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The application of miscibility parameter to the measurement of polymer-plasticizer compatibility

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SUMMARY

Poly(vinyl butyral) (PVB)was found to precipitate from a clear plasticizer solution as it was cooled and this unique temperature (T_P) (UCST) was noted. Poly(vinyl chloride) (PVC) did not precipitate and in this case the temperature at which it went into solution (T_S) was noted. A quantity, referred to previously as the miscibility parameter (MP), is an excellent relative quantitative indicator of the miscibility of poly(vinyl butyral) and poly(vinyl chloride) with plasticizers as demonstrated from a correlation of MP with T_P and T_S. Each polymer-plasticizer system is unique. A plot of MP vs. T_P or T_S for several polymer-plasticizer systems allows additional plasticizers to be evaluated for their plasticizing ability from calculated MP's without resorting to additional experimental measurements. The absolute level of MP acceptability is dictated by the application. For PVB, a copolymer which precipitates from a plasticizer/solvent, the interaction parameter chi(χ) is chi critical (χ_{cr}) at the T_P of PVB in plasticizer. Since T_P approximates the Θ temperature in the limit of molecular weight, the temperature of precipitation or Θ temperature, the solvent volume V_S, and the χ_{cr}, define the theoretical MP_{cr} as given by $\frac{(\chi_{cr} - 0.35)RT}{V_S}$. All MP_{cr}'s were ≈ 0.3 which represents the critical MP above which phase separation occurs. The low molecular weight plasticizers were estimated to drastically increase MP_{cr} to about 1 for acceptable application compatibility and this value compares favorably with (PVB) acceptability for a wide range of plasticizer-PVB combinations based on a plasticizer DP of about 20.

Introduction

Choosing an appropriate plasticizer to modify the properties of a glassy polymer ultimately depends on a judicious balancing of the final performance properties. This can typically range from polymer softness (plasticizer loading) to impact (loading, compatibility of plasticizers) to long term stability (loading, compatibility, and plasticizer molecular weight). The ability to estimate plasticizer/polymer compatibility is therefore a key factor in selecting a range of plasticizers for property modifications.

In a recent communication (1), we have reported on the use of the miscibility parameter (MP) to estimate the miscibility of polymer blends. This approach is based on the use of appropriate individual contributions of the solubility parameter and has been presented in detail.

Many polymers, as originally prepared, are of limited practical use without the addition of suitable additives. In fact, large volume applications for coatings, packaging, and other applications require the plasticization of glassy polymers or resins. This has resulted in extensive study and investigation of the mechanisms of plasticizer behavior and interactions in polymers and theories that account for polymer-plasticizer mixing. These aspects and others have been reviewed by Sears and Darby (2).

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Measurements that have been used to judge the relative ability or effectiveness of a plasticizer to "plasticize" or modify a resin's properties are: the power requirements during mixing as a function of residence time (3), peak power requirements of mixing as a function of the dielectric constant of the plasticizer, work to adequately fuse and mix as a function of plasticizer dielectric constant, and solubility parameter (3,4).

Much work has been done in relating the solubility parameter (δ) of the polymer additive to its solvent or plasticizing ability (3-8). There is no overall theory or technique that can be used to quantify the interaction between a specific polymer and a large variety of potential plasticizers for that polymer. Although Burrell (7,9,10) illustrated the merit of applying solubility parameter theory to polymer solutions, he saw that solvents which could hydrogen bond with themselves or with other solvents did not always fit simple theory. As a consequence, correction factors have been added to the solubility parameter for alcohols, esters, and ketones which did not follow the simple Hildebrand model. In view of these issues, we investigated the possibility of applying the miscibility parameter (MP) concept to the interaction of polymer-plasticizer systems as we had to polymer-polymer systems (1).

Approach

Theory

We will not review in detail the previous considerations which led to the development and use of the miscibility parameter, MP, for measuring polymer-polymer miscibility (1) since this is a straight forward application of MP to estimating polymer-plasticizer miscibility.

