ELSEVIER

polymer

Interactions between PVC and binary or ternary blends of plasticizers. Part I. PVC/plasticizer compatibility

J.T. van Oosterhout, M. Gilbert*

Institute of Polymer Technology and Materials Engineering, Loughborough University, Loughborough, Leicestershire LE11 3TU, UK

Received 14 April 2003; received in revised form 3 September 2003; accepted 10 September 2003

Abstract

Solid–gel transition temperatures, t_m, were measured for PVC in binary and ternary mixtures of plasticizers. Data were used to investigate interactions between plasticizers, and their effect on t_m and polymer–plasticizer interaction (χ) values. The UNIFAC-FV method was used to predict Gibbs free energy of mixing, and χ for a range of plasticizers, and interactions for one quaternary mixture. Synergy was observed when one or more branched phthalates were mixed with ODPP, but none when three phthalates were mixed. Mixtures of DOP with aliphatic ester plasticizers again produced synergy. Equations were produced to enable interaction coefficients of different plasticizer blends to be predicted. It was found that interaction coefficients increase as the difference in molar mass between the two plasticizers increases. Calculated χ values were generally similar to experimental values. The lower limit of Gibbs free energy of mixing required for plasticization of PVC using monomeric plasticizers was calculated to be about -0.9 J/g, and that for polymeric plasticizers -0.15 J/g. Equations were produced enabling Gibbs free energy of mixing to be predicted from the amount of C atoms in the plasticizer.
© 2003 Elsevier Ltd. All rights reserved.

Keywords: PVC; Plasticizers; Compatibility

1. Introduction

As a long established and widely used polymer, plasticized PVC has been discussed extensively in the literature. However, in real applications, in order to optimise properties two or more plasticizers are frequently used. The effect of binary and ternary blends of polymers on PVC/plasticizer compatibility, and product performance has been reported far less often. In a recent work programme, these effects have been considered in some detail for a number of different binary and ternary blend systems. In this paper the effect of these systems on PVC/plasticizer compatibility will be considered.

Theories of PVC/plasticizer compatibility have been discussed in detail by Sears and Darby [1]. Patel [2], Ramos DeValle [3] and Wilson [4] have also discussed various parameters indicative of compatibility, including polarity parameter, internal pressure, dielectric constant, solubility parameters, the combination of solubility parameters and dielectric constant, polarity parameter, modified polarity parameters, Flory–Huggins interaction parameter χ, and other derived parameters. In recent literature [5] particular attention has been given to the expanded solution parameters. These prediction parameters can be used alone, but the use of two or more predictors together is common practice.

Plasticizers act as solvents for amorphous regions of PVC. The PVC chains in the amorphous regions become solvated at elevated temperatures during processing. When more than one plasticizer is present, cosolvency needs to be considered. Dondos and Patterson [6] have shown that the sign and magnitude of the solvent–solvent interaction parameter χ_{12} could be considered as a guide to possible cosolvency. Thus, a mixture of two non-solvents might dissolve a polymer by acting as cosolvents, when χ_{12} is relatively large and positive. The phenomenon of cosolvency has been explained in terms of structural parameters, and preferential adsorption of the individual solvent components on polymer chains. For ternary systems composed of a polymer and two low molecular weight liquids, the simplest assumption is that the mixed solvent behaves like a single liquid represented by a single interaction parameter χ_{mix}. Scott [7] proposed the following

* Corresponding author. Fax: +44-1509-223-949.
E-mail address: m.gilbert@lboro.ac.uk (M. Gilbert).

relationship:

$$\chi_{mix} = \phi_1 \chi_{13} + \phi_2 \chi_{23} - \phi_1 \phi_2 \chi_{12} \qquad (1)$$

where subscripts 1 and 2 refer to the liquids, and 3 refers to the polymer. ϕ values are volume fractions of the various components. It is clear from Eq. (1) that χ_{mix} is smaller than is predicted by simple additivity when χ_{12} is positive. This means that the solvent power is higher than anticipated when the solvents are mixed.

Group contribution methods offer another route for investigating compatibility. One suitable method is UNI-FAC-FV, where UNIFAC means universal functional group activity coefficient [8]. Gottlieb and Herskowitz used this method for polymer solutions, and obtained reasonable predictions for the Flory–Huggins Interaction parameter χ [9]. More recently Boo and Shaw [10] and Price and Dent [11] have explored UNIFAC-FV for predicting liquid–liquid equilibrium in PVC-plasticizer systems, and calculated the activities and change of Gibbs free energy for multicomponent systems. The concentration-dependent Gibbs free energy was used to estimate the relative compatibility of various PVC based systems.

The present paper investigates solid–gel transition temperatures and χ values for several binary and ternary plasticizer blends. Other compatibility predictors are also considered briefly, and some data obtained using the UNIFAC-FV model for comparison.

2. Experimental

2.1. Experimental design

In view of the range of parameters involved in this investigation, a mixture design method was used. This is a more appropriate for plasticized PVC because the concentration of plasticizer used affects the concentration of PVC [12]. The Design-Expert® Software from Stat-Ease has been used for design of experiments and statistical treatment of results obtained.

The design matrix [13] used in this project is summarised in Table 1. This user-defined design is based on a triangular system, and contains:

the design points on each vertex for the three single plasticizers and their replicates (observation numbers 1–6),
the design points on the mid-points of the three sides and a replicate of one of these mid-points with equal quantities of two plasticizers (observation numbers 8, 11, 14 and 15)
the design points on 1/3 or 2/3 of the length of the three sides, whereby the quantity of one plasticizer is twice the quantity of the other plasticizer (observation numbers 7, 9, 10, 12, 13 and 16)
the design points inside the triangle, whereby the

Table 1
Design matrix

Observation number	Plasticizer A	Plasticizer B	Plasticizer C
1	1.000	0.000	0.000
2	1.000	0.000	0.000
3	0.000	1.000	0.000
4	0.000	1.000	0.000
5	0.000	0.000	1.000
6	0.000	0.000	1.000
7	0.667	0.333	0.000
8	0.500	0.500	0.000
9	0.333	0.667	0.000
10	0.000	0.667	0.333
11	0.000	0.500	0.500
12	0.000	0.333	0.667
13	0.333	0.000	0.667
14	0.500	0.000	0.500
15	0.500	0.000	0.500
16	0.667	0.000	0.333
17	0.667	0.167	0.167
18	0.167	0.667	0.167
19	0.167	0.167	0.667
20	0.333	0.333	0.333

quantity of one plasticizer is four times the quantity of each of the other two plasticizers. (observation numbers 17, 18 and 19)
a design point inside the triangle that contains equal quantities of each plasticizer. (observation number 20.)

The randomised run order was different for each series of experiments and all the experiments within a series were carried out within one day.

For the solid–gel transition temperature measurement and the subsequent calculation of the χ parameter, the above user-defined design was augmented with six more design points. These mixtures contained 95 vol% of one plasticizer and 5 vol% of another plasticizer. These mixtures are situated on the three sides of the triangle.

2.2. Materials

The emulsion PVC used for this investigation was E PVC (VINNOL P70) supplied by Wacker. This polymer has a K-value of 70, and was used for the production of free flowing plasticized PVC compounds used for instrument panels. Plasticizers are listed in Table 2. The phthalates were provided by Exxon, URAPLASTS by DSM Resins, ODPP by Monsanto and Akzo Nobel, the aliphatic esters by FMC and MESAMOLL by Bayer.

2.3. Measurement of solid–gel transition temperature

For PVC conventional methods of measuring melting temperature, such as measuring the last trace of crystallinity optically, or dilatometry are not possible because:

- the level of crystallinity in PVC is low

Table 2
Plasticizers used

Abbreviation	Structure
Linear phthalates	
DBP	di-butyl phthalate
C911P	di-911 phthalate
DUP	di-undecyl phthalate
Branched phthalates	
DIBP	di-iso-butyl phthalate
DOP	di-2-ethylhexyl phthalate
DINP	di-iso-nonyl phthalate
DIDP	di-iso-decyl phthalate
DIUP	di-iso-undecyl phthalate
DTDP	di-iso-tridecyl phthalate
Aliphatic dicarboxylic esters	
DOA	di-2-ethylhexyl adipate
DOZ	di-2-ethylhexyl azelate
DOS	di-2-ethylhexyl sebacate
Trimellitate	
TOTM	tri-2-ethylhexyl trimellitate
Phosphate	
ODPP	Octyl-diphenyl phosphate
Alkyl sulfonic ester of phenol	
MESAMOLL	Pentadecyl sulfonate of phenol
Polymeric plasticizers	
URAPLAST RA10 molar mass 3200	poly(butylene adipate), terminated by acetylation,
URAPLAST S5561 molar mass 2100	poly(butylene adipate) non-terminated,
URAPLAST RA11 molar mass 3100	poly(butylene adipate) non-terminated,
URAPLAST S5640 molar mass 4100	poly(butylene adipate) non-terminated,

