Compatibility among chlorinated polyethylenes

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Compatibility among chlorinated polyethylenes with different degrees of chlorination has been identified by the transparency of blended films cast from solvent. Dynamic mechanical measurements have been used to check these observations. The heats of mixing of pairs of chlorinated octadecanes with different degrees of chlorination have been measured and shown to be positive. It has been found that in this system, which is dominated by dispersion forces, compatibility is determined by similarity of the equation-of-state parameters. The Flory equation-of-state theory without the interaction entropy parameter Q_{12} generates a positive ΔG_m and hence fails to predict compatibility. A positive Q_{12} is needed to remedy this deficiency of the theory. This is in direct contrast to the negative Q_{12} which is introduced in the systems which are dominated by specific interactions.

Keywords Compatibility; chlorinated polyethylene; thermodynamics; thermodynamic mixing functions; the Flory equation-of-state theory

INTRODUCTION

Since the equation-of-state theory was first applied to the thermodynamics of polymer solutions by Flory, another factor has been introduced in addition to the interaction between the two components in solution and the combinatorial entropy term to explain the solution properties. This factor is the contribution of the equations of state of the pure components. This analysis has been quite successful. Solution properties such as the excess volume, the lower critical solution temperature (*LCST*) observed in some systems, the interaction parameter χ in athermal solutions and the χ dependence on concentration could be derived directly from the theory. These properties could not be predicted by the Flory–Huggins lattice model theory.

The theory was adapted to the study of the compatibility of polymer mixtures[1–3]. The thermodynamic mixing functions were calculated. The *LCST* behaviour was predicted to be a common phenomenon in polymer mixtures. The dependence of phase boundaries on the molecular weights, the equation-of-state parameters, the interaction parameter and pressure, etc., were predicted.

One problem immediately arose as to the relative magnitudes of the different contributions included in the theory. Since the combinatorial entropy is small in polymer mixtures, there remain to be considered two main contributions to the overall free energy of mixing: the equation-of-state contributions and the interaction between different species in the mixture. In McMaster's treatment[2], with the assumption that the interaction energy parameter $X_{12}=0$, the compatibility was discussed with emphasis on the contribution of the equation of state. The calculation predicted that two polymers having molecular weights of 2×10^5 (chain length ~2000 segments) required a difference in their thermal expansion coefficients of less than 4% in order to have significant mutual solubility. Even at molecular weights less than 5×10^4, a difference of 10% in the thermal expansion coefficients could lead to virtually complete immiscibility.

Patterson and Robard[3] considered that the role of free volume at *LCST* was exaggerated in McMaster's paper. They preferred the interpretation that rapid decrease of the specific interaction with increasing temperature brought about phase separation in polyblends at the *LCST*, because the balance between the unfavourable free-volume effect and the favourable specific interaction at low temperature broke down at higher temperatures.

Their discussion left two problems to be considered.

(1) It is generally recognized that specific interactions play a major role in determining the compatibility of polymer mixtures. But this does not mean that in some cases the equation-of-state contribution may not play an important role in compatibility behaviour. The problem is how to find the condition under which the usually less important equation-of-state contribution becomes important.

(2) The Flory equation-of-state theory only fits the experiment qualitatively. The theory probably does not take account correctly of both the equation of state and the interactions. That this theory works for polymer blends where dispersion forces dominate is not well verified, though Flory *et al.*[1] give an example in which the thermodynamic mixing function calculated from the theory was used as a criterion for predicting the compatibility of the system.

In practice these types of analysis lead to 'similarity' and 'dissimilarity' principles for choosing compatible polymer pairs. According to the 'similarity' principle the

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matched polymer pair should have similar chemical structures, their interaction should be small and the equation-of-state properties should be similar, i.e. the pair should have nearly the same thermal expansion coefficients. The 'dissimilarity' principle argues for rather different chemical structures which allow the formation of specific interactions through the functional groups on the matched molecules. Since even weak positive dispersion force interactions are large enough to bring about phase separation, the 'dissimilarity' principle should give the opportunity to identify a wider range of compatible polymer pairs.

In order to separate the factors influencing compatibility, studies are to be preferred of mixtures made up from members of two series of polymers, each series having a continuous gradation of chemical structures. Koningsveld[4] classified these mixtures as:

(1) mixtures of homopolymers consisting of chemically identical monomers, but differing in molecular weight and/or molecular weight distribution (chain length compatibility);
(2) mixtures of homopolymers differing in the chemical constitution of their monomers, at least one monomer series being homologues;
(3) random copolymer/homopolymer mixtures;
(4) mixtures of random copolymers built up from the same two monomers, but differing in composition.

