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Solubility Parameters and Some Structural Characteristics of Chlorinated Poly(vinyl Chloride)

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Synopsis

Measurements of solubility parameters of a series of chlorinated poly(vinyl chloride) (CPVC) samples were carried out. A maximum value of solubility parameter occurs at a chlorine content of 63–65% and is related to optimum packing.

INTRODUCTION

As is known, the solubility parameter is a quantity equal to the square root of the cohesive energy density, $\delta = (E/V)^{1/2}$. It is a characteristic not only of solubility behavior but also of other properties of polymers. For example, it is known[1] that the glass transition temperature (T_g) of polymers, among others, is a function of their solubility parameters.

In this work, measurements were made of the solubility parameters and densities of a series of chlorinated hydrocarbon polymers containing between 56% and 74% chlorine.

A method of measuring solubility parameters by turbidimetric titrations is described in the literature.[2–5] The method is based on the titration of a polymer solution with two nonsolvents, one with a high solubility parameter (δ_{2h}) and the other with a low value (δ_{2l}).

When the interaction between solvent and polymer is small compared with the interaction between solvent and nonsolvent, the solubility parameter of the polymer, δ_3, can be obtained by

$$\delta_3 = [(V_{ml})^{1/2}\delta_{ml} + (V_{mh})^{1/2}\delta_{mh}]/[(V_{ml})^{1/2} + (V_{mh})^{1/2}]. \qquad (1)$$

When the polymer interacts preferentially with the solvent, its solubility parameter may be expressed by

$$\delta_3^* = \delta_{ml} + (V_{mh}/V_{ml})^{1/2}(\delta_{mh} - \delta_1) \qquad (2)$$

where $\delta_m = \psi_1\delta_1 + \psi_2\delta_2$, the subscripts *mh* and *ml* represent the mixture of solvents with high and low values of δ, 1, 2, and 3 refer to solvent, nonsolvent, and polymer, respectively, ψ is the volume fraction, and V is the molar volume. The solubility parameter is evaluated by measuring the volume fraction of the solvent and nonsolvent at the cloud point.

EXPERIMENTAL

Studies were conducted on commercially available samples of chlorinated polyethylene (ICI, Haloflex PE-242, -235, and -227), poly(vinyl chloride) (Frutarom, Haifa, Epivyl-32 and -46), CPVC (ICI, Genclor 8), and laboratory-prepared samples of chlorinated polyethylene and CPVC obtained by chlorination of powdered material. The properties of PVC and CPVC samples are summarized in Table I. Chlorine analyses were performed by Israel Mining Industries, Institute for Research & Development Ltd., Haifa, Israel.

In order to determine solubility parameters, solutions were prepared containing 0.1 g polymer per 100 ml cyclohexanone. The solutions were titrated by nonsolvents, one of which was characterized by a high solubility parameter (methanol, δ_{2h} = 14.54 (cal/cm^3)$^{1/2}$; V_{2h} = 40.7 cm^3/mol) and the other, by a low solubility parameter (*n*-heptane, δ_{2l} = 7.45 (cal/cm^3)$^{1/2}$; V_{2l} = 147.5 cm^3/mole). Chemically pure grade solvents (Frutarom, Haifa) were used as received. Cloud points were observed visually. Duplicate measurements were made; reproducibility was within 0.2%.

Density determinations (Fig. 2) of polyethylene, chlorinated polyethylene, and chlorinated poly(vinyl chloride) were made on samples prepared by powder pressing. Since no additives were used, pressing conditions were mild. A small quantity of powdered polymer was allowed to fuse for a few seconds on a hot plate whose top was covered with aluminum foil. Density

TABLE I
Properties of Investigated CPCV Samples

Sample	Chlorine content,[a] %	$[\eta]$[b]	MW[c]	δ, (cal cm^{-3})$^{1/2}$
Epivyl 32	56.7	0.815	70,700	9.41
	60.4			9.85
Chlorinated	62.5			9.90
Epivyl 32	63.7			9.90
	65.9			9.80
	68.0			9.65
Epivyl 46	56.7	1.420	125,000	9.71
	59.6	1.386		9.86
	63.0	1.126	101,000	9.75
Chlorinated	65.5	1.050		9.87
Epivyl 46	67.1	1.080	90,000	9.75
	68.9	0.900		9.77
	73.2	0.455	47,000	
	74.0	0.350	59,000	9.25

[a] Determined by Analytical Department, Israel Mining Industry, Institute for Research & Development, Ltd.

[b] Intrinsic viscosity, measured in cyclohexanone at 23°C in Ubbelohde viscometer.