- PVC crystallites are small, and do not aggregate to form spherulites
- PVC possesses crystallites with a wide range of size and perfection

Anagostopoulos et al. [15–17] therefore used a microscopy method to measure an 'apparent' melting temperature derived from the observed behaviour of a single PVC grain in the diluent concerned. A similar method was used in Refs. [2,3]. In the present work the method used was different, being based on DIN 53408 which is widely used in the European PVC and plasticizer industry. Although this is a bulk method, rather than one based on an individual grain, heating is carried out slowly, and the principle is the same. Furthermore, results are very similar, as shown by the comparison of t_m in this paper with those in Refs. [2,3,13]. The solid–gel transition temperature or clear point t_m is defined as the temperature at which a mixture of PVC and plasticizer becomes clear. The PVC in the plasticizer passes from an opaque solid to a clear gel. This temperature gives an indication of the compatibility of the plasticizer with PVC; the lower the clear point, the greater the compatibility. The clear point of the plasticizer blends with PVC was measured according to DIN 53408. 48 ml of each plasticizer or plasticizer blend and 2 g PVC were transferred into a 100 ml beaker. The contents of this beaker were stirred and heated on an electric hot plate. The heating rate was 1 °C/min. The temperature of the beaker content was recorded. The temperature t_m belonging to the apparent phase change from an opaque mixture to a transparent solution was measured and used for further calculations. t_m could be reproduced to within ± 1 °C.

2.4. Calculation of Flory–Huggins interaction parameter χ

This interaction parameter was calculated for the various PVC/plasticizer blends using the formula originally due to Flory [14] modified by Anagostopoulos et al. [15–17]:

$$1/T_m = 0.002226 + 0.1351(1 - \chi_{(123)4})/V_{123} \qquad (2)$$

where $T_m = (t_m + 273)$ is the depressed melting temperature in K, and $\chi_{(123)4}$ represents the interaction between the plasticizer mixture consisting of plasticizers 1, 2 and 3 and the polymer 4. The molar volume of plasticizer mixture was calculated from,

$$V_{123} = M\{1 - \alpha(t_m - 25)\}/\rho \qquad (3)$$

where ρ is the density of the plasticizer mixture at 25 °C, M is its molar mass and α is the coefficient for thermal expansion. The volume fraction V_{123} is the molar volume of the plasticizer mixture at t_m. The value of V_{123} at temperature t_m can be calculated from the values V_1, V_2 and V_3 at the same temperature using the relationship:

$$V_{123} = \varphi_1 V_1 + \varphi_2 V_2 + (1 - \varphi_1 - \varphi_2)V_2 \qquad (4)$$

The values of V_1, V_2 and V_3 at temperature t_m were calculated by use of the formula

$$V_{tm} = V_{25}(1 + \alpha(t_m - 25)) = M(1 + \alpha(t_m - 25))/\rho \qquad (5)$$

where α is the coefficient of thermal expansion, M is the molecular weight and ρ is the density, at 25 °C, for the plasticizer

Eq. (4) assumes that:

1. the excess volume of mixing is zero and
2. the variation in volume fraction with temperature is negligible.

As regard to the latter the coefficient for thermal expansion α was always taken to be 0.00080 cm^3 cm^{-3} K^{-1}.

The constants in Eq. (2) assume a value for the heat of fusion of 2742 J/mol of polymer repeat unit, and a polymer melting temperature of 174 °C [15]. Both of these values are lower than those reported subsequently; certainly a fraction of PVC crystallites melt well above 174 °C, as seen by thermal analysis. However, these low values have been used

in calculations; justification for continuing to use these values has been provided previously [2].

2.5. Calculation of Bigg interaction parameter α^*

Bigg [18] proposed that the final term in Eq. (2) could be used as a measure of compatibility, which he described as the activity parameter α. For simplification, he replaced the molar volume term V by the molar mass of the polymer. However, since values of V_{123} terms have already been calculated in the present work, the activity coefficient has been redefined as:

$$\alpha^* = 1000(1 - \chi_{(123)4})/V_{123} \tag{6}$$

The multiplying factor of 1000 is used to give numbers on a convenient scale. Activity values have been calculated using data obtained in the present work.

2.6. Calculation of Hildebrand solubility parameter δ

For a ternary blend of plasticizers, the solubility parameter δ can be calculated from:

$$\delta = \delta_1\phi_1 + \delta_2\phi_2 + \delta_3\phi_3 + 0.22\phi_1\phi_2 + 0.30\phi_1\phi_3 \tag{7}$$

where the last two terms are corrections suggested by Fedors [19].

2.7. Theoretical prediction of compatibility

UNIFAC is a group contribution technique, which splits each molecule being considered into a number of functional groups such as methyl, methylene, carbonyl, etc and treats the solution as a mixture of these groups.

In the UNIFAC-FV model the activity of component i is given in terms of combinatorial, residual and free volume contributions [8]:

$$\ln a_i = \ln a_i^C + \ln a_i^R + \ln a_i^{FV} \tag{8}$$

The combinatorial combination takes into account the entropy effect, which arises from differences in molecular size and shape. The residual contribution accounts for energetic interactions between the functional groups in the mixture, and the free volume contribution accounts for changes in free volume, which are caused by mixing. While the latter is often negligible, for systems in which one of the components is more tightly packed, such as a polymer and solvent, free volume effects are far from negligible, and should be taken into account.

The change in the Gibbs free energy on mixing can be calculated from the activities determined from Eq. (8) by the expression:

$$\Delta G_{\text{mix}} = RT \sum_i x_i \ln a_i \tag{9}$$

where R is the gas constant, T is absolute temperature and x_i is the mole fraction of component i in the mixture. Using this method, plasticizer blends can be treated as a single solvent, and for this binary polymer–solvent system, the interaction parameter χ is defined by the Flory–Huggins equation:

$$\chi = 1/(\Phi_1)^2[\ln a_1 - \ln \Phi_1 - (1 - 1/x)\Phi_2] \tag{10}$$

where Φ_1 and Φ_2 are volume fractions of solvent and polymer, respectively, and x is the number average ratio of the molar volume of the polymer relative to the solvent.

3. Results

3.1. Individual plasticizers

Values for solid–gel transition temperatures for the individual plasticizers are shown in increasing order in Table 3. Molar volumes and χ values are also included in this table. For the four polymeric plasticizers the molar volume of the polymer repeat unit has been used to calculate χ; reasons for this are discussed later.

3.2. Binary plasticizer mixtures

The results for t_m and χ were processed using Design Expert software, which provided a mathematical model which could be represented by a 2D or 3D graph. Clearly a considerable amount of results have been obtained from the experiments described. A selection of these will be presented.

A set of t_m equations for binary systems based on ODPP with branched phthalates is shown in Table 4, where ϕ is the plasticizer volume fraction, and R^2 reflects the fit of the equation to experimental data ($R^2 \times 100$ is the degree of fit in % for the model equations. $R^2 \geq 0.98$ corresponds with a

Table 3
Solubility data for individual plasticizers

Plasticizer	t_m (°C)	V_1 (cm^3 mol^{-1})	χ
ODPP	88	338.91	−0.41
DIBP	88	280.81	−0.13
DBP	92	290.39	−0.10
MESAMOLL	115	383.87	0.00
DOP	115	424.84	−0.10
DINP	123	464.03	−0.03
DIDP	127	499.12	−0.01
C911P	130	503.08	0.05
DIUP	135	537.21	0.11
DOA	136	435.99	0.29
DUP	140	543.71	0.21
DTDP	144	610.64	0.22
DOS	148	511.39	0.43
URAPLAST RA10	146	215.83	0.74[a]
URAPLAST S5561	159	199.54	0.87[a]
URAPLAST RA11	159	199.54	0.87[a]
URAPLAST S5640	159	199.54	0.87[a]

[a] Calculated using polyester repeat unit.

Table 4
Equations relating t_m to volume fractions for ODPP with branched phthalates

Binary system	t_m (°C)	R^2
ODPP–DIBP	$88.5\phi_{ODPP} + 87.3\phi_{DIBP} + 4.90\phi_{ODPP}\phi_{DIBP}$	0.9540
ODPP–DOP	$88.5\phi_{ODPP} + 114.1\phi_{DOP} - 22.40\phi_{ODPP}\phi_{DOP}$	0.9930
ODPP–DIDP	$88.5\phi_{ODPP} + 127.8\phi_{DIDP} - 25.02\phi_{ODPP}\phi_{DIDP}$	0.9983
ODPP–DIUP	$89.3\phi_{ODPP} + 133.5\phi_{DIUP} - 28.64\phi_{ODPP}\phi_{DIUP}$	0.9963
ODPP–DTDP	$88.8\phi_{ODPP} + 143.0\phi_{DTDP} - 40.03\phi_{ODPP}\phi_{DTDP}$	0.9951

correlation coefficient between 0.99 and 1). Similar data for χ values for these systems are shown in Table 5. The mixture ODPP–DIBP shows a low antagonistic interaction due to the identical t_ms of these blends. When plasticizers with higher t_m values are added to ODPP, a gradual increase in t_m is observed in all cases, and the fit between the model and experimental data, represented by R^2 is excellent. Similar results are observed for χ, but the cubic terms lower the χ values of the mixture when the volume fraction of ODPP is larger than the volume fraction of the associated branched phthalate as illustrated in Figs. 1 and 2.