In previous reports[5-7] the compatibility of poly(methyl methacrylate) (PMMA) with chlorinated polyethylene (CPE) was discussed. These mixtures belong to type 3 in the above list, if CPE is regarded as a random copolymer. It was found that the specific interaction was the driving force promoting compatibility in these systems. Compatibility is only possible when the chlorine content of CPE reaches a certain level (around 50% by weight). The compatibility has been explained using the equation-of-state theory with some parameters obtained from the model studies of corresponding oligomer mixtures. The molecular weight dependence of phase boundaries was not so pronounced as predicted in McMaster's paper[2]. It was found that the interaction entropy parameter Q_{12} was decisive in calculation; this reduces the usefulness of the theory since Q_{12}, as an empirical parameter, was set arbitrarily.

In this paper the compatibility of pairs of chlorinated polyethylenes has also been studied. These are type 4 mixtures in the above list. With increasing degree of chlorination, CPE transforms from a polyethylene-like crystalline plastic to a rubber and ultimately to a poly(vinyl chloride)-like polar plastic. The properties of the equation of state are very different for these three types of material. The polarity increases with the chlorine content. Thus the system provides a unique opportunity to explore the cause of compatibility in the polymer mixtures. Compatibility has been determined from visual inspection of the films and dynamic mechanical measurements. The heats of mixing between chlorinated octadecanes (COD) and the thermal expansion coefficients of CPE have been measured. The thermodynamic mixing functions have been calculated using the equation-of-state theory. This analysis has revealed the hitherto unrecognized fact that polymer mixtures dominated by dispersion forces will be compatible if the matched pairs have similar equation-of-state parameters.

THEORETICAL

The constituent equations of the equation-of-state theory were summarized in a previous paper[7], specially for the study of polymer compatibility. The main equations are given below. In Flory's formulation[8], the free energy of mixing, the heat of mixing, the entropy of mixing and the chemical potential of component 1 are:

$$\Delta G_{\mathrm{m}} = \Delta H_{\mathrm{m}} - T\Delta S_{\mathrm{m}} \tag{1}$$

$$\begin{aligned}\Delta H_{\mathrm{m}} = \bar{r}Nv^*[&\phi_1 P_1^*(\tilde{v}_1^{-1} - \tilde{v}^{-1}) + \phi_2 P_2^*(\tilde{v}_2^{-1} - \tilde{v}^{-1}) \\ &+ \phi_1\theta_2 X_{12}/\tilde{v}]\end{aligned} \tag{2}$$

$$\begin{aligned}-T\Delta S_{\mathrm{m}} = RT&(n_1 \ln\phi_1 + n_2 \ln\phi_2) \\ &+ 3\bar{r}Nv^*\{\phi_1 P_1^*\tilde{T}_1 \ln[(\tilde{v}_1^{1/3} - 1)/(\tilde{v}^{1/3} - 1)] \\ &+ \phi_2 P_2^* T_2 \ln[(\tilde{v}_2^{1/2} - 1)/(\tilde{v}^{1/3} - 1)]\}\end{aligned} \tag{3}$$

$$\begin{aligned}\Delta\mu_1 = RT[\ln\phi_1 + (1 - r_1/r_2)\phi_2] + P_1^* V_1^*\{3\tilde{T}_1 \ln[(\tilde{v}_1^{1/3} \\ - 1)/(\tilde{v}^{1/3} - 1)] + (\tilde{v}_1^{-1} - \tilde{v}^{-1}) + \tilde{P}_1(\tilde{v} - \tilde{v}_1)\} + X_{12} V_1^* \theta_2^2/\tilde{v}\end{aligned} \tag{4}$$

with

$$P^* = \phi_1 P_1^* + \phi_2 P_2^* - \phi_1\theta_2 X_{12} \tag{5}$$

$$1/T^* = (\phi_1 P_1^*/T_1^* - \phi_2 P_2^*/T_2^*)/P^* \tag{6}$$

The segment fraction ϕ and interaction site fraction θ are given by

$$\phi_2 = 1 - \phi_1 = r_2 N_2/\bar{r}N \tag{7}$$

$$\theta_2 = 1 - \theta_1 = S_2\phi_2/(S_1\phi_1 + S_2\phi_2) \tag{8}$$

The spinodal is given by

$$\left.\frac{\partial(\Delta\mu_1/RT)}{\partial\phi_2}\right|_{T,P} = 0 \tag{9}$$

i.e.