The technique we utilize is based on the well known and widely used solubility parameter concept (11). In this instance we use the individual solubility parameter contributions for each repeat unit or block of the polymer and also the individual contributions for the plasticizer, i.e., dispersive (δ_d), polar (δ_p), and hydrogen bonding (δ_h).

The cohesive energy E_{coh} of a substance in a condensed state is defined as the increase in internal energy, U, per mole of substance if all the intermolecular forces are eliminated. And the solubility parameter, δ, is:

$$\delta = \left(\frac{E_{coh}}{V}\right)^{1/2} \text{ (dimensions: } J^{1/2}/cm^{3/2} \text{ or } cal^{1/2}/cm^{3/2}\text{)} \qquad (1)$$

and

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \qquad (2)$$

For monomers 1 and 2 of the polymer, we have

$$(\delta_1^{poly})^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \qquad (3)$$

$$(\delta_2^{poly})^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \qquad (4)$$

and for the plasticizer

$$(\delta^{plas})^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \qquad (5)$$

Weight fractions of monomer units were multiplied by their respective individual solubility parameter contributions to give a single solubility parameter characterizing the polymers as discussed and illustrated previously (1).

$$\delta^{poly} = \delta_1^{poly}\phi_1' + \delta_2^{poly}\phi_2' \qquad (6)$$

and similarly for the plasticizer, we have:

$$\delta^{plas} = \delta_3^{plas}\phi_3' + \delta_4^{plas}\phi_4' \qquad (7)$$

where ϕ' is the weight fraction of the particular component and δ_3^{plas} and δ_4^{plas} are the respective solubility parameters for each plasticizer in cases where mixed plasticizers are used. We utilized weight fractions in our work since for most industrial applications this is convenient and does not introduce errors which would in any way change interpretation of plasticizer compatibility. Additionally, densities are often not known accurately.

The miscibility parameter is then given by:

$$MP = (\delta^{poly} - \delta^{plas})^2 \qquad (8)$$

The calculated MP's for a set of different plasticizers were then compared with the results of two experimental techniques used for measuring the "goodness" or effectiveness of plasticizer compatibility with a given polymer. We used both poly(vinyl butyral) and poly(vinyl chloride) for testing this approach. It will be recalled that the well known Flory-Huggins interaction parameter, χ, is related to MP in the following way(12):

$$\chi = \beta + \frac{V_s}{RT}(\delta_1 - \delta_2)^2 \tag{9}$$

where δ_1 and δ_2 relate to the solvent (plasticizer in this case) and polymer respectively, and β is a lattice constant, usually 0.35 ± 0.1(normally assumed to be zero when dealing exclusively with high polymers), V_s is the molar volume of solvent or plasticizer, and T is in °K. For the case of a copolymer or polymer which precipitates from a plasticizer/solvent, the temperature of precipitation or Θ temperature, the solvent volume V_s, and the χ_{cr} define the theoretical MP_{cr} as:

$$\frac{(\chi_{cr} - 0.35)RT}{V_S} = MP_{cr} \tag{10}$$

Thermodynamics of Plasticizer Compatibility

Although it is easy to calculate solubility parameters and apply these to the calculation of miscibility parameters (13), there is no quantitative technique that we are aware that has been used to estimate polymer plasticizer compatibilities.

We investigated the use of adding a small amount of polymer to a plasticizer ($\approx$ 2.5% solution) in a test tube, and heating the resultant mixture until the polymer dissolved. At this point, the temperature of the solution was carefully lowered while stirring, until the polymer precipitated, and the temperature noted. The temperature of precipitation, T_P(UCST), then becomes a quantitative measure of polymer/plasticizer compatibility which can be compared with MP to estimate compatibility.

Since this is a single point determination, the only significant aspect of the polymer concentration is that it should be low. This makes it easier to observe the precipitation or "cloud point" of the polymer solution.