3.3. Ternary plasticizer mixtures

Table 6 shows equations for t_m, and Table 7 for χ for various ternary mixtures. Different behaviours are observed for different systems. A two-dimensional t_m plot for DOP–DINP–DIDP is shown in Fig. 3. In this case, where there is no interaction between plasticizers (Table 6) lines of constant t_m are equally spaced, but in Fig. 4, for DOP–DIDP–ODPP mixtures some interaction occurs, and the lines become closer together at high DIDP concentrations. The plot for DOP–DOA–DOS is similar to Fig. 4. A 3D representation for DOP–DIDP–ODPP (Fig. 5) shows the effect of the different plasticizers, and the response diagram in Fig. 6 shows the effects of changing the concentration of each plasticizer from equal concentrations of all three.

Table 5
Equations relating χ to volume fractions for ODPP with branched phthalates

ODPP–DIBP
$\chi = -0.40\phi_{ODPP} - 0.14\phi_{DIBP} + 0.14\phi_{ODPP}\phi_{DIBP}$　　$R^2 = 0.9989$

ODPP–DOP
$\chi = -0.39\phi_{ODPP} - 0.13\phi_{DOP} - 0.41\phi_{ODPP}\phi_{DOP} - 0.37\phi_{ODPP}\phi_{DOP}(\phi_{ODPP} - \phi_{DOP})$　　$R^2 = 0.9989$

ODPP–DIDP
$\chi = -0.39\phi_{ODPP} + 0.00\phi_{DIDP} - 0.58\phi_{ODPP}\phi_{DIDP}$　　$R^2 = 0.9944$

ODPP–DIUP
$\chi = -0.38\phi_{ODPP} + 0.13\phi_{DIUP} - 0.67\phi_{ODPP}\phi_{DIUP} - 0.60\phi_{ODPP}\phi_{DIUP}(\phi_{ODPP} - \phi_{DIUP})$　　$R^2 = 0.9981$

ODPP–DTDP
$\chi = -0.38\phi_{ODPP} + 0.22\phi_{DTDP} - 1.12\phi_{ODPP}\phi_{DTDP} - 0.81\phi_{ODPP}\phi_{DTDP}(\phi_{ODPP} - \phi_{DTDP})$　　$R^2 = 0.9964$
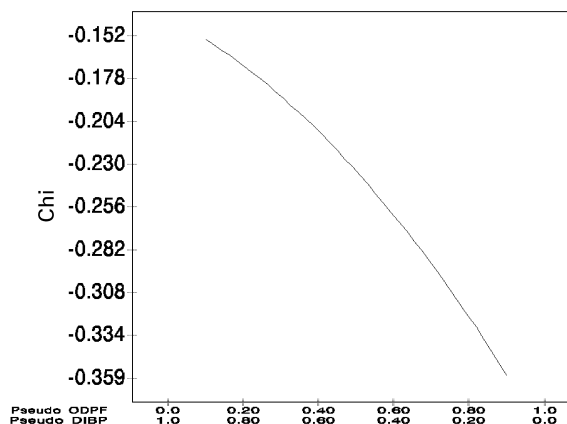
Fig. 1. χ versus plasticizer composition for ODPP–DIBP blend.

Results for χ values are similar; a response plot for χ for DOP–DOA–DOS is shown in Fig. 7.

3.4. Polymeric plasticizer mixtures

Equations were obtained for mixtures containing two monomeric phthalates. Results fitted model equations well, and were generally similar to those discussed above. A response diagram for DOP–DIUP–URAPLAST RA11 is shown in Fig. 8. It is seen here that neither DIUP nor URAPLAST RA11 cause linear changes in t_m with change in their concentration. A 2D t_m-plot for MESAMOLL–DOA–URAPLAST RA10 is shown in Fig. 9. Considerable curvature is shown in the t_m contours.

For the χ values for this system, considerable curvature is again observed (c.f. Fig. 10).

3.5. Other compatibility predictors

Bigg interaction parameter. A limited number of investigations were carried out to see whether the equations described previously could be used to predict the Bigg interaction parameter for various plasticizer mixtures. A typical response trace is shown in Fig. 11 (c.f. Fig. 7).

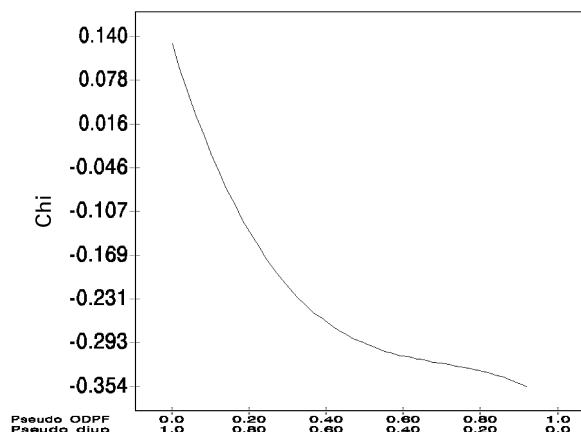*Hildebrand solubility parameter.* The following equation

Fig. 2. χ versus plasticizer composition for ODPP–DIUP blend.

Table 6
Equations relating t_m to volume fractions for various ternary systems

---

Mixtures containing only monomeric plasticizers

DOP–DINP–DIDP
$t_m = 112.9\phi_{DOP} + 123\phi_{DINP} + 128.1\phi_{DIDP}$
Standard error = 0.3 °C $\hfill R^2 = 0.9851$

DOP–C911P–DIUP
$t_m = 115.4\phi_{DOP} + 130\phi_{C911P} + 134.8\phi_{DIUP}$
Standard error = 0.2 °C $\hfill R^2 = 0.9997$

DOP–DIDP–ODDP
$t_m = 114.4\phi_{DOP} + 127.8\phi_{DIDP} + 87.6\phi_{ODDP} - 19.9\phi_{ODPP}\phi_{DOP} -$
$23.2\phi_{ODPP}\phi_{DIDP}$
Standard error = 0.5 °C $\hfill R^2 = 0.9962$

DOP–DOA–DOS
$t_m = 119.4\phi_{DOP} + 136\phi_{DOA} + 147.8\phi_{DOS} - 16.4\phi_{DOA}\phi_{DOP} -$
$22.5\phi_{DOP}\phi_{DOS}$
Standard error = 0.65 °C $\hfill R^2 = 0.9893$

Mixtures containing polymeric plasticizers

DOP–DBP–RA11
$t_m = 114.9\phi_{DOP} + 90.9\phi_{DBP} + 159\phi_{RA11} - 32.8\phi_{DOP}\phi_{RA11}$
Standard error ≤ 0.9 °C $\hfill R^2 = 0.9967$

DOP–DINP–RA11
$t_m = 117.2\phi_{DOP} + 127.5\phi_{DINP} + 159.3\phi_{RA11} - 34.6\phi_{DOP}\phi_{RA11} -$
$46.8\phi_{DINP}\phi_{RA11}$
Standard error ≤ 0.9 °C $\hfill R^2 = 0.9909$

DOP–DUP–RA11
$t_m = 116.6\phi_{DOP} + 139.4\phi_{DUP} + 158.8\phi_{RA11} - 32.8\phi_{DOP}\phi_{RA11} -$
$47.8\phi_{DUP}\phi_{RA11}$
Standard error ≤ 0.9 °C $\hfill R^2 = 0.9850$

DOP–DIUP–RA11
$t_m = 114.4\phi_{DOP} + 134.2\phi_{DIUP} + 160.0\phi_{RA11} - 33.4\phi_{DOP}\phi_{RA11} -$
$48.0\phi_{DIUP}\phi_{RA11}$
Standard error ≤ 0.9 °C $\hfill R^2 = 0.9993$

MESAMOLL–DOA–RA10
$t_m = 115.2\phi_{MES} + 135.6\phi_{DOA} + 145.5\phi_{RA10} - 23.2\phi_{MES}\phi_{DOA} -$
$22.2\phi_{MES}\phi_{RA10} - 47.5\phi_{DOA}\phi_{RA10} - 57.6\phi_{MES}\phi_{RA10}(\phi_{MES} - \phi_{RA10})$
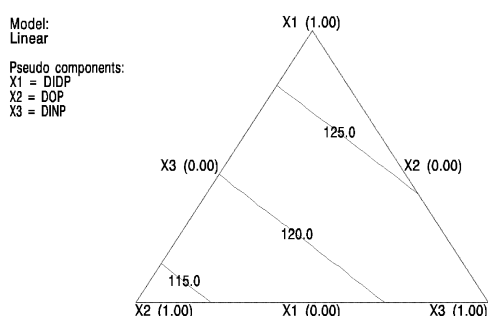Standard error ≤ 0.9 °C $\hfill R^2 = 0.9977$

