A Comparison of Methods for Assessing the Degree of Interaction Between Plasticizers and Poly(vinyl Chloride)

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Synopsis

The Hildebrand solubility parameter δ, the Flory-Huggins interaction parameter χ, dilute-solution viscosities, apparent melting temperatures, and the equilibrium swelling of poly(vinyl chloride) (PVC) granules in plasticizer are compared as methods for assessing the degree of PVC–plasticizer interaction. Results from the empirical methods agree well with each other, but not with δ or χ. A quantitative activity parameter α, derived from χ, correlates well with all results other than δ values. A relative order of plasticizer solvent power has been established for nine plasticizers of widely differing structures and activities.

INTRODUCTION

A knowledge of the interaction between plasticizers and poly(vinyl chloride) (PVC) is basic to the understanding of more complex processes such as the behavior of pastes and the gelation and extrusion of plasticized compounds. Considerable work is reported in the literature on polymer–plasticizer interaction[1–43] and on the development of methods for its assessment. These include empirical methods based on dilute-solution viscosities[6,7] or on the temperature at which a mixture of polymer and diluent undergoes an apparent phase change, for example, the "clear point" of Graham and Derby,[36] the "dissolving temperature" of Luther et al.,[37] and the "critical solution temperature" of Thinius.[32] Theoretical approaches based on solution thermodynamics have led to the Hildebrand solubility parameter δ and the Flory-Huggins interaction parameter χ.

The empirical methods, while they give results which are in broad agreement with each other, are difficult to apply to the understanding of more complex problems because of their qualitative nature. As for the theoretical approaches, it is inherent in the derivation of the Hildebrand solubility parameter that it is most successful when applied to polymer–diluent interactions which are nonpolar. The Flory-Huggins interaction parameter, based on statistical thermodynamics, agrees well with observed PVC-plasticizer compatibilities,[10,35,38] but has not been shown to relate to plasticizer solvent power or to the processing behavior of plasticized PVC.

The purpose of the present work was to compare methods of assessing

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PVC–plasticizer interaction, and to establish the extent of agreement and, if possible, a reliable index (preferably quantitative) of plasticizer solvent power.

EXPERIMENTAL

Materials

The poly(vinyl chloride) used in this work was Corvic D65/02 (Imperial Chemical Industries Ltd., Plastics Division). All plasticizers were of commercial quality and were used as received. Their full names, abbreviations, and sources of supply are listed below:

Dioctyl adipate (DOA) and dioctyl sebacate (DOS): Ciba-Geigy Ltd.; Cereclor S 52 (S52): Imperial Chemical Industries Ltd.; trioctyl trimellitate (TOTM): Chas. Pfizer and Co.; butyl benzyl phthalate (BBP) and dibutyl phthalate (DBP): Lankro Chemicals Ltd.; dioctyl phthalate (DOP): BP Chemicals International Ltd.; octyl diphenyl phosphate (ODP): Monsanto Chemicals Ltd.; Mesamoll (MM): Bayer Chemicals Ltd.

Methods

Equilibrium Swelling. Microscope slides with granules of PVC polymer suspended in an excess of plasticizer were heated in an air-circulating oven maintained at 74°C.

The slides were examined daily, and the increase in area determined from photomicrographs (100×) using a planimeter. Heating was continued until no further expansion was evident (about 48 hours).

Dilute-Solution Viscosity (μ). The viscosities of PVC solutions, ranging in concentration from 0.2 to 3.0 g/l. in tetrahydrofuran (THF)/plasticizer (1:1 by volume) were determined using a U-tube viscometer calibrated against a standard sucrose solution.

The results were plotted as reduced viscosity against concentration and the intrinsic viscosity estimated from these graphs:

$$\mu_{reduced} = \frac{\mu_{solution} - \mu_{solvent}}{\mu_{solvent}} \frac{1}{C}$$

where μ is the viscosity in centipoises and C is the concentration of polymer in g/l.

$$\text{intrinsic viscosity} = \mu_{reduced} \lim_{C \to 0}$$

Apparent Melting Temperature (T_m). Individual granules of PVC powder, chosen to be roughly equidimensional, were suspended in an excess of plasticizer and examined by transmitted-light hot-stage microscopy. The temperature was increased by 10°C/min to 30°C below the apparent melting temperature, and then by 1°C/min.