Experimental

Poly(vinyl butyral) (PVB) of molecular weight of about 200,000 and poly(vinyl chloride) (PVC) of molecular weight of about 190,000 were utilized in all experiments. Both had a polydispersity of approximately 2.5. The PVB was prepared by acetalization (14) in our laboratories as described previously and the PVC was obtained from Aldrich Chemicals. Approximately 0.05 g of the polymers were added to 1.95 g of specific plasticizers to provide a 2.5% solution. The mixtures were continuously stirred and heated to effect solubility and then subsequently cooled while digitally monitoring the temperature at which the polymer precipitated. Slight changes in polymer concentrations did not influence repeatability of T_P.

Results and Discussion

Poly(vinyl butyral)(PVB)/Plasticizer Compatibilities

A series of plasticizers was selected that provided a range of compatibilities with PVB. The compatibility of the polymer with the plasticizer was further controlled by varying both the hydroxyl level of the PVB and the structure of the polymer backbone as described previously(14). The resulting MP's, T_P's, aldehydes used for acetalization of poly(vinyl alcohol), and PVB hydroxyl concentrations are shown in Table 1 and a plot of the calculated MP's vs. T_P's is shown in figure 1.

It can be seen that the MP can be used effectively for estimating PVB/plasticizer compatibility as judged by the temperature at which that specific polymer precipitates from solution in that plasticizer. The MP represents a viable technique for estimating compatibility that we have extended from the previous polymer blend work to polymer plasticizer compatibilities.

While the T_P represents a more reliable number since it is obtained experimentally, the advantage of the MP is that it can be quickly and conveniently calculated for unknown materials particularly in those cases where a T_P cannot be determined. An example of this occurs in the case of poly(tetra methylene

Table 1
Data for Plasticizer type, Temperature of Precipitation, Aldehyde Used, Hydroxyl Concentration of Poly(vinyl butyral), and Critical Miscibility Parameter

PLASTICIZER	*T_p, ° C*	*ALDEHYDE*	*MP_{dph}*	*PVOH*	*MP_{cr}*
tri-propyleneglycol dibenzoate	60.0	butanal	0.02	18.2	0.27
di-propyleneglycol dibenzoate	47.0	butanal	0.02	18.2	0.31
di-tetrahydro furural adipate	68.0	butanal	0.37	18.2	0.31
di-2-ethyl hexyl adipate	134.0	butanal:decanal (90:10)	1.92	18.1	0.30
di-2-ethyl hexyl adipate	169.0	butanal:decanal (90:10)	2.41	20.6	0.33
di-2-ethyl hexyl adipate	126.0	butanal:decanal (80:20)	1.75	17.9	0.30
di-2-ethyl hexyl adipate	150.0	butanal:decanal (80:20)	1.90	18.7	0.31
di-2-ethyl hexyl adipate	184.0	butanal:decanal (80:20)	2.32	20.9	0.34
di-2-ethyl hexyl adipate	132.0	butanal:2-ethyl hexanal(90:10)	1.89	17.8	0.30
di-2-ethyl hexyl adipate	167.0	butanal:2-ethyl hexanal(90:10)	2.32	20.1	0.33
tetraethylene glycol di-heptanoate	68.0	butanal	1.34	18.6	0.24
triethylene glycol di-2-ethylbutyrate	102.0	butanal	1.64	18.6	0.32
di-isononyl adipate	147.0	butanal:decanal (90:10)	2.03	19.0	0.29
di-isononyl adipate	161.0	butanal:2-ethyl hexanal(70:30)	2.14	19.6	0.30
di-n-hexyl adipate	97.0	butanal:2-ethyl hexanal(70:30)	1.45	18.2	0.33
poly(tetramethylene ether glycol)	----	butanal	0.05	18.2	----
di-isoheptyl phthalate	98.0	butanal	1.04	18.2	0.30
di-isoheptyl phthalate	120.0	butanal	1.39	20.4	0.32

glycol) (PTMEG) where T_p could not be obtained since this material is so compatible that the temperature cannot be lowered to the point where precipitation occurs (Table I). Nevertheless, the MP for PTMEG (0.05) not only corroborates that this plasticizer is very compatible but also gives a quantitative measure of its compatibility.

