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Correlation of the glass transition temperature of plasticized PVC using a lattice fluid model

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Abstract

A model has been developed to estimate the glass transition temperature of polymer + plasticizer mixtures (up to 30 wt% plasticizer). The model is based on the Sanchez–Lacombe equation of state and the Gibbs–DiMarzio criterion, which states that the entropy of a mixture is zero at the glass transition. The polymers studied included polystyrene and poly(vinyl chloride). The plasticizers studied included a wide range of chemicals from methyl acetate to di-undecyl phthalate. The model qualitatively accounted for the effect of different plasticizers on the mixture glass transition temperature.

Keywords: Glass transition temperature; Gibbs-DiMarzio; Sanchez-Lacombe

1. Introduction

The plasticizer is the most important formulating ingredient as a polymer modifier [1]. The major function of a plasticizer is to impart flexibility and workability to the polymer. One measure of increased flexibility is a reduction in the glass transition temperature. Approximately 85% of the plasticizers used worldwide are used in the manufacture of flexible polyvinyl chloride (PVC) [1]. The most significant monomeric plasticizer family is the phthalates, which constitute about 70% of the plasticizers used. There have been many studies on the glass transition temperature of PVC + phthalate mixtures [2–8]. It is the goal of this study to develop a correlation for the glass transition temperature of polymer + plasticizer mixtures. This was done with the hope to be able to estimate the glass transition temperature of PVC + plasticizer mixtures for plasticizers for which no experimental data is available.

There have been many attempts at correlating the glass transition temperature of plasticized polymer mixtures [3–12]. Some researchers have used empirical mixing rules to determine the glass transition temperature of polymer + plasticizer mixtures [3,5,8]. The mixing rule developed by Couchman and Karasz [13,14] yielded the best fit to experimental glass transition temperature data [5]. Their equation is based on the assumption that the entropy of the mixture is continuous at the glass transition temperature. In other words, the entropy of the mixture in the glass state is equal to that in the liquid state. The Couchman and Karasz equation is given by

$$\ln(T_g/T_{g,1}) = \frac{w_2 \Delta C_{p,2} \ln(T_{g,2}/T_{g,1})}{w_1 \Delta C_{p,1} + w_2 \Delta C_{p,2}} \qquad (1)$$

where T_g is the glass transition temperature of the mixture, $T_{g,i}$ is the glass transition temperature of component i in the mixture, $\Delta C_{p,i}$ is difference in specific heat between the liquid and glass states at T_g, and w_i is the weight fraction of component i. Since literature T_g data rarely includes values for $\Delta C_{p,i}$ it is difficult to apply Eq. (1) to many systems. However, it has been shown that the product $T_g \Delta C_p$ is approximately constant for thirty polymers [15], and several plasticizers [5]. If one allows the product $T_g \Delta C_p$ to be constant, upon rearrangement Eq. (1) becomes [5]

$$\ln(T_g/T_{g,1}) = \frac{w_2 \ln(T_{g,2}/T_{g,1})}{w_1 (T_{g,2}/T_{g,1}) + w_2} \qquad (2)$$

This equation can then be used to calculate the mixture glass transition temperature given the glass transition temperature

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of the pure components and the mixture composition. While this method has been shown to match the composition dependence of the glass transition temperature on the mixture composition [5] it still requires the glass transition temperature for the plasticizers, which to the authors' knowledge, are not widely available.

Other researchers used empirical mixing rules that include an adjustable constant [4,6,7]. Ceccorulli et al. [4] used the following logarithmic relation

$$\ln(T_g/T_{g,2}) = \frac{\ln(T_{g,1}/T_{g,2})}{1 + k_1 w_2/w_1} \tag{3}$$

(where k_1 is a dimensionless constant) to model data for PVC plasticized by *n*-butyl acetate and di-*n*-butyl phthalate over the entire composition range. Mauritz and co-workers [6,7] used the following linear equation developed from diffusion theory

$$T_g = T_{g,2} - k_2 w_1 \tag{4}$$

(where k_2 is a constant known as the plasticizer efficiency parameter) to model data for PVC plasticized by several higher order di-alkyl phthalates. The plasticizer efficiency parameter was shown to decrease as the molecular weight of the plasticizer increased. It must be noted that Eq. (4) is only valid at small diluent concentrations since the experimental T_g for PVC mixed with similar phthalates is highly nonlinear at higher concentrations (greater than 40 wt% diluent) [3–5,8].

