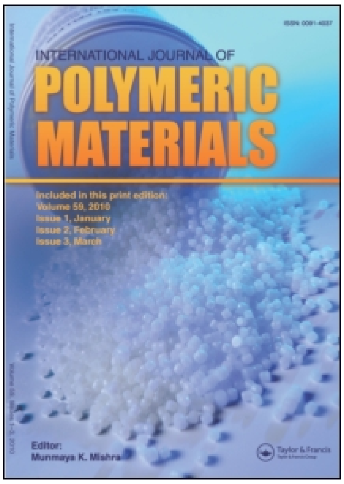

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MISCIBILITY OF PVC WITH CHLORINATED PE AND CHLORINATED PVC

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Miscibility of PVC with chlorinated PE and chlorinated PVC was reviewed. The miscible region of chlorine content ranged from 44 wt% to 65 wt%, which was not symmetric to the chlorine content of PVC, 56.7 wt%. Two group contribution methods were used to calculate solubility parameters of polymers. The results of solubility parameters showed a more symmetric miscible region with respect to the value of PVC. However, the ranges of miscibility were different. It was 2.3 $(J/cm^3)^{0.5}$ in a three-dimensional method and was 1.5 $(J/cm^3)^{0.5}$ in the Fedors method.

Keywords: PE, chlorinated PE, PVC, CPVC, solubility parameter, blends

INTRODUCTION

Poly (vinyl chloride), commercially known as PVC, was first recognized and characterized more than 100 years ago. Due to its poor thermal stability and processing difficulty, it was not until about 1930 that PVC started to gain commercial importance. The problems of poor thermal stability were overcome by the development of copolymerization techniques and suitable additives, such as stabilizers, fillers, and plasticizers.

PVC is frequently compounded with other materials acting as stabilizers or plasticizers. This makes the study of polymer blending a

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natural extension. When large amounts of rubbery polymers are added into PVC, they can act as macromolecular plasticizers and impact modifiers. The use of another polymer to blend with PVC offers three advantages: (1) It improves impact strength of PVC; (2) it improves processibility; and (3) it gives a higher heat deflection temperature than a system using liquid plasticizers. Many reviews on PVC blends have been made in the past [1–5].

There are several definitions of compatibility and miscibility of polymer blends. Some studies consider a compatible blend as one that exhibits desirable physical properties, such as improvement of impact strength. Others define compatible blends as polymer mixtures that do not exhibit symptoms of phase separation. Generally, "miscibility" is used for dissolution of molecules at the molecular level with only one glass transition temperature (Tg), while "compatibility" is used for more general cases that blends have useful properties. The experimental methods most often used for the measurement of Tg are differential scanning chlorimetry (DSC) and dynamic mechanical analysis using the Rheovibron. A partially miscible blend is expected to exhibit two Tg's intermediate between those of the pure components. If the change of Tg is a function of the relative amounts of each component in the blend, a phase diagram can be constructed for a partially miscible blend [1,2].

Normally, elastomers do not need to be miscible with a glassy polymer on a molecular level to improve the impact properties. A separate rubbery phase with Tg about 60°C below room temperature is necessary for impact improvement [6]. But good adhesion between the two phases is still necessary [7]. Therefore two polymers need to be at least compatible. For PVC, impact modifiers should also maintain a sufficient size of rubbery domains in a network structure [8–10].

THEORETICAL BACKGROUND

Equilibrium miscibility of polymers is the most basic thermodynamic element in the analysis of blend compatibility. The classical theory of solution begins with the equation for free energy of mixing [1,2]:

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

where ΔG_{mix} is Gibbs free energy of mixing, ΔH_{mix} is the heat of mixing, and ΔS_{mix} is the entropy change due to mixing. Two conditions are necessary for miscibility [1,2]:

$$\Delta G_{mix} < 0 \tag{2}$$

and

$$\frac{\partial^2 G_{\text{mix}}}{\partial \phi^2} > 0 \tag{3}$$

where ϕ is the volume fraction of one component. R. L. Scott was among the first to adapt the Flory-Huggins equation to polymer blends. The expression of ΔG_{mix} is [1,2]:

$$\Delta G_{\text{mix}} = (\text{RTV/Vr})\left[\left(\frac{\phi_A}{X_A}\right)\ln\phi_A + \left(\frac{\phi_B}{X_B}\right)\ln\phi_B + \chi\phi_A\phi_B\right] \tag{4}$$

where V is the total volume, Vr is a reference volume taken as the smallest repeat unit of components, ϕ_A and ϕ_B are the volume fraction of components A and B, X_A and X_B are the degree of polymerization of A and B in terms of Vr, and χ is the polymer−polymer interaction parameter. The two terms containing X_A and X_B are entropy terms, which provide a negative contribution to the free energy of mixing. But for polymer blends these two terms are essentially zero because of the large value of X's. This leaves the last term of Eq. (4), which is the enthalpy of mixing, dominating the free energy of mixing of polymer blends.