$$\begin{aligned}-\frac{1}{\phi_1} + \Bigg(1 - \frac{r_1}{r_{2w}} - \frac{(P_1^* V_1^*/RT_1^*)\partial\tilde{v}/\partial\phi_2}{\tilde{v}^{2/3}(\tilde{v}^{1/3} - 1)} \\ + \frac{P_1^* V_1^*}{RT}\left(\frac{1}{\tilde{v}^2} - \tilde{P}_1\right)\frac{\partial\tilde{v}}{\partial\phi_2} \\ + \frac{V_1^* X_{12}}{RT}\left(\frac{2\theta_1\theta_2^2}{\tilde{v}\phi_1\phi_2} - \frac{\theta_2^2}{\tilde{v}^2}\frac{\partial\tilde{v}}{\partial\phi_2}\right) = 0\end{aligned} \tag{10}$$

where

$$\frac{\partial\tilde{v}}{\partial\phi_2} = \frac{\partial\tilde{P}/\partial\phi_2 - (1/\tilde{T})(\tilde{P} + 1/\tilde{v}^2)\partial\tilde{T}/\partial\phi_2}{2/\tilde{v}^3 - \tilde{T}(\tilde{v}^{1/3} - 2/3)/[\tilde{v}^{5/3}(\tilde{v}^{1/3} - 1)^2]} \tag{11}$$

$$\frac{\partial\tilde{P}}{\partial\phi_2} = \frac{[P_1^* - P_2^* + X_{12}\theta_2(\theta_1/\theta_2 - 1)]P}{P^{*2}} \tag{12}$$

$$\frac{\partial\tilde{T}}{\partial\phi_2} = \frac{(P_2^*/T_2^* - P_1^*/T_1^*)T}{P^*} + \frac{[P_1^* - P_2^* + X_{12}\theta_2(\theta_1/\phi_2 - 1)]\tilde{T}}{P^*}$$

In these equations the interaction entropy parameter Q_{12} is not considered. Calculations require the equation-of-state coefficients, S_1/S_2 and X_{12}. First the characteristic parameters P_i^*, T_i^* and v^* ($v^* = v_1^* = v_2^*$) are calculated and then the thermodynamic mixing functions can be evaluated.

EXPERIMENTAL

Materials

CPE and COD were prepared by photochlorination. Commercial polyethylene and octadecane were used for the purpose. The details of the reactions were described in a previous paper[6]. The properties of the materials are listed in *Tables 1* and *2*, respectively. The degrees of chlorination were determined by elemental analysis. The molecular weights were measured by g.p.c. relative to polystyrene standards or by v.p.o. in the case of oligomers. The densities d of CPE and COD were determined by equal density titration[7] and by pycnometer, respectively. The thermal expansion coefficients α were calculated from the densities at two temperatures. Dynamic mechanical loss peaks and hence glass transition temperatures were measured using a Rheovibron at 11 Hz to determine tan δ as a function of temperature, $f(T)$.

The polyblends at fixed weight fraction 50/50 were prepared by casting films from chlorobenzene (A.R.) solutions in petri dishes. The rate of evaporation was controlled by partial covering of the dishes. The films were then dried in a vacuum oven at 1 mmHg and 50°C for 1 week.

Compatibility was determined by visual inspection to assess the transparency of the film. The blends of transparent films are compatible while the blends of turbid or translucent films are judged incompatible.

Dynamic mechanical measurements

Dynamic mechanical measurements were carried out on a Rheovibron (model DDV-2, Toyo Measuring Instrument Co. Ltd). A strip of the sample was subjected to an imposed oscillatory frequency of 11 Hz. A temperature range from $-60°$ to 120°C was scanned at 1°C min^{-1} heating rate and a plot of tan δ vs. temperature obtained. A maximum in tan δ curve was taken as a measure of T_g.

Heat of mixing

The heat of mixing of various pairs of oligomers was measured using a modified NBS batch type calorimeter[9]. The machine has an accuracy of ± 0.02 J g^{-1} as determined by an acid–base reaction. However, the viscosity of the oligomers made mixing difficult and we estimate an error of ± 0.1 J g^{-1} for our systems. The machine was calibrated using a heating coil immersed in the COD mixtures.