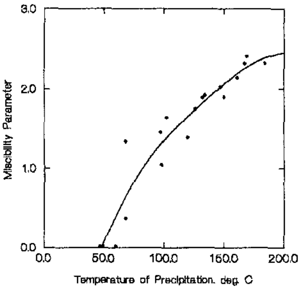


Figure 1
Miscibility Parameter (MP_{dph}) of Poly(Vinyl Butyral)/Plasticizer vs. Temperature of Precipitation(T_p)

We interpret the inability to obtain a precipitation temperature as being due to the fact that the PVB is so compatible with the PTMEG that the hydroxyls on the polymer backbone prefer the plasticizer /solvent at all temperatures so that hydroxyl agglomeration accompanied by phase separation does not occur above room temperature.

We have demonstrated previously (1) that an acceptable criteria to be used for MP to indicate polymer/polymer compatibility is ≈ 0.1 It will be noted from the accompanying table that most values are substantially higher. These data show that plasticizer/polymer system requirements are different from high polymer systems, as would be expected. The additional free volume introduced in a plasticized system due to the chain ends of a low molecular weight material mixed with a high polymer will lower the overall criteria for miscibility and correspondingly raise the MP level necessary for miscibility. Also, differences between the entropic contributions to the free energy of mixing of the polymer-plasticizer blend compared to the polymer-polymer system will also affect the criteria for miscibility and raise the MP level necessary for miscibility.

The precipitation of the PVB is consistent with our previous interpretation (1) in that the hydoxyl blocks of the copolymer tend to interact primarily between themselves which was the rationale for not employing the hydrogen bonding portion of the solubility parameter in our previous study of PVB/polymer miscibility. This was quantitatively indicated by the much higher values of the hydrogen bonding solubility parameter component relative to the vinyl butyral blocks or the block components of the polymers used for blending and this allows a "cloud point" or T_p determination in a single solvent to be used as an indicator of hydroxyl concentration for those polymers prepared from identical aldehydes.

The temperature, T_p, is unique in that this is the temperature at which the partial molar free energy due to polymer-solvent interactions is zero and deviations from ideal solution behavior vanish. The excluded volume becomes smaller as the solvent becomes poorer and vanishes at $T = \Theta$, and when the polymer molecules interpenetrate one another they do so freely with no net interactions. At temperatures below, Θ, they attract one another and the excluded volume is negative. Much below Θ, precipitation occurs and therefore at Θ, χ is really χ critical (χ_{cr}).

Since T_p approximates the Θ temperature (the critical miscibility temperature in the limit of infinite molecular weight), (χ_{cr}) should approach 1/2 (15) at T_p since the molecular weight of the PVB is ≈ 200,000 and it is at or is approaching the limiting value required.

The calculated MP_{cr}'s, from equation 10, are all ≈ 0.3 (Table I). When these MP values are exceeded the polymers-plasticizers will no longer be miscible with resultant phase separation. This is the case in all but the first two instances. For high polymers of molecular weight of about 200,000, the difference criteria in solubility parameters (MP's) that should not be exceeded for miscibility is 0.077 (16). This value is much more restrictive than the calculated values because of the low molecular weights of the plasticizers and the corresponding entropic effects introduced.

These results dramatically illustrate the effect of molecular weight on the miscibility of two materials and its influence on the MP's since the entropy contribution is small to negligible for high polymer systems and large in low molecular weight or solvent (plasticizer)-polymer systems. Using the data of Krause , we estimated MP_{cr} based upon a DP ≈ 20. This DP is a representative value of the number of structural units of the plasticizers used. A MP_{cr} value of 0.8≈1.0 was obtained. This estimate assumes that the number of structural units in the plasticizer is the determining factor.