When χ is zero or negative a miscible blend could be obtained. For a small χ a partially miscible blend is obtained. In this case the mutual solubility depends on temperature and molecular weight [1,2]. The effects of temperature on miscibility of polymer blends are complex, and both lower critical solution temperature (LCST) and upper critical solution temperature (UCST) may be observed. UCST behavior, in which a homogeneous blend at a given temperature undergoes phase separation on cooling, is characteristic of endothermic mixing and positive entropy of mixing. Such behavior is common in mixtures of low molecular weight materials and polymer solutions, and is predicted by traditional thermodynamic theories. In contrast, LCST behavior, in which components of a mixture undergo phase separation on heating, is characteristic of negative heats of mixing and negative excess entropy. This type of behavior is more frequently seen in polymer blends and is predicted by newer theories [1,2].

Chlorinated polyethylene (CPE) and chlorinated PVC (CPVC) are structurally similar to PVC with the only difference in their chlorine content. The mutual miscibility of these modifiers depends upon the chlorine content and the distribution of the chlorine atoms on the polyethylene backbone. CPE is prepared by chlorination of PE and CPVC is prepared by chlorination of PVC. Chlorination of PE and PVC can be conducted in solid state or in solutions. PE is a highly crystalline material. If the polymer is in solid state, chlorination begins at amorphous areas and crystalline surfaces, followed by melting and exposure of fresh areas for chlorination. Chlorine frequently concentrates unevenly in certain regions of the polymer during chlorination. This uneven distribution is referred to as block chlorination. The most widely used commercial process for chlorination employs an aqueous suspension. Chlorination in solution, on the other hand, tends to be more uniform, being limited only by solvation, *i.e.*, how well the chains are stretched out. The crystallinity of PE is gradually destroyed in chlorination. For example, it has been shown that the crystallinity of polyethylene can be destroyed by random chlorination in solution when the chlorine content exceeds 35 wt% [11].

PVC also contains a small amount of crystallinity, which accounts for its unusual properties. X-ray studies indicate that PVC is substantially amorphous although some small percentage (<5%) of crystallinity is present. Studies using nuclear magnetic resonance (NMR) techniques indicate that conventional PVC is about 55% syndiotatic and the rest largely atactic in structure. When chlorinated, PVC also gradually losses its crystallinity. But in block chlorination it has been reported that there was an increase of the syndiotactic fraction because the atactic portion was selectively chlorinated first [12].

LITERATURE REVIEW

Ajroldi et al. [13] studied the dynamic mechanical properties of melt-mixed blends comprised of 15% PVC and 85% CPVC of either 67.1% or 67.4% Cl, and found them incompatible. Carmoin et al. [14] studied blends of PVC and heterogeneously chlorinated PVC prepared by Brabender and milling cylinder. Blends with CPVC of 62.5% Cl showed a single Tg's which varied quasi-linearly with blend composition. For CPVC with 67.5% Cl the blend exhibited two Tg's.

Double and Walsh [15] studied phase diagrams of a solution of PVC and a chlorinated polyethylene. The latter contained 42 wt% Cl and 1 wt% S as SO_2Cl group. The blends were found to be compatible over some range of composition and exhibited the phenomenon of a lower critical solution temperature (LCST). Since the blends behaved as a single phase at low temperature, the chlorine content at 42% was likely the boundary of miscibility with PVC.

Clark *et al.* [16] studied blends of PVC with several CPVCs with Cl content ranging from 63% to 68%. It was concluded that compatibility decreased with increasing molecular weight and Cl content. CPVC with Cl content 65% and below had only one Tg and could be regarded as miscible with PVC.

Xu et al. [17] studied binary blends of PVC, CPE, high-density polyethylene (HDPE), and low-density polyethylene (LDPE), and their ternary blends. Their CPE contained 36% chlorine. They concluded that a small amount of PE increased the impact strength of PVC. As little as 3% PE showed a significant effect. A small amount of PE also improved the impact strength of PVC/CPE blends. Electron micrographs showed that PE contributed to the formation and perfection of a CPE network structure and increased the impact strength of the PVC/CPE blends. The dynamic viscoelastic spectra data revealed that CPE was incompatible with PVC but might act as a compatibilizer for PVC/PE. In the blends CPE/HDPE and CPE/LDPE the Tg's moved toward each other, indicating a partial miscibility.

