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Dedicated to Prof. Edith A. Turi in recognition of her leadership in education

MISCIBILITY OF SOME POLYCARBONATES WITH POLYVINYL CHLORIDE AND CHLORINATED POLYVINYL CHLORIDE

J. T. Neill and F. E. Karasz[*]

Department of Polymer Science and Engineering, University of Massachusetts, Amherst
Massachusetts 01003, USA

Abstract

The phase behavior of several polycarbonate homopolymers and copolymers blended with PVC and chlorinated PVCs (CPVCs) has been investigated. Tetrachlorobisphenol-A polycarbonate (TCPC) is miscible in all proportions with PVC and CPVCs containing up to 70.2 wt% chlorine. CPVCs having chlorine contents greater than 70.2% (by weight) are immiscible with TCPC. Tetrabromobisphenol-A polycarbonate (TBPC) exhibits phase mixing with PVC and CPVCs; however, the high T_g of this polycarbonate (260°C) prevents adequate investigation of equilibrium phase behavior. Bisphenol-A polycarbonate (BPC), tetramethylbisphenol-A polycarbonate (TMPC), and hexafluorobisphenol-A polycarbonate (HFPC) form two-phase mixtures with the vinyl polymers. Microstructural differences in the CPVCs due to chlorination method (solution chlorination *vs.* slurry chlorination) have no effect on the miscibility results. Miscibility was observed in several copolycarbonate/CPVC blends and was found to be dependent on copolymer composition. Using a binary interaction, mean-field theory, segmental interaction parameters were estimated for repeat unit interactions. Based on the estimated interaction parameters, miscibility in these blends is primarily the result of intramolecular repulsive effects, rather than strong intermolecular attractive forces.

Keywords: chlorinated polyvinyl chloride, polycarbonates, polymer miscibility, polyvinyl chloride

Introduction

Blends of polycarbonates with PVC have been studied for many years, and several patents exist for PVC/polycarbonate compounds [1–10]. Although ‘polycarbonate’ is synonymous with bisphenol-A polycarbonate (BPC, Fig. 1), these patented compounds typically contain novel bisphenol-A-derived repeat units, such as tetramethyl bisulfone polycarbonate (TMSPC, Fig. 1). Robeson *et al*. [8] investigated blends of PVC with poly(BPC-alt-TMSPC). Using dynamic mechanical analysis, it was found that this copolymer forms single-phase blends with PVC. Another polycarbonate, oligomeric tetrabromobisphenol-A polycarbonate (TBPC, Fig. 1), has been reported

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[*] Author to whom all correspondence should be addressed.

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to be an effective heat distortion temperature modifier and smoke retardant for PVC and chlorinated PVC (CPVC) [11].

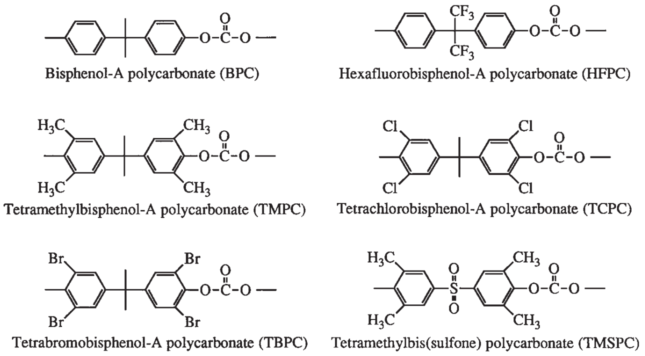
Bisphenol-A polycarbonate (BPC)
Hexafluorobisphenol-A polycarbonate (HFPC)
Tetramethylbisphenol-A polycarbonate (TMPC)
Tetrachlorobisphenol-A polycarbonate (TCPC)
Tetrabromobisphenol-A polycarbonate (TBPC)
Tetramethylbis(sulfone) polycarbonate (TMSPC)

Fig. 1 Repeat unit structure of bisphenol-A polycarbonate (BPC)

Excluding the patent literature, there is little published research on polycarbonate/PVC blends. BPC and tetramethylbisphenol-A polycarbonate (TMPC, Fig. 1) have been reported to be immiscible with PVC in all proportions [12, 13]. These polycarbonates were found to be miscible with vinyl chloride-vinylidene chloride copolymers [12, 13]. Braun *et al.* [12] suggested that the increased chlorination created more sites for interaction between the polycarbonate and the vinyl copolymer. This conclusion was based on observed shifts in the carbonyl region of the IR spectrum.

In this research, the phase behavior of polycarbonate/PVC and polycarbonate/CPVC blends were investigated. Polycarbonates studied included both homopolymers and copolymers. The CPVCs were produced via solution-chlorination and slurry-chlorination. Using a mean-field, binary interaction model, developed to explain miscibility in copolymer-containing blends, segmental interaction parameters were estimated from miscibility data.

Estimation of segmental interaction parameters, $\chi_{i,j}$

It has been found that blends containing copolymers may form miscible blends even though the homopolymer pairs are immiscible [14–17]. This effect has been attributed to an intramolecular, repulsive interaction acting within the copolymer, and a theory to describe this behavior has been developed [18–20]. In this mean-field theory, the overall interaction parameter for the blend, χ_{blend}, is a function of the individual segmental interaction parameters, $\chi_{i,j}$, acting within the blend system. The $\chi_{i,j}$ quantify the interaction between monomer pairs. In the mean-field approach, the Flory-Huggins equation [21, 22] is retained for the free energy change of mixing, ΔG_M, where

$$\Delta G_M/RT=(\phi_1/N_1)\ln(\phi_1)+(\phi_2/N_2)\ln(\phi_2)+\chi_{\mathrm{blend}}\phi_1\phi_2 \tag{1}$$

ϕ_i and N_i are the volume fraction and degree of polymerization, respectively, of component *i*. For a blend of poly(A-*co*-B) and poly(C-*co*-D), χ_{blend} is given by [18]

$$\chi_{blend}=(1-x)(1-y)\chi_{AC}+(1-x)y\chi_{AD}+x(1-y)\chi_{BC}+xy\chi_{BD}-x(1-x)\chi_{AB}-y(1-y)\chi_{CD} \quad (2)$$

where x and y are the volume fractions of monomer residues B and D, respectively, within their respective copolymers. The designation for this type of blend system is $(A_{1-x}B_x)/(C_{1-y}D_y)$.

For miscibility to occur, ΔG_M must be negative. If the polymers are of infinite molecular weight, the first two terms on the right-hand side of Eq. (1) become negligible, and ΔG_M depends only on the χ_{blend}-term. Inspection of Eq. (2) shows that χ_{blend} can be less than zero when all $\chi_{i,j}$'s are positive. This occurs when $\chi_{A,B}$ and $\chi_{C,D}$ are of sufficient magnitude to overcome the four intermolecular $\chi_{i,j}$'s. The copolymer composition range in which single-phase blends are formed is known as a 'miscibility window'. This theory also predicts that immiscible blends may result when the comonomers attract one another, that is, when all the segmental interaction parameters are negative. A 'window of immiscibility' has been shown to exist in blends of poly(vinyl chloride-*co*-vinyl acetate) and poly(*n*-butyl methacrylate-*co*-isobutyl methacrylate) even though all binary combinations of the homopolymers are miscible [23].

Experimental

The homopolymers and copolymers used in this investigation are listed in Tables 1 and 2. Repeat unit structures of the aromatic polycarbonates are shown in Fig. 1. PVC-0 and the slurry-chlorinated PVCs (slurry-CPVCs) were generously donated by the B. F. Goodrich Company. BPC-1, BPC-2, and BPC-3 were obtained from Aldrich Chemical (cat. no. 18,167-6), as was PVC-2 (cat. no. 34,676-4). TMPC-1 was donated by General Electric Company. PVC-1, the solution-chlorinated PVCs (solution-CPVCs), and the remaining polycarbonate homopolymers and copolymers were acquired from LARK Enterprises (Webster, MA). The solution-CPVCs were produced by the chlorination of PVC-1.