---

shows the relationship between the solubility parameter and the components of the plasticizer blend DOP–DOA–DOS at 25 °C:

$$\delta = 18.08\phi_{DOP} + 17.3\phi_{DOA} + 17.17\phi_{DOS} \qquad (11)$$

where δ is in MPa$^{0.5}$ and $R^2 = 0.9965$, i.e. the fit to the experimental data is excellent. Fedors [19] showed that solubility parameters could be obtained at t_m using the following equation:

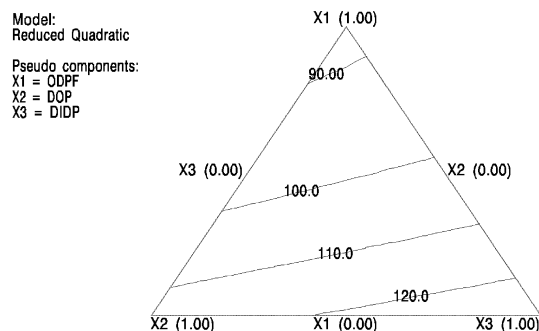$$\delta_{tm} = \delta_1 \{V_1/V_{tm}\}^{1.13} \qquad (12)$$

Fig. 3. t_m versus plasticizer composition for DOP–DINP–DIDP blend.

Fig. 4. t_m versus plasticizer composition for DOP–DIDP–ODPP blend.

Table 7
Equations relating χ to volume fractions for various ternary systems

Mixtures containing only monomeric plasticizers

DOP–DINP–DIDP

$\chi = -0.15\phi_{DOP} - 0.03\phi_{DINP} + 0.01\phi_{DIDP}$ $R^2 = 0.9495$

DOP–C911P–DIUP

$\chi = -0.10\phi_{DOP} + 0.05\phi_{C911P} + 0.10\phi_{DIUP}$ $R^2 = 0.9860$

DOP–DIDP–ODPP

$\chi = -0.12\phi_{DOP} - 0.00\phi_{DIDP} - 0.40\phi_{ODPP} - 0.44\phi_{ODPP}\phi_{DOP} - 0.58\phi_{ODPP}\phi_{DIDP}$ $R^2 = 0.9882$

DOP–DOA–DOS

$\chi = -0.02\phi_{DOP} + 0.30\phi_{DOA} + 0.43\phi_{DOS} - 0.30\phi_{DOA}\phi_{DOP} - 0.50\phi_{DOP}\phi_{DOS}$ $R^2 = 0.9840$

Mixtures containing polymeric plasticizers

DOP–DBP–RA11

$\chi = -0.10\phi_{DOP} - 0.11\phi_{DBP} + 0.86\phi_{RA11} + 0.39\phi_{DOP}\phi_{RA11} + 0.50\phi_{DBP}\phi_{RA11}$ $R^2 = 0.9986$

DOP–DINP–RA11

$\chi = -0.06\phi_{DOP} + 0.06\phi_{DINP} + 0.86\phi_{RA11} + 0.34\phi_{DOP}\phi_{RA11} + 0.15\phi_{DINP}\phi_{RA11}$ $R^2 = 0.9960$

DOP–DUP–RA11

$\chi = -0.09\phi_{DOP} + 0.20\phi_{DUP} + 0.87\phi_{RA11} + 0.4\phi_{DOP}\phi_{RA11}$ $R^2 = 0.9965$

DOP–DIUP–RA11

$\chi = -0.12\phi_{DOP} + 0.09\phi_{DIUP} + 0.87\phi_{RA11} + 0.41\phi_{DOP}\phi_{RA11} + 0.18\phi_{DIUP}\phi_{RA11}$ $R^2 = 0.9995$

MESAMOLL–DOA–RA10

$\chi = 0.00\phi_{MES} + 0.28\phi_{DOA} + 0.75\phi_{RA10} - 0.42\phi_{MES}\phi_{DOA} + 0.21\phi_{MES}\phi_{RA10} - 0.22\phi_{DOA}\phi_{RA10} - 0.68\phi_{MES}\phi_{RA10}(\phi_{MES} - \phi_{RA10})$ $R^2 = 0.9987$

where V_1 and V_{tm} are the molar volumes and δ_1 and δ_{tm} the solubility parameters of the plasticizer at 25 °C and t_m, respectively.

When δ is corrected for temperature, the model for solubility parameters becomes:

$$\delta = 16.7\phi_{DOP} + 15.7\phi_{DOA} + 15.4\phi_{DOS} + 0.22\phi_{DOP}\phi_{DOA} + 0.30\phi_{DOP}\phi_{DOS}$$

For this relationship $R^2 = 0.9987$.

3.6. Theoretical prediction of compatibility

The UNIFAC-FV method was used to calculate the activities, χ values, and the Gibbs free energy of mixing versus composition for several PVC/plasticizer systems, and also for systems containing more than one plasticizer. χ versus composition has been predicted for one plasticizer at different temperatures, and activities and χ versus composition for the

DOP–DOA–DOS blend at 25 °C have also been predicted. Figs. 12 and 13 show plots of Gibbs free energy of mixing for a series of phthalate plasticizers and various other plasticizers respectively. The number average molar mass of PVC was assumed to be 50,000. Table 8 shows equations for χ values at 27 °C predicted by the UNIFAC method. Excellent fits are observed. Table 9 compares χ values calculated by the UNIFAC method with those reported experimentally. Reasonable agreement is obtained, except for higher χ values, where the plasticizer concerned is a poor solvent for PVC. The relative compatibility, starting from the most compatible plasticizer is:

$$DBP > DOP > DINP > DIDP > DIUP > DOA > DTDP$$

$$> DOS$$
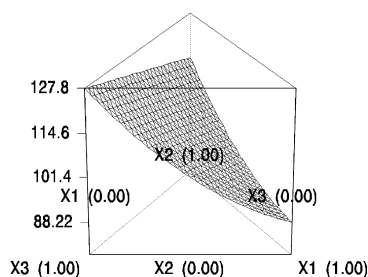
Fig. 5. 3D plot showing t_m variation for DOP–DIDP–ODPP blend.
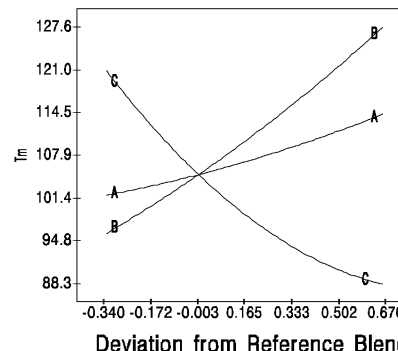
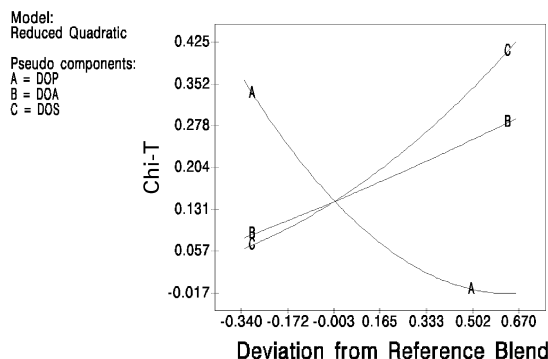Fig. 6. Response plot showing t_m variation for DOP–DIDP–ODPP blend.

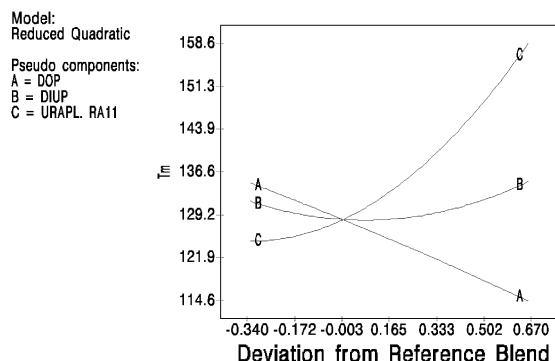Fig. 7. Response plot showing χ variation for DOP–DOA–DOS blend.