Xu et al. [18] also studied the compatibility, morphology, fusion behavior, and mechanical properties of blends of PVC, acrylic resin, and CPE. The acrylic was a copolymer of methyl methacrylate and ethyl acrylate at a ratio of 9:1. The CPE contained 36% chlorine. The results indicated that PVC and acrylate were miscible with only one Tg in both DSC and Rheovibron studies. PVC and CPE were immiscible with two Tg's. With increasing acrylic content in PVC/CPE blends, the'interfacial adhesion improved, resulting in the increasing compatibility of the blends. Acrylic was more effective in promoting fusion while CPE with a small amount of acrylic enhanced impact strength.

Several practical properties of PVC-acrylonitrile-butadiene-styrene (ABS) and PVC-CPE blends were reported by Deanin and Chuang [19]. Both ABS and CPE worked as impact modifiers. The impact strength increased substantially with concentration, while flexural modulus and heat deflection temperature decreased slightly. CPE containing less than 24 wt% Cl were incompatible with PVC and generally were not used with PVC. Those with 25–40 wt% Cl were the best impact modifiers having practical compatibility [5].

Table 1 summarizes the conclusions about miscibility of PVC with CPVC and CPE. It can be concluded that CPE with 42 wt% Cl was the lower bound of miscibility while CPVC with 65 wt% Cl was the upper bound of miscibility. It can be noticed that this range is not completely symmetric with respect to chlorine content of PVC, which is 56.7 wt%. Toward the low Cl side there is a difference of about 14% and toward the high Cl side the difference is about 8%. This variation is a result of chlorine concentration and density change, which is explained later through the solubility parameter discussion.

SOLUBILITY PARAMETER

In 1916 Hildebrand pointed out that the order of solubility of a given solute in a series of solvents is determined by the internal pressure of the solvents. Later, Scatchard introduced the concept of cohesive

TABLE 1 Conclusions of Miscibility of PVC with CPE and CPVC

Polymer	Ci content (%)	Comments	Reference
CPE	36	Immiscible	[17,18]
CPE	42	LCST	[15]
PVC	56.7		
CPVC	62.5	miscible	[14]
CPVC	63	miscible	[16]
CPVC	64	miscible	[16]
CPVC	65	miscible	[16]
CPVC	67.1	immiscible	[13]
CPVC	67.4	immiscible	[13]
CPVC	67.5	immiscible	[14]
CPVC	68	immiscible	[16]

energy density into Hildebrand's theory, identifying this quantity with the cohesive energy per unit volume. Finally, Hildebrand gave a comprehensive treatment of his concept and proposed the square root of the cohesive energy as a parameter identifying the behavior of specific solvents. In 1949, he proposed the term "solubility parameter" and the symbol "δ" which is defined as:

$$\delta = \left(\frac{-\Delta E_{\text{vap}}}{V}\right)^{(1/2)} \tag{5}$$

The square of δ is often called the cohesive energy density. The concept of the solubility parameter was initially used in polymer-solvent systems, in particular by the coating industry and also by the elastomer industry. The former was interested in providing compatibility of the solvent system with a coating resin; the latter was more concerned with the unfavorable swelling of a cured rubber by solvents. Years later, the extension of the concept of the solubility parameter to polymer–polymer systems was popularized by Bohn [20]. The solubility of a given polymer in various solvents is largely determined by its chemical structure. As a general rule, structural similarity favors solubility. This means that the solubility of a given polymer in a given solvent is probable if solubility parameters of the polymers and the solvent are within one to two units of each other.

It has been shown that the Flory-Huggins interaction parameter can be related to the solubility parameter of two components by [1,2]:

$$\chi = \frac{(\delta_1 - \delta_2)^2 V_r}{RT} \tag{6}$$

where V_r is the volume of repeat units of the polymers. The above equation implies that χ is always positive and most polymer blends will not be miscible unless their structures are very similar and bring the two solubility parameters close together. A negative value of χ can occur when a specific interaction exists and is not accounted for by Eq. (6). Since LCST was observed in the CPE/PVC blend, a small positive heat of mixing and χ are expected. Therefore, the use of the solubility parameter concept in discussing miscibility is appropriate.