The chlorination process leads to significant microstructure differences between solution-CPVCs and slurry-CPVCs. Solution chlorination proceeds by random placement of Cl within the PVC macromolecule. Komoroski *et al.* [24] have shown that chlorine atoms preferentially add to $-CH_2-$ groups, and only at high chlorine levels (>64 wt% Cl) do $-CCl_2-$ groups become evident. In slurry chlorination, PVC particles are chlorinated while in suspension. Those portions of PVC macromolecules at the particle surface become highly chlorinated while chain segments within the particle remained unaffected by the chlorination process. The differences in microstructure are apparent in the thermal behavior of the CPVCs (Fig. 2). Solution-CPVCs exhibit narrow glass transition widths, ΔT_g; the ΔT_g's are less than 10°C. The ΔT_g of slurry-CPVCs increases with increasing chlorine content, reflecting the structural heterogeneity of these polymers. The slurry-CPVCs also exhibit a melt endotherm because of residual PVC sequence content.

Table 1 Polycarbonate characterization

PC	$M_n(10^{-3})$	M_w/M_n	M_z/M_w	T_g/°C	ΔC_p/J (g K)$^{-1}$
Homopolymers					
BPC-0	13.1	2.63	2.01	139	0.248
BPC-1	22.4	1.90	1.55	145	0.248
BPC-2	24.9	2.14	1.57	149	0.248
BPC-3	38.0	1.98	1.59	151	0.248
TMPC-0	6.6	1.61	1.66	176	0.263
TMPC-1	25.6	2.16	1.75	197	0.263
TMPC-2	45.1	2.08	1.63	200	0.263
TCPC-0	14.2	1.96	1.59	222	0.195
TCPC-1	22.3	1.43	1.39	225	0.195
TCPC-2	41.0	1.90	1.69	226	0.195
HFPC	23.0	2.48	2.81	159	0.201
TBPC	49.6	2.04	1.66	262	0.152
Copolymers					
BPC-TCPC-25	12.3	1.96	1.94	157	0.261
BPC-TCPC-50	10.6	2.02	1.67	180	0.236
BPC-TCPC-53	57.4	2.87	1.90	200	0.195
BPC-TCPC-75	14.1	2.07	1.66	202	0.209
TMPC-TCPC-42	10.1	1.39	1.43	195	0.250
TMPC-TCPC-52	52.7	2.36	1.78	214	0.211
TMPC-TCPC-58	14.3	1.77	1.48	206	0.230
TMPC-TCPC-92	13.3	1.76	1.46	213	0.200
BPC-TBPC-50	39.0	2.03	1.59	209	0.150
HFPC-TMPC-50	9.3	1.61	1.59	161	0.215

Molecular weights listed for these polymers were determined by gel permeation chromatography (GPC) (Waters Model 410 Differential Refractometer and Data Module). The columns were maintained at 30°C, and THF was the solvent. Molecular weights are relative to polystyrene standards (Polymer Laboratories).

Glass transition temperatures, T_g's, and specific heat increments at T_g, ΔC_p, were measured by differential scanning calorimetry (DSC) (Perkin Elmer System 7 with 7700 Series Computer). The glass transition data was measured at a heating rate of 20°C min^{-1}, and the DSC cell was continuously purged with dry nitrogen. T_g's were measured after cooling the sample from $T>T_g$ at the natural cooling rate of the instrument (>70°C min^{-1}); ice/water was used in the calorimeter coolant reservoir. T_g is defined as the midpoint in the heat capacity increment at the glass transition.

Table 2 Characteristics of PVCs and CPVCs

	%Cl	$M_n(10^{-3})$	M_w/M_n	M_z/M_w	T_g/°C	ΔC_p/J (g K)$^{-1}$	% DCE Repeat Units
PVC							
PVC-0	56.7	22.3	2.66	1.89	76	0.350	
PVC-1	56.7	56.9	2.09	2.01	86	0.295	
PVC-2	56.7	108.0	2.28	1.74	90	0.290	
Solution-Chlorinated PVC							
CPVC-1	58.3	63.3	2.21	2.48	88	0.304	6
CPVC-3	59.2	67.7	2.12	2.29	91	0.315	10
CPVC-4	60.0	68.7	2.11	2.45	95	0.322	13
CPVC-5	61.4	71.7	2.10	2.48	100	0.320	21
CPVC-6	62.2	72.1	2.03	2.25	106	0.283	24
CPVC-7	63.5	68.5	1.94	2.09	115	0.272	31
CPVC-8	65.4	69.4	1.82	1.80	127	0.225	42
CPVC-9	67.3	69.5	1.90	1.74	147	0.197	54
CPVC-10	69.2	62.1	1.90	1.71	178	0.161	67
CPVC-11	70.2	54.8	1.97	1.76	195	0.159	75
CPVC-12	70.6	48.1	1.95	1.82	211	0.150	78
Slurry-Chlorinated PVC							
BFG-63	63.5	33.3	2.08	1.79	107	0.260	
DSP-63	63.5	29.0	2.30	1.76	106	0.260	
BFG-68	68.3	25.1	2.53	1.90	130	0.230	
DSP-68	68.3	24.1	2.64	1.84	130	0.2	

Elemental analysis was performed by the University of Massachusetts Microanalysis Laboratory to determine the chlorine content of the CPVCs and the polycarbonate copolymers. For the copolymers, chlorine content was used to determine copolymer composition. In Table 1, the number following the copolycarbonate abbreviation is the mol% TCPC repeat unit, e.g., copolymer BPC-TCPC-25 is composed of 75 mol% BPC repeat units and 25 mol% TCPC repeat units.

The chlorine content of the solution-CPVCs was used to determine the ‘copolymer composition’ of the CPVC, assuming the polymer resembles a copolymer of vinyl chloride (VC, $-CH_2-CHCl-$) and 1,2-dichloroethylene (DCE, $-CHCl-CHCl-$). This assumption is based on ^{13}C NMR analysis [24]. The percentages of DCE repeat units in the solution-CPVCs are listed in Table 2.

Preparation of PVC-containing blends depended upon the PVC used. PVC-0 was soluble in methylene chloride, also a good solvent for all of the polycarbonates, and blends were cast into thin films from 4% w/v methylene chloride solutions. PVC-1 and PVC-2 were soluble in THF, and blends containing these PVCs were cast from THF solutions (4% w/v) to form thin films, and/or precipitated in an eleven-fold

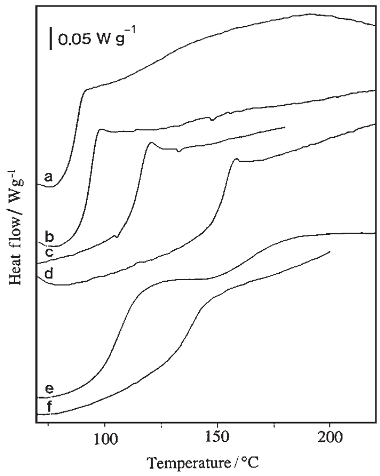

Fig. 2 Effect of chlorination and chlorination method of PVC glass transition temperature behavior as measured by DSC. (a) PVC-1; (b) CPVC-3; (c) CPVC-7; (d) CPVC-9; (e) BFG-63; (f) BFG-68

excess of methanol. Precipitated samples were placed under vacuum at 60°C until dry (determined by thermogravimetric analysis). Films cast from methylene chloride were dried under the same conditions. THF-cast films, however, required higher drying temperatures to remove solvent. Under nitrogen, the temperature was cycled to as high as 140°C. Cycling minimized exposure to degradative thermal conditions. Color changes in the samples indicated some degradation was occurring; however, the films were still soluble in THF and the glass transition behavior was not affected.

All CPVC-containing blends were cast as thin films from 4% w/v methylene chloride solutions. Methylene chloride was allowed to evaporate at 30°C under a nitrogen stream. Once the films formed, the temperature was raised to 50°C. One to two days was sufficient to remove all traces of the solvent from the films. Thermogravimetric analysis (TGA) was used to monitor levels of residual methylene chloride in the films.

Blend samples were thermally treated within the DSC cell prior to glass transition measurements. Data presented represents second heatings of samples following the initial treatment. Annealing temperatures up to 230°C were used to treat the samples. Anneal times at high temperatures were short, 5 to 10 min. At lower temperatures, e.g., 160°C, anneal times greater than one hour were possible without noticeable degradation of the polymers. Typically, 20 to 30 min was used at these lower temperatures. Another thermal pretreatment was heating the sample to high temperatures (>240°C), followed by rapid cooling. This treatment was used to determine if phase separation could be induced at very high temperatures. Heating rates utilized for T_g measurements were 20°C min^{-1} and 40°C min^{-1}. The higher rate was chosen to minimize PVC and CPVC degradation. Blends exhibiting a single glass transition were judged to be miscible. Samples were removed from DSC pans to observe color changes due to degradation. Discoloration of the samples was seen, varying from yellow to red depending upon the thermal treatment and the blend composition.

