# Solubility Parameter of a Polyester Composite Material

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**ABSTRACT:** The solubility parameters of a BMC composite material, its polyester matrix, and its low profile additive [poly(vinyl acetate)] were determined by using several methods. For Hildebrand's solubility parameter : calculation from molar additive laws and determination from unrelaxed elastic constants, these latter being determined from the propagation rate of ultrasonic waves. For partial solubility parameters from sorption test in saturated solvent atmosphere, using bidimensional solubility maps. The effect of glass fibers and mineral fillers on solvent absorption can be considered negligible. In contrast, the presence of the low profile additive significantly modifies the solubility parameter values. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 2663–2671, 1998

**Key words:** BMC; unsaturated polyester; solvents; solubility parameters

## INTRODUCTION

Although criticized for their lack of precision, the concepts of the cohesive energy density $e$ and solubility parameter $\delta = e^{1/2}$ have been largely applied to the prediction of thermophysical, mechanical properties, and behavior in solvent atmosphere of glassy polymers.[1–6] We tentatively apply these approaches to bulk molding compounds that are possibly in contact with organic solvents in many applications, for instance, painting of automotive parts. These latter can promote damagement from their swelling effect, so that the knowledge of material–solvent interactions is of practical interest. Experimentally, the degree of interaction between a polymer and a solvent is assumed by the equilibrium concentration $v_\infty$ of the solvent in the polymer, determined from a classical sorption test. From the theoretical point of view, there are essentially two approaches. The first one, derived from thermodynamics of solutions, is based on the consideration of Hildebrand's solubility parameters[7] ($\delta_P$ for the polymer, $\delta_S$ for the solvent) and can be resumed by the following rule:

$$v_\infty \text{ increases when } |\delta_P - \delta_S| \to 0.$$

This rule allows prediction of overall trends (sensitivity to nonpolar or polar or hydrogen bonding solvents), it displays relatively good predictive properties in the case of nonpolar polymers, but it is clearly insufficient in the case of polar polymers. In this case, better results are obtained using the Hansen's method,[8,9] in which three partial solubility parameters corresponding respectively to the three types of intermolecular forces: dispersion (London) $\delta_d$; polar (Debye and Keesom) $\delta_p$, and hydrogen bonds $\delta_h$. The degree of interaction then obeys the following rule:

$$|\delta_{dP} - \delta_{dS}| \to 0$$
$$v_\infty \text{ increases when } |\delta_{pP} - \delta_{pS}| \to 0$$
$$|\delta_{hP} - \delta_{hS}| \to 0$$

We use in this work two methods: (1) a theoretical approach in which the solubility parameter is calculated by using an additive law of elemental group contributions established by several authors; (2) a graphical approach [10] in which the representative points of the polymer ($P$) and the solvent ($S$) are located in a bidimensional space of partial solubility parameters ($0, \delta_v, \delta_h$), where $\delta_v = \sqrt{\delta_d^2 + \delta_p^2}$. Their mutual interaction is a decreasing function of the distance PS:

$$v_\infty \text{ increases when } (\overrightarrow{PS})^2 \text{ decreases.}$$

Both methods are questionable because the elemental group contribution is considered as independent of the neighboring, and because of possible sorption anomalies due to relaxation phenomena, damaging. Despite this, they have been applied successfully to epoxy–amine networks. [11]

But whatever the chosen method, we get three additional problems: (1) for polar polymers such as polyester and poly(vinyl acetate), the equilibrium concentration of the solvent in the polymer does not vary in an isotropic and monotonous way with $\overrightarrow{PS_i}$. (2) The composite material is polyphase—polyester and poly(vinyl acetate) form two distinct phases. Could this composite be considered as an homogenous material of which the properties would be an additive function of the polyester and poly(vinyl acetate) properties? (3) The microvoid concentration in the BMC polyester is around 10%. [12] How will these microvoids affect the behavior independently of solubility parameter considerations?

## EXPERIMENTAL

### Materials

#### Composite Material (BMC)

It is composed of styrene crosslinked polyester (20.2 wt %), poly(vinylacetate) (3.6 wt %), short glass fibers (18 wt %), calcium carbonate (56.8 wt %), and various additives in low concentration. The plaques were injection molded at 170°C, 9 MPa during 90 s. The chosen plaque was a large size rectangular plate that was arbitrarily divided into six zones differing by the distance to the injection gate (Fig. 1).