The solubility parameters of solvents can be determined experimentally from heat of vaporization data. For polymers, the solubility parameter can be determined from the swelling of polymers by a series of solvents. Similar to other thermodynamic properties, solubility parameters can be estimated based upon the chemical structure of molecules. Small [21] was the first to propose a group calculation method for solubility parameters. Fedors [22] developed another system of group molar attraction constants together with constants of molar volume. Both approaches calculate heat of vaporization and molar volume separately from values of each structural group and calculate the solubility parameter using Eq. (5). These approaches are considered to be one-dimensional approaches.

The cohesive energy of organic compounds may be divided into three parts, corresponding to three types of interaction forces: dispersive, polar, and hydrogen bonding [23]. Dispersive forces are the result of a fluctuating atomic dipole formed from a positive nucleus and a negative electron cloud. They occur in all molecules and usually contribute a dominating portion of intermolecular interaction. Polar forces include both permanent and induced dipoles. Hydrogen bonding interaction exists between a hydrogen donor and a hydrogen acceptor. PVC is known to be a weak hydrogen donor and contains a small amount of hydrogen bonding interaction energy. The cohesive energy density can be properly separated into three components, and the corresponding solubility parameter expression is:

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \tag{7}$$

where δ_d = the dispersion compound of δ, δ_p = the polar component of δ, and δ_h = the hydrogen-bonding component of δ. For each of the three components of the solubility parameter, a group calculation method and a comprehensive table of characteristic values for functional groups are given by van Krevelen [24].

In calculating the properties of CPE, PVC, and CPVC the chlorine is assumed to exist as −CHCl−. This is true in PVC and is likely to be true in CPE with low chlorine content. For CPVC a finite amount of chlorine exists as $-CC1_2-$ which is discussed later. The molar volume of polymers can also be calculated by a group addition method given in van Krevelen. The value for methylene in the calculation is 16.45 cm^3/mol and for the chloromethylene group, −CHCl−, is 28.25 cm^3/mol. Table 2 compares the experimental values of density of CPVC measured by Ajroldi *et al.* [13] and calculated results. The agreement of results is within 1.5% up to 66% of Cl. Density calculated using the constants of Fedors shows much larger difference. It should be noted that the molar volume constants in the Fedors method were generated for computing solubility parameter and were not for density calculations.

Table 3 compares the solubility parameters calculated using the three-dimensional method and Fedors method for CPE, PVC, and CPVC. It can be seen that the miscible region in terms of solubility parameter is more symmetric. In the three-dimensional method the difference of the solubility parameter between 44% and 57.6% is 2.45 $(J/mol)^{0.5}$ and the difference between 57.6% and 65% is 2.12 $(J/mol)^{0.5}$. In the Fedors method the difference are 1.61 $(J/mol)^{0.5}$ and 1.43 $(J/mol)^{0.5}$, respectively. In both methods the difference between 44% and PVC is larger than the difference between PVC and 65%. The range of solubility parameter is wider in the three-dimensional method

TABLE 2 Comparison of Density of CPVC

Cl content (wt%)	Density (g/cm^3)	
	Experimental*	*Calculated*
56.6	1.405	1.396
58.9	1.440	1.433
61	1.470	1.469
62	1.485	1.487
63.3	1.500	1.510
64.6	1.520	1.534
65.4	1.530	1.550
66.2	1.545	1.565
67.2	1.555	1.585
68	1.570	1.602
68.6	1.580	1.614
70.6	1.605	1.657

*Experimental results were obtained from Reference [13].

TABLE 3 Calculated Solubility Parameters

Cl content (wt%)	Solubility parameter (J/cm^3)$^{0.5}$	
	Three-dimensional	Fedors
38	18.66	20.33
40	18.91	20.53
42	19.18	20.74
44	19.47	20.96
46	19.79	21.18
48	20.12	21.42
50	20.49	21.66
52	20.88	21.92
54	21.30	22.19
56	21.75	22.47
56.7	21.92	22.57
58	22.24	23.06
60	22.76	23.39
62	23.32	23.39
64	23.92	23.72
65	24.04	23.90
66	24.57	24.08
68	25.26	24.45
70	26.01	24.85

than the Fedors method. The reason for this difference is because of the introduction of polar and hydrogen bonding components into the three-dimensional method. This difference increases proportionally to the chlorine content. Also the Fedors method tends to overestimate molar volume and underestimate density when chlorine content increases. Another possibility is the existence of the dichlorinated group, $-CCl_2-$, in CPVC. According to the study of Komorsoki et al. [25] using C-13 NMR there was about 5 mol% of the $-CCl_2-$ group in CPVC of 65 wt%. The exact percentage varies with the method of preparation. The group constant of $-CCl_2-$ is available in the Fedors method but not in the three-dimensional method. A refined calculation including the $-CCl_2-$group in the Fedors method tends to lower solubility parameters because of the partial cancellation of the dipole interaction in the $-CCl_2-$ group. It also increases molar volume slightly. This will make a better estimation of density but will decrease the solubility parameter of 64 wt% in the Fedors method by about 0.1 (J/cm^3)$^{0.5}$ and is unlikely to change the conclusion discussed above.