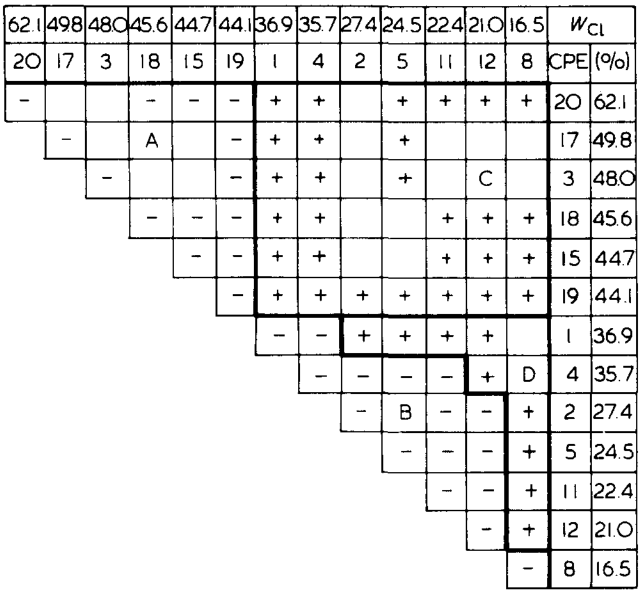
RESULTS AND DISCUSSION

Comptability among CPE

Out of 78 possible, 55 pairs of CPE were blended. Their compatibilities are mapped in *Figure 1* where '+' means the pair is immiscible while '−' is miscible. The triangle can be divided into four regions. A is a 'polar plastic' region where the polymers mix with each other. B is a 'rubber' region where the polymers also mix with each

Table 2 Data for chlorinated octadecane (COD)

Sample	Degree of chlorination (wt %)	M_n	d, 70°C (g ml^{-1})	α, 70°C x10^4 (K^{-1})
1	17.3	314	0.865	8.20
2	24.6	356	0.918	7.87
3	33.4	412	1.017	7.82
3A	34.9	421	1.046	7.32
4	43.2	467	1.105	7.18
5	52.9	546	1.217	7.36



62.1	49.8	48.0	45.6	44.7	44.1	36.9	35.7	27.4	24.5	22.4	21.0	16.5	W_{Cl}	
20	17	3	18	15	19	1	4	2	5	11	12	8	CPE	(%)
−			−	−	−	+	+		+	+	+	+	20	62.1
	−		A		−	+	+		+				17	49.8
		−			−	+	+		+		C		3	48.0
			−	−	−	+	+			+	+	+	18	45.6
				−	−	+	+			+	+	+	15	44.7
					−	+	+	+	+	+	+	+	19	44.1
						−	−	+	+	+	+		1	36.9
							−	−	−	−	+	D	4	35.7
								−	B	−	−	+	2	27.4
									−	−	−	+	5	24.5
										−	−	+	11	22.4
											−	+	12	21.0
												−	8	16.5

Figure 1 **Compatibility among chlorinated polyethylenes: '−', miscible; '+', immiscible**

Table 1 Data for chlorinated polyethylene (CPE)

Sample	Degree of chlorination (wt %)	$M_w \times 10^{-5}$	$M_n \times 10^{-4}$	M_w/M_n	d, 25°C (g ml^{-1})	α, 25°–45°C x10^4 (K^{-1})	T_g (°C)
1	36.9	1.10	1.58	6.96	1.159	6.25	−10
2	27.4	1.08	1.52	7.11	1.071	13.24	−8
3	48.0	1.20	1.80	6.67	1.301	4.43	27
4	35.7	1.15	1.89	6.08	1.127	8.73	−10
5	24.8				1.062	12.25	−10
8	16.5				1.015	9.10	
11	22.4				1.066	12.30	−12
12	21.0				1.036	11.57	
15	44.7	1.70	1.81	9.38	1.311	5.66	27
17	49.8	1.82	2.08	8.78	1.365	3.85	32
18	45.6	2.02	2.29	8.81	1.319	4.93	27
19	44.1	1.79	2.09	8.56	1.304	5.47	25
20	62.1	2.42	2.58	9.41	1.487	3.72	78

other because they have similar equation-of-state parameters. In region C the 'polar plastics' do not mix with the corresponding 'rubber' components. Region D is a 'rubber' region too (cf. B), but one in which the polymers cannot mix with each other because the difference in their equation-of-state properties is too large. CPEs with low chlorine content have been excluded from the study because they are crystalline and therefore lie outside the scope of the analysis which can only be applied to amorphous systems. The blends identified as compatible by visual inspection were checked by measurements of their dynamic mechanical loss spectra. In *Figure 2* is shown a typical example in which the pair exhibits the largest difference in chlorine contents among the tested blends. The compatible blends in region B were not tested because the difference between the glass transition temperatures of the pure polymers was too small. The fact that the T_g of the blend is a linear function of weight fraction (*Figure 2*) indicates that the influence of specific interaction in the system is not strong.

The compatibility identified in this way can be unreliable if the chlorine contents of the components are close, because the samples have similar refractive indices ($\Delta n < 0.01$) and glass transition temperatures. Our measurements[6] on COD showed that the difference in the refractive indices would be greater than 0.01 if the chlorine contents had a difference larger than 6 wt%. For the high molecular homologues studied the difficulty lies in the judgement of compatible pairs of larger difference in the chlorine contents. Fortunately, these pairs have quite different refractive indices and glass transition temperatures.