Table 8
Polymer solvent interaction parameters predicted using UNIFAC-FV

|		
PVC/DBP	$\chi = -0.1745 - 0.153\phi_{DBP} + 0.033\phi_{DBP}^2$	$R_{val} = 0.9993$
PVC/DOP	$\chi = -0.0674 - 0.108\phi_{DOP} + 0.029\phi_{DOP}^2$	$R_{val} = 0.9988$
PVC/DINP	$\chi = 0.0481 - 0.100\phi_{DINP} + 0.022\phi_{DINP}^2$	$R_{val} = 0.9998$
PVC/DIDP	$\chi = 0.1492 - 0.056\phi_{DIDP} + 0.013\phi_{DIDP}^2$	$R_{val} = 0.9998$
PVC/DIUP	$\chi = 0.2657 - 0.006\phi_{DIUP} + 0.020\phi_{DIUP}^2$	$R_{val} = 0.9840$
PVC/DOA	$\chi = 0.4354 + 0.006\phi_{DOA} - 0.009\phi_{DOA}^2$	$R_{val} = 0.9967$
PVC/DTDP	$\chi = 0.5168 + 0.094\phi_{DTDP} - 0.015\phi_{DTDP}^2$	$R_{val} = 0.9999$
PVC/DOS	$\chi = 0.6829 + 0.212\phi_{DOS} - 0.051\phi_{DOS}^2$	$R_{val} = 0.9984$

Table 9
Comparison of predicted and measured χ parameters

	Literature values [22,23]	From Table 3	Predicted (UNIFAC-FV)
PVC/DBP	-0.06 to -0.22	-0.10	-0.28
PVC/DOP	-0.04 to -0.24	-0.10	-0.14
PVC/DINP		-0.03	-0.02
PVC/DIDP	0.20 to -0.07	-0.01	0.04
PVC/DIUP		0.11	0.20
PVC/DOA	0.23 to 0.33	0.29	0.48
PVC/DTDP	0.48	0.22	0.59
PVC/DOS	0.47 to 0.52	0.43	0.84

Fig. 8. Response plot showing t_m variation for DOP–DIUP–RA11 blend.

Equations for predicting the concentration, and temperature dependence (T) are shown in Table 10, and these relationships are illustrated in Fig. 14 for PVC–DOS, and in Fig. 15 for PVC–DOP. The temperature and concentration dependence for the compatibility of DOP differs from that for DIOP
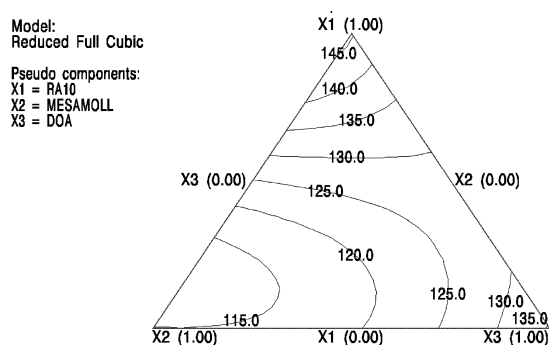

Fig. 9. t_m versus plasticizer composition for MESAMOL–DOA–URAPLAST RA10 blend.

published by Holly [20], with the signs for the quadratic terms reversed. DOA and DOS confirm the theoretical expectations of a decrease in χ with increasing temperature and plasticizer concentration. Fig. 15 shows that DOP behaves differently: χ decreases with increasing temperature up to 105 °C, and afterwards increases.

The UNIFAC-FV method was also used to predict the activity versus plasticizer concentration for each of the sixteen blends of the quaternary PVC–DOP–DOA–DOS system, and to predict the density of each of these blends. This information was used to calculate χ for each of these plasticizer blends at ten concentrations. The results were processed by regression analysis using the Design-Expert® Software, which resulted in a general equation for calculating χ:

$$\chi = -0.16\phi_{DOP} + 0.43\phi_{DOA} + 1.04\phi_{DOS} + 0.43\phi_{PVC}$$
$$+ 3.58\phi_{DOP}\phi_{DOA} + 5.26\phi_{DOP}\phi_{DOS} - 1.16\phi_{DOP}\phi_{PVC}$$
$$+ 1.96\phi_{DOA}\phi_{DOS} + 0.16\phi_{DOA}\phi_{PVC} + 0.19\phi_{DOS}\phi_{PVC}$$
$$- 6.25\phi_{DOA}\phi_{DOS}\phi_{PVC} + 2.71\phi_{DOP}\phi_{DOS}(\phi_{DOP}$$
$$- \phi_{DOS}) + 1.38\phi_{DOP}\phi_{PVC}(\phi_{DOP} - \phi_{PVC})$$
$$- 1.64\phi_{DOS}\phi_{PVC}(\phi_{DOS} - \phi_{PVC})$$

for which $R^2 = 0.9729$.
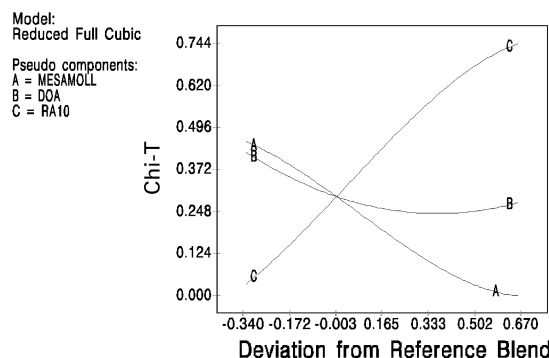
Fig. 10. Response plot showing χ variation for MESAMOL–DOA–URAPLAST RA10 blend.
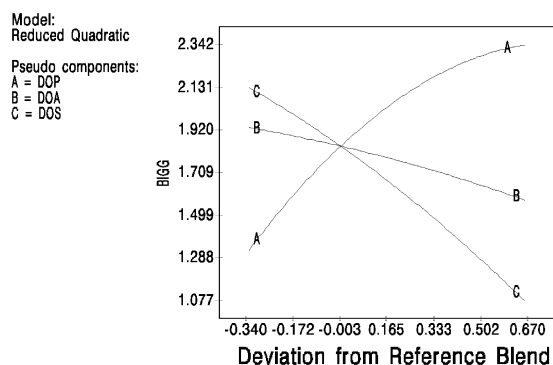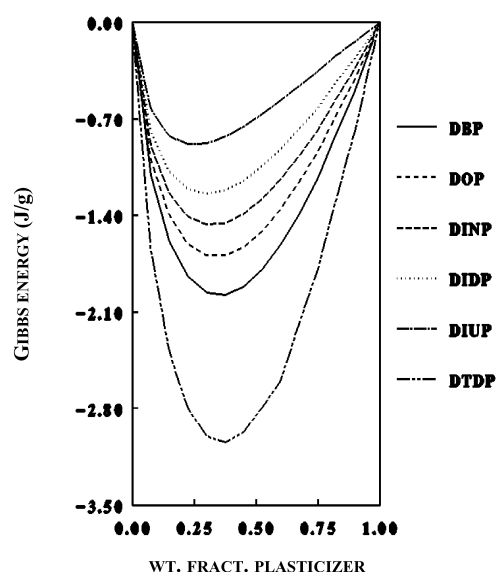
Fig. 11. Response plot showing α^* variation for DOP–DOA–DOS blend.

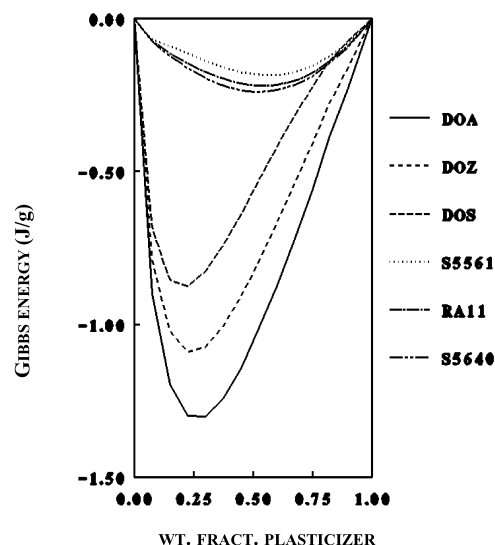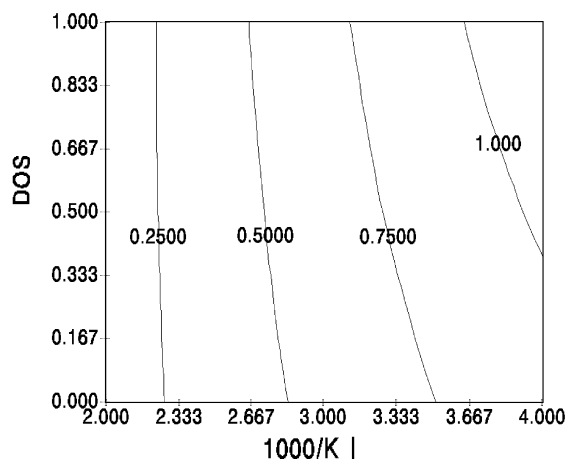Fig. 12. Gibbs free energy of mixing for various phthalate plasticizers.