#### Unsaturated Polyester (UP)

We prepared styrene crosslinked polyester plates in molds of $145 \times 135 \times 0.7$ mm$^3$. A mold remov-
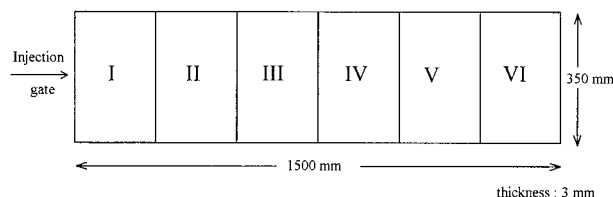


**Figure 1**    Cutout scheme of the plaque.

ing agent (QZ13F; Ciba Geigy) is first sprayed on the mold, the compound that is composed of 28 g of polyester, 12 g of styrene, and 0.1 g of 2-butanone peroxide (initiator dissolved at 50% in some dimethyl phthalate) is degassed under a reduced pressure of 2000 Pa (3 min at 50°C). This operation enables us to get rid of gas-derivated products that were created and trapped during the synthesis. The compound is then run into the mold. The plate is removed after a 24 h cooling at room temperature. A postcure is performed, first at 80°C for 8 h, then at 120°C for 4 h.

#### Poly(vinyl acetate) (PVAc)

It is provided in small 3–4 mm diameter balls. Two grams of PVAc are layed down in an aluminium plate of 5.5 cm diameter. This plate is then heated up at 60°C under vacuum for 1 h and 30 min. After removing the sample, it is pressed for 5 min at 80°C and 15 MPa.

### Solvent Interactions

#### Gravimetry

Samples of $30 \times 45 \times 3$ mm$^3$ for BMC and $30 \times 45 \times 0.7$ mm$^3$ for polyester were dried under vacuum at 50°C until constant weight. Then they were placed in a solvent saturated atmosphere for 500 h in a thermostated chamber at 30°C. They are not immersed because: (1) extraction phenomena are limited; (2) the difference of the solvent concentration at the surface of the composite is supposed insignificant; (3) the process is slower and can be observed by regular weighings; and (4) the equilibrium volume is the same.

They were periodically weighed with a $10^{-4}$ relative precision balance. To compare the solvent effects, we took into account the density of solvents and expressed the results in cm$^3$ of solvent per 100 g of material. The characteristics of the 33 solvents and the equilibrium concentration $v_\infty$ in BMC zone II and polyester are presented in Table I. These solvents were chosen because they

