$, at 23°C and the residual energy parameter. This parameter, related to the capability of the body to perform work after the yield point, was ob-

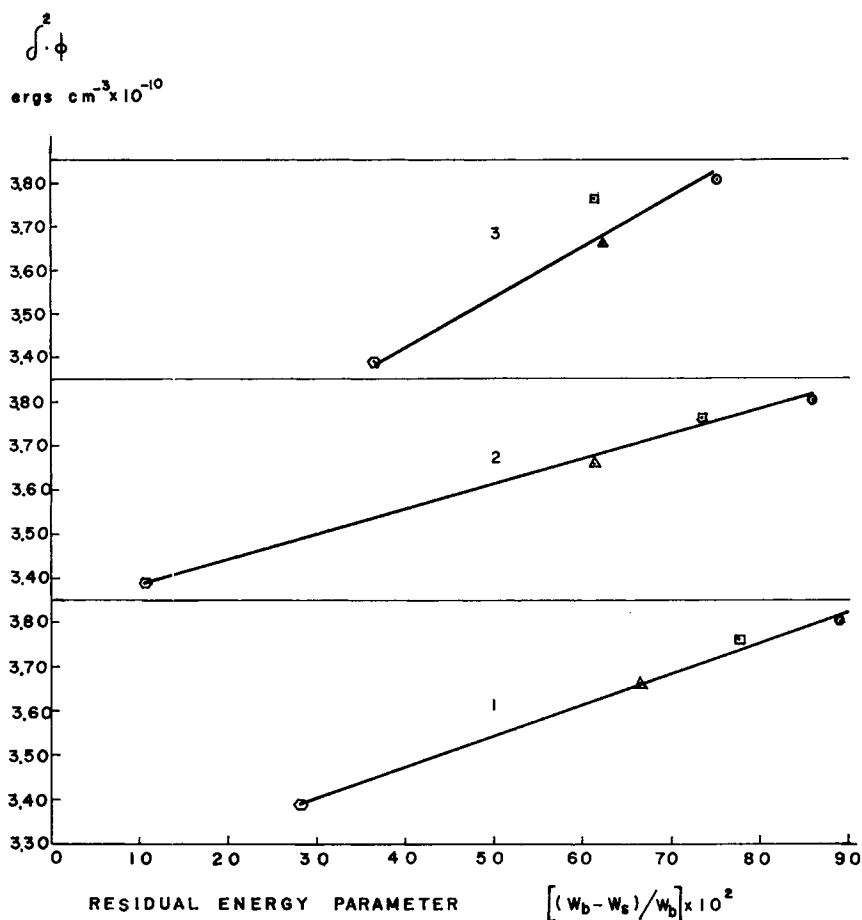


Fig. 6. Plot of potential energy parameter, $\delta^2\phi$, vs. residual energy parameter. Symbols and numbers 1, 2, and 3 refer respectively to PVC and CPVC type as given in Fig. 5 and strain rate ($\dot{\epsilon}$) as given in Fig. 1.

tained as per cent difference between the total work and work to yield point. $[(W_b - W_s)/W_b] \times 100$. The data point out that a linear relationship exists between the potential energy parameter of the bodies, $\delta^2\phi$, and the residual energy parameter. At all strain rates, a direct relationship was observed (Table II). The residual work parameter decreased in the order PVC, CPVC 64.6, CPVC 65.9, and CPVC 69.9. The capability of PVC to perform work remained high, higher than 75%, while that of CPVC 69.9 was relatively low, less than 35%. This capability was retained by the PVC sample at all strain rates that were investigated, but decreased with increasing chlorine content and strain rate.

The residual work consists mainly of the dissipated work. This work arises from the resistance of the body to viscous deformation which takes place almost exclusively after the yield point. As a result, the work that is

obtained is converted to heat. From these data it can be inferred that the resistance to breaking under rapid loading conditions would be in the order

$$\text{PVC} > \text{CPVC 64.6} > \text{CPVC 65.9} > \text{CPVC 69.9}.$$

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