Unsupported films for FT-IR were prepared by solution casting onto glass plates. Typical thickness of these films was 0.020 mm. Measurements were made in a Nicolet Instruments IR Spectrometer.

A Polymer Laboratories Mk I DMTA was used for measuring the dynamic mechanical loss tangent of the polymers and their blends. Thick films for dynamic mechanical analysis were prepared by solvent casting in layers, each layer being allowed to form before application of additional polymer/solvent solution.

Results and discussion

PVC blended with polycarbonate homopolymers

DSC curves of PVC-0/BPC-3 blends are shown in Fig. 3. The DSC behavior of three PVC-0/polycarbonate blend systems, including PVC-0/BPC-3, as a function of blend composition are summarized in Table 3. The other two polycarbonates are TMPC-2 and HFPC (Fig. 1 for repeat unit structures). The results in Fig. 3 and Table 3 are for blends annealed at 180°C for 20 min (BPC, HFPC) and 210°C for 15 min (TMPC). Annealing at higher temperatures did not change the results, i.e., UCST behavior was not observed. In these blends, the polycarbonate glass transition is partly, or wholly, obscured by the PVC melt endotherm; this effect is most prominent in PVC-rich blends. Despite the difficulty in locating the polycarbonate T_g in some blends, the PVC T_g is detectable and is not affected by the addition of polycarbonate.

BPC-3 and TMPC-2 clearly form two-phase blends with PVC-0, a result consistent with previously published results [12, 13]. Despite its low molecular weight, HFPC is also immiscible with PVC. The glass transition temperatures of each phase correspond to those of the pure components. In polycarbonate-rich compositions,

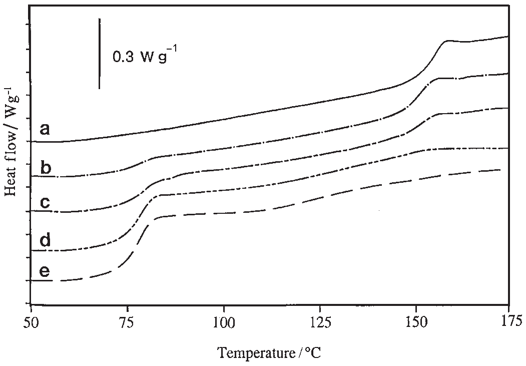

Fig. 3 DSC behavior of BPC-3/PVC-0 blends. (a) 100/0 (wt/wt); (b) 80/20; (c) 50/50; (d) 20/80; (e) 0/100

where ΔC_p could be measured for both PC and PVC phases, the ratio of $\Delta C_{p,\mathrm{measured}}$ to $\Delta C_{p,\mathrm{calculated}}$ lies between 0.95 and 1.06, where $\Delta C_{p,\mathrm{calculated}}$ is the product of the pure component ΔC_p and w, its weight fraction in the blend. In phase-separated blends, a $\Delta C_{p,\mathrm{measured}}/\Delta C_{p,\mathrm{calculated}}$ of unity indicates that the phase is pure [25]. Thus, both the glass transition temperatures and the ΔC_p behavior indicate a lack of mixing in these blends [24].

Table 3 Results from DSC experiments for blends of PVC with polycarbonate homopolymers

Blend	Weight proportion	Glass transition temperature/°C
BPC-3/PVC-0	20/80	76/–
	40/60	77/148
	60/40	77/149
	80/20	77/150
TMPC-2/PVC-0	20/80	79/–
	35/65	79/–
	50/50	80/198
	65/35	80/199
	80/20	80/200
HFPC/PVC-0	25/75	79/–
	50/50	79/–
	75/25	80/161

Blends of lower molecular weight BPC and TMPC with PVC-0 were studied to determine the effect of chain length on miscibility. Decreasing molecular weight will enhance the possibility of creating a miscible blend (see Eq. (1)). BPC-0/PVC-0 blends were found to be immiscible, and as in the high molecular weight blends, there was no indication of mixing within each phase. A TMPC-0/PVC-0 blend (50/50 by weight) exhibited a PVC-phase glass transition temperature at 83°C, 7°C higher than pure PVC-0. The TMPC T_g was not observable within the PVC melt endotherm. It is likely that a low molecular weight TMPC fraction is present in the PVC-rich phase, leading to this increase in the PVC T_g.

The addition of TBPC to PVC leads to an increase in the PVC T_g (Fig. 4). Because of the high glass transition temperature of TBPC (260°C) and the thermal instability of PVC above 240°C, it was not possible to anneal samples at high temperatures, where thermal equilibrium could be reached. The measured blend T_g is seen to be sensitive to the thermal history of the sample. Using annealing temperatures up to 220°C, a single T_g is seen in 50/50 (wt/wt) blends. As the annealing temperature and time are increased, it is observed that the blend glass transition temperature increases. This glass transition is broad (>15°C) and the T_g is much lower than the T_g predicted by either the Fox equation [26]

$$1/T_g=w_1/T_{g1}+w_2/T_{g2} \qquad (3)$$

or the Couchman equation [27]

$$\ln T_g=(w_1\Delta C_{p1}\ln T_{g1}+w_2\Delta C_{p2}\ln T_{g2})/(w_1\Delta C_{p1}+w_2\Delta C_{p2}) \qquad (4)$$

In both equations, absolute temperature is used. The Fox and Couchman equations predict T_g's of 157 and 130°C, respectively, for a miscible, 50/50 (wt/wt) blend. In the DSC experiments, a sample annealed at 180°C for 20 min had a T_g of 101°C, 29°C below the T_g value calculated from Eq. (4). The highest measured T_g after heat treatment was 114°C. This was achieved after heating the sample twice to 210°C at a rate of 30°C min^{-1}. This suggests that phase mixing is enhanced by elevating temperature.

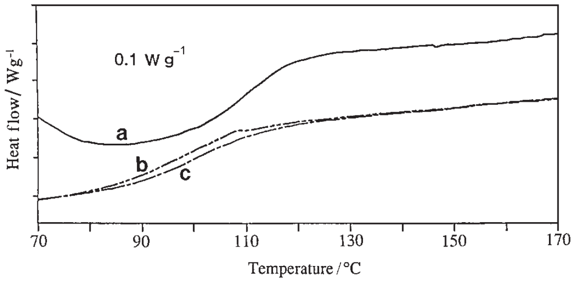

Fig. 4 Effect of annealing on 50/50 blends of TBPC/PVC-0. (a) sample previously heated to 200°C and 210°C; (b) sample annealed at 180°C for 5 min; (c) sample annealed at 180°C for 20 min

An explanation for this behavior is a state of non-equilibrium existing in the cast films. It is desirable in blend studies to anneal at temperatures above the T_g's of the blend components. This treatment is necessary to reduce the high solution viscosity that may hinder phase separation or mixing. The high T_g of TBPC and the poor thermal stability of PVC make it impossible to anneal at the proper temperatures to reach thermodynamic equilibrium. The 180°C annealing temperature is only 25°C above the predicted blend T_g and is not great enough for the high-viscosity polymer system to achieve equilibrium.

Tetrachlorobisphenol-A polycarbonate (TCPC), which is similar in structure to TBPC, with –Cl substituted for –Br, forms single phase blends with PVC. Films cast from solution are transparent, and thermal analysis (DSC and DMA) shows that the blends have single, composition-dependent glass transition temperature. T_g's for PVC-0/ TCPC-2 blends as a function of TCPC weight fraction are shown in Fig. 5. Plotted with the experimental data are the predicted T_g's based on Eqs (3) and (4). The Couchman equation comes close to predicting the blend T_g. TCPC/PVC blends do not exhibit the dependence upon thermal history seen in the TBPC/PVC blends. Several annealing temperatures were used (to as high as 260°C, with a 1 min anneal time), yet there was no indication of phase separation. Blends of the highest molecular weight materials, PVC-3 and TCPC-2, were also found to be miscible in all proportions.