**Table I Correspondence Between the Name of Solvents and Numbers Located on the Solubility Spectra**

| Solvent | No. | $\rho$ (kg m$^{-3}$) | $\delta$ (J$^{1/2}$ cm$^{-3/2}$) | $\delta_d$ (J$^{1/2}$ cm$^{-3/2}$) | $\delta_p$ (J$^{1/2}$ cm$^{-3/2}$) | $\delta_h$ (J$^{1/2}$ cm$^{-3/2}$) | $v_\infty$ (cm$^3$/100 g) BMC | UP |
|---|---|---|---|---|---|---|---|---|
| Toluene | 1 | 865 | 18.2 | 17.7 | 1.4 | 2.0 | 5.1 | 6.6 |
| Ethyl acetate | 2 | 900 | 18.6 | 15.2 | 5.3 | 9.2 | 5.2 | 20.0 |
| Chloroform | 3 | 1480 | 19.0 | 17.9 | 3.1 | 5.7 | 11.3 | 23.7 |
| Methyl acetate | 4 | 930 | 18.7 | 15.5 | 7.2 | 7.6 | 5.5 | 22.5 |
| Dioxane | 5 | 1034 | 20.2 | 18.2 | 1.8 | 7.4 | 6.6 | 27.4 |
| Nitrobenzene | 6 | 1100 | 20.5 | 18.7 | 12.3 | 4.1 | 6.0 | 8.5 |
| Aniline | 7 | 1021 | 22.6 | 19.5 | 5.1 | 10.2 | 7.4 | 10.7 |
| Acrylonitrile | 8 | 800 | 21.5 | 16.4 | 17.4 | 6.8 | 5.8 | 22.0 |
| Pyridine | 9 | 982 | 21.9 | 19.5 | 8.8 | 5.9 | 8.1 | 26.9 |
| Dimethylphthalate | 10 | 1190 | 21.9 | 18.6 | 10.8 | 4.9 | 1.3 | 1.3 |
| N,N-Dimethylacetamide | 11 | 940 | 22.1 | 16.8 | 11.5 | 10.2 | 5.8 | 1.6 |
| 1-Pentanol | 12 | 815 | 21.7 | 16.0 | 4.5 | 13.9 | 2.7 | 1.4 |
| Nitroethane | 13 | 1050 | 22.7 | 16.3 | 15.6 | 4.5 | 5.8 | 22.7 |
| 2-Propanol | 14 | 785 | 23.6 | 15.8 | 6.1 | 16.4 | 4.3 | 5.2 |
| Acetonitrile | 15 | 782 | 24.1 | 15.8 | 18.0 | 6.1 | 5.3 | 18.5 |
| 1-Propanol | 16 | 804 | 24.4 | 15.9 | 6.8 | 17.4 | 4.5 | 2.5 |
| 2-Methoxyethanol | 17 | 920 | 24.7 | 16.2 | 9.2 | 16.4 | 4.6 | 21.4 |
| N,N-Dimethylformamide | 18 | 950 | 24.9 | 17.4 | 13.7 | 11.3 | 5.8 | 29.0 |
| Ethanol | 19 | 810 | 26.0 | 15.8 | 8.8 | 19.5 | 4.2 | 14.0 |
| Nitromethane | 20 | 1130 | 26.0 | 16.1 | 18.8 | 5.1 | 5.9 | 28.0 |
| 2-Pyrrolidone | 21 | 1110 | 28.4 | 19.5 | 17.4 | 11.3 | 1.2 | 3.4 |
| Methanol | 22 | 792 | 29.6 | 15.2 | 12.3 | 22.3 | 4.8 | 14.0 |
| Formamide | 23 | 1130 | 36.7 | 17.2 | 26.2 | 19.0 | 1.0 | 3.5 |
| Heptane | 24 | 684 | 15.2 | 15.2 | 0.0 | 0.0 | 0.1 | 0.3 |
| Styrene | 25 | 910 | 19.0 | 17.7 | 1.0 | 4.1 | 5.2 | 3.6 |
| Butyl acetate | 26 | 875 | 17.4 | 15.7 | 3.7 | 6.4 | 5.0 | 2.3 |
| Methylisobutylketone | 27 | 800 | 17.5 | 15.3 | 6.1 | 4.1 | 4.6 | 2.0 |
| 1-Methyl-2-pyrrolidone | 28 | 1030 | 22.9 | 17.9 | 12.3 | 7.2 | 6.4 | 6.5 |
| 1,4-Dimethylbenzene | 29 | 860 | 18.0 | 17.0 | 1.0 | 1.0 | 5.0 | 1.8 |
| 1-Acetoxy-2-ethoxy ethane | 30 | 970 | 18.3 | 15.7 | 4.6 | 8.6 | 5.3 | 6.5 |
| 1-Methoxy-2-propanol | 31 | 921 | 22.8 | 15.3 | 6.5 | 15.3 | 4.7 | 4.5 |
| 2-(2-Butoxyethoxy)ethyl acetate | 32 | 977 | 18.1 | 15.9 | 3.6 | 7.9 | 2.0 | 3.8 |
| Water | 35 | 1000 | 47.9 | 13.3 | 31.3 | 34.2 | 0.7 | 1.9 |

Density and solubility parameters and of the solvents[2,8,9] and equilibrium concentration $v_\infty$ of solvents in BMC zone II and polyester.

are used in this kind of study[11] or contained in car paint formulations. They represent a large distribution of solubility parameters $\delta$. The reproducibility on $v_\infty$ is 4%.

PVAc is soluble in most of solvents; thus, it is impossible to do the same experiment. We will present only the results obtained from calculation and ultrasonic tests.

## Solubility Parameter Determination

Two experimental methods allow the determination of the solubility parameter of a material: one is the analytical, and the other is the graphical method.

### Analytical Method

To analytically determine the solubility parameters of BMC and polyester, we have to know the values of the equilibrium concentration $v_\infty$ of the solvents determined on the gravimetric curves for BMC and polyester. Solubility parameters of BMC and polyester are considered as the barycenter of the points $(\delta_{si}; v_{\infty i})$. Interactions between a solvent and a polymer are strong when the solu-

bility parameters $\delta_S$ of the solvent and $\delta_P$ of the polymer are close. So the solubility parameter of the polymer is equal to the parameter of the solvent of which $v_\infty$ is the highest. Solvents are divided in three families according to their behavior, the most active solvents towards the material, the less active ones, and the intermediate ones.

