# Solubility Parameters of Polymers from Swelling Measurements at 60°C

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## SYNOPSIS

The swelling behavior of the networks of natural rubber, an epoxidized natural rubber, low-density polyethylene, polystyrene, and poly(methyl methacrylate) are studied in six classes of solvents at 60°C. The data of the swelling coefficient are successfully treated by a modified version of the empirical equation proposed by Gee, as to determine the solubility parameter of a polymer, $\delta_2$. It is found that increasing the temperature would decrease the $\delta_2$'s of these polymers with a common rate of 0.02 $(J/mL)^{1/2}/K$. A semiempirical model is proposed to rationalize the present finding satisfactorily. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

Data of solubility parameter ($\delta$) have been compiled for numerous solvents and polymers.[1-3] They are particularly useful for studying the solution and bulk properties of these materials. For example, the miscibility of two components including polymer blends may be predicted if their $\delta$'s are adequately close.[4-6] Other practical implications of this important parameter have been reviewed by Barton[3] recently.

However, most of the foregoing information on $\delta$ refer to temperatures at or around 25°C, except those obtained from inverse gas chromatography (IGC). The present study offers new $\delta$ data for five distinct polymers at 60°C by means of the equilibrium swelling measurements. This would facilitate the development of a novel approach for estimating the $\delta$ of polymers above ambient temperature.

## CORRELATION OF SOLUBILITY PARAMETER AND TEMPERATURE

The $\delta$ of a liquid at the temperature $T$ may be readily computed by

$$\delta_1 = [(\Delta \bar{H}_v - RT)/\bar{V}_1]^{1/2} \qquad (1)$$

where $R$ is the gas constant; $\bar{V}_1$, the molar volume; and $\Delta \bar{H}_v$, the molar enthalpy of vaporization accessible by

$$\Delta \bar{H}_v = D - ET \qquad (1a)$$

with $D$ and $E$ being the empirical constants. Hereafter, subscript "1" refers to the liquid. In the event of the lack of information on $D$ and $E$, one could resort to

$$\delta_1 = \delta_1'[1 - 1.13\alpha_1 \Delta T] \qquad (2)$$

where $\alpha_1$ is the isothermal expansion coefficient, $\Delta T = T - T'$, and the superscript "'" refers to the temperature $T'$ hereafter. Since eq. (1) cannot be extended to polymers, and eq. (2) is, rather, based on a semiempirical approach, the following considerations are in order:

By definition, the square of $\delta$ is given by

$$\delta^2 = E_c/V \qquad (3)$$

where $E_c$ is the cohesive energy, and $V$, the volume. The quantity $E_c$ is, in turn, equal to the decrease of internal energy ($-\Delta U$). Hence, eq. (3) becomes

$$\delta^2 = -\Delta U/V \qquad (4)$$

**Table I  Preparation of Crosslinked Polymers**

| No. | Polymer Network (Designation) | Formulation | Temperature (°C) | Cure Time (h) |
|-----|-------------------------------|-------------|------------------|---------------|
| 1 | XNR | NR + BZP (10 wt %) | 140 | 3 |
| 2 | XENR | ENR 50 + DCP (5 wt %) | 140 | 3 |
| 3 | XPE | LDPE + DCP (4 wt %) | 160 | 3 |
| 4 | XPS | St. (20 mL) + DVB (0.8 mL) + BZP (0.21 g) | 80 | 96[a] |
| 5 | XPMMA | MMA (15 mL) + p-dioxane (10 mL) + EGDM (0.06 mL) + AZBN (0.45 g) | 60 | 24[a] |

[a] Vacuum-dried for 2 days at 60°C after curing.

It follows that

$$\left(\frac{\partial \delta^2}{\partial T}\right)_p = -\left(\frac{\partial \Delta U}{\partial T}\right)_p \Big/ V + \Delta U \left(\frac{\partial V}{\partial T}\right)_p \Big/ V^2 \quad (5)$$

In general, heating a material would result in volume expansion and weakening of intermolecular forces. This means that the two partial derivatives on the right-hand side of eq. (5) are positive, indicating the depression of $\delta$ at higher $T$ as confirmed experimentally later.