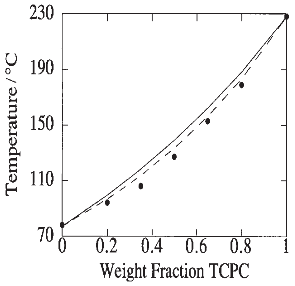

Fig. 5 Glass transition temperature of TCPC-2/PVC-0 blends. Solid curve, T_g, blend predicted by Eq. (3); dashed curve, blend glass transition temperature predicted by Eq. (4)

The dynamic mechanical loss tangent as a function of temperature (measurement frequency=1 Hz) for two TCPC/PVC blend compositions is shown in Fig. 6. The peaks having the greatest magnitude for each blend are assigned to the glass transition. Below the T_g, each blend exhibits two secondary relaxations. These processes correspond to the secondary relaxations of the PVC (–50°C) and TCPC (+70°C). Because these relaxations are due to localized motions in the polymer backbone, they are sensitive to interactions occurring between the polymers. The presence of two secondary relaxations suggests that the two polymers do not interact strongly.

Infrared spectroscopy was used to determine the effect of blending on the carbonyl stretching band of the polycarbonate. A reduction in the frequency of vibration of this band with increasing PVC concentration would indicate an interaction between the two polymers involving this functional group. The carbonyl stretch region for some TCPC/PVC and BPC/PVC blends is shown in Fig. 7. The high wavenumber shoulder of pure TCPC results from frozen-in conformations, a result of sample preparation. Comparing the spectra of the two PCs, there is little effect on the carbonyl stretch as a result of blending. The peak values for pure TCPC, 50/50 TCPC/PVC, and 25/75 TCPC/PVC are 1799.8, 1799.3, and 1798.9 cm^{-1}, respectively; the shifts are less than 1 cm^{-1}. Similar behavior is seen in immiscible BPC/PVC blends. If a specific interaction exists between TCPC and PVC, these measurements indicate that it does not involve the polycarbonate carbonyl group.

Kim and Paul [28] have advanced the argument that the changes in electron density within the polycarbonate with halogen substitution create favorable interactions with other polymers, such as polystyrene, PMMA, and polyesters. Electron density calculations indicate that the effect of chlorination or bromination at the 3,3′- and 5,5′-phenyl positions is to increase the polarity of the ring. Fluorine substitution for hydrogen in the isopropylidene group affects only the polarity within that group and does not exert an effect upon the phenyl rings. The calculations further show that the effect of these substitutions to the bisphenol unit have no effect on the electron density of the carbonate linkage. The changes in aromatic electron distribution in the

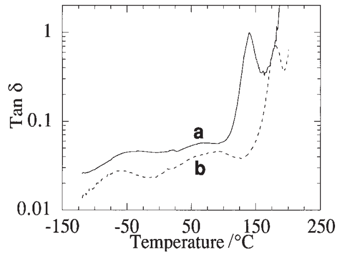

Fig. 6 Loss tangent of TCPC-2/PVC-0 blends. (a) 50/50 (wt/wt); (b) 75/25 (wt/wt). Measurement frequency is 1 Hz

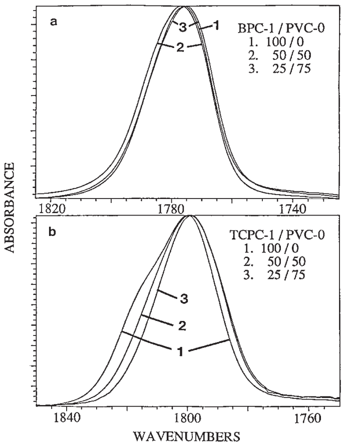

Fig. 7 Carbonyl stretch region of IR spectrum for (a) TCPC/PVC blends and BPC/PVC blends

chloro- and bromo-substituted polycarbonates may induce a π-π complex interaction between the polycarbonate phenyl rings and the chlorine atoms of PVC.

Chlorinated-PVC/polycarbonate homopolymer blends

There are two means by which chlorination of PVC may lead to miscibility with polycarbonates. First, the addition of chlorine may increase the number of interaction sites on the vinyl polymer backbone. The second factor is based on intramolecular repulsive effects within the CPVC. To a good approximation, solution-chlorinated PVC samples resemble copolymers of vinyl chloride and 1,2-dichloroethylene. Shiomi *et al.* [29] investigated solution-CPVC-containing blends, and determined the interaction parameter for this pair, $\chi_{\mathrm{VC,DCE}}$, to be 0.042. The positive value of this interaction parameter is a driving force for miscibility.

In Table 4, DSC results for 50/50 (wt/wt) blends of BPC-3, HFPC, and TMPC-1 with several solution-CPVCs are summarized. Annealing temperatures for these blends were as high as 220°C. All blends exhibit two glass transitions, though slight shifts in CPVC-phase T_g's are observed in some blends. These 3 to 5°C shifts in CPVC T_g result from the presence of low molecular weight polycarbonate fractions within this phase. Lowering the molecular weight of the polycarbonate does not change experimental results; BPC-0 and TMPC-0 blends with solution-CPVCs are phase separated. Like the higher molecular weight blends, the CPVC-phase has a T_g that is 4°C greater than the pure CPVC, while the T_g of the PC phase is unaffected. Thus, PVC chlorination is unable to affect miscibility with these polycarbonate homopolymers.

Table 4 Glass transition temperatures of 50/50 blends of polycarbonates with solution-chlorinated PVCs

Blend system	Glass transition temperature/°C
BPC-3/CPVC-4	98/150
BPC-3/CPVC-6	112/149
BPC-3/CPVC-7	122/151
BPC-3/CPVC-8	133/152
HFPC/CPVC-4	160/94
HFPC/CPVC-6	160/106
HFPC/CPVC-8	160/128
HFPC/CPVC-10	160/178
TMPC-1/CPVC-3	199/95
TMPC-1/CPVC-4	199/99
TMPC-1/CPVC-6	196/108
TMPC-1/CPVC-8	197/131
TMPC-1/CPVC-9	200/154
TMPC-1/CPVC-10	198/179

The results for BPC and TMPC blends with CPVC contrast with previously reported results in two respects. First, Braun *et al*. [12] found that certain compositions (10/90 and 90/10 PC/CPVC) of these PCs blended with a CPVC having 60 wt% chlorine were miscible. These compositions were not investigated in this study, but miscibility previously reported may be explained by the use of a low molecular weight CPVC. Second, the conclusion that increased chlorination of a vinyl polymer enhances miscibility with BPC and TMPC did not take into consideration the vinyl polymers chosen for the study. The highly chlorinated materials used in earlier investigations [12, 13] were vinyl chloride (VC)-vinylidene chloride (VDC) copolymers. The source of miscibility in blends of the vinyl chloride-vinylidene chloride copolymers with BPC and TMPC is either (1) a copolymer effect, as it has been reported that PVC and poly(vinylidene chloride) are immiscible [30] or (2) a favorable interaction between polycarbonate and vinylidene chloride repeat units.

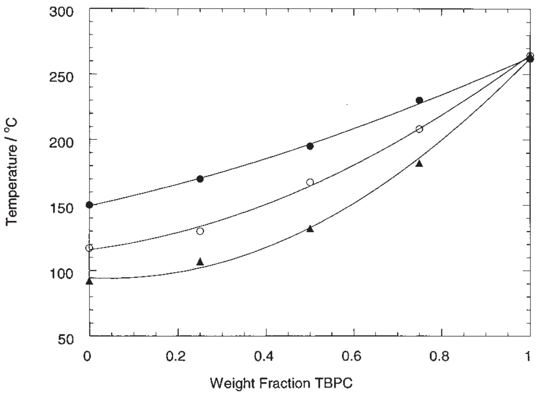

Fig. 8 Glass transition temperatures for blends of TBPC with ▲ CPVC-3; ○ CPVC-7; and ● CPVC-9. Solid curves, Couchman, Eq. (4) predicted T_g

TBPC blends with solution-CPVCs show a single glass transition in the accessible temperature range (<230°C) (Fig. 8). The blend T_g's increase as the quantity of TBPC in the blend increases. In general, a 25% (by weight) loading of TBPC leads to an increase in the CPVC T_g of 11 to 15°C, and a 50% loading increases the T_g by 40°C over the pure CPVC transition temperature. The experimental blend T_g's are fitted well by the Couchman equation. These temperature shifts are much greater than those seen in TBPC/PVC blends. These data suggest that the solution-CPVCs are miscible with TBPC, while PVC is not.