[c] Molecular weight of CPVC, determined by ultracentrifuge and diffusion measurements of cyclohexanone solutions.

was determined by titration of a zinc chloride solution with water or water with methanol. The density of the final solution was determined with a hydrometer; reproducibility was within 0.1%.

DISCUSSION

The solubility parameter data indicate that a maximum value occurs at an approximate chlorine content of 63%. Figure 1 illustrates the change of solubility parameter with chlorine content as calculated by means of eqs. (1) and (2). A statistical analysis (by M. Goldberg, Applied Mathematics Department, Centre for Industrial Research, Haifa) indicates that a maximum value for δ_3*, eq. (2), has a small probability. The technique used was

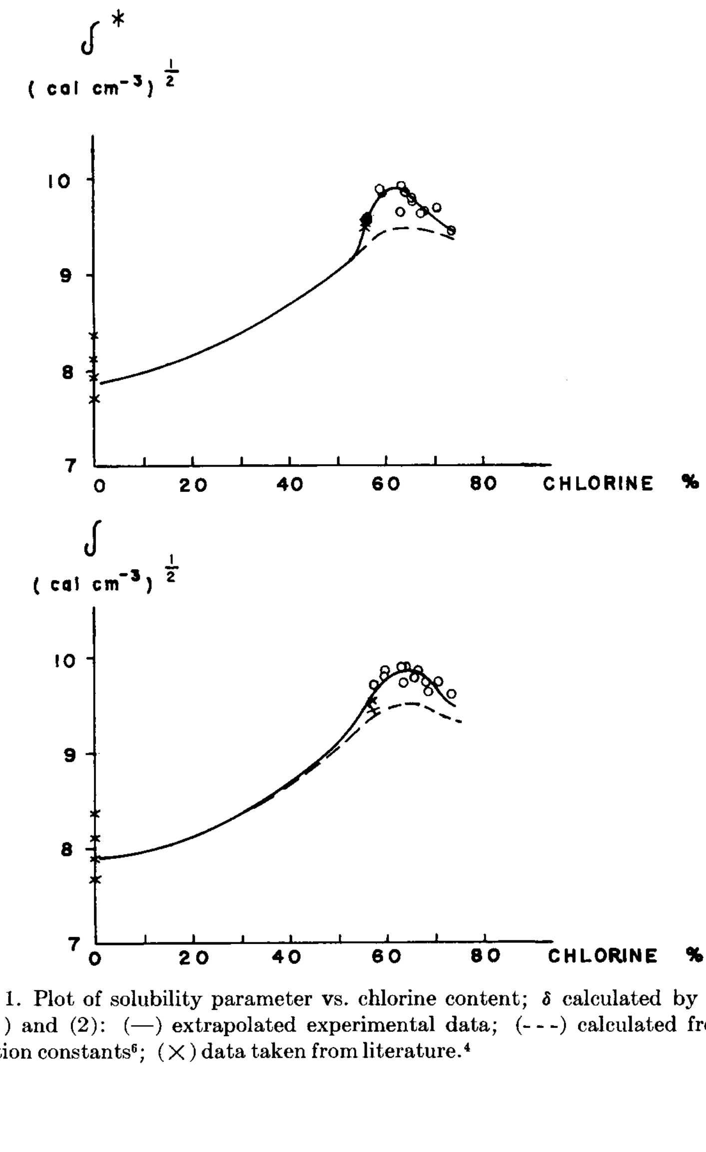

Fig. 1. Plot of solubility parameter vs. chlorine content; δ calculated by means of eqs. (1) and (2): (—) extrapolated experimental data; (- - -) calculated from molar attraction constants[6]; (×) data taken from literature.[4]

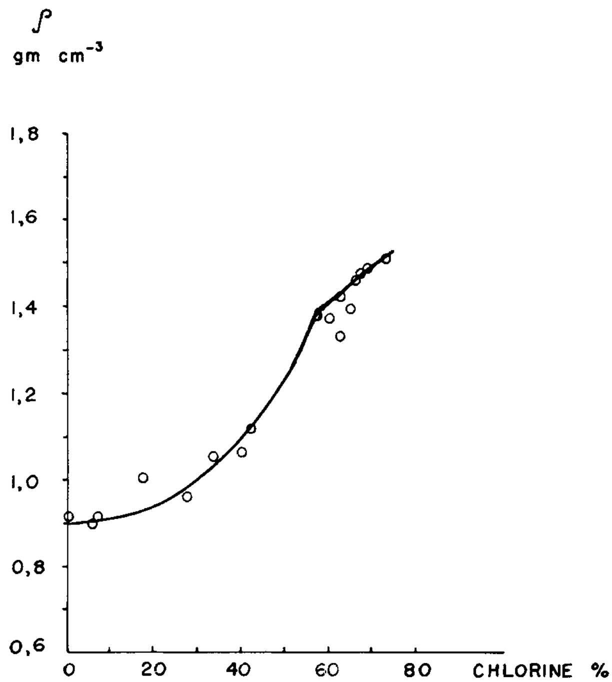

Fig. 2. Density vs. chlorine content for polyethylene, chlorinated polyethylene, poly(vinyl chloride), and chlorinated poly(vinyl chloride).