Panayiotou [9] developed an equation of state approach to correlate the glass transition temperature of mixtures. His approach is based on the lattice-fluid theory of Sanchez and Lacombe [16,17] and the Gibbs and DiMarzio criterion of zero total system entropy for the glass transition [18–21]. The system entropy is given by [10]

$$\frac{-S}{krN} = (1/\tilde{\rho} - 1)\ln(1 - \tilde{\rho}) + \frac{\ln\tilde{\rho}}{r} + \frac{\phi_1}{r_1}\ln\frac{\phi_1}{r_1} + \frac{\phi_2}{r_2}\ln\frac{\phi_2}{r_2} + 1 + \frac{\ln(2/z) - 1}{r} + \frac{\phi_1}{r_1}(r_1 - 2)\left[\ln(1 - f_1) - f_1\frac{\Delta\varepsilon_1}{kT}\right] + \frac{\phi_2}{r_2}(r_2 - 2)\left[\ln(1 - f_2) - f_2\frac{\Delta\varepsilon_2}{kT}\right] \tag{5}$$

where S is the system entropy, k is Boltzmann's constant, r is the number of sites occupied per hypothetical mixture molecule, N is the number of molecules in the system, $\tilde{\rho}$ is the reduced density of the mixture, r_i is the number of segments per molecule i, ϕ_i is the close-packed volume fraction of component i, and z is the lattice coordination number. In this study component 1 refers to the diluent or plasticizer and component 2 refers to the polymer. The equilibrium fraction of bonds of type i in the bent conformation, f_i, is given by

$$f_i = \frac{(z - 2)\exp(-\Delta\varepsilon_i/kT)}{1 + (z - 2)\exp(-\Delta\varepsilon_i/kT)} \tag{6}$$

where $\Delta\varepsilon_i$ is the flex energy of bonds of type i. For convenience the lattice coordination number, z, for the polymer and the plasticizer are assumed to be equal.

The reduced density of the mixture is determined by solving the PVT form of the Sanchez–Lacombe equation of state [16]

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}[\ln(1 - \tilde{\rho}) + (1 - 1/r)\tilde{\rho}] = 0 \tag{7}$$

where $\tilde{P}$ and $\tilde{T}$ are the reduced pressure and temperature, respectively. The reduced temperature, pressure and density are given by

$$\tilde{T} = \frac{T}{T^*};\ \tilde{P} = \frac{P}{P^*};\ \tilde{\rho} = \frac{\rho}{\rho^*} \tag{8}$$

where T^*, P^*, and ρ^* are the characteristic temperature, pressure and density of the mixture, respectively. The characteristic parameters of a pure component are typically obtained from regressions of thermodynamic data such as density and vapor pressure measurements. The characteristic parameters of a mixture are determined using a set of mixing rules. In this study we utilized the mixing rules summarized by Xiong and Kiran [22]. For completeness they are listed in the Appendix. The glass transition temperature is determined by finding the temperature at which the total system entropy in Eq. (5) is zero. The density is simultaneously determined using Eq. (7). The pressure in the system is assumed to be ambient pressure.

Panayiotou [9] modeled the T_g for several polymer blends. Panayiotou was able to match the concentration dependence of the T_g data by making the flex energy ($\Delta\varepsilon_i$) of one of the components to be a function of mixture composition or temperature. Condo and co-workers [10,11] modeled the T_g for several polymers plasticized by carbon dioxide using the equation of state approach developed by Panayiotou [9]. The model was able to account for the effect of carbon dioxide solubility on the glass transition temperature. The Chow equation [23] was able to yield comparable T_g estimates when a lattice coordination number of unity was used.

Dong and Fried [12] developed a similar model for determining the glass transition temperature of polymer + diluent mixtures. Their model is based on a slightly different lattice model and their T_g criterion is based on the entropy of the polymer instead of that of the mixture

$$\frac{-S_2}{kn_2r_2} = \left(\frac{\phi_0+\phi_1}{\phi_2}\right)\ln(\phi_0+\phi_1)+1+f_2\ln f_2 + (1-f_2)\ln(1-f_2) - f_2\ln(z_{22}-2) = 0 \qquad (9)$$

where n_i is the number of molecules of component i, ϕ_i is the close-packed volume fraction of component i, ϕ_0 is the close-packed volume fraction of the holes in the lattice, z_{22} is the lattice coordination number for the polymer, and all other variables are as defined in the model of Panayiotou. Since the method of Dong and Fried is based on the entropy of the polymer, it does not require the flex energy of the diluent ($\Delta\varepsilon_1$). However, the method of Dong and Fried does require an additional parameter, ε_{ij}, the energy density of interaction between species i and j. Dong and Fried used this model to correlate T_g data for polystyrene (PS) plasticized by several organic solvents for diluent concentrations ranging from 0–30 wt% [12].