Manipulation of eq. (5) with the aid of the relevant thermodynamic functions yields

$$\left(\frac{\partial \delta^2}{\partial T}\right)_p + \alpha \delta^2 = -\rho \bar{c}_p \quad (6)$$

where $\rho$ is the density, and $\bar{c}_p$, the specific heat capacity at constant pressure $P$. We assume the coefficient $\alpha$ to be $T$-independent and that

$$\bar{c}_p = \bar{c}'_p + \left(\frac{\partial \bar{c}_p}{\partial T}\right)_p \Delta T \quad (7)$$

where $\bar{c}_p$ and $\bar{c}'_p$ refer to $T$ and $T'$, respectively. Now, eq. (6) is solved for the $\delta$ of a polymer to give

$$\delta_2^2 = \left\{ \delta_2'^2 - \rho_2' \Delta T \left[ \bar{c}'_{p2} + \left(\frac{\partial \bar{c}_{p2}}{\partial T}\right)_p \Delta T/2 \right] \right\}$$

$$\times \exp(-\alpha_2 \Delta T) \quad (8)$$

where the subscript "2" refers to the polymer hereafter. Equation (8) holds if $\Delta T$ is not too large.

## EXPERIMENTAL

A sample of natural rubber (NR) of grade SMR L and a 50 mol % epoxidized natural rubber (ENR 50) were supplied by the courtesy of Rubber Research Institute of Malaysia and Kumpulan Guthrie Berhad, Malaysia, respectively. Another commercial product was the low-density polyethylene (LDPE) of melt flow index 0.3. Dicumy peroxide (DCP), benzoyl peroxide (BZP), and azobisisobutyronitrile (AZBN) were purchased from BDH, Merck, and Kasei (Tokyo), respectively. They were recrystallized, respectively, from ethanol, chloroform/methanol (13 : 1), and methanol. Styrene (St) and methyl methacrylate (MMA) obtained from Fluka were purified by vacuum-distillation and kept in a refrigerator before use. Divinylbenzene (DVB) and ethylene glycol dimethacrylate (EGDM) as well as all the solvents were supplied by Fluka, except 1-butanol, which was obtained from BDH. The solvents were of reagent grade and used as received and so were the crosslinking agents.

Table I lists the formulations and conditions for preparing the crosslinked polymers. Samples of NR and ENR50 were mixed with their respective initiators on a twin-roll mill, while both LDPE and DCP were first dissolved in p-xylene at 90°C. The solvent was removed under reduced pressure at ambient temperature. These mixtures were heated at the designated temperatures in a hot press between two aluminum foils. The polymerization and curing of St and MMA were performed in the sealed containers under nitrogen atmosphere. The vulcanizates were extracted with boiling butanone (for XNR and XENR) and toluene (for XPE, XPS, and XPMMA) for ca. 4 h. At last, the samples were vacuum-dried at 60°C for 3 days.

The swelling measurements were performed on the vulcanizates, using a series of solvents covering

**Table II    Thermodynamic Properties of Various Solvents at 60°C**

| No. | Solvent | $\alpha_1 \times 10^3$ (K$^{-1}$) | $\delta_1$ (J/mL)$^{1/2}$ | $\bar{V}_1$ (mL/mol) | $\Delta \bar{H}_v{}^a$ (kJ mol$^{-1}$) |
|-----|---------|------|------|------|------|
| 1 | 2-Butanone | 1.28 | 17.8 | 94.4 | 32.58 |
| 2 | $p$-Xylene | 1.08 | 17.2 | 128.6 | 40.73 |
| 3 | $n$-Butyl acetate | 1.13 | 17.4$^b$ | 138.1 | (40.65)$^c$ |
| 4 | 1,4-Dioxane | 1.09 | 19.2$^d$ | 89.1 | (36.61) |
| 5 | Carbon tetrachloride | 1.21 | 16.6 | 101.4 | 30.71 |
| 6 | Toluene | 1.09 | 17.3 | 111.1 | 36.13 |
| 7 | $n$-Hexane | 1.37 | 13.9 | 138.4 | 29.41 |
| 8 | $n$-Butyl chloride | 1.23 | 16.1 | 109.8 | 31.38 |
| 9 | 1-Butanol | 0.93 | 22.1$^e$ | 95.1 | (39.29) |
| 10 | Chloroform | 1.24 | 17.5 | 84.7 | 28.74 |

$^a$ Computed by eq. (1a) unless specified, otherwise.

$^b$ 1.2 (J/mL)$^{1/2}$ is added to the value computed by combining eqs. (1) and (2) (Ref. 3, p. 111).