The blends were solvent cast. The final state of the blend is determined by the route of evaporation of solvent, which may make a compatible blend phase-separated. Owing to chemical adsorptions, solvent may persist in the cast films. In this work chlorobenzene has been chosen as the solvent. It can dissolve CPE of high and low chlorine content properly. Obviously, the solvent should have no specific interactions with CPE.

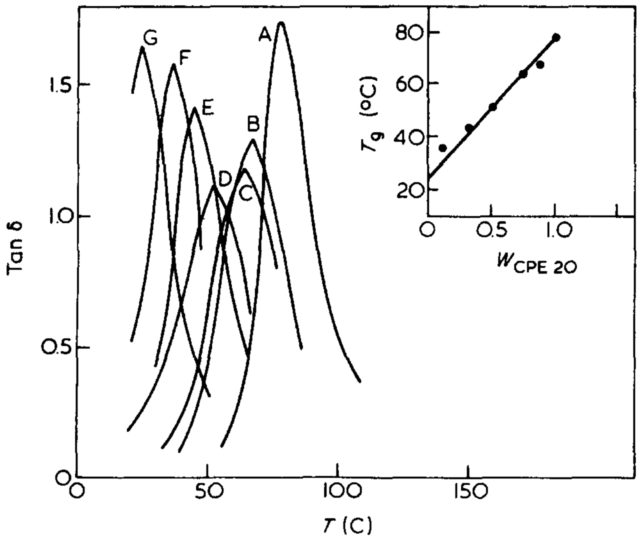


Figure 2 Dynamic mechanical measurements for CPEs 19/20 blends. Curve A, CPE 20; curves B–F, weight fractions of CPE 19: B, 0.1227, C, 0.2646, D, 0.5025, E, 0.7445, F, 0.8911; curve G, CPE 19

Interaction energy parameter X_{12}

Heats of mixing of chlorinated octadecanes were measured at 0.5 weight fraction for each pair. The results are shown in *Figure 3*. One system COD 3/COD 5 was measured over the complete concentration range as shown in *Figure 4*. X_{12} can be evaluated from equation (2) and one of the computed curves is shown in *Figure 4* for the system COD 3/COD 5. For other systems X_{12} was estimated from the values of ΔH_m at 0.5 weight fraction. The X_{12} values are all positive. In *Figure 5* they are plotted as a function of the difference between the chlorine content of the pairs of oligomers. The curve is characteristic of mixtures in which dispersion forces dominate.

The parameters of COD used in these calculation are listed in *Table 2*. The thermal pressure coefficient γ was assumed to be 10 atm K^{-1} for each component; inspection showed that the precise value of the parameter had little influence on the final results. The ratios S_1/S_2 were calculated using Bondi's technique[10], and it runs from 0.97 to 1.02 according to the difference in chlorine content of the pairs of oligomers.

Thermodynamic mixing functions

The free energies of mixing, heats of mixing and entropies of mixing were calculated for CPE/CPE mixtures from equations (1)–(3) at 25°C. The results for 20 polymer pairs are listed in *Table 3*. The parameters used for calculations are given in *Table 1*. The weight-average molecular weights were used. The M_w of CPE 8 and CPE 12 were not available because they were not sufficiently soluble in THF for g.p.c. measurements. M_w was taken as 1×10^5 in both cases. It is apparent that the thermal expansion coefficient α decreases significantly when the

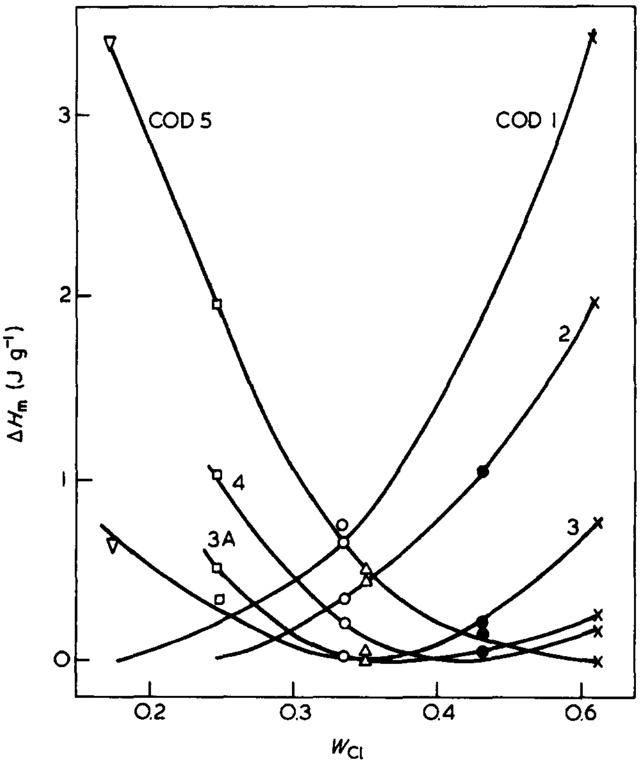


Figure 3 Heats of mixing between chlorinated octadecanes at weight fraction 0.5. One oligomer is denoted on the curve, the other is: ▽, COD 1; □, COD 2; ○, COD 3; △, COD 3A; ●, COD 4; x, COD 5