In this study we attempted to correlate the glass transition temperature of polymer–plasticizer mixtures using the method of Panayiotou [9]. We chose this approach since the diluent parameters can be obtained from pure component thermodynamic data such as vapor pressure and density data. To the authors' knowledge, this method has only been applied to polymer–polymer mixtures [9] and polymer + compressed fluid mixtures [10,11] but not to polymer–liquid plasticizer mixtures.

2. Experimental

In order to determine the glass transition temperature of a polymer + diluent mixture one needs the characteristic parameters (T^*, P^*, and ρ^*) of each component, the bond flex energies ($\Delta\varepsilon_i$) of each component, the lattice coordination number (z), and the Sanchez–Lacombe interaction parameter (δ_{ij}) for the binary mixture.

The characteristic parameters of the components used in this study are given in Table 1. The parameters for most of the phthalate esters were not available in the literature. The parameters are generally fit to vapor pressure data and the density at the normal boiling point (Sanchez and Lacombe, 1976). The parameters for the phthalates were fit to experimental vapor pressure data [24–27] and the density at ambient conditions [1,24] (since the values at the normal boiling point were not generally available). The parameters were fit using the Levenberg–Marquardt algorithm [28]. The characteristic pressure and density decreased slightly with increasing alkyl chain length. The characteristic temperature had a parabolic dependence on the alkyl chain length. The parameters for the isoalkyl phthalates (see Table 1) behaved similarly. The parameters for amyl butyrate were fit to the vapor pressure data of propyl hexanoate since the normal boiling points of the two isomers only differed by 2 K. The characteristic parameters for PVC and PS were obtained from the literature [29]. The parameters for these polymers were fit to liquid density data since polymers have no appreciable vapor pressure.

Table 1
Characteristic parameters of pure components

Substance	T^* (K)	P^* (bar)	ρ (g/cm^3)	Reference
Poly(vinyl chloride)	721	4130	1.464	[29]
Polystyrene	735	3570	1.105	[29]
Dimethyl phthalate	633	4924	1.297	This study
Diethyl phthalate	578	4446	1.151	This study
Di-*n*-propyl phthalate	603	3998	1.146	This study
Di-*n*-butyl phthalate	569	3708	1.002	This study
Di-*n*-hexyl phthalate	578	3809	1.103	This study
Di-*n*-heptyl phthalate	592	3372	1.032	This study
Di-*n*-octyl phthalate	572	3424	1.067	This study
Di-*n*-nonyl phthalate	658	2716	1.012	This study
Di-*n*-decyl phthalate	667	2314	0.889	This study
Di-*n*-undecyl phthalate	757	2208	0.957	This study
Diisobutyl phthalate	570	3925	1.133	This study
Diisooctyl phthalate	619	3265	1.030	This study
Diisononyl phthalate	625	2785	1.036	This study
Diisodecyl phthalate	803	2156	1.030	This study
Di(2-ethyl hexyl) phthalate	514	4436	1.178	This study
Di(2-ethyl hexyl) adipate	634	3024	0.972	This study
Methyl acetate	468	5170	1.094	[29]
Ethyl acetate	468	4580	1.052	[16]
n-Butyl acetate	498	3940	1.003	[16]
Amyl butyrate	512	3654	0.982	This study
Methyl salicylate	618	4990	1.297	This study
Benzene	523	4440	0.994	[16]
Toluene	543	4023	0.966	[16]
Nitrobenzene	653	5463	1.241	This study
Carbon disulfide	567	5160	1.398	[16]

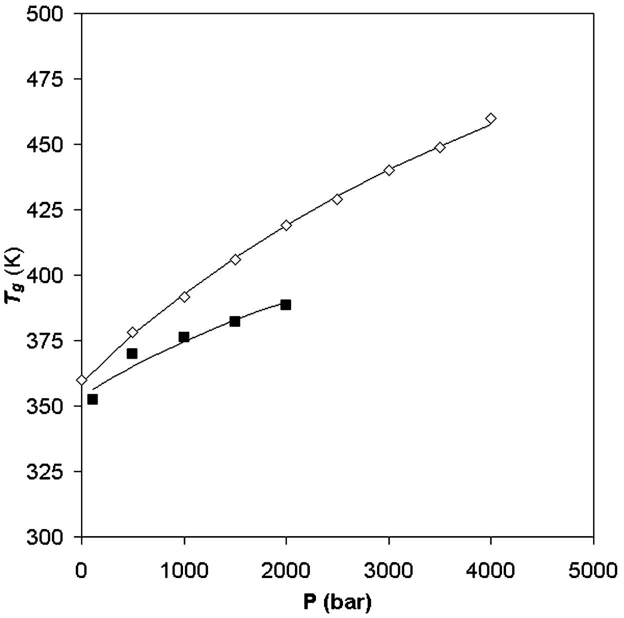

Fig. 1. Glass transition temperature behavior as a function of pressure. Data: (◇) PS [33] and (■) PVC [34]. Curves are theoretical regressions.