to fit to a least-squares quadratic equation to the δ_3 and δ_3^* data obtained on PVC and CPVC. An F-test was used to compare the residual variance after the quadratic equation was fitted to the data and to the variance resulting from the arithmetic mean. The quadratic equation was statistically significant for δ_3 only (F-ratio significant at the 97% level); for this parameter the equation gave a maximum value of 9.88 and 63.4% chlorine.

The evaluation of δ_3 from "molar attraction constants"[6,7] and density measurements also indicates the existence of a maximum value at 63% chlorine. These results indicate that the values of δ_3 are correct and that the polymer does not interact preferentially with cyclohexanone. The results given in Table I show again that the materials prepared by chlorination of poly(vinyl chloride) exhibit an almost linear decrease in molecular weight with increasing chlorine content.

From results of density measurements (Fig. 2), the quantity $V_\rho = M_0/N_A\rho$ (M_0 = monomer molecular weight, N_A = Avogadro's number) was evaluated. V_ρ could be taken as proportional to the total volume occupied by a monomer unit of the polymer. The quantity V_c, proportional to the volume occupied by the atoms forming the monomer, was evaluated as the sum of the volumes occupied by spheres with radii equal to the covalent radii of the atoms in the monomer unit (H = 0.136×10^{-24} cm^3, C = 1.87×10^{-24} cm^3, Cl = 4.00×10^{-24} cm^3). Thus, for PVC

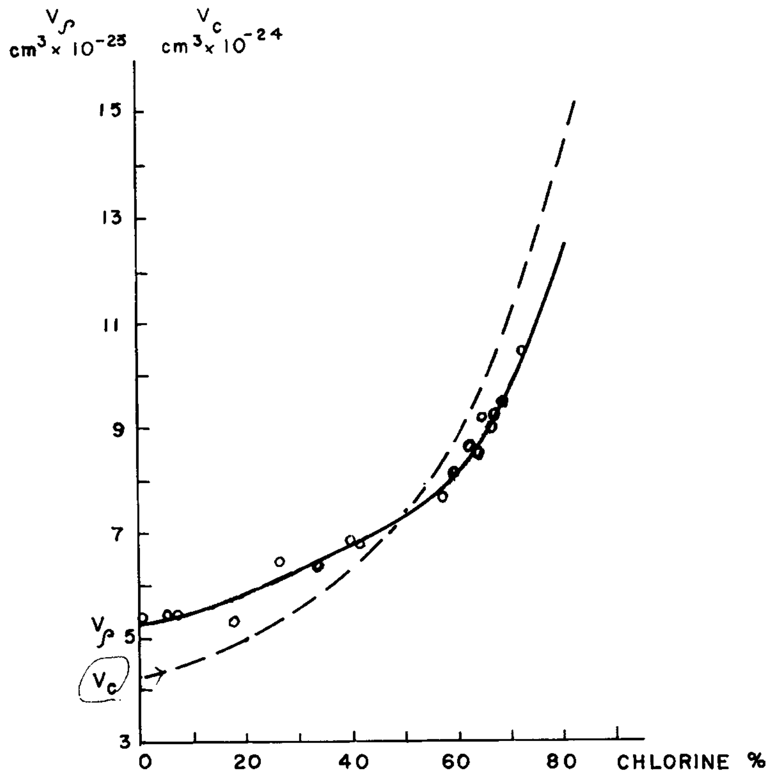

Fig. 3. Variation of V_ρ and V_c with chlorine content: (—) $V_\rho = M_0/N_A\rho$, where M_0 is the monomer molecular weight, N_A is Avogadro's number, and ρ is density (Fig. 2); (- - -) $V_c = 4/3\ \pi\Sigma r_{ci}^3$, where r_{ci} is the covalent radius of i species. The variations of the degree of packing of the monomer unit in the polymer owing to configuration and bulkiness of the atoms is reflected by the variations of the values V_ρ and V_c.