Deviations of the MP's for phase separation, as in the first two examples, occurs in those instances of a more polar solvent/plasticizer, i.e., one having greater compatibility with the copolymer where combinatorial entropic effects and deviations from ideal behavior at T_p might be expected. This is consistent with the polymer expansion factor, α, and its dependence on ψ, the entropic probability term as indicated in the relationship (15):

$$\alpha^5 - \alpha^3 = 2C_m\psi(1-\frac{\theta}{T})M_w^{1/2} \qquad (11)$$

where C_m is a constant dependent upon the system. The expansion factor, α, is expected to be larger in better solvents and should approach one at the Θ temperature. Normal impurities in the plasticizers (solvents), errors in calculating MP's, and experimental errors may also be involved in predicting MP_{cr}.

However, the correlation of the calculated MP's with the experimentally determined TP's indicates no serious discrepancies.

Poly(vinyl chloride)/Plasticizer Compatibilities

Since poly(vinyl chloride)(PVC) is a polymer that has a wide range of uses in its plasticized form we investigated the extension of this technique to PVC plasticized systems. As before, a 2.5% solution of PVC in plasticizer was cooled to obtain T_P. With the PVC systems, it proved impossible to obtain a T_P even when the polymer concentrations were increased and the temperatures were lowered to the point at which the freezing point of the plasticizer was reached. Thus the PVC plasticized systems exhibited a fundamental difference in behavior from the PVB systems.

The inability to obtain a T_P for the PVC plasticized systems is indicative of the compatibility of the polymer with the plasticizer at all temperatures. This is similar to the case of the PTMEG compatibility with PVB. The key difference between the behavior of the PVC vs. the PVB is that the PVC is a homopolymer and does not contain groups which are very dissimilar from those of the plasticizer. Therefore, precipitation is not experienced at any temperature since there are no groups on the PVC polymer backbone which will agglomerate due to preference for each other. This again illustrates the importance of hydrogen bonding and the unique properties of PVB.

In order to evaluate whether or not the miscibility parameter concept had more general applicability for estimating polymer/plasticizer miscibility, the temperature at which the polymer dissolved or went into solution (T_s) was measured for a number of PVC plasticizer systems that were qualitatively established to have different degrees of compatibility with PVC (2). In addition, plasticizers were selected that provided a range of MP's for comparison to the T_s.

The temperature at which PVC goes into solution in a plasticizer has been used previously to judge the qualitative plasticizing capability of materials(17,18,19). The disappearance of a polymer particle (PVC) in a plasticizer was termed a melting phenomenon and the temperature recorded as T_m. A pictorial example of this has been given(20). This approach allowed adoption of Flory's equation to be used for calculating the value of χ based on an experimental determination of T_m. The χ values were used as predictors of compatibility, with each class of plasticizers, e.g., sebacates, fumarates, maleates, etc., showing a distinct relationship and dependence on the molecular weight of the plasticizer (20).

The temperature of solution, T_s, was found to have a larger amount of variance compared to the T_P since the polymer went into solution over a temperature range. Therefore, the initial temperature was recorded and compared with the MP. These data are listed in Table2.

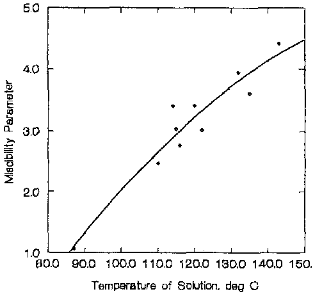
Table 2

Data for Plasticizer type, Polymer, Temperature of Solution, and Miscibility Parameters

Plasticizer	*Polymer*	T_s, °C	MP_{dph}
di isononyl phthalate	PVC	122.0	3.01
di isoheptyl phthalate	PVC	110.0	2.48
di isononyl adipate	PVC	143.0	4.41
di isohexyl adipate	PVC	120.0	3.40
di-n-hexyl adipate	PVC	115.0	3.04
heptyl nonyl adipate	PVC	135.0	3.60
di-2-ethylhexyl adipate	PVC	132.0	3.93
di-2-methylpentyl adipate	PVC	114.0	3.40
di-octyl phthalate	PVC	116.0	2.78
di-butyl phthalate	PVC	87.0	1.07

These data are presented graphically in figure 2.