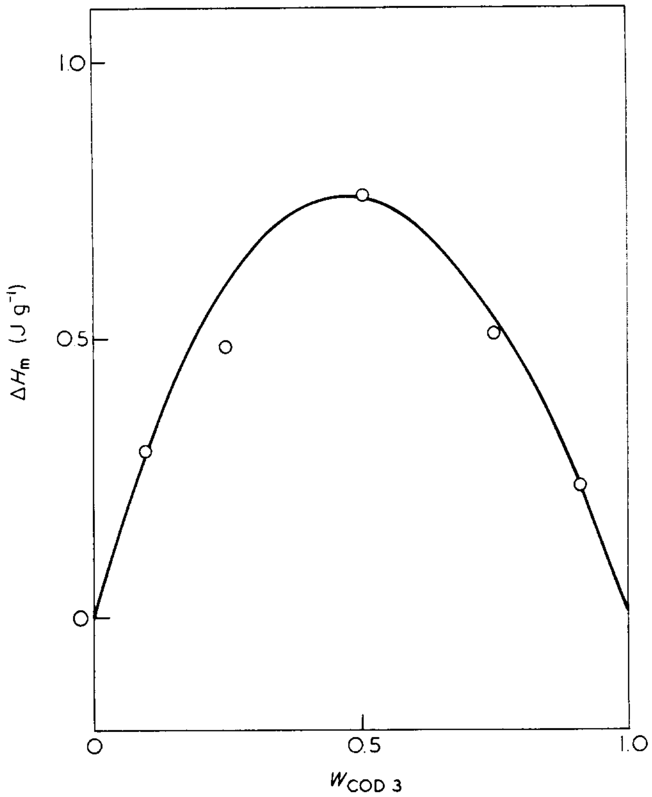


Figure 4 Heat of mixing of COD 3/COD 5 mixture. The theoretical curve is calculated from equation (2)

polymer changes from rubber at low chlorine content to polar plastic-type material at high chlorine content, as shown in *Figure 6*. The thermal pressure coefficients γ were again assumed to be 10 atm K^{-1}. It was found that the sensitivity of the calculation of thermodynamic mixing functions on the value of γ depends on the difference in α values of a CPE pair. The larger this difference, the greater is the influence of γ on the thermodynamic mixing functions. We examined three model cases in which the values of γ_1 and γ_2 were set equal to 10 and 10, or 20 and 10, or 20 and 20 atm K^{-1}, respectively. Calculations showed that ΔG_m could increase as much as 50% with increase of γ for the pairs where the difference in α values was relatively large, i.e. $\alpha_1 \sim 2\alpha_2$ or *vice versa*. For most compatible pairs such as CPEs 15/19, 3/18, 3/19, 3/2 and 20/17, etc., ΔG_m was substantially independent of the values of γ_1 and γ_2. Thus we are confident that the selected values of γ will not influence significantly the conclusions to be presented in the following discussion. The range of γ values covers most of polymers. X_{12} values were determined from *Figure 5* as a function of the difference in chlorine content between two polymers. X_{12} is molecular weight dependent. According to Flory[11], X_{12} decreases with molecular weight for the polyisobutylene/n-alkanes system in which dispersion forces dominate. For this reason the thermodynamic functions were calculated for $X_{12}=0$ as well as for $X_{12}\neq 0$; the results will be discussed in the following paragraph. The ratios S_1/S_2 were evaluated by Bondi's technique[10]. They run from 0.97 to 1.00 according to the difference in chlorine contents between two polymers.

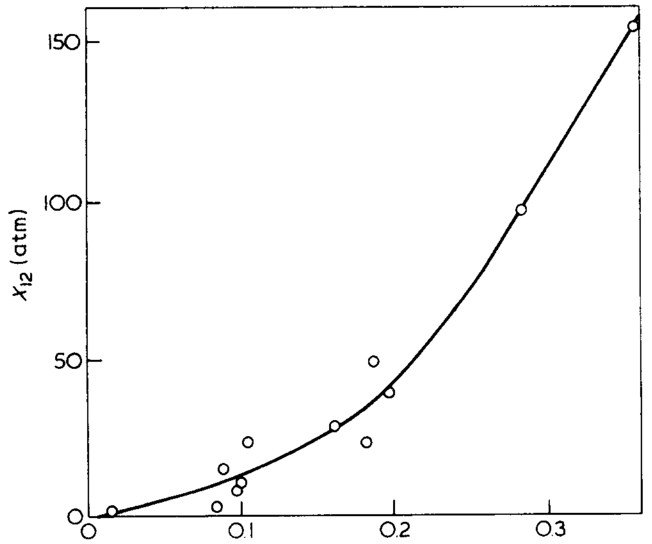


Figure 5 Interaction energy parameter X_{12} vs. difference in chlorine contents of mixed oligomers