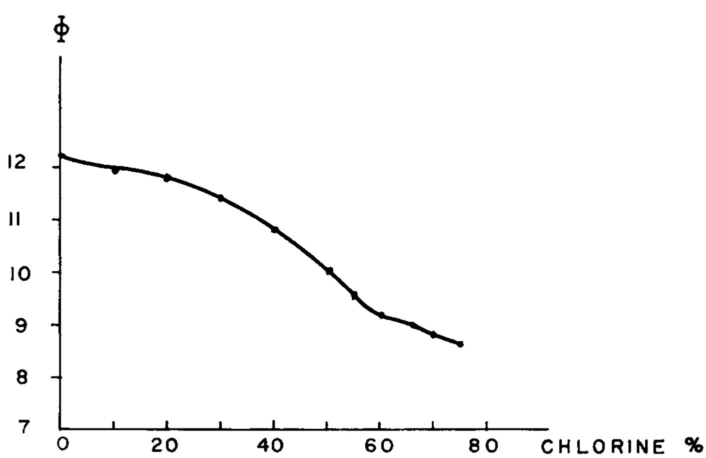

Fig. 4. Plot of $\phi(= V_\rho/V_s)$ vs. chlorine content. Value of ϕ is a criterion selected to indicate the extent of packing and shape of the molecules.

(—CH_2CHCl—), V_c is equal to 8.148×10^{-24} cm^3 and V_p is equal to 9.45×10^{-23} cm^3. The value $\phi = V_p/V_c$ is a criterion selected to indicate the extent of packing and shape of the molecules. Figure 3 shows the variations in V_p and V_c with chlorine content, and Figure 4 shows a plot of the ratio V_p/V_c versus chlorine content. The change in ln ϕ with glass transition temperature is shown in Figure 5.

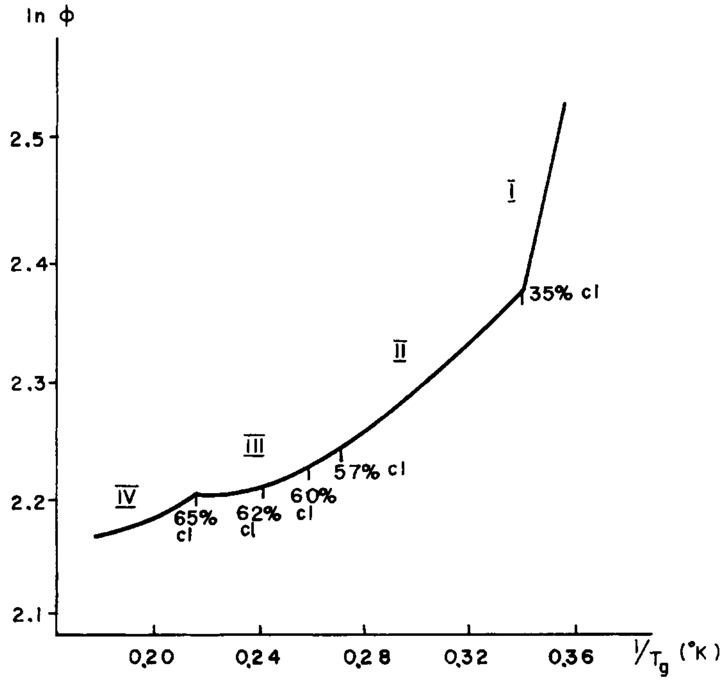

Fig. 5. Variation of ln ϕ vs. reciprocal of glass transition temperature; T_g data taken from Oswald and Kubu.[9] The first part of the curve I is linear to 35% chlorine. The beginning (at ca. 60% chlorine) of the second part (II) is still linear. The third part (III), from ca. 60% to ca. 65%, corresponds to maximum packing and to the maximum value of solubility parameter δ. The fourth part of the curve (IV) corresponds to the very highly chlorinated PVC, for which the solubility parameter decreases.

Figure 4 shows that, as the chlorine content increases, a distinct change in the nature of the packing occurs in the transition from chlorinated polyethylene to PVC and in CPVC containing approximately 63% chlorine; this change has an effect on the solubility parameter (Fig. 1), on density (Fig. 2), and on apparent segmentation in Figure 5.

CONCLUSIONS

1. A maximum of solubility parameter is by inhibited chlorinated poly(vinyl chloride) at 63–65% chlorine content.
2. The existence of this maximum is related to optimum packing.

Samples of chlorinated polyethylene were prepared by N. Sofer (Israel Mining Industries). CPCV was prepared by G. Salee. Molecular weight measurements were made by H. Silberstein, The Israel Institute of Technology (Technion). Solubility parameter and density measurements were made with the technical assistance of D. Davidi, H. Ohana, and F. Gutman. The author is indebted to Dr. M. Goldberg for the statistical analysis and to Dr. D. Henis, Dr. L. Shorr, Dr. J. Waterman, and B. Schneier for helpful comments.

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