The next set of parameters to be determined were the lattice coordination number, z, and the bond flex energy, $\Delta\varepsilon_i$, for each component. In this study it was assumed that the coordination number for the polymer and the diluent were approximately equal as was done by Condo et al. for polymer + carbon dioxide mixtures [10]. The lattice coordination number, z, and the bond flex energy for the polymer, $\Delta\varepsilon_2$, can be fit to pure polymer data (glass transition temperature as a function of pressure) [12]. The results of the fit are given in Fig. 1 and the parameters obtained from the fit are given in Table 2. The coordination number for PVC was slightly larger than that for PS because the glass transition temperature was a weaker function of pressure. Dong and Fried [12] obtained similar parameters for PS ($z = 4.267$ and $\Delta\varepsilon_2 = 5634$), although they used a slightly different lattice model. It was determined that Panayiotou [9] used a value of about four to model the glass transition temperature of several polymer blends.

Condo et al. [10] assumed that the bond flex energy, $\Delta\varepsilon_1$, for their diluent (carbon dioxide) was zero. In this study we will assume that the bond flex energy of all the plasticizers (including the higher molecular weight phthalates) is zero. The advantage of this assumption is that we do not need the experimental glass transition temperature of the pure diluent. The disadvantage of this assumption is that one cannot calculate the glass transition temperature over the entire composition range (since the glass transition temperature of the pure diluent will be undefined). In this study we will show that reasonable estimates can be achieved in the range of 0–30 wt% diluent using this assumption.

The binary interaction parameter, δ_{12}, as defined by Kiran et al. [30] was set equal to zero for our glass transition temperature calculations. Using a relatively large value for the interaction parameter value, 0.05, only changed the estimated T_g for 50 wt% PVC/50 wt% DOP by 0.58 K. Panayiotou [9] also observed a negligible change in the estimated T_g for polymer blends for comparable changes in the interaction parameter used in his study. In general the Sanchez–Lacombe equation of state predicts that the phthalates will be soluble in PVC (up to an alkyl number of 8) using an interaction parameter of 0.0 at the experimental conditions. The solubility was calculated using the standard thermodynamic relation that the chemical potential of each component in each phase is equal. In order to facilitate these calculations we assumed that both compounds are in the liquid state. However in reality PVC consists of amorphous and crystalline fractions [2]. Thus our estimate of the solubility is only a rough approximation. A review of the equations needed to perform phase equilibria calculations using the Sanchez–Lacombe equation of state is available in the literature [22]. According to Scandola et al. [8], PVC and dimethyl phthalate undergo a phase transition for dimethyl phthalate concentrations greater than 70 wt% (which corresponds to a temperature of about 200 K). The Sanchez–Lacombe equation state predicts a solubility of 70 wt% at 200 K using a value of 0.0035. Since this value is much less than 0.05, we do not incur appreciable error in the glass transition temperature by assuming that the interaction parameter is fixed at zero.

There are conflicting reports [2,7] on the solubility of diisodecyl phthalate (DIDP) in PVC. Bair and Warren [2] have shown that PVC–DIDP mixtures exhibit two distinct glass transitions (for 1–25 wt% DIDP). They attribute this phenomenon to the presence of two distinct glassy phases. This indicates that near the glass transition temperature of PVC, the solubility of DIDP in PVC is less than 1 wt%. Mauritz et al. [7] reported glass transition temperatures for up to 15 wt % DIDP in PVC but did not report the occurrence of multiple glass transitions. Using a δ_{12} value of 0.0, the Sanchez–Lacombe equation of state predicts a solubility of 0.7 wt% DIDP at the glass transition temperature of PVC. In order for DIDP to be soluble at 15 wt% and 313 K (the T_g reported by Mauritz et al. [7] at 15% DIDP) the interaction parameter would have to be −0.0316. This value for the interaction parameter has a negligible impact on the estimated T_g. Thus estimates using an interaction parameter of 0.0 will be reasonably accurate assuming that DIDP is soluble in PVC for up to 15 wt% DIDP.