TCPC was found to be miscible with solution-CPVCs having chlorine contents of up to 70.2 wt% (CPVC-11). This is indicated by a single T_g in DSC experiments as well as by the optical clarity of the film samples. Blends of TCPC/CPVC-12 cast from THF and methylene chloride were cloudy, and this system was deemed immiscible on this basis. The glass transition temperatures of 50/50 (by weight) blends of TCPC with solution-CPVCs are shown in Fig. 9. All blends exhibit a single T_g intermediate between the pure component T_g's.

Infrared analysis of the carbonyl stretch region does not implicate this functional group as a contributor to blend miscibility in these TBPC/CPVC or TCPC/CPVC blends. If a specific interaction exists, it must involve the phenyl rings and either the methyne protons or chlorines of solution-CPVC.

In solution-CPVCs/TCPC blends, there is (1) an attractive, or negligibly repulsive, interaction between vinyl chloride and TCPC repeat units and (2) an intramolecular, repulsive interaction between vinyl chloride and 1,2-dichloroethylene repeat units, which promote miscible behavior. In the nomenclature of the mean-field approach for estimating χ_{blend}, the TCPC/solution-CPVC blend system is of the type $A/B_{1-x}C_x$, where A=TCPC, B=VC, and C=DCE. χ_{blend} for this system is defined as

$$\chi_{\mathrm{blend}}=(1-x)\chi_{\mathrm{VC,TCPC}}+x\chi_{\mathrm{DCE,TCPC}}-x(1-x)\chi_{\mathrm{VC,DCE}} \tag{5}$$

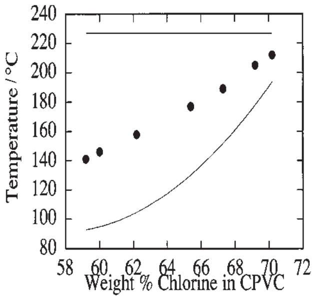

Fig. 9 Glass transition temperature of 50/50 (wt/wt) TCPC/solution-CPVC blends

Each $\chi_{i,j}$ will contribute to χ_{blend}, and the relative contribution of each χ_{ij} will change with x, the fraction of DCE repeat units. For example, at small x, $\chi_{\text{TCPC,VC}}$ is expected to be the predominant factor leading to miscibility, while at higher x-values, within the single-phase region and close to the miscible-immiscible boundary, $\chi_{\text{VC,DCE}}$ will dominate. The effects of these two contributions are shown schematically in Fig. 10. The magnitudes of curves a and b in Fig. 10 are arbitrary. The sum of their effect (curve c) determines the size of the miscibility window.

As x increases in Eq. (5) and Fig. 10, the favorable contribution to χ_{blend} from $\chi_{\text{TCPC,VC}}$ decreases, and the unfavorable contribution from $\chi_{\text{TCPC,DCE}}$ increases. The contribution due to VC-DCE intramolecular repulsion, which is always favorable to mixing, has its optimal effect at $x=0.5$. As x is increased above 0.5, the contributions of $\chi_{\text{VC,DCE}}$ and $\chi_{\text{TCPC,VC}}$ to χ_{blend} diminish and $\chi_{\text{TCPC,DCE}}$ determines the value of χ_{blend}.

Differences in CPVC microstructure do not have an effect on the miscibility behavior with the polycarbonate homopolymers. In Fig. 11, the behavior of TCPC/DSP-68 and BPC/DSP-63 are shown. In spite of their low molecular weight, the slurry-chlorinated CPVCs are immiscible with BPC, HFPC, and TMPC. Blends with TCPC have a single, composition dependent glass transition temperature. In the miscible blends of TCPC with DSP-68 (Fig. 11), the glass transition breadth was large, between 14 and 18°C. This, however, is still lower than the transition breadth of pure DSP-68, which is greater than 30°C. Thus, the heterogeneity of the CPVC is reflected in the T_g behavior of these miscible blends.

BPC-TCPC copolymers blended with PVC and solution-CPVCs

The glass transition temperatures of 50/50 (wt/wt) blends of BPC-2 and BPC-TCPC-copolymers with PVC-1 and solution-CPVCs are shown in Fig. 12. The polycarbonate copolymers begin to exhibit single-phase behavior in their blends with PVC. This immiscible-to-miscible transition is expected to occur as the TCPC repeat unit content increases and BPC repeat units become diluted. The volume fraction of TCPC repeat units in the copolycarbonate at which the immiscible-miscible transition occurs will depend not only on TCPC content but also on the intramolecular in-

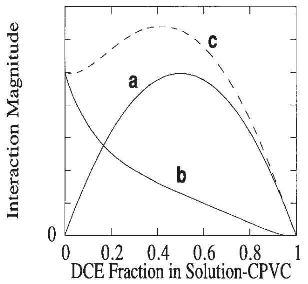

Fig. 10 Contribution from the (a) intramolecular and (b) intermolecular effects to the favorable interaction (c) between TCPC and solution-CPVCs

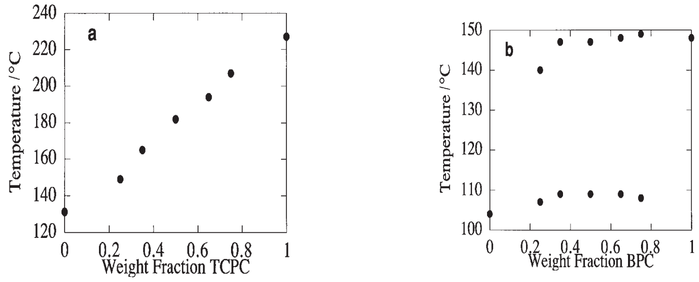

Fig. 11 Polycarbonate blends with slurry-CPVCs. (a) TCPC-2/DSP-68; (b) BPC-2/DSP-63

teraction between the BPC and TCPC repeat units. The reasoning is identical to that used to explain miscibility in TCPC/solution-CPVC blends.

In Fig. 12, it is seen that BPC-TCPC-25 exhibits a miscibility window between 24 mol% and 66 mol% DCE content (63–68 wt% Cl) in the CPVC. The two CPVCs showing miscible behavior, CPVC-7 and CPVC-8, have T_g's that are 30 and 43°C, respectively, below the polycarbonate T_g. Thus, it is not likely that the observed, single T_g (filled triangles) is the product of two mixed phases having nearly similar T_g's. The wide data gap in which the upper limit of the miscibility window is found is caused by the T_g similarity of BPC-TCPC-25 and CPVC-9. The single-T_g criterion for assessing miscibility cannot be used for this particular blend. Though solvent-cast films of CPVC-9/BPC-TCPC-25 are transparent, this is not a sufficient indicator of blend miscibility.

As TCPC content increases in the BPC-TCPC copolymer, so does the width of the miscibility window in their blends with the CPVCs. In 50/50 (wt/wt) CPVC/BPC-TCPC-50 blends, the miscibility window (filled squares) extends from 13% to nearly 70% DCE repeat units in the CPVC. BPC-TCPC-75 is miscible with PVC (filled diamonds) and solution-CPVCs containing up to 70.2 wt% chlorine (CPVC-10). Gaps in the data for blends containing high chlorine-content CPVCs are due to the similarity of blend component T_g's. It is coincidental that those blends for which the difference

($T_{g,PC}$–$T_{g,CPVC}$) approaches zero lie close to the miscibility window boundary at high DCE contents. The miscibility boundaries in blends that contain BPC-TCPC-25 and BPC-TCPC-50 were found not to change with increasing annealing temperature; annealing at temperatures from 160 to 230°C does not lead to phase separation in these blends.

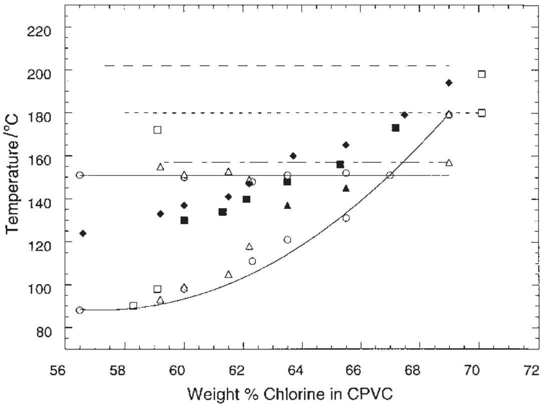

Fig. 12 Glass transition temperature of 50/50 (wt/wt) blends of BPC and BPC-TCPC copolymers with solution-CPVCs. Open symbols represent immiscible blends; closed symbols represent miscible blends. — BPC-2; – - – BPC-TCPC-25; ---- BPC-TCPC-50; – – – BPC-TCPC-75

The miscibility windows in the polycarbonate copolymer/CPVC blends are created by the action of three forces: (1) the favorable, or negligibly unfavorable, interaction of VC and TCPC repeat units, (2) the intramolecular repulsion between VC and DCE repeat units within the vinyl copolymer, and (3) the intramolecular effect within the copolycarbonate. The favorable intermolecular interaction between VC and TCPC cannot be the primary driving force leading to a miscibility window; if it were, then BPC-TCPC-25 should be miscible with PVC. Therefore, the primary factor leading to miscibility must be the intramolecular repulsive effects present within the copolymers. That the window occurs in BPC-TCPC-25/CPVC blends in the VC-DCE composition range where the intramolecular effect is at a maximum (1:1 ratio of VC to DCE) is evidence that the 'copolymer effect' within the vinyl polymer is driving miscibility in these copolymer/copolymer blends.