From the above results it can be concluded that the solubility parameter method can give a reasonable estimation of the mutual miscibility of polymer blends. Since the solubility parameters of polymers can not be determined from the heat of vaporization measurement an estimation method is necessary to assign a value. Although the two estimation methods give close solubility parameter values, when calculating the difference of the solubility parameters of two polymers a large percentage of variation can occur. Therefore, the use of calculation method and group constants must be consistent when comparisons are made.

CONCLUSIONS

Two group methods were used to compare the miscibility compositions of CPE, PVC, and CPVC at different chlorine content. Both methods correctly demonstrated a more symmetric boundary for miscibility but the miscibility ranges were different.

REFERENCES

[1] Olabisi, O., Robeson, L. M. and Shaw, M. T. (1979). "Polymer-Polymer Miscibility", Academic Press, New York.

[2] Paul, D. R. and Newman, S. (1978). "Polymer Blends", Academic Press, New York.

[3] Robeson, L. M. (1990). *J. Vinyl. Tech.*, **12**, 89.

[4] Huang, J. C., Chang, D. C. and Deanin, R. D. (1993). *Adv. Polym. Tech.*, **12**, 81.

[5] Nass, L. I. and Heiberger, C. A. (1988). "Encyclopedia of PVC", 2nd edn., Vol. 2, Chapter 5, Marcel Dekker, New York.

[6] Bucknall, C. B. (1977). "*Toughened Plastics*", Applied Science Publishers, London.

[7] Wu, S. (1982). "*Polymer Interface and Adhesion*", Marcel Dekker Inc., New York.

[8] Kiss, L., Aztankai, G., Nagy, P. and Karger-Kocsis, J. (1984). *J. Vinyl. Tech.*, **6**, 125.

[9] Fleischer, D., Fischer, E. and Brandrup, J. (1977). *J. Macromol. Sci. Phys.*, **B14**, 17.

[10] Siegmann, A. and Hiltner, A. (1984). *Polym. Eng. Sci.*, **24**, 869.

[11] Era, V. A. (1974). *Makromol. Chem.*, **175**, 2191.

[12] Nass, L. I. and Heiberger, C. A. (1988). "Encyclopedia of PVC", 2nd edn., Vol. 1, Chapter 11, Marcel Dekker, New York.

[13] Ajroldi, G., Gatta, G., Gugelmetto, P. D., Rettore, R. and Talamini, G. P. (1971). In: "*Multicomponent Polymer Systems*", Gould, R. F., Ed., *Adv. Chem. Ser.*, **99**, 119, *Am. Chem. Soc.*, Washington, DC.

[14] Carmoin, B., Villoutreix, G. and Berlot, R. (1977). *J. Macromol. Sci. Phy.*, **B14**, 307.

[15] Double, C. P. and Walsh, D. J. (1978). *Polymer*, **20**, 1115.

[16] Clark, D. D., Collins, E. A. and Kleiner, L. W. (1982). *Polym. Eng. Sci.*, **22**, 698.

[17] Xu, X., Meng, X. and Chen, K. (1987). *Polym. Eng. Sci.*, **27**, 391.

[18] Xu, X., Zang, L. and Li, H. (1987). *Polym. Eng. Sci.*, **27**, 398.

[19] Deanin, R. D. and Chuang, W. Z. L. (1986). *SPE ANTEC*, 1239.

[20] Bohn, L. (1969). *Rubber Chem. Tech.*, **41**, 459.

[21] Small, P. A. (1953). *J. Appl. Chem.*, **3**, 71.

[22] Fedors, R. F. (1974). *Polym. Eng. Sci.*, **14**, 471.

[23] Deanin, R. D. (1972). "*Polymer Structure, Properties, and Applications*", Cahners Books, Boston, MA.

[24] van Krevelen, D. W. (1976). "*Properties of Polymers – Their Estimation and Correlation with Chemical Structure*", 2nd edn., Elsevier, Amsterdam.

[25] Komorsoki, R. A., Parker, R. G. and Shockcor, J. P. (1985). *Macromolecules*, **18**, 1257.