Table 2
Parameters for the pure polymers

Polymer	z	$\Delta\varepsilon_2$ (J/mol)
PVC	5.214	6993
PS	4.277	5393

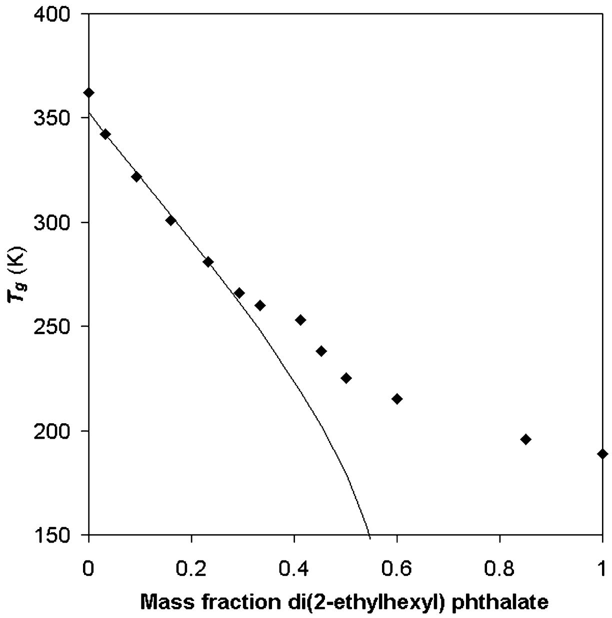

Fig. 2. Glass transition temperature of PVC as function of plasticizer (di(2-ethylhexyl)phthalate). Data: (◆) [3]. Curve is model prediction.

In the glass transition temperature data [3,4,7,8] modeled in this study, the molecular weight of the polymer, PVC, is not listed. However, the Panayiotou model predicts that the glass transition temperature of pure PVC will only change by 2 K as the molecular weight changes from 10^4 to 10^6. Therefore to facilitate our calculations we assumed a value of 50,000 for the molecular weight of PVC.

3. Results and discussion

Typical estimation results are shown in Fig. 2 for the PVC/di(2-ethylhexyl) phthalate system. The model is able to match the composition dependence of the experimental data up to 30 wt % di(2-ethylhexyl) phthalate. Mauritz et al. [6,7] define the initial slope of the curve as the plasticizer efficiency parameter (k_2 in Eq. (4)). Since our estimations are only accurate up to 30 wt% diluent and the experimental data is fairly linear in this region, we chose to compare our estimation results for different plasticizers using plasticizer efficiency parameters. The advantage of using efficiency parameters to make comparisons is that it does not matter if the pure polymer glass transition temperatures vary slightly from study to study. The efficiency parameters for all the systems studied are given in Table 3.

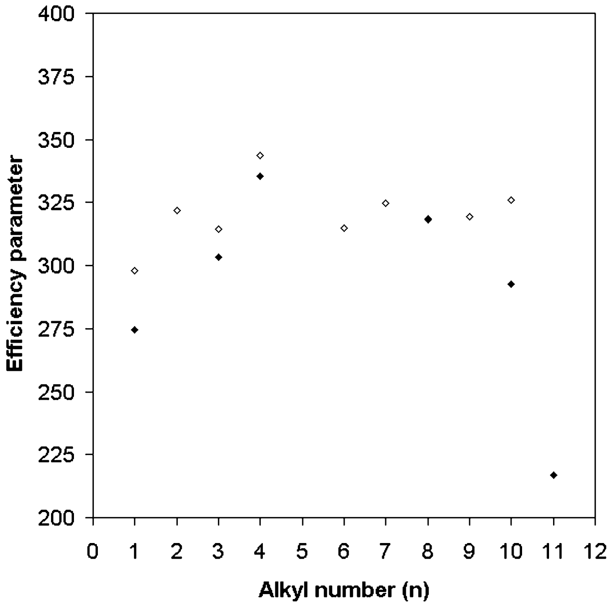

Fig. 3. Plasticizer efficiency parameter as a function of chain length for n-alkyl phthalates. Filled in symbols are experimental data points. Open symbols are model predictions.