The hot-stage used was a Mettler FP2, which has a low thermal capacity and high thermal stability. Good contrast was achieved using a Wollaston

prism in conjunction with a polarizing microscope, and could be further improved by electronic processing and display on a TV monitor screen.

RESULTS AND DISCUSSION

Equilibrium Swelling

The simplest method of determining solvent power would be to measure the solubility of PVC in the plasticizer. This is, however, impractical for most plasticizers (especially secondary plasticizers) because of their very poor solvent action on PVC. We have, therefore, considered the converse system, i.e., the solubility of plasticizer in polymer, and assumed that the greater the interaction the greater will be the swelling of PVC granules when heated in an excess of plasticizer.[44]

The results are shown in Table I.

TABLE I
The Equilibrium Swelling of PVC Granules in Plasticizer (at 74°C)

Plasticizer	Average increase in area of granule, %
DOS	15
S52	21.7
TOTM	22.4
DOA	28.6
DOP	42
MM	44.5
BBP	72
ODP	373
DBP	384

The results are consistent with qualitative ideas of plasticizer activity; secondary plasticizers such as DOS and S52 causing little swelling, DOP intermediate, and "active" plasticizers such as BBP and DBP causing most swelling.

Dilute-Solution Viscosity

Dilute-solution viscosities have been used to assess the solvent power of liquids for a variety of polymers. It is assumed that liquids with high solvent power for the polymer cause an expansion of the chain above random coil dimensions and therefore increase the resistance to flow.[45] For liquids of low solvent power, polymer–polymer and diluent–diluent interactions are preferred, and hence the polymer chains remain more tightly coiled.

The reduced viscosity/concentration curves in THF/plasticizer solution are shown in Figures 1 and 2. Frith[7] used cyclohexanone/plasticizer in an earlier study, but in our hands even some relatively good plasticizers failed to give clear solutions at a ratio of 1:1 plasticizer:cosolvent.

The relative solvent power of the plasticizers, as indicated by intrinsic viscosity, is DOA < DOS < S52 < TOTM < DOP < MM < DBP < ODP. This order is similar to that suggested by equilibrium swellings. Differences are in the surprisingly low placing of DOA and in the reversal of DBP and ODP.
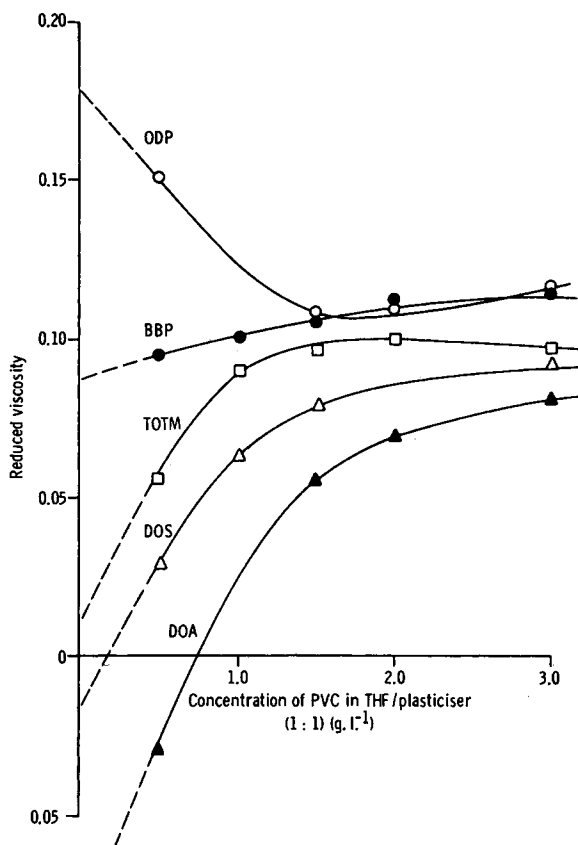
Fig. 1. Dilute-solution viscosities of PVC–plasticizer solutions.

The slopes of reduced viscosity-against-concentration curves have also been used to assess solvent power, but its interpretation is open to doubt. Frith,[7] for example, has shown the steeper slope to correspond to the better solvent for PVC, whereas Spurlin[9] has shown the opposite to be true of cellulose derivatives. Our own results show slopes of varying sign, as shown in Figures 1 and 2.