The data in Fig. 12 can be replotted in the form of a 'miscibility map'. This representation is given in Fig. 13. The abscissa and ordinate represent the copolymer composition, expressed in mole fraction, of the vinyl and polycarbonate copolymers, respectively. Blend compositions are constant (50/50 by weight). The map is an isothermal slice through a three-dimensional composition-composition-temperature diagram. 'Composition' refers to copolymer composition. The region within the elliptical boundaries is the single-phase, miscibility window. The equation describing the boundary may be used to estimate the segmental interaction parameters, χ_{ij}'s. Be-

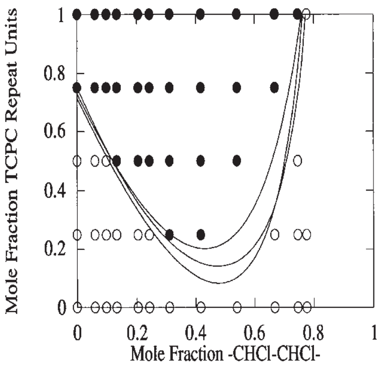

Fig. 13 Isothermal, miscibility map for solution-CPVCs blended with PBC-TCPC copolymers. Blend compositions are 50/50 by weight. Closed circles represent miscible blends; open circles are two-phase blends

cause of gaps in copolymer composition and CPVC-copolycarbonate T_g differences approaching zero, it is possible to fit more than one curve to the miscible-immiscible boundary. Three elliptical boundaries fitting the data are shown in Fig. 13. The minimum in the boundary curves, with respect to TCPC content in the copolycarbonate, varies from approximately 15 mol% (curve 3) to 25 mol% (curve 1).

At the miscibility-immiscibility boundary, $\chi_{\text{critical}}=\chi_{\text{blend}}$. From Flory-Huggins theory

$$\chi_{\text{critical}}=(1/2)(N_1^{-1/2}+N_2^{-1/2})^2 \tag{6}$$

where N_i is the degree of polymerization of component i. A function $f(x,y)$ can be defined

$$f(x,y)=\chi_{\text{blend}}-\chi_{\text{critical}} \tag{7}$$

At the miscible-immiscible boundary, $f(x,y)=0$. Substituting Eq. (2) into Eq. (7), the boundary may be defined by the function

$$f(x,y)=ax^2+bxy+cy^2+dx+ey+f=0 \tag{8}$$

where

$$a=\chi_{\text{VC,DCE}} \tag{9}$$

$$b=\chi_{\text{VC,BPC}}+\chi_{\text{DCE,TCPC}}-\chi_{\text{VC,TCPC}}-\chi_{\text{DCE,BPC}} \tag{10}$$

$$c=\chi_{\text{BPC,TCPC}} \tag{11}$$

$$d=\chi_{\text{DCE,BPC}}-\chi_{\text{VC,BPC}}-\chi_{\text{VC,DCE}} \tag{12}$$

$$e=\chi_{\text{VC,TCPC}}-\chi_{\text{VC,BPC}}-\chi_{\text{BPC,TCPC}} \tag{13}$$

$$f=\chi_{\text{VC,BPC}}-\chi_{\text{critical}} \tag{14}$$

Equation (8) may describe an ellipse, an hyperbola, or a parabola.

A computer program was written for fitting the boundary of the miscibility window [31]. Using this program, it is possible to place an ellipse or a hyperbola on the diagram, user-defining the position, the angle of orientation, and the aspect ratio of the conic section. The boundary is fit by trial-and-error, and curves are chosen that best fit the miscible-immiscible boundary data. From the inputted information, the coefficients of the generalized quadratic function for the conic section are generated. Using $\chi_{\mathrm{VC,DCE}}$=0.042 [29], the equations describing the boundaries shown in Fig. 13 were normalized, and values of the segmental interaction parameters, $\chi_{\mathrm{i,j}}$'s, were determined from Eqs (9) to (14). The normalized equations for the three curves shown in Fig. 13 are

curve 1:

$$0.042x^2+0.017xy+0.006y^2-0.047x-0.026y+0.017=0 \tag{15}$$

curve 2:

$$0.042x^2+0.020xy+0.004y^2-0.049x-0.024y+0.017=0 \tag{16}$$

curve 3:

$$0.042x^2+0.020xy+0.003y^2-0.050x-0.023y+0.017=0 \tag{17}$$

Segmental interaction parameters for each of the elliptical boundaries are listed in Table 5. A χ_{critical}-value of 0.004 was used in Eq. (14). This value is determined from Eq. (6) and depends on the degree of polymerization, DP, of the polymers. The DP was estimated from the weight-average molecular weight, M_w. To account for the size disparity between vinyl polymer and polycarbonate repeat units, M_w for the polycarbonates was multiplied by 5/2. The numerator represents the volume ratio of a polycarbonate repeat unit to a vinyl polymer repeat unit [32]; division by 2 is based on the observation that the GPC measured molecular weights of secondary polycarbonate standards are two-times greater than their molecular weight determined by light scattering.

Table 5 Segmental interaction parameters estimated from the elliptical boundaries (shown in Fig. 13)

	curve 1	curve 2	curve 3
$\chi_{\mathrm{VC,DCE}}$	0.042 [29]	0.042	0.042
$\chi_{\mathrm{BPC,TCPC}}$	0.006	0.004	0.003
$\chi_{\mathrm{VC,BPC}}$	0.021	0.021	0.021
$\chi_{\mathrm{VC,TCPC}}$	0.001	0.001	0.001
$\chi_{\mathrm{DCE,BPC}}$	0.016	0.014	0.013
$\chi_{\mathrm{DCE,TCPC}}$	0.013	0.014	0.013

Comparing the three boundaries in Fig. 13, and the derived $\chi_{i,j}$'s, it is interesting to note how little the segmental interaction parameters vary. $\chi_{DCE,TCPC}$, $\chi_{VC,TCPC}$, and $\chi_{VC,BPC}$ remain nearly constant as the boundary changes. The magnitude of $\chi_{VC,TCPC}$ is consistent with experimental results for PVC/TCPC blends. The FT-IR and DMA data, indicating a lack of strong interaction between the two polymers, would suggest that $\chi_{PVC,TCPC}$ is a very small, positive number. $\chi_{BPC,TCPC}$ and $\chi_{DCE,BPC}$ both decrease by 0.003 as the boundary changes from curve 1 to curve 3; these two parameters are the only two showing significant change with the position of the miscible-immiscible boundary. It is the decrease in $\chi_{DCE,BPC}$ that brings the boundary closer to the BPC axis (y=0).

Using the $\chi_{i,j}$'s calculated for curve 1, Fig. 13, χ_{blend} can be determined using Eq. (2). χ_{blend} is plotted *vs*. DCE content for each polycarbonate copolymer in Fig. 14. When χ_{blend} falls below 0.004, $\chi_{critical}$, miscibility results. The locus of crossover points forms the boundary shown in Fig. 13. For infinite molecular weight components, for which $\chi_{critical}$=0, the miscibility window would contract significantly. BPC-TCPC-25 and BPC-TCPC-50 would not be miscible with the CPVCs. Also, PVC and TCPC would be immiscible. There still would be a miscibility window in TCPC/solution-CPVC blends, due to the repulsive, copolymer effect within the vinyl polymer.