Table 3
Plasticizer efficiency parameters

Polymer	Plasticizer	k_2, exp* [a]	Fit error,* [b] exp	k_2, this study	Fit error, this study
PVC	*n*-Butyl acetate	516 [4]	39	399	7
PVC	Bis(2-ethylhexyl) adipate	370 [3]	19	332	2
PVC	Dimethyl phthalate	274 [8]	13	298	2
PVC	Diethyl phthalate			322	2
PVC	Di-*n*-propyl phthalate	303 [8]	15	314	2
PVC	Di-*n*-butyl phthalate	335 [4]	18	343	2
PVC	Di-*n*-hexyl phthalate			315	2
PVC	Di-*n*-heptyl phthalate			325	2
PVC	Di-*n*-octyl phthalate	318 [6]	10	319	2
PVC	Di-*n*-nonyl phthalate			319	2
PVC	Di-*n*-decyl phthalate	293 [6]	8	326	2
PVC	Di-*n*-undecyl phthalate	217 [7]	5		
PVC	Di(2-ethylhexyl) phthalate	317 [3]	19	309	1
PVC	Diisodecyl phthalate	305 [7]	12	305	5
PS	Methyl acetate	491 [32]	36	403	18
PS	Ethyl acetate	524 [32]	33	414	13
PS	*n*-Butyl acetate	357 [32]	24	344	9
PS	Amyl butyrate	329 [32]	30	322	7
PS	Methyl salicylate	331 [32]	14	271	9
PS	Methylene chloride	348 [32]	20	332	11
PS	Chloroform	286 [32]	15	276	5
PS	Carbon tetrachloride	241 [32]	30	251	7
PS	Benzene	415 [32]	18	392	15
PS	Toluene	377 [32]	25	325	9
PS	Nitrobenzene	325 [32]	25	283	9
PS	Carbon disulfide	521 [32]	19	364	11

[a] Each k value (efficiency parameter) was determined from the slope of the experimental glass transition temperature curve from 0.0 to 0.3 mass fraction plasticizer.

[b] Fit error is the standard absolute error of the slope of the linear regression of the glass transition temperature as a function of the plasticizer mass fraction.

As shown in Fig. 3, the model is able to qualitatively match the parabolic dependence of the efficiency parameter on the alkyl chain length for linear alkyl phthalates (up to about di-*n*-octyl phthalate). That is the efficiency increases as you go from methyl to *n*-butyl phthalate and decreases as the molecular weight increases beyond *n*-butyl phthalate. However, the model does not appear to yield a smooth curve. The reason for this is that there is some scatter in the Sanchez–Lacombe parameters for the plasticizers. This is due to the fact that phthalate esters have fairly low vapor pressures (some have values as low as 10^{-10} bar at room temperature), which makes accurate measurements of the vapor pressure more difficult. Since the experimental efficiency parameter for di-*n*-undecyl phthalate is appreciably lower than that of di-*n*-decyl phthalate it is likely that di-*n*-undecyl phthalate may not have been completely soluble over the entire experimental composition range (up to 15 wt% plasticizer). Therefore we did not attempt to make an estimate for di-*n*-undecyl phthalate.

As shown in Fig. 4, the model is able to estimate the plasticizer efficiency for a wide range of plasticizers for PS ($R^2 = 0.87$). However, the slope of the regression line is 0.62, which indicates that the model consistently underestimates the plasticizer efficiency. Carbon disulfide was not included in Figure 4 because it was a significant outlier. To model the PS/carbon disulfide system, Dong and Fried [12] used an interaction parameter that was significantly smaller than the values used for the other plasticizers in their study. This indicates that methods utilizing lattice models tend to underpredict the plasticizing efficiency of compounds with relatively high plasticizing efficiencies.

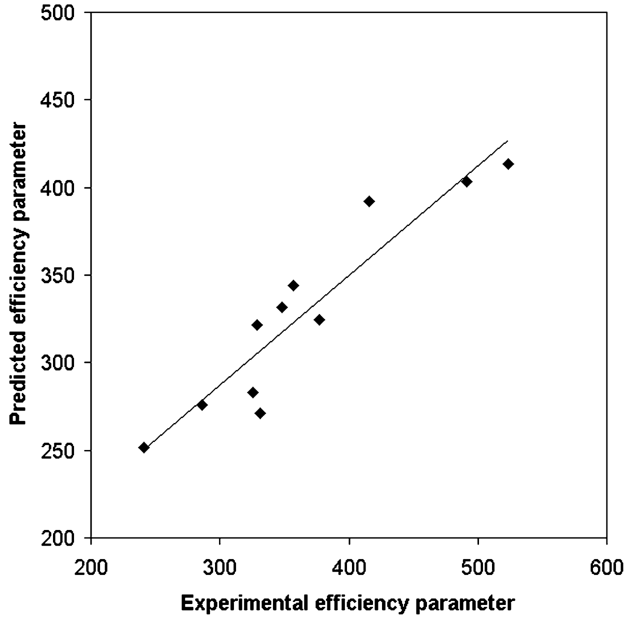

Fig. 4. Predicted vs. experimental plasticizer efficiency parameters for PS/plasticizer mixtures. Line is linear regression ($y = 0.624x + 99.925$, $R^2 = 0.872$) for the predictions.