Figure 2
Miscibility Parameter (MP_{dph}) of Poly(Vinyl Chloride)/Plasticizer vs. Temperature of Solution



The current work demonstrates that for systems other than high molecular weight polymers, the absolute magnitude of the MP that defines compatibility will vary from system to system and must be experimentally established. This reflects the specific backbone structure of the polymer and its group intra and intermolecular interactions with itself and the low molecular weight species. In this case, this amounts to polymer-plasticizer interaction of the structural groups. For low molecular weight materials interacting with high molecular weight polymers, the extent of interaction cannot be thermodynamically related, on a theoretical basis to a single level of MP below which miscibility will be indicated. Nevertheless, for given polymer systems (Tables 1 and 2), the MP's within each system allow quantitative comparisons of relative plasticization of candidate materials without requiring prior experimental determinations. The MP's are easily estimated for most conceivable structures thus eliminating the need for literature values and this leads to valid relative comparisons.

Application of MP to Evaluation and Selection of Suitable Plasticizers for Commercial Use With High Polymers

For a final example of the use of MP as a quantitative indicator of polymer/plasticizer compatibility we chose a practical application of MP to plasticizer compatibility of poly(vinyl butyral). This resin when plasticized and formed into sheets becomes an interlayer that is used to prepare safety glazings.

The preparation of this resin has been discussed previously(14) and will not be repeated here. The plasticization of PVB is a critical application, compared to PVC and other plasticized polymers since it is a carefully formulated system that is balanced to simultaneously provide compatibility with the plasticizer, edge stability of the laminated sheet, low volatility of the plasticizer, and impact strength of the laminate.

Quite often the edges of safety glazings are exposed to view within 1/8" of the glass edge. For this reason and also because safety glazings are exposed to the elements for years, particularly in architectural applications, the "edge stability" of the glazing or the glazings' resistance to deterioration must be excellent.

A key experimental indicator of plasticizer compatibility with PVB is plasticizer exudation under controlled conditions of relative humidity (R.H.) and temperature. High relative humidities cause displacement of the plasticizer by moisture, depending upon the plasticizer's compatibility with the resin. Plasticizer that exudes from an experimentally prepared sheet is compared to a standard sheet with both systems formulated to provide identical glass transition temperatures. Each system then has a figure of merit which is called the exudation ratio(ER).

Exudation ratios higher than 1 are unacceptable. The estimated MP_{cr} of $\approx$0.8-1.0, based on a DP$\approx$20, compares favorably with application acceptability of an ER of 1.

The hydroxyl concentrations of the PVB resins varied from 18.2% to 21.8% hydroxyl,(wt.%) calculated as residual poly(vinyl alcohol) in PVB as well as a small number of resins which were prepared using aldehydes other than butyraldehyde. The calculated MP was used as a selection guide for plasticizers and the ER was measured for 113 formulations. A correlation coefficient of 0.89 and an R^2 value of 0.79 were found by correlating the ER with the MP for each formulation. The measured exudation ratio plotted against the ER estimated from MP isillustrated graphically in figure 3.

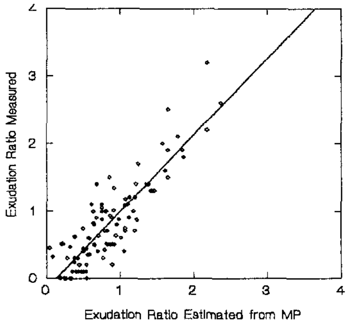


Figure 3
Measured Exudation Ratio of Plasticized Poly(Vinyl Butyral) vs. Exudation Ratio Estimations from Miscibility Parameters

We believe the observed scatter is primarily due to non-reproducibilities of the ER measurement, impurities, and mixed esters in the plasticizers.

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