Fig. 13. Gibbs free energy of mixing for various aliphatic polyester plasticizers.

Fig. 14. Influence of temperature and plasticizer concentration on χ for PVC–DOS blends.

This equation shows nearly all possible interactions between the components of this quaternary system. Comparison of these results with those for the same plasticizer blend in Table 7, obtained by applying Eq. (2) to experimental results, shows the same order of compatibility as for the single plasticizers. The quadratic terms for DOP–DOA and DOP–DOS show large interactions, but with opposite sign to those in Table 7. The remaining terms are smaller, but significant with a positive sign, except for

the interaction between DOP and PVC. The cubic terms have larger interactions. UNIFAC-FV has not succeeded in predicting the observed synergistic interactions between DOP–DOA and DOP–DOS. Both of these interactions

Table 10
Effect of temperature on predicted χ parameters

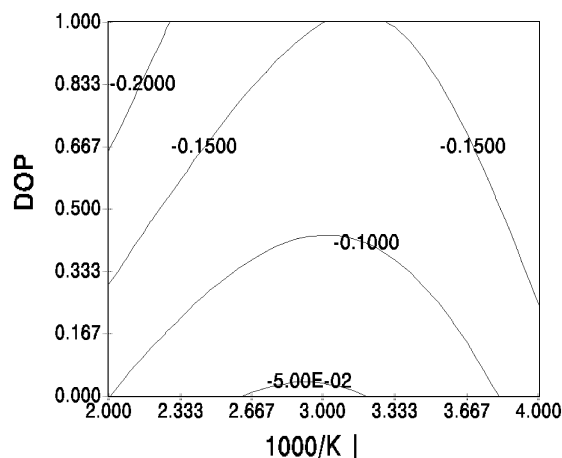|	
PVC/DOP	
$\chi = -0.62 - 0.243\phi_{DOP} + 394/T + 0.039\phi_{DOP}^2 - 67000/T^2 + 32\phi_{DOP}/T$	$R^2 = 0.9809$
PVC/DOA	
$\chi = -0.76 - 0.174\phi_{DOA} + 502/T - 0.003\phi_{DOA}^2 - 43000/T^2 + 67\phi_{DOA}/T$	$R^2 = 0.9999$
PVC/DOS	
$\chi = -1.11 - 0.273\phi_{DOS} + 733/T - 0.017\phi_{DOS}^2 - 58000/T^2 + 137\phi_{DOS}/T$	$R^2 = 0.9998$

Fig. 15. Influence of temperature and plasticizer concentration on χ for PVC–DOP blends.

have been overshadowed by the interactions between PVC and one or more plasticizers.

4. Discussion

The solid–gel transition temperature t_m varies to some extent due to the precise method used for its measurement. However, the order of different monomeric plasticizers shown in Table 3, varying from ODPP which has very good solvent power, to the polymeric plasticizers with low solvent power is consistent with previous literature [15,20]. Ordering of χ values is similar except for MESAMOLL and DOA, which both have relatively higher χ values due to their low molar volumes.

When binary mixtures of ODPP and branched phthalates are considered (Table 4), the first multiplier in the equations obviously corresponds to the t_m value for ODPP, and it is seen that the predicted values are close to that which has been measured (Table 3). As the molar mass of the branched phthalate increases, the other two multipliers change systematically for phthalates producing a higher t_m than ODPP. As an example, t_m is plotted against composition in Fig. 16. It is seen that there is a negative deviation from a straight line correlation. The plasticizer mixture therefore possesses a higher solvent power than expected. This synergistic effect increases with chain length of the branched phthalate. Further, it is shown that an increase of one CH$_2$ group in a phthalate branch produces a reduction of about 1 °C in the solid–gel transition temperature of binary mixtures containing equal volumes of each plasticizer. The synergistic effect is also observed for χ values as shown in Fig. 2. It is likely to be due to cosolvency effects [6]. ODPP molecules will preferentially interact with the PVC, reducing the interactions between the PVC chains, hence facilitating interaction with the branched phthalate. The maximum synergy occurs for the composition that has the lowest calculated free energy of mixing as shown in Fig. 12.

The parallel lines for t_m in Fig. 3, and the equations for DOP–DINP–DIDP and DOP–C911P–DIUP in Table 6 show a linear relationship between these plasticizer systems, with no interactions. This is in accordance with the results of Tomaselli et al [21,22], who showed that there was no interaction between members of the same group of plasticizers.

The remaining ternary plasticizer blends show interactions between members of different groups. The synergistic interactions for the mixture DOP–DIDP–ODPP are very similar to the results for binary mixtures discussed above, because of interactions between DOP and ODPP and DIDP and ODPP, as seen in Fig. 5. A response trace plot (Fig. 6) provides silhouette views of the response surfaces, and shows the effects of changing each component along an imaginary line from the reference blend containing equal volumes of each plasticizer. As the amount of one component increases, the amounts of the other components decrease, but their ratio to one another remains constant. The curvature of the three traces shows that t_m is quite sensitive to changes in all three components.

The coefficients in the equation for DOP–DOA–DOS produce a decrease in t_m due to interactions between DOP and the aliphatic dibasic esters. As before, these interactions increase with increasing t_m of the aliphatic dibasic ester used. The magnitude of coefficients associated with the interacting plasticizers in this system is similar to those for interacting plasticizers DOP–DIDP–ODPP. The introduction of one additional CH$_2$ group into the aliphatic dibasic chain gives a reduction of about 0.5 °C for the t_m for binary mixtures containing equal amounts of DOP–DOA and DOP. Again, there is a significant reduction in the free energy of mixing for these pairs (Fig. 13).

The relationship between the quadratic interaction coefficients A for t_m found for each pair of monomeric plasticizers for the binary and ternary mixtures above, and the difference in t_m for each pair is shown in Fig. 17. A least squares fit with a correlation coefficient of 0.9659 gives:
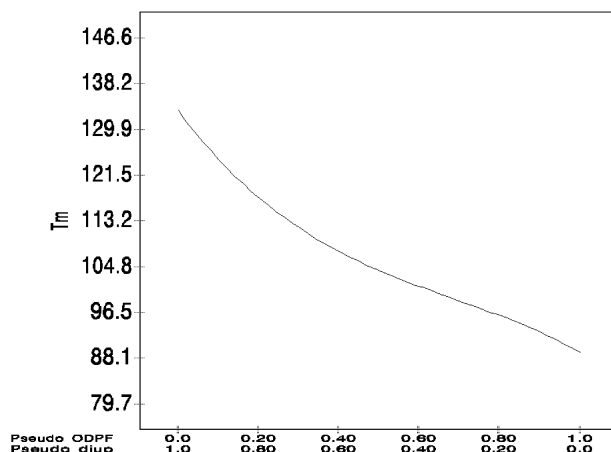
$$A = -1.21 - 0.71\Delta t_m$$

Fig. 16. t_m versus plasticizer composition for ODPP–DIUP blend.

This enables interaction coefficients of other plasticizer blends to be predicted. Tomaselli et al. [22] produced a t_m versus concentration plot for DOP–TOTM mixtures, although the technique used to measure t_m was different. A quadratic equation produced an interaction coefficient of -19.8, compared with a value of -14.4 using the above equation, a reasonable agreement in the circumstances.

The coefficients for plasticizers in Table 7 correspond well with the measured χ parameters for these plasticizers. Synergistic effects for DOP–DIDP–ODPP and DOP–DOA–DOS are observed as for t_m values, and coefficients increase with increasing molar mass of the plasticizer. Although these models still show a good fit, they are not as good as the corresponding t_m equations (Table 6). This is because t_m is used twice in Eq. (2), to calculate T_m, and the molar volume at t_m, magnifying the effect of any errors in this value. Fig. 7 shows that χ is generally more sensitive to changes in DOP concentration than DOA and DOS.

Like t_m, the quadratic coefficients for χ can be related to the difference between the two monomeric plasticizers as shown in Fig. 18. A least squares fit with a correlation coefficient of 0.9521 gives:

$$C = 0.10 - 0.02\Delta t_m$$

where C is the quadratic interaction coefficient. Interaction parameters for other plasticizer blends can therefore be predicted. In practice, it is also important to know the sensitivity of χ to small errors in the measurement of t_m, and the effect of using weight fractions instead of volume fractions that are normally used for the calculation of χ. Table 11 shows the relevant equations for DOP–DOA–DOS plasticizer mixtures for $t_m + 1\,°C$, t_m and $t_m - 1\,°C$. A decrease of $1\,°C$ in t_m causes a decrease of 0.02 units in χ, which is larger than the standard error for these systems. The interactions are insensitive to such changes in temperature, and the fit of the models is unaffected. The
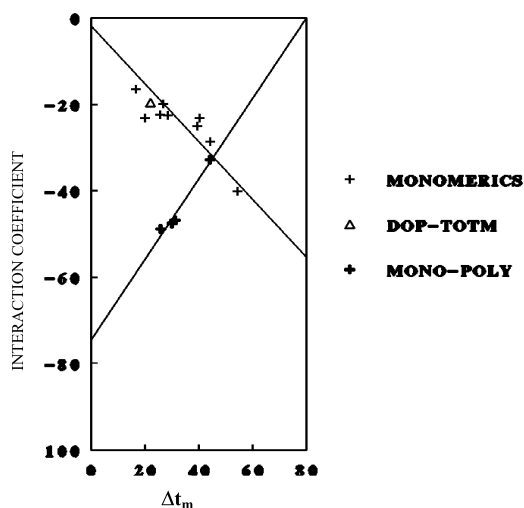
introduction of weight rather than volume fractions has only a slight effect on the interactions.