To compare the different zones of the BMC plaque and the polyester, we calculated their global solubility parameter $\delta$ and the partial parameters corresponding to dispersion forces, dipole–dipole forces and hydrogen bonding:

$$\delta = \frac{\sum \delta_{s_i} \times v_{\infty_i}}{\sum v_{\infty_i}} \quad \delta_d = \frac{\sum \delta_{d_i} \times v_{\infty_i}}{\sum v_{\infty_i}}$$

$$\delta_p = \frac{\sum \delta_{p_i} \times v_{\infty_i}}{\sum v_{\infty_i}} \quad \delta_h = \frac{\sum \delta_{h_i} v_{\infty_i}}{\sum v_{\infty_i}}$$

### Graphical Method

We plot three different level curves corresponding to the activity levels: strong, moderate, and weak. One then proceeds by successive approximation, on the three solubility maps of the studied material simultaneously[2]: $\delta_d = f(\delta_a)$, $\delta_h = f(\delta_v)$, $\delta_p = f(\delta_u)$, with

$$\delta_a = \sqrt{\delta_p^2 + \delta_h^2} \quad \delta_v = \sqrt{\delta_p^2 + \delta_d^2} \quad \delta_u = \sqrt{\delta_d^2 + \delta_h^2}$$

We obtain bidimensional maps taking into account all three figures. The solvent family must be the same in the three cases and for a given material. Maps of $\delta_h = f(\delta_v)$ are the only ones shown here. For each $(\delta_a, \delta_d)$, $(\delta_v, \delta_h)$, $(\delta_p, \delta_u)$ diagram, three maps are plotted: (1) the first attempt corresponds to the chosen answer; (2) the second attempt represents the case where the boundaries between the most active solvents and the moderate ones cannot be distinguished; (3) the third attempt represents the case where the boundaries between the less active solvents and the moderate ones cannot be distinguished.

The computed point of the solubility parameter of PVAc and the graphically determined ones (center of the level curve of the most active solvents) of polyester and BMC are printed on the maps.

### Ultrasonic Tests

The propagation rate of the ultrasonic waves was determined, for transverse ($v_t$) and longitudinal ($v_l$) modes, using a Sofranel 5055 PR pulser/receiver wave generator with 5 MHz probes for longitudinal and transversal waves using mineral oil or grease as coupling agent. The bulk modulus $B_u$ and Poisson's ratio $\nu_u$ were determined from the following relationships[2]:

$$R = \frac{v_l}{v_t} \quad \nu_u = \frac{2 - R^2}{2(1 - R^2)} \quad B_u = v_l^2 \rho \frac{1 + \nu}{3(1 - \nu)}$$

where $\rho$ is the density.

These measurements were made only on polyester and PVAc for which there are no fibers and fillers.

## RESULTS

### Theoretical Calculation of the Solubility Parameters

We calculate the theoretical solubility parameters of the polyester and the PVAc by an additive law of molar contributions to cohesive energy from each chemical group[2] and by an additive law of the three partial solubility parameters calculated by Hansen.[8] The solubility parameter is the square root of the cohesive energy density:

$$\delta = \sqrt{\frac{\sum n_i Hs_i}{V}}$$

### Poly(vinyl acetate)



$M = 86$ g
$\rho_{\exp} = 1187$ kg m$^{-3}$
$V = 72.4$ cm$^3$ mol$^{-1}$
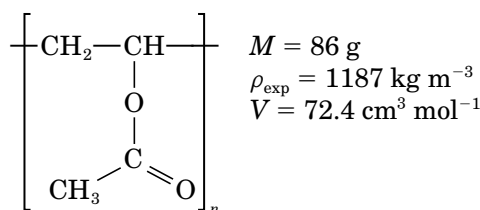
| group | $n_i$ | $Hs_i$ | $\Sigma n_i Hs_i$ |
|---|---|---|---|
| COO | 1 | 18000 | |
| CH | 1 | 3430 | |
| CH$_2$ | 1 | 4940 | |
| CH$_3$ | 1 | 4710 | |
| total: | | | 31080 J mol$^{-1}$ |

$$\frac{\Sigma Hs_i}{V} = 0.429 \text{ kJ cm}^{-3} \quad \underline{\delta = 20.7 \text{ J}^{1/2} \text{ cm}^{-3/2}}$$

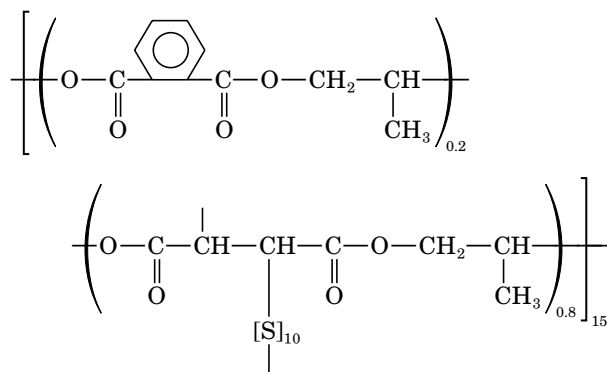$$\delta = (\delta_h^2 + \delta_p^2 + \delta_d^2)^{1/2} = 19.2 \text{ J}^{1/2} \text{ cm}^{-3/2}$$

calculated by an additive law of the three partial solubility parameters by Hansen.[8]

## Polyester

We determine by steric exclusion chromatography the number average molecular weight: $\overline{M}_n = 2520$

g mol$^{-1}$. The network corresponds to the following structure in which the molar ratio maleate/phthalate is about 0.8/0.2, and where all the styrene molecules are assumed to participate to the reaction, which gives an average of 10 styrene units (S) per structural unit.