TABLE II
Apparent Melting Temperature (°C) of PVC–Plasticizer Mixtures

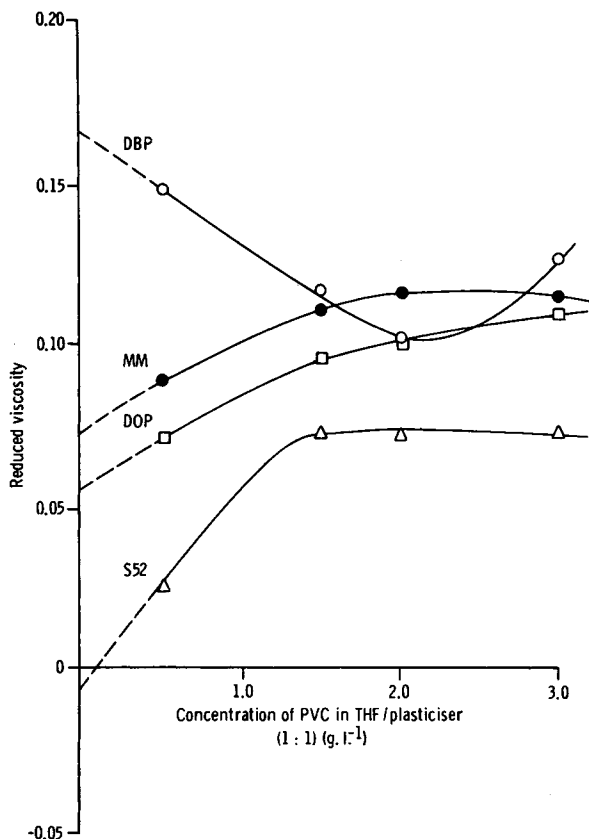| Plasticizer	T_m, °C	Gel-sol transition,[35,38] °C	Clear point,[36] °C	Dissolving temp.,[33] °C	Critical solution temp.,[32] °C
DOS	156–7	151–2	155	—	—
S52	144–6	—	—	—	—
TOTM	143–7	—	—	—	—
DOA	142–6	134–8	144	151	131–140
DOP	121–2	116–8	127	129	116–120
MM	117–121	—	—	122	—
BBP	115–117	104–118	89	126	96–100
ODP	99	88–92	105	—	—
DBP	98–99	90–94	97	105	90

Fig. 2. Dilute-solution viscosities of PVC–plasticizer solutions.

Apparent Melting Temperature (T_m)

The temperature at which a mixture of PVC and plasticizer becomes clear, or undergoes an apparent phase change, has been taken by several authors as a measure of the solvent power of the plasticizer.[28,32,36,37]

Our results for apparent melting temperature T_m are compared with those of other workers in Table II.

Although there is considerable variation in the values quoted, probably due to differences in experimental techniques and in variation of polymer and plasticizer samples, the relative order of the plasticizers is fairly consistent.

Hildebrand Solubility Parameter (δ)[46]

Hildebrand solubility parameters were calculated from surface tension measurements (Du Noüy tensiometer) on the plasticizers, using eq. (1) below, and from heats of vaporization using eq. (2). The equations of Hildebrand,[46] (3) and (4), were used to calculate the heats of vaporization from literature boiling points:

$$\delta = 4.1 \left(\gamma/V^{1/3}\right)^{0.43} \tag{1}$$

$$\delta = (\Delta E/V)^{1/2} \tag{2}$$

$$\Delta H_{25°C} = 23.7\,T_b + 0.020\,T_b{}^2 - 2950 \tag{3}$$

$$\Delta E_{25°C} = \Delta H_{25°C} - RT \tag{4}$$

where δ = Hildebrand solubility parameter, γ = surface tension of the plasticizer (dynes/cm), V = molar volume of the plasticizer, ΔE = energy of vaporization, ΔH = latent heat of vaporization, T_b = boiling point of the plasticizer (°K), R = the gas constant, and T = temperature (°K).

The calculated values of δ are shown in Table III.

TABLE III
Hildebrand Solubility Parameters

Plasticizer	δ Calculated from surface tension, (cal/cc)$^{1/2a}$	δ Calculated from boiling points, (cal/cc)$^{1/2}$
TOTM	7.2	
DOS	7.4	
DOA	7.5	7.3
DOP	7.5	7.7
MM	7.7	
ODP	8.1	8.4
S52	8.5	
DBP	8.6	8.9
BDP	8.8	

[a] A correction term of +0.6 has been added to these δ values to allow for hydrogen bonding to the esters.[36]

The agreement between the δ values calculated by the two methods is good, but the order of plasticizer solvent powers obtained is unreasonable, with, for example, the secondary plasticizer S52 apparently a much better plasticizer than ODP or DOP.