$^c$ Values in the parentheses refer to $\Delta \bar{H}_v$ at 25°C computed by $\Delta \bar{H}_v$ (J·mol$^{-1}$) = $-12340 + 99.2 T_b + 0.084 T_b^2$, where $T_b(K)$ is the normal boiling point (Ref. 3, p. 110).

$^d$ Computed by combining eqs. (1) and (2).

$^e$ 2.9 (J/mL)$^{1/2}$ is added to the value computed by combining eqs. (1) and (2).

a practical range of $\delta_1$'s. In a typical run, a piece of sample weighing about 0.3 g was immersed in a test liquid for about 1 week in an oven at 60 ± 2°C. After being surface-dried, the swollen polymer was weighed in a closed vessel. This procedure was repeated daily in order to achieve the equilibrium or maximum weight ($W_e$) for the sample. The swelling coefficient ($Q$) was computed by

$$Q = (W_e - W_0)/\rho_1 W_0 \qquad (9)$$

where $W_0$ is the initial weight of the sample, and $\rho_1$, the density of the solvent at 60°C. A linear least-squares method was applied to process the data.

## RESULTS AND DISCUSSION

The values of $\delta_1$ at 60°C for a total of 10 solvents used are computed by eqs. (1) and (2) using the literature data of $\alpha_1$, $D$, and $E$.[7,8] They are displayed in Table II, together with other relevant information.

A distinct feature of the swelling tests is that they provide a simple means to estimate $\delta_2$ by a Gaussian function after Gee.[9] The original expression can be readily modified to

$$Q = Q_m \exp[-\kappa \bar{V}_1 (\delta_1 - \delta_2)^2 / RT] \qquad (10)$$

where $Q_m$ is the maximum $Q$, and $\kappa$, an empirical constant. Accordingly, a plot of $[(RT \ln Q_m/Q)/\bar{V}_1]^{1/2}$ against $\delta_1$ would result in a straight line with gradient $S$ and intercept $I$. Figure 1 demonstrates
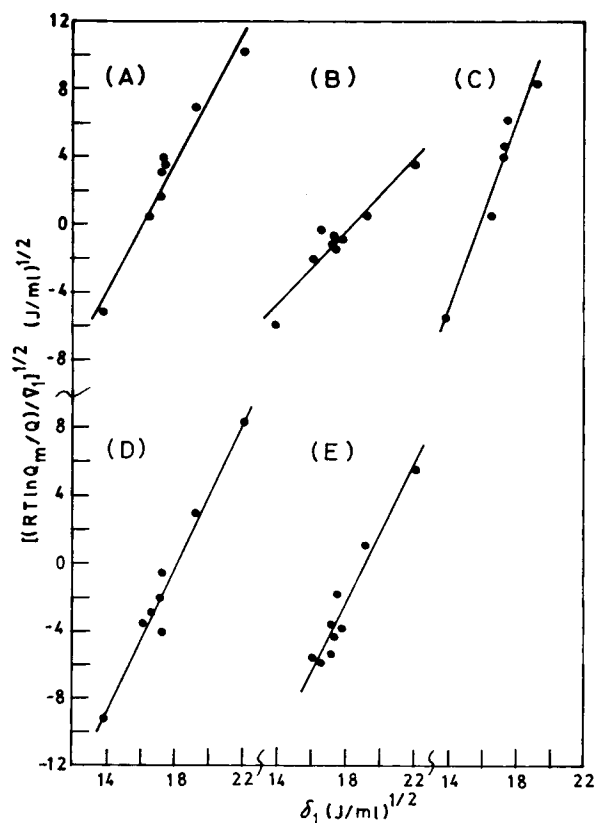


**Figure 1**    Linear plots of $[(RT \ln Q_m/Q)/\bar{V}_1]^{1/2}$ against $\delta_1$ for (A) XNR, (B) XENR50, (C) XPE, (D) XPS, and (E) XPMMA. All at 60°C.

**Table III  Results of Swelling Measurements of Various Polymers at 60°C**

| No. | Polymer Network | $\delta_2$ $(J/mL)^{1/2}$ | $\kappa$ | $Q_m$ (mL/g) | $r^a$ | $N^b$ |
|---|---|---|---|---|---|---|
| 1 | XNR | 16.0 | 3.57 | 20.0 | 0.9727 | 8 |
| 2 | XENR | 18.3 | 1.11 | 6.5 | 0.9507 | 9 |
| 3 | XPE | 15.8 | 7.44 | 3.0 | 0.9688 | 6 |
| 4 | XPS | 18.1 | 4.55 | 2.0 | 0.9763 | 8 |
| 5 | XPMMA | 19.2 | 4.11 | 6.0 | 0.9632 | 9 |