Constitutive repeat unit:



| | group | $n_i$ | $Hs_i$ (J mol$^{-1}$) | $\Sigma n_i Hs_i$ (J mol$^{-1}$) |
|---|---|---|---|---|
| prepolymer | —COO— | 2   × 15 | 18000 | |
| | CH | 2.6 × 15 | 3430 | |
| | CH$_2$ | 1   × 15 | 4940 | |
| | CH$_3$ | 1   × 15 | 4710 | |
| | phenyl | 0.2 × 15 | 31940 | 914340 |
| styrene | phenyl | 10 | 31940 | |
| | CH | 10 | 3430 | |
| | CH$_2$ | 10 | 4940 | 403100 |
| total: | | | | 13170 kJ mol$^{-1}$ |

$M_{\text{calc}} = 3568$ g     $V = 2854$ cm$^3$ mol$^{-1}$     $\rho_{\text{exp}} = 1250$ kg m$^{-3}$

$$\frac{\Sigma Hs_i}{V} = 0.46 \text{ kJ cm}^{-3}$$

$$\underline{\delta = 21.5 \text{ J}^{1/2} \text{ cm}^{-3/2}}$$

## Analytical Determination of the Solubility Parameters

We determine here the Hildebrand's solubility parameter $\delta$ and the Hansen's partial solubility parameters $\delta_d$ (dispersion), $\delta_p$ (dipole–dipole) and $\delta_h$ (hydrogen bonding). The idea is that each point representing the solvent is affected by a weight equal to its equilibrium concentration in the polymer, the point representing the polymer is the barycenter of the solvent representative points. A (global or partial) solubility parameter $\delta_x$ can be calculated by

$$\delta_x = \frac{\Sigma \, \delta_{xi} v_i}{\Sigma \, v_i}$$

The obtained results are presented in Table II for the different zones of the plaque and the polyester. These results call for the following comments: (1) For the composite, the solubility parameters are independent (within experimental scatter) of the location in the plaque. This confirms previous analytical results[12] showing that there are no differences in structure and composition of the organic phase between different sites of the plaque. Incidentally, the low variations of solubility parameters from one site to another give an idea of the reproducibility of these experiments. (2) We compared the solubility parameters of the BMC and the polyester, considering that the concentrations of styrene used for the

**Table II Solubility Parameters ($J^{1/2}$ cm$^{-3/2}$), Determined Analytically, of Polyester and the Different Zones of the Plaque**

| | BMC Zone I | BMC Zone II | BMC Zone III | BMC Zone IV | BMC Zone V | BMC Zone VI | Polyester |
|---|---|---|---|---|---|---|---|
| $\delta$ | 21.9 | 21.8 | 21.7 | 21.8 | 21.8 | 21.8 | 22.6 |
| $\delta_h$ | 8.9 | 8.8 | 8.7 | 8.7 | 8.6 | 8.7 | 9.3 |
| $\delta_p$ | 8.6 | 8.5 | 8.5 | 8.6 | 8.7 | 8.6 | 10.3 |
| $\delta_d$ | 16.8 | 16.9 | 16.9 | 16.9 | 16.9 | 16.8 | 16.8 |

crosslinking, 40 wt % for BMC and 30 wt % for polyester, are close. The polyester is more polar than the BMC: its values of $\delta$, $\delta_p$, and $\delta_h$ are stronger but the $\delta_d$ values are the same. This is consistent with the results obtained by calculation: PVAc is less polar than polyester. (3) BMC has a higher absorption capacity than the polyester. For the most "reactive" solvent (chloroform), $\nu_\infty = 11$ cm$^3$/100 g for BMC (therefore, 40 cm$^3$/100 g, considering only the organic part of BMC) and 24 cm$^3$/100 g for neat polyester. This difference can be attributed to the effect of PVAc or fillers, or a difference in porosity. We have no quantitative data for PVAc, but looking at an eventual effect of fillers, we have calculated the interface volume between CaCO$_3$ and organic phase to compare its value with the volume of the matrix phase able to absorb solvent. The average radius of a CaCO$_3$ grain is $r = 1.5$ $\mu$m, its volume is