The agreement between the order suggested by δ values and the above empirical methods is, as might be expected, poor.

Flory-Huggins Interaction Parameter (χ)

Anagnostopoulus and co-workers[35,38] have shown that the Flory theory of melting in the presence of a diluent could be applied with success to PVC and that the χ values obtained correlated well with observed compatibilities (better than 90%). Our technique for measuring the apparent melting temperature is similar, but the use of more sophisticated apparatus to achieve better contrast leads to higher values of T_m, as shown by a comparison of columns 2 and 3 in Table II. This also gives somewhat different values for χ, although the relative order is unchanged, as shown in Table IV. χ Values were calculated from the apparent melting temperature (T_m) using the preferred eq. (5) of Anagnostopoulus et al.[35,38]:

$$1/Tm = 0.002226 + 0.3151\,(1 - x)/V_1 \tag{5}$$

where V_1 is the molar volume of the plasticizer at the apparent melting temperature T_m.

TABLE IV
Flory-Huggins Interaction Parameters (χ)

Plasticizer	χ	Lit. value of χ[35,38]
DOS	0.62	0.53
S52	0.52	—
DOA	0.48	0.28
TOTM	0.32	—
BBP	0.17	0.10
MM	0.07	—
DOP	0.05	−0.03
DBP	0.04	−0.05
ODP	−0.20	−0.35

It is generally accepted that a χ value of about 0.55 is the dividing line between compatibility and noncompatibility, that $0.30 < \chi < 0.55$ is the area of poor-moderate compatibility, and that good solvents have χ values <0.30. The results in Table IV broadly conform to practical experience in this respect, but it is noteworthy that the order is quite different from that suggested by the empirical methods above, which agree with each other.

How does this work out in practice? The Flory-Huggins interaction parameter has been shown to correlate well with compatibility,[35,38] as might be expected, since by definition it refers to the thermodynamic interaction between one molecule of plasticizer and an equivalent segment of the PVC chain. On the other hand, empirical methods related to those above are useful methods of assessing the effect of plasticizers on processing characteristics.

It would be extremely useful if these sets of data could be combined to give a simple quantitative measure of the degree of PVC–plasticizer interaction. Equation (5) suggests a way in which this might be done, since the degree of interaction, represented by $1/T_m$, is proportional to $(1 - \chi)/V_1$. V_1, the molar volume of the plasticizer at the apparent melting temperature of the mixture is, however, not a readily accessible figure. We propose, therefore, an activity parameter α, defined as in eq (6), where V_1 is replaced by the molecular weight MW of the plasticizer, a simplification which will not result in great differences in most cases. A factor of 10^3 is added to give numbers on a

TABLE V
α Values and Plasticizer Solvent Powers from Empirical Experiments[a]

Plasticizer	α	Equilibrium swelling	Dilute-soln. viscosity	Apparent melting temp.
			DOA	
DOS	0.8	DOS	DOS	DOS
S52	1.0	S52	S52	S52
TOTM	1.2	TOTM	TOTM	TOTM
DOA	1.4	DOA		DOA
DOP	2.4	DOP	DOP	DOP
MM	2.5	MM	MM	MM
BBP	2.6	BBP	BBP	BBP
ODP	3.3	ODP	DBP	ODP
DBP	3.4	DBP	ODP	DBP

[a] Arranged in order of increasing solvent power.

convenient scale, where the greater the value of α, the greater is the plasticizer activity:

$$\alpha = \frac{(1 - x)}{MW} \, 10^3 \tag{6}$$

The advantage of this simple equation is that α values will be readily accessible for the large number of PVC plasticizers for which χ-values are already known.

Table V shows the calculated values of α and the agreement with the order of plasticizer solvent powers obtained by the above empirical methods. Moreover, we have evidence, which we hope to publish shortly, that α values relate well to some practical aspects of PVC processing.

CONCLUSIONS

The methods of dilute-solution viscosities, equilibrium swellings, and apparent melting temperatures agree well, in the present study, in their assessment of relative plasticizer solvent power. Moreover, they also show excellent agreement with our proposed plasticizer activity parameter α (derived from the Flory-Huggins interaction parameter χ).

Neither the Hildebrand solubility parameter δ nor χ agree with the results of the three empirical methods of assessing plasticizer activity, although χ is known to correlate well with observed plasticizer compatibility.

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