[a] Correlation coefficient.
[b] Sample population.

such linear plots for the five systems of interest, with the results shown in Table III. Here, the solvents are judiciously chosen in order that the resulting correlation coefficients are close to unity as noted in the table. The parameters $\delta_2$ and $\kappa$ are computed by $\delta_2 = -I/S$ and $\kappa = S^2$. The latter is a dimensionless quantity, with values varying approximately from 1 to 8 and may roughly depict the kurtosis of the Gaussian curve defined by eq. (10). This implies that among the thermosets in Table III, the XPE with the highest $\kappa$ would exhibit the sharpest peak when $Q$ is plotted against $\delta_1$.

In fact, the swelling behavior of four of the foregoing polymers has been observed at lower temperatures by other workers. Applying the present algorithm to these studies by plotting $[(RT \ln Q_m/Q)/\bar{V}_1]^{1/2}$ against $\delta_1$ leads to the results presented in Table IV. Although Bristow and Watson[10] employed a wide spectrum of solvents to swell the cured rubber, the pertaining plot is grossly scattered, due to the considerable difference in the specific inter-

actions between the polymer segments and solvent molecules. As such, only 17 data points derived from the hydrocarbons and some other solvents common to those listed in Table II were chosen for the present purpose to yield a reasonable $r = .9248$. Improved linear relationships are apparent for the two samples of semicrystalline LDPE studied by Richards.[11] The same situation is observed for a glassy PS[12] and the two crosslinked PMMAs prepared by using the same curing agent EGDM[13] as in the present study, but in higher concentrations.

As noted, it is important to employ the appropriate solvents, which would produce the coherent $Q$ data, to ensure the success of the present method. Tables III and IV further reveal that the $\delta_2$ of a polymer changes primarily with $T$, whereas $\kappa$ and $Q_m$ depend not only on $T$ but also its molecular parameters. Apparently, the parameter $Q_m$ increases with increasing average crosslinking density, if the latter is not too large. The low-temperature $\delta_2$ values do compare favorably with those cited in the literature

**Table IV  Results of Swelling Measurements of Various Polymers at Low Temperatures From the Literature**

| No. | Polymer/Crosslinking Polymer | $\delta_2$ $(J/mL)^{1/2}$ | $\kappa$ | $Q_m$ (mL/g) | $r$ | $N$ | Solvents[a] | $T$ (°C) | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| 1 | NR + DCP (3%) | 16.7 | 4.75 | 7.20 | 0.9248 | 17 | (1)–(5) | 25 | 10 |
| 2 | LDPE $(0.94 \times 10^4)^b$ | 16.6 | 2.65 | 0.45 | 0.9989 | 10 | (1)–(3), (7), (8) | 20 | 11 |
| 3 | LDPE $(1.4 \times 10^4)^b$ | 16.6 | 2.67 | 0.25 | 0.9780 | 10 | As above | 20 | 11 |
| 4 | PS (commercial grade, $M_n = 1.25 \times 10^5$, $M_w = 3.9 \times 10^5)^c$ | 18.7 | 1.88 | 1.50 | 0.9791 | 16 | (1), (4), (6)–(9) | 23 | 12 |
| 5 | MMA + EGDM (0.5 vol %) | 19.9 | 4.97 | 12.40 | 0.9609 | 8 | (4) | 20 | 13 |
| 6 | MMA + EGDM (1.0 vol %) | 19.8 | 6.82 | 12.00 | 0.9799 | 7 | As above | 20 | 13 |

[a] Classes of solvents used: (1) alkanes, (2) aromatic hydrocarbons, (3) halohydrocarbons, (4) esters, (5) ketones, (6) ethers, (7) nitrocompounds, (8) alcohols, and (9) Si compounds.
[b] Nominal molecular weight.
[c] $M_n$ = number-average molecular weight, $M_w$ = weight-average molecular weight.

and are shown in Table V. We believe that the former obtained by the linear least-squares treatment are more reliable, and, hence, they will be utilized for the ensuring exercise.