$$v = \tfrac{4}{3}\pi r^3 = 14.10^{-18} \text{ m}^3$$

By supposing that the thickness of the "disturbed" layer around the grain is $10^{-9}$ m and the external surface of the grain being $4\pi r^2$, the interface volume around one grain is $28.10^{-21}$ m$^3$. Fillers ($\rho = 2700$ kg m$^{-3}$) represent about 57 wt %, that is to say 21.1 cm$^3$/100 g; the organic part ($\rho = 1200$ kg m$^{-3}$) represents 25 wt %, that is to say 20.8 cm$^3$/100 g. The volume of the matrix corresponding to the volume of fillers equal to $14.10^{-18}$ m$^3$, able to absorb solvent ($14.10^{-18}$ m$^3$), is 1000 times higher than the interface volume ($28.10^{-21}$ m$^3$). We cannot exclude the role of PVAc, but the volumic % of porosity[12] (10%) could partly explain this difference.
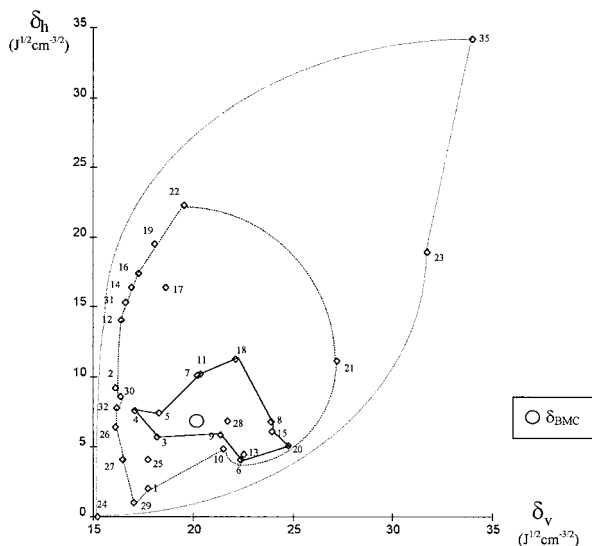
## Graphical Determination of the Solubility Parameters

Both analytical and graphical methods have been used to determine Hansen's partial solubility pa-

rameters. For the graphical method, solvents are classified in three families, respectively, weakly, moderately, and strongly interactive solvents. For each family, the representative points in bidimensional maps are expected to belong to a closed envelope containing the envelopes of the more interactive families. Ideally, each family would correspond to a $\nu_\infty$ value, the corresponding envelope would be a circle, and the representative point of the polymer would be the center of the smallest circle corresponding to the most interactive family. In reality, the nonisotropy of the ($\delta_d$, $\delta_p$, $\delta_h$) space and the limited number of solvents under study, imposing to limit to three the number of families, are responsible for the noncircular, even nonconvex, shape of the envelopes, as shown in Figures 2 and 3, where the weakly and moderately interacting families are represented by dotted lines, whereas the most interactive family is represented by a full line. It will be arbitrarily
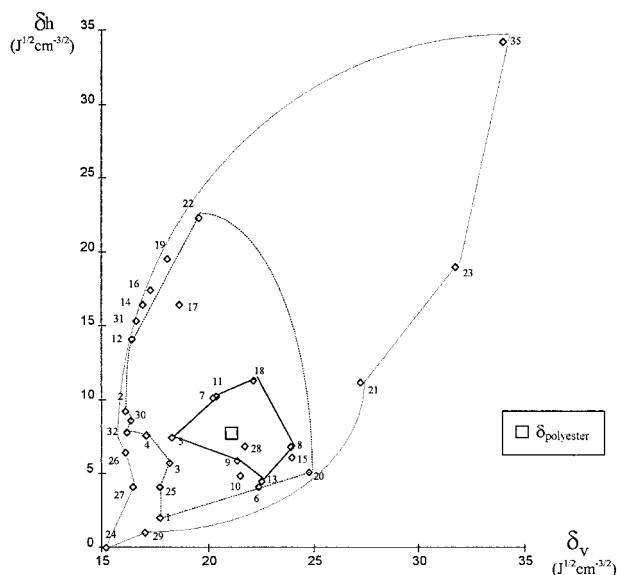


**Figure 2** Bidimensional solubility map of polyester: $\delta_h = f(\delta_v)$. See "Graphical determination of the solubility parameters" for the location of "region" centers.
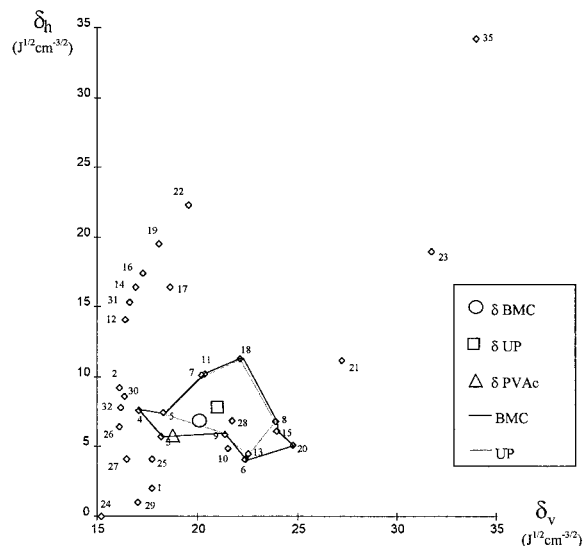
**Figure 3** Bidimensional solubility map of the zone II of the plaque: $\delta_h = f(\delta_v)$. See "Graphical determination of the solubility parameters" for the location of "region" centers.