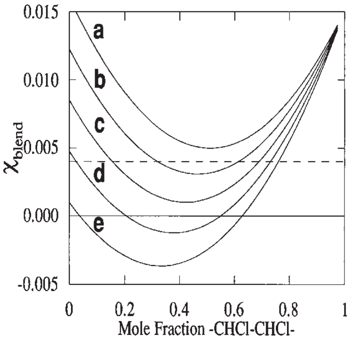

Fig. 14 χ_{blend} as a function of copolymer composition for VC-DCE/BPC-TCPC copolymer 50/50 blends. Values of y (the mole fraction of TCPC repeat units in the PC copolymer) are: (a) 0.0; (b) 0.25; (c) 0.50; (d) 0.75; (e) 1.0. Dashed line, $\chi_{critical}$ (0.004)

The boundaries in the miscibility map have been assumed to be elliptical. This allows both intramolecular segmental interaction parameters, $\chi_{VC,DCE}$ and $\chi_{BPC,TCPC}$ to be positive. The choice of a hyperbolic boundary would mean that one of these two should be less than zero, since $\chi_{VC,DCE}$>0, $\chi_{BPC,TCPC}$ would be negative. This result, however, is not consistent with experimental data on BPC/TCPC blends, which will be discussed below.

TMPC-TCPC copolymers blended with PVC and CPVCs

DSC curves of 50/50 (wt/wt) blends of PVC-0 with TMPC-TCPC copolymers are presented in Fig. 15. The TCPC repeat unit level in these copolycarbonates at which miscibility begins is lower than that found in the BPC-TCPC copolymers. This effect may be attributed to a greater intramolecular effect within the TMPC-TCPC copolymer than that present in the BPC-TCPC copolymers. A relatively large positive value of $\chi_{\mathrm{TMPC,TCPC}}$, coupled with a very small, positive value of $\chi_{\mathrm{TCPC,VC}}$, is needed to overcome the positive $\chi_{\mathrm{TMPC,VC}}$ and produce a negative χ_{blend}.

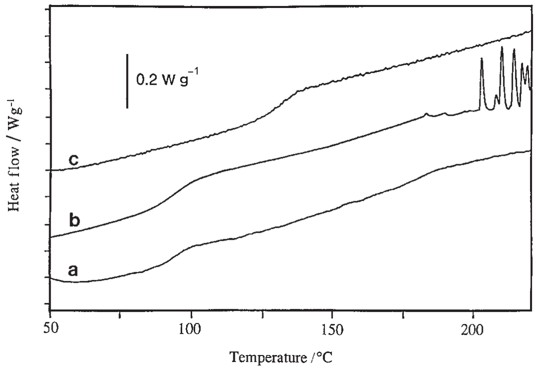

Fig. 15 DSC curves of 50/50 (wt/wt) blends of PVC-1. (a) TMPC-0; (b) TMPC-TCPC-41; (c) TMPC-TCPC-58

Glass transition temperatures for the CPVC/copolycarbonate blends (50/50, wt/wt) are plotted *vs*. DCE content in Fig. 16. TMPC-TCPC-42 exhibits a miscibility window, forming single-phase blends with chlorinated polymers CPVC-6 through CPVC-9. TMPC-TCPC-58 and TMPC-91 form miscible blends with all CPVCs, up to, and including, CPVC-11. Like the BPC-TCPC copolymer/CPVC blends, raising the annealing temperature does not induce phase separation in the miscible blends along the miscible-immiscible boundary.

The miscibility map for VC-DCE/TMPC-TCPC blends is shown in Fig. 17. The miscible region does not extend into the TMPC-rich copolycarbonates. The interaction parameters $\chi_{\mathrm{TMPC,VC}}$ and $\chi_{\mathrm{TMPC,DCE}}$ are responsible for this effect. With BPC-TCPC and TMPC-TCPC copolymers having similar molecular weights, one may predict that $\chi_{\mathrm{TMPC,VC}}>\chi_{\mathrm{BPC,VC}}$ and $\chi_{\mathrm{TMPC,DCE}}>\chi_{\mathrm{BPC,DCE}}$, based on the difference in the shape of miscibility window boundaries. The right-hand portion of the single-phase region ($x>0.75$) is the result of intramolecular repulsion between the TMPC and TCPC repeat units. This repulsion also affects the boundary intercept at $x=0$ (PVC).

The function describing the boundary shown in Fig. 17 is

$$2.858x^2+1.021xy+7.077y^2-2.994x-11.364y+3.947=0 \qquad (18)$$

Normalizing Eq. (18) using $\chi_{\mathrm{VC,DCE}}=0.042$,

$$0.042x^2+0.015xy+0.104y^2-0.044x-0.167y+0.058=0 \qquad (19)$$

The $\chi_{i,j}$'s estimated from the coefficients of the normalized equation are $\chi_{TMPC,TCPC}=0.104$, $\chi_{VC,TMPC}=0.063$, $\chi_{DCE,TMPC}=0.061$, $\chi_{VC,TCPC}=0.000$, and $\chi_{DCE,TCPC}=0.015$. $\chi_{critical}$ equals 0.005. As predicted, the estimated values of $\chi_{TMPC,VC}$ and $\chi_{TMPC,DCE}$ are greater than their counterparts in the BPC-TCPC copolymer system. Their effect is to push the miscible-immiscible boundary away from the lower corners of the miscibility map. The large $\chi_{TMPC,TCPC}$-value widens the miscibility window to include x-values greater than 0.8, and enhances copolycarbonate miscibility with PVC. The later effect is demonstrated by the lower TCPC content (relative to the BPC-TCPC copolymers) needed in the copolycarbonate in order to create miscibility with PVC; this oc-

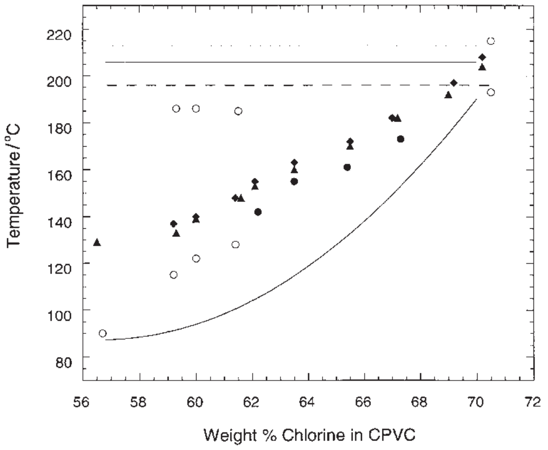

Fig. 16 Glass transition temperature of 50/50 blends of TMPC-TCPC-copolymers with solution-CPVCs. Horizontal lines, T_g's of copolycarbonates; upward curving solid line, T_g's of CPVCs. – – – TMPC-TCPC-42; — TMPC-TCPC-58; --- TMPC-TCPC-91

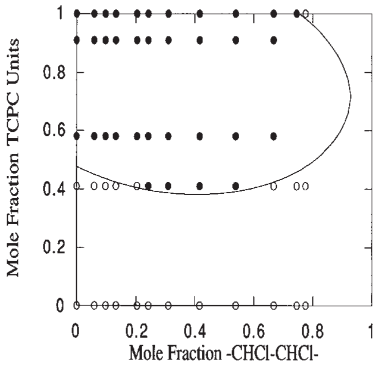

Fig. 17 Isothermal, miscibility map for VC-DCE/TMPC-TCPC copolymer blends. Filled circles represent miscible blends. Blend composition is 50/50 by weight

curs despite a high $\chi_{\mathrm{VC,TMPC}}$-value. The miscibility window with PVC is predicted when the polymers are of infinite molecular weight ($\chi_{\mathrm{critical}}=0$), as shown by the dashed boundary line in Fig. 17.

The $\chi_{\mathrm{VC,TCPC}}$ and $\chi_{\mathrm{DCE,TCPC}}$ values estimated from the two miscibility maps are in good agreement. Though both maps share data for TCPC/CPVC blends, this does not guarantee that the calculated segmental interaction parameters will be similar. The shape of the miscibility window boundary and χ_{critical} are the critical factors that determine the two TCPC-vinyl repeat unit interaction parameters. This example demonstrates the self-consistency of the mean-field approach for the determination of segmental interaction parameters.

Segmental interaction parameters from $A/(A_{1-x}B_x)$-type blends

The segmental interaction parameters for the polycarbonate repeat units, $\chi_{\mathrm{TMPC,TCPC}}$ and $\chi_{\mathrm{BPC,TCPC}}$, can be determined from polycarbonate homopolymer/copolymer blends. By investigating $\mathrm{A}/(\mathrm{A}_{1-x}\mathrm{B}_x)$-type blends, $\chi_{\mathrm{A,B}}$ can be estimated if homopolymers poly(A) and poly(B) are immiscible. At some x-value, there will be a miscible-to-immiscible transition. $\chi_{\mathrm{A,B}}$ for this blend system is calculated by

$$\chi_{\mathrm{A,B}}=\chi_{\mathrm{critical}}/y^2 \tag{20}$$

where y is the x-value at which the miscible-to-immiscible transition takes place.