It has been shown for polymers exhibiting relatively weak intermolecular forces[16] that

$$\delta_2^3 = 59 T_g / \sqrt{C_\infty} \quad (\text{J/mL})^{3/2} \quad (11)$$

where $T_g$ is the glass-transition temperature, and $C_\infty$, the characteristic ratio. Roland[14] estimated the $C_\infty$ and $T_g$ for ENR50 to be 5.0 and 260 K, respectively, leading to $\delta_2 = 19.0$ (J/mL)$^{1/2}$ via eq. (11). Since there is no experimental value of $\delta_2$ available for this particular copolymer,[17] the foregoing figure is accepted tentatively and included in Table V.

The present study utilizes eq. (8) to predict the $\delta_2$. In this connection, Table V shows the relevant thermodynamic data. At 333.2 K, the estimated $\delta_2$'s for NR, ENR50, LDPE, PS, and PMMA are, respectively, found to be 14.5, 16.9, 14.5, 17.3, and 18.1 (J/ml)$^{1/2}$. Clearly, these values are consistently lower than are the corresponding ones determined by experiments (Table III) with the standard deviation of the differences between the two sets of results equal to 1.2 (J/mL)$^{1/2}$. Hence, the foregoing figure is added to the value of $\delta_2$ computed by eq. (8), as a practical means to correct for the inadequacy of the proposed model. It follows that

$$\delta_2 = 0.035 \Delta T$$

$$+ \left\{ \delta_2'^2 - \rho_2'^2 \Delta T \left[ \bar{c}_{p2}' + \left( \frac{\partial \bar{c}_{p2}}{\partial T} \right)_p \Delta T / 2 \right] \right\}^{1/2}$$

$$\exp(-\alpha_2 \Delta T / 2) \quad (12)$$

where $T' = 298$ K. Equation (12) predicts the $\delta_2$ (J/mL)$^{1/2}$ values with an average deviation of ca. 2% in the present study.

It has been established that $\delta_1$ varies with $T$ (Ref. 18) according to

$$\delta_1 = mT + b \quad (13)$$

where $m$ and $b$ are the empirical constants. For $C_3$ and $C_5$ hydrocarbons, the values of the coefficient $m$ reportedly vary from $-0.018$ to $-0.041$ (J/ml)$^{1/2}$/K. If eq. (13) is applied to the polymer with $\delta_2$ replacing $\delta_1$, the present results (Tables III and IV) indicate that

$$\delta_2 = \delta_2' - 0.02 \Delta T \quad (14)$$

where $T' = 298$ K. Although eq. (14) agrees remarkably well with experiments at least for the five polymers reported in this work, its thermodynamic origin is obscure and, hence, should be used with caution.

In conclusion, we have demonstrated a simple method to determine the $\delta_2$ above ambient temperature, i.e., by swelling tests. Unlike the IGC which only operates above the $T_g$, this particular technique works equally well for both rubbery and glassy polymers. The present study observes that $\delta_2$ decreases linearly with increasing $T$. However, this feature seems to defy a precise thermodynamic description.

**Table V  Thermodynamic Characteristics[a] of Various Polymers Cited in the Literature**

| No. | Polymer | $\delta_2'$ (J/mL)$^{1/2}$ | $\rho_2'$ (g/mL) | $\alpha_2 \times 10^4$ (K$^{-1}$) | $\bar{c}_{p2}'$ (J/g K) | $\left(\frac{\partial \bar{c}}{\partial T}\right)_p \times 10^3$ (J/g K$^2$) |
|---|---|---|---|---|---|---|
| 1 | NR | 16.6[b] | 0.913 | 6.70 | 1.91 | 3.54 |
| 2 | ENR50[c] | 19.0 | 1.01[d] | 6.20 | 1.87 | 2.25 |
| 3 | LDPE | 16.2[e] | 0.925 | 5.30 | 1.76[f] | 5.28[f] |
| 4 | PS | 18.8[e] | 1.05 | 2.86 | 1.22[f] | 4.15[f] |
| 5 | PMMA | 19.4[g] | 1.19 | 2.50 | 1.42 | 4.50 |

[a] Unless specified otherwise, data are obtained from Ref. 1 as follows: L. A. Wood, p. V-7 for NR; R. P. Quirk and M. A. A. Alasmarraic, p. V-15 for LDPE; J. F. Rudd, p. V-81 and P. Zoller, p. V-475 for PS; and W. Wunderlich, p. V-77 for PMMA.
[b] Ref. 10.
[c] All data except $\delta_2'$ and $\rho_2'$ for ENR50 are estimated by methods detailed in Ref. 2, Chaps. 4 and 5.
[d] Ref. 14.
[e] Ref. 15.
[f] Ref. 2, chap. 5.
[g] Ref. 13.

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