For the mixtures containing polymeric plasticizers (Table 6), the coefficients of synergistic interaction between DOP and RA11 are almost constant, while those between RA11 and the other phthalates increase with increasing t_m for those phthalates. The interaction is negligible for a binary mixture of DBP and RA11 because of the low molar mass of DBP. The plasticizer blend MESAMOLL–DOA–RA10 (an acetyl terminated polyester plasticizer) displays synergistic interactions between all its components, and also possesses cubic interactions, which lower the t_m of the mixture MESAMOLL–RA10 further when $\phi_{RA10} < \phi_{MES}$.

Fig. 8 shows that t_m is more sensitive to changes in DOP and RA11 concentrations than DIUP concentration in DOP–DIUP–RA11 mixtures.

For the systems containing a polymeric plasticizer, interaction coefficients with this plasticizer tend to increase as the t_m of the monomeric plasticizer increases. This is an opposite effect to that observed for the monomeric plasticizer mixtures (see Fig. 17). A least squares fit with a correlation coefficient of 0.9938 gives:

$$B = -83 + 1.19\Delta t_m$$

where B is the quadratic interaction coefficient. It is concluded that the highest interactions are obtained for those mixtures containing the highest molar mass monomerics in both series.

In order to calculate χ parameters for polymeric plasticizers, three mixtures were prepared consisting of DOP, DIUP and polyester plasticizers produced from the same diol and dibasic acid, but with different molar masses. Equations for these are shown in Table 12. Clearly the coefficients in all these equations are very similar, thus producing similar t_m values. These polymeric plasticizers
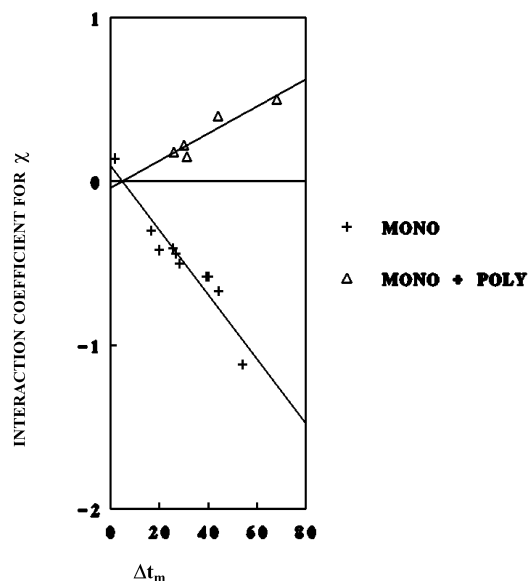

Fig. 17. Relationship between the difference in t_m between two plasticizers, and their t_m values.

Fig. 18. Relationship between the difference in t_m between two plasticizers, and their χ values.

Table 11
Effect of changes in t_m and volume/weight ratios on calculated χ parameters

$t_m - 1\,^\circ C$ $\chi = -0.04\phi_{DOP} + 0.27\phi_{DOA} + 0.41\phi_{DOS} - 0.31\phi_{DOA}\phi_{DOP} - 0.50\phi_{DOP}\phi_{DOS}$	$R^2 = 0.9839$
t_m $\chi = -0.02\phi_{DOP} + 0.30\phi_{DOA} + 0.43\phi_{DOS} - 0.30\phi_{DOA}\phi_{DOP} - 0.50\phi_{DOP}\phi_{DOS}$	$R^2 = 0.9840$
$t_m + 1\,^\circ C$ $\chi = -0.00\phi_{DOP} + 0.23\phi_{DOA} + 0.45\phi_{DOS} - 0.30\phi_{DOA}\phi_{DOP} - 0.50\phi_{DOP}\phi_{DOS}$	$R^2 = 0.9841$
Weight fraction $\chi = -0.02\phi_{DOP} + 0.30\phi_{DOA} + 0.43\phi_{DOS} - 0.28\phi_{DOA}\phi_{DOP} - 0.49\phi_{DOP}\phi_{DOS}$	$R^2 = 0.9821$

have in common only a polymeric repeat unit, of molar mass 200.16. The introduction of the repeat unit molar mass rather than the polymer molar mass rationalises the results in Fig. 17, i.e. the interaction coefficients increase as the difference between the molar masses of the two plasticizers increases. Ramos DeValle [23] also concluded that it was not appropriate to use the molar volume of the plasticizer in calculating χ for polymeric plasticizers, since the χ values obtained using this molar volume implied high compatibility, while the measured t_m values implied low compatibility. He suggested that the interaction between PVC and a polymeric plasticizer would involve the repeat unit of PVC and an equivalent small volume of the plasticizer chain. More realistic χ values (in line with other data) were obtained if the plasticizer molar volume was divided by 3–4. In the present work, both experimental measurements, and equations in Table 12 produce a t_m of 159 °C for all the polymeric plasticizers, independent of molar mass, so the repeat unit was used to calculate χ values, although the values obtained (Table 3) were theoretically too high, such as to imply that the polymeric plasticizers were totally incompatible with PVC. Data in Table 7 show that χ values calculated as above correlate with those from the models. However, while interactions with other plasticizers are synergistic for the t_m values (Table 6), they are antagonistic for χ values. The antagonistic interactions between RA11 and the phthalates become smaller with increasing molar mass of the phthalates, as seen in Fig. 18. Therefore, the

blends become more compatible with increasing molar mass of the phthalates, which is consistent with results discussed earlier. A least squares fit with a correlation coefficient of 0.9394 for data for mixtures of monomeric and polymeric plasticizers in Fig. 18 is given by:

$$D = -0.04 + 0.08\Delta t_m$$

where D is the quadratic coefficient for χ.

Both synergistic and antagonistic interactions are observed in the MESAMOLL–DOA–RA10 blend as shown in Fig. 10. The cubic interactions between MESA-MOLL and RA10 compensate partly for the antagonistic interaction between these two plasticizers at higher MESAMOLL concentrations (Table 7). The interactions between MESAMOLL and DOA are synergistic for both t_m and χ; the strong interaction for t_m between RA10 and DOA changes to a very weak interaction for χ due to the low molar mass of the repeat unit.

For DOP–DOA–DOS similar interactions are obtained for the Bigg activity parameter α^*, as illustrated by comparison of Figs. 7 and 11. α^* is quite sensitive to changes in the concentration of DOP or DOS.

Solubility parameters for the same system show no interaction at 25 °C. If values are corrected to produce the same equation at t_m, low synergistic interactions are observed.

The UNIFAC-FV model provides further information about the compatibility of PVC with plasticizers. Figs. 12

Table 12
Equations relating t_m to volume fractions for various ternary systems containing poly(butylene adipate)

DOP–DIUP–S5561 $t_m = 114.3\phi_{DOP} + 134.1\phi_{DIUP} + 158.8\phi_{S5561} - 31.8\phi_{DOP}\phi_{S5561} - 46.9\phi_{DIUP}\phi_{S5561}$	$R^2 = 0.9981$
DOP–DIUP–RA11 $t_m = 114.4\phi_{DOP} + 134.2\phi_{DIUP} + 160.0\phi_{RA11} - 33.4\phi_{DOP}\phi_{RA11} - 48.5\phi_{DIUP}\phi_{RA11}$	$R^2 = 0.9993$
DOP–DIUP–S5640 $t_m = 114.4\phi_{DOP} + 135.2\phi_{DIUP} + 160.8\phi_{S5640} - 33.9\phi_{DOP}\phi_{S5640} - 47.9\phi_{DIUP}\phi_{S5640}$	$R^2 = 0.9989$

and 13 predict that the Gibbs free energy of mixing is always negative, with a minimum value at a concentration dependant on the type of plasticizer. For the phthalates studied (Fig. 12) the shape of the curves is similar, and the value of the free energy of mixing becomes more negative as the alkane chain length becomes shorter. This correlates well with their observed compatibilities with PVC. Fig. 19 shows the relationship between the minima of the above values and the number C atoms in the aliphatic alcohol moiety. A least squares fit with a correlation coefficient of 0.9985 gives:

Minimum Gibbs free energy of mixing $= -3.95 + 0.24C$

where C is the number of C atoms.