**Figure 4** Curves connecting the stronger interaction solvents of BMC zone II (full line) and polyester (small dotted line). The solubility parameters of the three materials are plotted: BMC (circle), polyester (square) and PVAc[8] (triangle). See "Graphical determination of the solubility parameters" for the location of "region" centers.

considered that the representative point of the polymer $P$ is the barycenter of the points representative of the most interactive solvents of which the numerical code in the figure, is given in Table I. Indeed, in this approach, the result can depend on the criteria taken to distinguish the three families. Various criteria were tested and those giving the most consistent solution were chosen. They are represented in Figures 2 and 3 for, respectively, polyester and BMC (zone II). The results are summarized in Table III. In the case of polyester, the graphically determined value of $\delta$ is slightly lower than the analytical one, whereas both values are equal in the case of BMC. For polyester, where the theoretical value of $\delta$ can be determined, it appears significantly lower than the experimental one: 21.5 against 22.4 ± 0.2 J$^{1/2}$ cm$^{-3/2}$.

The envelopes of strongly interactive solvents have been plotted in the same diagram $\delta_h = f(\delta_v)$

**Table III  Solubility Parameters (J$^{1/2}$ cm$^{-3/2}$) Determined Graphically**

|            | BMC Zone II | Polyester |
| ---------- | ----------- | --------- |
| $\delta$   | 21.8        | 22.2      |
| $\delta_h$ | 7.1         | 7.8       |
| $\delta_p$ | 9.9         | 11.2      |
| $\delta_d$ | 17.6        | 17.5      |

in Figure 4, which calls for two interesting remarks: (1) as expected, the curve of BMC includes the curve of polyester and the area excess of BMC contains the representative point of PVAc; and (2) logically, the point representative of BMC is located on the segment linking the representative points of polyester and PVAc, between these points.

It appears, thus, that in the case under study, the effect of additives can be predicted in terms of quasi linear effects and that fillers (glass fibers and calcium carbonate) play no significant role in polymer–solvent interactions.

From a comparison of the analytical and graphical methods, it appears that graphical method overestimates $\delta_p$ and $\delta_d$ and underestimates $\delta_h$:

$$\Delta\delta_h = 1.7 \text{ (BMC) and } 1.5 \text{ (polyester)}$$
$$\Delta\delta_p = -1.4 \text{ (BMC) and } -0.9 \text{ (polyester)}$$
$$\Delta\delta_d = -0.7 \text{ (BMC) and } -0.7 \text{ (polyester)}$$

However, the hierarchy of values is not modified from one method to another. It can be reasonably supposed that these systematic errors mainly come from nonuniformity in the distribution of the solvent representative points in the space of partial solubility parameters.

**Table IV   Results of Ultrasonic Measurements of Polyester and PVAc**

|  | Polyester | PVAc |
|---|---|---|
| $\rho$ (kg m$^{-3}$) | 1250 | 1187 |
| $\nu$ | 0.38 | 0.33 |
| $E_u$ (MPa) | 4160 | 4540 |
| $G_u$ (MPa) | 1440 | 1680 |
| $B_u$ (MPa) | 5780 | 4460 |
| $\delta_u = \sqrt{B_u/11}$ (J$^{1/2}$ cm$^{-3/2}$) | 22.9 | 20.1 |

### Ultrasonic Measurements

Gruneisen[13] showed that the bulk modulus of molecular crystals is linked to the sublimation enthalpy by the equation

$$B = 8.04 \frac{\Delta H}{V}$$

Tobolsky[14] transposed this relation to amorphous polymers:

$$B = 8.04 \frac{E_{\text{coh}}}{V} = 8.04 \, \delta^2$$

In the case of epoxy[15] and vinylester[16] networks, this coefficient is closer to $11 \pm 1$ than 8 if we admit that the calculation of the cohesive energy density with the Van Krevelen[2] increments is reliable. The ultrasonic elastic quantities are determined on a time scale ($<10^{-6}$ s) inferior to the characteristic time of the majority of the relaxations associated to local motions in polymers. They are, therefore, not very affected by these relaxations and should depend on only two parameters: the cohesive energy density, and the packing density. We measured from ultrasonic propagation rates the bulk modulus and deduced a value for the solubility parameter,[17] the results of which are shown in Table IV.