Table 3 Thermodynamic functions calculated at $X_{12} \neq 0$

CPEs	ΔW_{Cl} (wt %)	Miscibility	ΔH_m (J g^{-1})	$-T\Delta S_m$ (J g^{-1})	ΔG_m (J g^{-1})
15/19	0.6	–	0.009	–0.009	0
3/18	2.4	–	0.027	0.014	0.041
3/19	3.9	–	0.031	0.101	0.132
12/8	4.5	+	–0.015	0.252	0.237
2/12	6.4	–	0.089	0.043	0.132
15/1	7.8	+	0.039	0.451	0.490
4/2	8.3	–	–0.108	0.761	0.653
3/1	11.1	+	–0.003	1.185	1.182
20/17	12.3	–	0.293	–0.036	0.258
4/12	14.7	+	0.348	0.248	0.596
15/2	17.3	+	–0.284	2.703	2.418
20/19	18.0	–	0.519	0.276	0.795
4/8	19.2	+	0.803	–0.176	0.627
3/2	20.6	+	–0.381	4.222	3.841
15/12	23.7	+	0.648	1.731	2.379
20/1	25.2	+	0.917	1.576	2.493
3/12	27.0	+	0.786	3.018	3.804
15/8	28.2	+	1.651	0.492	2.143
3/8	31.5	+	1.947	1.387	3.334
20/2	34.7	+	1.175	4.653	5.827

It can be seen from *Table 3* that the values of ΔG_m are positive for all 20 polymer pairs. The spinodals have been calculated and they show that the polymer pairs are immiscible at 25°C. Thus, if we assume that the X_{12} values of the oligomers can be used for polymers, all the polymers should be immiscible according to this analysis. As discussed above, the situation for $X_{12}=0$ has been evaluated for comparison to check the possible effect of the molecular weight dependence of X_{12}. The results do not improve very much. Out of seven compatible polymer pairs, only two pairs (CPEs 15/19 and 20/17) are calculated to have a negative ΔG_m and for the third pair (CPE 3/18) ΔG_m is almost zero. The remaining pairs still have positive values of ΔG_m. The spinodals calculated also confirm these results. As can be seen in *Table 3*, ΔH_m is not important when the difference in chlorine contents of the polymer pair in the mixture is large. It is the large negative entropy term from the disparity of the equation-of-state parameters that determines the positive ΔG_m. In practice the calculation with $X_{12}=0$ does not change the value of ΔG_m for these systems very much.

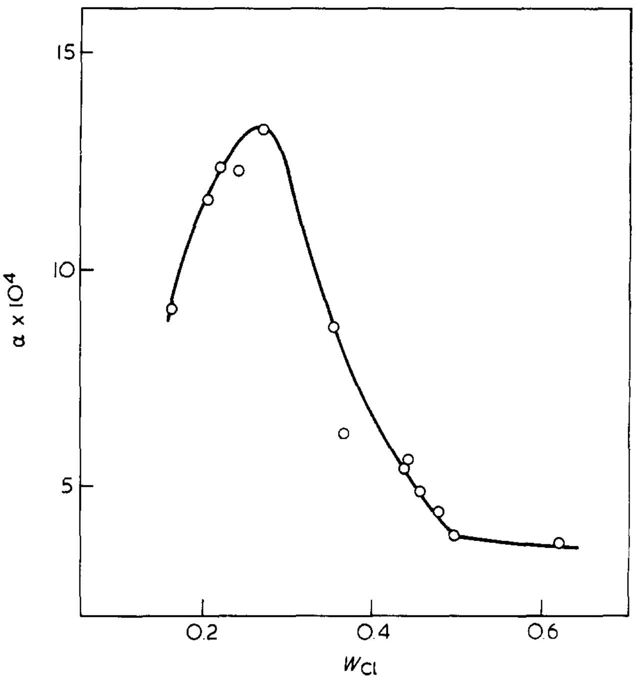


Figure 6 The thermal expansion coefficient α as a function of chlorine content in CPE

An analysis of some compatible and incompatible pairs shows some interesting features:

(1) CPEs 20/19–this compatible pair is in the region A. Because the chlorine difference reaches 18 wt%, the ΔH_m is relatively large (+0.519 J g^{-1}). Owing to the large difference in their thermal expansion coefficients, $-T\Delta S_m$ is positive (+0.276 J g^{-1}). In total the ΔG_m for the pair is +0.795 J g^{-1}. Thus by this analysis the pair should be immiscible.