The shape of the curves in Fig. 12 changes gradually from DBP to DTDP. For weight fractions of plasticizers greater than 0.5, the curvature decreases and finally becomes a straight line. This straight line is the borderline for miscibility. If straight lines, starting from the right hand side (weight fraction of plasticizer = 1) are drawn, it is seen that the line for DTDP, the least polar phthalate studied, applies to a wide concentration range. In practice, this phthalate has the highest alcohol chain length for use as an effective plasticizer.

Similar results are observed for other plasticizer types (Fig. 13). The method of drawing tangents described above shows partial miscibility for DOS with PVC. Again, it is known in practice that the compatibility of PVC with DOS is low, i.e. PVC/DOS dry blends with more than 40 wt% of DOS are sticky and wet. A linear relationship is observed in a plot of the minimum Gibbs free energy of mixing against the number of CH_2 groups in the dicarboxylic acids used in DOA, DOZ and DOS. A least squares fit with a correlation

coefficient of 0.9644 gives:

Minimum Gibbs free energy of mixing $= -1.72 + 0.10C$

From both Figs. 12 and 13, the lower limit for the Gibbs free energy of mixing is -0.88 J/g. It is concluded that the lower limit of Gibbs free energy of mixing required for plasticization of PVC using monomeric plasticizers is about -0.9 J/g.

The curves for polymeric plasticizers in Fig. 13 are very similar. There is a small effect of plasticizer molar mass, with higher molar mass compounds having more negative values. This correlates well with the observed compatibilities of these compounds (5). It is well known that non-terminated low molar mass (~ 1000) polymerics are incompatible due to the relatively high level of hydroxyl groups in the plasticizer. It is concluded that the lower limit for Gibbs free energy of mixing is less negative than for monomerics, and is of the order of -0.15 J/g for non-terminated polyester plasticizers with a molar mass of 1000.

Boo and Shaw [10] and Price and Dent [11] also obtained convex-downward curves for mixtures of PVC with both plasticizers and lubricants. All these workers used the older UNIFAC-FV parameters without including temperature dependency, so that the results reported here generally correlate better with experimental results.

Equations in Table 8 show that χ values increase with increasing molar mass of both phthalates and dibasic esters, due to the value of the constant term. This constant relates to PVC alone ($\phi = 1$) so should be constant, but the values were obtained by curve fitting. The 'constant' therefore applies to χ for PVC with an infinitely small quantity of the plasticizer present, explaining why it increases for the less compatible plasticizers. Other terms in the equations in Table 8 cause a gradual transition from a decrease in χ at increasing plasticizer concentrations χ for compatible plasticizers to an increase in χ at increasing plasticizer concentrations for less compatible plasticizers, as illustrated for some plasticizers in Fig. 20.

5. Conclusions

The ordering of different monomeric plasticizers with respect to their compatibility was similar to that reported previously. Synergy is observed when branched phthalates are mixed with ODPP, which was the most compatible of the plasticizers studied, with a greater than anticipated reduction in the solid–gel transition temperature. The synergistic effect increased with the chain length of the branched phthalate. The maximum synergy occurred for the composition with the lowest calculated free energy of mixing. Similar synergy was observed when two phthalates were mixed with ODPP, but none when three phthalates were mixed. Mixtures of DOP with aliphatic ester plasticizers again produced synergy of a similar magnitude. Unsurprisingly, similar synergistic effects were also
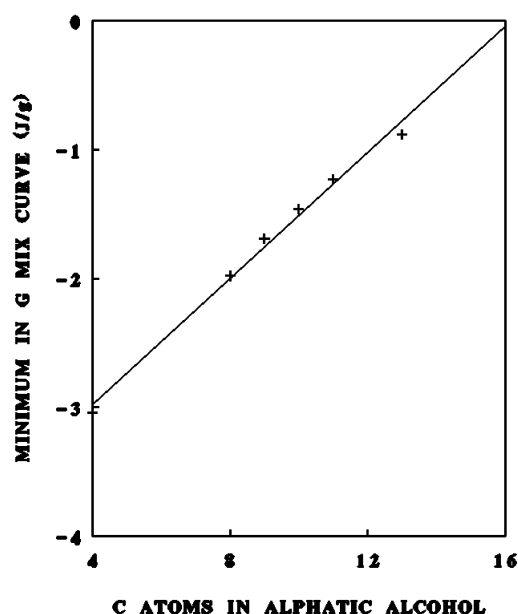

Fig. 19. Relationship between the minimum Gibbs free energy of mixing and the number of C-atoms in the aliphatic alcohol in phthalate plasticizers.
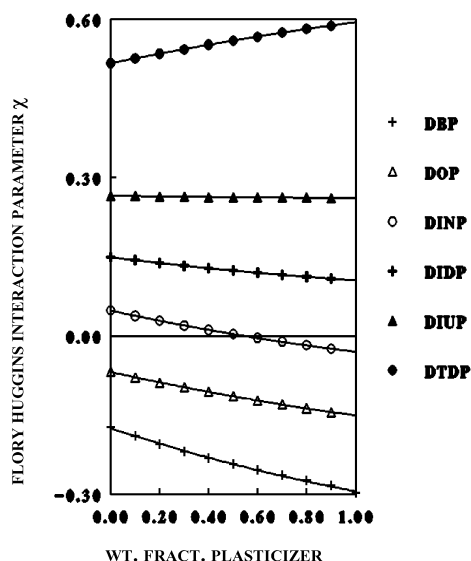
Fig. 20. Relationship between χ and weight fraction for various phthalate plasticizers.

observed when χ values were considered, although the fit for equations produced was poorer. Measured interaction parameters are unaffected by variations in t_m measurement of $\pm 1\,^{\circ}C$.

Equations were produced for both monomeric and polymeric plasticizers, which would enable interaction coefficients of different plasticizer blends to be predicted.

For the systems containing a polymeric plasticizer, interaction coefficients with this plasticizer tend to increase as the t_m of the monomeric plasticizer increases. This is an opposite effect to that observed for the monomeric plasticizer mixtures. t_m was found to be independent of the molar mass of the polymeric plasticizer, suggesting that the plasticizer repeat unit should be used for calculation of χ. It was then possible to conclude that interaction coefficients will increase when the difference between the molar mass of the two plasticizers is greatest.

χ values calculated using the UNIFAC-FV method were similar to experimental values, except for the poorer plasticizers, when calculated values were too high. The lower limit of Gibbs free energy of mixing required for plasticization of PVC using monomeric plasticizers was

calculated to be about -0.9 J/g. That for polymeric plasticizers was less negative, of the order of -0.15 J/g. Equations were produced enabling Gibbs free energy of mixing to be predicted from the amount of C atoms in the plasticizer.

Acknowledgements

References

[1] Sears JK, Darby JR. The technology of plasticizers. New York: Wiley; 1982.
[2] Patel SV, Gilbert M. Plast Rubb Proc Appl 1986;6:321–30.
[3] Ramos DeValle LF, Gilbert M. Plast Rubb Proc Appl 1990;13:151–6.
[4] Wilson AS. Plasticizers. London: Institute of Materials; 1995.
[5] Huang JC, Chang DC, Deanin RD. Adv Polym Technol 1993;12: 81–90.
[6] Dondos A, Patterson D. J Polym Sci Part A-2 1969;7:209–17.
[7] Scott RL. J Chem Phys 1981;17:279–84.
[8] Fredenslund A. Fluid Phase Equilibria 1989;52:135–50.
[9] Gottlieb M, Herskowitz M. Macromolecules 1981;14:1468–71.
[10] Boo H-K, Shaw MT. J Vinyl Technol 1988;10:77–83.
[11] Price GJ, Dent MR. Polymer 1990;31:1745–9.
[12] Cornell JA. Experiments with mixtures. New York: Wiley; 1990.
[13] Design-Expert User's Guide; 1993.
[14] Flory PJ. Principles of polymer chemistry. New York: Cornell University Press; 1953.
[15] Anagostopoulos CE, Coran AY, Gamrath HR. J Appl Polym Sci 1960; 4:181–92.
[16] Anagostopoulos CE, Coran AY. J Polym Sci 1962;57:1–11.
[17] Anagostopoulos CE, Coran AY, Gamrath HR. Mod Plast 1965;43: 141–4.
[18] Bigg DCH. J Appl Polym Sci 1975;19:3119–27.
[19] Fedors RF. Polym Engng Sci 1974;14:147–54.
[20] Holly ED. J Polym Sci Part A 1964;2:5267–76.
[21] Tomaselli F, Gupta VP, Calderon HS, Brown GR. J Vinyl Technol 1988;10:72–6.
[22] Tomaselli F, Gupta VP, Calderon HS, Brown GR. J Vinyl Technol 1989;11:9–14.
[23] Ramos-DeValle LF. PhD Thesis. Loughborough University; 1988.