It is understood that applying this method to BMC would be nonsense because the important contribution of mineral fillers would be taken into account, which has no sense.

The values of the solubility parameter $\delta_u$ of the polyester and of the PVAc, determined from ultrasonic measurements, are respectively 22.9 and 20.1 J$^{1/2}$ cm$^{-3/2}$. The value for polyester is significantly higher than the values given above, but the hierarchy between polyester and PVAc remains the same.

## DISCUSSION

The summing up of the Hildebrand's solubility parameters values is given in Table V. If the difference between the calculated value of the solubility parameter from the cohesive energy density and the values determined from the experimental maps of solubility is reasonable, a large number of possible reasons of discrepancy exists up to 5% on the solubility parameter. To significantly improve the resolution of our determination methods, the amount of information would have to be multiply by one order of magnitude, which is not very realistic. The difference between the "mechanical" value of the Hildebrand's solubility parameter $\delta_u$ and the "physico-chemical" values is more important. $\delta_u$ is higher than $\delta$ (analytical, graphical, or calculated solubility parameter). Such a difference has already been observed for PMMA[17] and seems to be systematic.

One of the reasons that could explain this difference may be attributed to the plasticizing effect of solvents.[18,19] Indeed, according to the glass transition temperature of the blend "polymer–solvent," two cases must be distinguished: (1) $T_g < T_{\text{test}}$ that is to say in the rubbery state, the equilibrium concentration depends only on the interaction coefficient $\chi$ and the molar volume of the solvent. The solubility parameter determined by sorption tests will have a value close to the one determined from ultrasonic experiments. This is effectively the case of the PVAc; (2) $T_g > T_{\text{test}}$ that is to say in the glassy state, the behavior of the blend will be closely linked to the intensity of the plasticizing effect of the solvent, which can be determined from the free volume theory[18,19]:

$$T_g = \frac{\alpha_P T_{g_P}(1 - \varphi) + \alpha_S \varphi T_{g_S}}{\alpha_P(1 - \varphi) + \alpha_S \varphi} \quad (1)$$

where $S$ and $P$ refer to the solvent and the polymer. $\alpha$ is the expansivity coefficient of the free volume and $\varphi$ the solvent volume fraction. If we consider $\alpha T_g$ as constant (Simha-Boyer[20] law), eq. (1) can be simplified as follows:

$$\frac{1}{T_g} = \frac{1}{T_{g_P}} + A\varphi$$

where

$$A = \frac{1}{T_{g_S}} - \frac{1}{T_{g_P}}$$

**Table V   Summing Up of the Solubility Parameters ($J^{1/2}$ cm$^{-3/2}$) Determined by Different Methods**

|  | Polyester | PVAc | BMC Zone II |
|---|---|---|---|
| $\delta$ theoretical | 21.5 | 20.7 | — |
| $\delta$ analytical | 22.6 | — | 21.8 |
| $\delta$ graphical | 22.2 | — | 21.8 |
| $\delta_u$ | 22.9 | 20.1 | — |

can be called the plasticizing effect.

It so appears that the plasticizing effect is governed by the $T_g$ of the solvent, which depends on a couple of molecular factors, among which, its cohesive energy $e_{coh}$. $T_{g_S}$ rises according to the following scheme: nonpolar solvents < polar solvents < hydrogen bonding solvents.

The higher absorption of nonpolar solvents and low-polar solvents is therefore a consequence of their higher plasticizing effect. For polymers such as UP, the "polymer–solvent" blend always shows a $T_g > T_{test}$, and the solubility parameter determined by the sorption test is systematically lower than the one determined from ultrasonic tests.

## CONCLUSION

The solubility parameters of a bulk molding compound and its main organic components, polyester and poly(vinyl acetate), were determined by various ways: calculation using molar increments, experimental determination from bidimensional solubility maps, and from the ultrasonic bulk modulus. The methods based on solvent absorption experiments are often criticized because of their lack of precision and because they partly depend on the solvent choice, but it should be noticed that the maximum discrepancy between the four methods is less than 10% for polyester (this article) epoxy[11,15] and vinylester[16] networks. Despite this standard deviation of 10%, it can be assumed that inorganic fillers play no significant role, and that the BMC characteristics are logically intermediate between polyester and PVAc. These data, especially partial solubility parameters, can be used to predict the behavior of the material in the presence of solvents of known characteristics, one possible application being the rational choice among a range of paint solvents.

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