The model correctly predicts that the plasticizer efficiency will also be a parabolic function of molecular weight for several ester compounds in PS. That is the model predicts that as you go from methyl acetate to ethyl acetate the efficiency increases and then the efficiency decreases from ethyl acetate to *n*-butyl acetate to amyl butyrate. The model also correctly predicts that the efficiency decreases as the molecular weight increases as you go from methylene chloride to carbon tetrachloride and from benzene to toluene.

In a recent article, DiMarzio and co-workers [31] developed a simple theory for the glass temperature depression of polymers by small plasticizer molecules. According to their theory, the depression in the glass transition temperature was only a function of the plasticizer mole fraction (for a given polymer). For this theory to be valid, the coefficient of variation for dT_g/dm_1 should be small (for a polymer mixed with several different plasticizers). For the PVC/plasticizer mixtures examined in this study, the coefficient of variation (standard deviation divided by the mean) for dT_g/dm_1 was actually larger than that of dT_g/dw_1 (0.31 compared to 0.24). This can be explained by the fact that our data set includes phthalate esters, which have a large number of flexible bonds in each molecule so that the simple theory of DiMarzio may not be applicable. However an earlier theory of DiMarzio predicts that the depression of T_g decreases with increasing plasticizer molecular weight [21]. For the PS/plasticizer mixtures in this study, the coefficient of variation for dT_g/dm_1 was smaller than that for dT_g/dw_1 (0.18 compared to 0.24). This can be explained by the fact that the plasticizers (for PS) in this study did not have a large amount of flexible bonds (*n*-butyl acetate had the largest number of flexible bonds with 3). Thus the simple theory of DiMarzio was found to be valid for these compounds.

4. Conclusions

A model based on the Sanchez–Lacombe equation of state and the Gibbs–DiMarzio criterion has been developed to describe the composition dependence of the glass transition temperature for PVC + plasticizer mixtures using pure component thermodynamic data. The model correctly predicted that the plasticizer efficiency parameter is a parabolic function of molecular weight for phthalate esters in PVC. A similar result was achieved for smaller molecular weight esters in PS. In general the model made fairly good estimations considering only pure component data was used in the calculations.

Appendix A

Listed below are additional equations that further describe the Sanchez–Lacombe equation of state.

The characteristic pressure is defined as the interaction energy per volume for each mer (or segment of a molecule)

$$P^* \equiv \varepsilon^*/v^* \tag{A1}$$

where ε^* is the interaction energy per mer and ν^* is the close-packed volume of a mer. The characteristic temperature is defined as follows

$$T^* = \frac{P^* v_0}{R} \tag{A2}$$

thus the characteristic temperature is proportional to the interaction energy per mer. The characteristic density is defined as the close-packed density of a mer

$$\rho^* \equiv M/v^* \tag{A3}$$

where M is the molecular weight.

Now that the pure component characteristic parameters have been defined, the determination of the characteristic parameters for the mixture will be given. The number of sites occupied per mixture molecule, r, is given by

$$r = v^*/v_0 \tag{A4}$$

The average close-packed volume of a mer in the mixture, v^*, is given by the following mixing rule

$$\frac{1}{v^*} = \sum_i \frac{\phi_i}{v_i^*} \tag{A5}$$

the close-packed volume fraction of component i in the incompressible state, ϕ_i, is given by

$$\phi_i = \frac{w_i/\rho_i^*}{\sum_j w_j/\rho_j^*} \tag{A6}$$

the close-packed volume of a mer of component i, v_i^*, is given by

$$v_i^* = \frac{M_i}{\rho_i^*} \tag{A7}$$

The volume of a lattice site, v_0, is given by the following reciprocal rule

$$\frac{1}{v_0} = \sum_i \phi_i \left(\frac{P_i^*}{RT_i^*} \right) \tag{A8}$$

the number of segments per molecule i in the mixture, r_i, is defined as follows

$$r_i = \frac{P_i^* v_i^*}{RT_i^*} \tag{A9}$$

the characteristic pressure of the mixture is given by the following mixing rule

$$P^* = \sum_j \phi_j P_j^* - RT \sum_j \sum_{i<j} \phi_i \phi_j \chi_{ij} \tag{A10}$$

where χ_{ij} is the interaction parameter given by

$$\chi_{ij} = \frac{P_j^* + P_j^* - 2\sqrt{P_i^* P_j^*}(1 - \delta_{ij})}{RT} \tag{A11}$$

the characteristic temperature of the mixture, T^*, is given by Eq. (A2). Using the mixing rules listed above, the chemical potential of component i is given by