(2) CPEs 4/2–this compatible pair is in the region B. Their chlorine contents are similar, and the dispersion forces between two species are likely to lead to a small degree of interaction. By calculation, the great difference in the thermal expansion coefficients makes ΔH_m small and negative (−0.108 J g^{-1}). But this difference in turn generates a large positive $-T\Delta S_m$(+0.761 J g^{-1}). The resultant ΔG_m (+0.653 J g^{-1}) is still unfavourable for mixing.

(3) CPEs 15/1 and 3/1–these two pairs are incompatible and are in the region C. Immiscibility stems from the very different properties of the equation of state; two polymers CPEs 3 and 15 are polar plastics while CPE 1 is a rubber. The two pairs have closely similar chlorine contents, and in each case ΔH_m is nearly zero.

(4) CPEs 12/8, 4/12 and 4/8–these three incompatible pairs are in the region D. The polymers in this region are rubbers. The range of chlorine content explored in this region is quite similar to that in the region A. Hence the polymer pairs are expected to be miscible. The observed immiscibility stems from a moderate difference in the thermal expansion coefficients. In the mixture CPEs 12/8 the chlorine content difference is so small that ΔH_m is only −0.015 J g^{-1}. However $\alpha_1/\alpha_2 = 1.27$, and this leads to $-T\Delta S_m = +0.252$ J g^{-1}. Hence a small positive ΔG_m (+0.227 J g^{-1}) leads to incompatibility of the pair. With increasing difference of chlorine contents, the unfavourable ΔH_m increases and becomes equal in magnitude to $-T\Delta S_m$ for the mixture CPEs 4/12 CPEs 4/8 is an interesting mixture. Because the components have nearly equal thermal expansion coefficients, $-T\Delta S_m$ is negative (−0.176 J g^{-1}). But the moderate dispersion forces result in a ΔH_m of +0.803 J g^{-1}. The resultant ΔG_m (+0.627 J g^{-1}) leads to incompatibility of the pair.

CONCLUSIONS

Several conclusions can be drawn from the above discussion:

(1) Compatibility in the systems in which dispersion forces dominate is determined by the degree of similarity of the equation-of-state parameters of pure components. Without introducing the empirical parameter Q_{12}, the Flory equation-of-state theory cannot generate a negative ΔG_m and hence fails to predict the observed compatibility of these systems.

(2) It seems that we can draw a dotted line through the data for ΔG_m in *Figure 7*. Above the line the polymer pairs are immiscible, below the line the pairs are miscible. Considering that X_{12} for high polymers should be smaller than the values measured for the corresponding oligomers, the slope of this line for high polymers may be lower. The line represents the boundary of effectiveness of the theory without the introduction of the empirical parameter Q_{12}.

(3) One way to remedy this inadequacy of the scope of the theory is by introducing Q_{12}. Q_{12} is expected to be positive and proportional to the difference in chlorine content of the two polymers in the mixture. This is in contrast to the systems in which specific interactions dominate, i.e. where a negative Q_{12} is needed to calculate the spinodals[7]. This conclusion is quite similar to that reported for polymer solutions[12].

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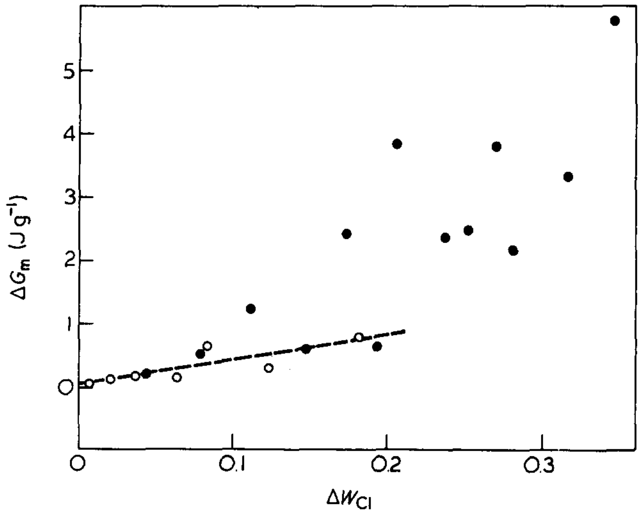

Figure 7 ΔG_m vs. difference in chlorine contents of mixed CPE polymers: ●, immiscible; ○, miscible

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