$$\begin{aligned} \frac{\mu_i}{RT} &= \ln \phi_i + 1 - \frac{\nu_i^*}{\nu^*} \\ &\quad + \tilde{\rho} \nu_i^* \left(\sum_j \phi_j \chi_{ij} - \sum_i \sum_{j<i} \phi_i \phi_j \chi_{ij} \right) \\ &\quad + r_i \left[\frac{-\tilde{\rho} + \tilde{P}_i \tilde{\nu}}{\tilde{T}_i} + \tilde{\nu} \left((1 - \tilde{\rho}) \ln(1 - \tilde{\rho}) + \frac{\tilde{\rho} \ln \tilde{\rho}}{r_i} \right) \right] \end{aligned} \tag{A12}$$

where $\tilde{\nu} = 1/\tilde{\rho}$, $\tilde{T}_i = T/T_i^*$, $\tilde{P}_i = P/P_i^*$.

References

[1] Krauskopf LG. In: EdenBaum J, editor. Plastics additives and modifiers handbook. Part III. Plasticizers, New York: Van Nostrand Reinhold; 1992.

[2] Bair HE, Warren PC. J Macromol Sci Phys 1981;B20:381–402.

[3] Beirnes KJ, Burns CM. J Appl Polym Sci 1986;31:2561–7.

[4] Ceccorulli G, Pizzoli M, Scandola M. Polymer 1987;28:2077–84.

[5] Fried JR, Lai S-Y. J Appl Polym Sci 1982;27:2869–83.

[6] Mauritz KA, Storey RF, George SE. Macromolecules 1990;23:441–50.

[7] Mauritz KA, Storey RF, Wilson BS. J Vinyl Technol 1990;12(3):165–73.

[8] Scandola M, Ceccorulli G, Pizzoli M, Pezzin G. Polym Bull 1982;6:653–60.

[9] Panayiotou CG. Polymer J 1986;18(12):895–902.

[10] Condo PD, Sanchez IC, Panayiotou CG, Johnston KP. Macromolecules 1992;25:6119–27.

[11] Condo PD, Paul DR, Johnston KP. Macromolecules 1994;27:365–71.

[12] Dong Z, Fried JR. Computational and theoretical polymer science 1997;7(1):53–64.

[13] Couchman PR, Karasz FE. Macromolecules 1978;11:117.

[14] Couchman PR. Macromolecules 1978;11:1156.

[15] Boyer RF. J Macromol Sci Phys 1973;B7(3):487.

[16] Sanchez IC, Lacombe RH. J Phys Chem 1976;80(21):2352–62.

[17] Sanchez IC, Lacombe RH. Macromolecules 1978;11(6):1145–56.

[18] Gibbs JH. In: MacKenzie JD, editor. Modern aspects of the vitreous state. London: Butterworths; 1960. Chapter 7.
[19] Gibbs JH, DiMarzio EA. J Chem Phys 1958;28:373.
[20] DiMarzio EA, Gibbs JH. J Chem Phys 1958;28:807.
[21] DiMarzio EA, Gibbs JH. J Polym Sci, Part A 1963;1:1417–28.
[22] Xiong Y, Kiran E. Polymer 1994;35(20):4408–15.
[23] Chow TS. Macromolecules 1980;13:362.
[24] Daubert TE, Danner RP, Sibul HM, Stebbins CC, editors. Physical and thermodynamic properties of pure chemicals. Evaluated process design data. New York: AIChE/DIPPR; 1980.
[25] Lide DR, editor. Handbook of chemistry and physics, 81st ed. Cleveland, OH: Chemical Rubber Co. Press; 2000.
[26] Frostling H. Aerosol Sci 1970;1:341–56.
[27] Yaws CL. Handbook of vapor pressure. Houston: Gulf Pub. Co; 1994.
[28] Press WH, Teukolsky SA, Vetterling WT, Flannery BP. Numerical recipes in C, 2nd ed. New York: Press Syndicate of the University of Cambridge; 1995.
[29] Sandler SI. Models for thermodynamic and phase equilibria calculations. New York: Marcel Dekker; 1994.
[30] Kiran E, Xiong Y, Zhuang W. J Supercrit Fluids 1993;6:193–203.
[31] DiMarzio EA, Castellano C, Yang A. J Polym Sci Part B 1996;34:535–43.
[32] Jenckel VE, Heusch R. Kolloid-Z 1953;130:89–105.
[33] Oels H, Rehage G. Macromolecules 1977;10:1036.
[34] Schneider HA, Rudolf B, Kariou K, Cantow H-J. Polym Bull 1994;32:645–52.