To use Eq. (20), DSC results for several blends were studied. All BPC and TCPC homopolymers are miscible with the BPC-TCPC copolymers; only BPC/TCPC binary, homopolymer blends are immiscible (Fig. 18). TCPC-2 is miscible with TMPC-TCPC-58 but immiscible with TMPC-TCPC-42. TMPC-0 is miscible with TMPC-TCPC-58 but not with TMPC-TCPC-92. Because of the spacing in copolymer TCPC-composition, ranges for the interaction parameter values are calculated. Using volume corrected degrees of polymerization (reference volume is that of

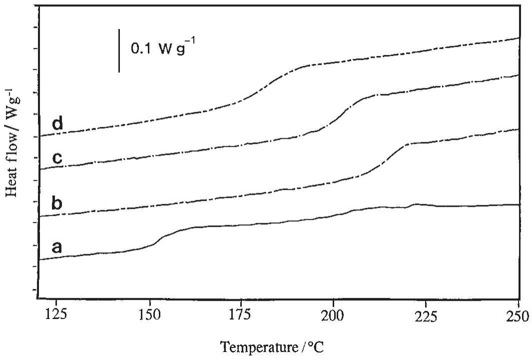

Fig. 18 DSC curves for 50/50 (wt/wt) blends of TCPC-0 with (a) BPC-0; (b) BPC-TCPC-75; (c) BPC-TCPC-50; (d) BPC-TCPC-25. Samples were annealed at 265°C for 20 min and quenched to room temperature prior to measurement

a vinyl chloride repeat unit) for the χ_{critical} calculations, it is found that $0.008 < \chi_{\mathrm{BPC,TCPC}} < 0.014$ (265°C) and $0.035 < \chi_{\mathrm{TMPC,TCPC}} < 0.041$ (250°C).

There are differences between $\chi_{i,j}$'s calculated from the A/AB and the AB/CD systems. $\chi_{\mathrm{BPC,TCPC}}$ is at least two times smaller, and $\chi_{\mathrm{TMPC,TCPC}}$ more than two times greater when estimated from the AB/CD system. Though the magnitudes differ, both methods of calculation reveal that $\chi_{\mathrm{TMPC,TCPC}} > \chi_{\mathrm{BPC,TCPC}}$.

The discrepancy in the magnitudes of the parameters may be explained by several factors. $\chi_{i,j}$'s are temperature dependent. The enthalpic and entropic contributions to $\chi_{i,j}$, χ_H, and χ_S, respectively, will have their own temperature dependencies. As temperature is increased, the magnitude of χ_H to $\chi_{i,j}$ will decrease, while χ_S, which is always positive, increases. This is illustrated in Fig. 19. There are two possible paths for $\chi_{i,j}$; $\chi_{i,j}$ may show a minima with increasing temperature (curve 4, Fig. 19), or increase monotonically with increasing temperature (curve 5, Fig. 19). Polycarbonate homopolymer/copolymer blends were annealed at temperatures at least 30 to 45°C greater than the annealing temperatures for AB/CD blend systems. Because $\chi_{\mathrm{BPC,TCPC}}$ has a larger value at 265°C, its behavior may follow either curve 4 or curve 5 (Fig. 19). $\chi_{\mathrm{TMPC,TCPC}}$ must follow curve 4, because only this path allows a decrease in $\chi_{i,j}$ with increasing temperature.

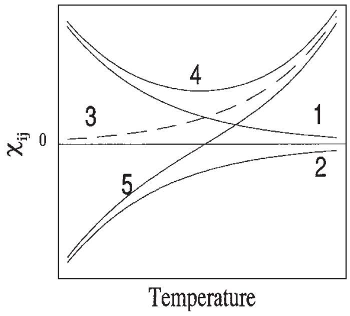

Fig. 19 Temperature dependence of $\chi_{i,j}$ (curve 4 or 5) in terms of contributions from $\chi_{\mathrm{enthalpic}}$ (curves 1 and 2) and χ_{entropic} (curve 3). Curve 4 represents the sum of curves 1 and 3; curve 5 is the sum of curves 2 and 3

The size difference between polycarbonate and vinyl polymer repeat units may also lead to differences in calculated $\chi_{i,j}$'s. In fact, ten Brinke [18] warned against comparison of $\chi_{i,j}$'s calculated from different blend systems. Calculated $\chi_{i,j}$'s that quantify polycarbonate repeat unit interaction in the AB/CD system are 'effective' segmental interaction parameters because the reference volume is that of a vinyl chloride repeat unit. In this case, the $\chi_{i,j}$-value between the polycarbonate repeat units is estimated assuming that the polycarbonate repeat units are the size of a vinyl chloride residue. In the A/AB blends, the intermolecular interactions are between polycarbonate repeat units. Despite the volume correction for χ_{critical} estimation, these interactions are not identical to polycarbonate/vinyl-polymer interactions.

Conclusions

Modification of polycarbonate repeat unit structure has been shown to affect miscibility with PVC. The substitution of chlorine at the 3,3′ and 5,5′-phenyl ring positions of the bisphenol-A repeat unit results in a polycarbonate homopolymer exhibiting miscibility with PVC in all proportions. Modifying PVC by increasing the chlorine content does not enhance miscibility with the polycarbonate homopolymers investigated. In fact, TCPC is immiscible with the CPVC having the highest chlorine loading (70.6 wt%). Thus, too great a chlorine content will induce phase separation. This observation does not support the conclusion of previous investigations in which increased chlorination was thought to enhance vinyl-polymer miscibility with polycarbonates.

Polycarbonate copolymer/CPVC blends exhibit phase behavior that is dependent on (1) chlorine content of the solution-CPVC and (2) copolycarbonate composition. Miscibility windows are observed in blends of BPC-TCPC-25, BPC-TCPC-50, and TMPC-TCPC-42 with solution-CPVCs. This behavior is explained by a mean-field, binary interaction model that considers both intermolecular and intramolecular contributions to the overall interaction parameter in these copolymer containing blends. Repulsive intramolecular interactions between copolymerized units are favorable to miscibility. Calculations for the blend systems studied reveal that

$$\chi_{\mathrm{VC,TMPC}}>\chi_{\mathrm{VC,BPC}}>\chi_{\mathrm{VC,TCPC}}$$

$\chi_{\mathrm{VC,TCPC}}$ is positive and close to zero. A $\chi_{\mathrm{VC,PC}}$ greater than or equal to 0.014 ($\chi_{\mathrm{VC,BPC}}$) is sufficient to cause phase separation in the PVC/PC blend. Interaction parameters between the polycarbonate repeat units and the model chlorinated vinyl repeat unit, DCE, show a different relationship

$$\chi_{\mathrm{DCE,TMPC}}>\chi_{\mathrm{DCE,BPC}}\approx\chi_{\mathrm{DCE,TCPC}}$$

The mean-field approach is self-consistent, shown by the similarity of $\chi_{\mathrm{VC,TCPC}}$ and $\chi_{\mathrm{DCE,TCPC}}$ estimated from two different copolycarbonate systems. That the two copolymer blends system share TCPC/CPVC blend data does not ensure that the $\chi_{\mathrm{i,j}}$'s will be similar; it is the experimental miscibility window boundary that determines the $\chi_{\mathrm{i,j}}$.

It was found that $\chi_{\mathrm{TMPC,TCPC}}\gg\chi_{\mathrm{BPC,TCPC}}$. The greater intramolecular repulsion within the TMPC-TCPC copolymer leads to a broader range of copolycarbonate compositions that are miscible with PVC. In fact, a miscibility window is predicted in infinite molecular weight blends of TMPC-TCPC copolycarbonate and PVC. Because of the large repulsive interactions between TMPC and the vinyl repeat units (VC and DCE) the miscibility window does not extend into TMPC-rich copolycarbonate compositions. This demonstrates the sensitivity of immiscible-miscible boundaries in copolymer-containing blends to variations in segmental interaction parameter values. With knowledge of $\chi_{\mathrm{i,j}}$'s it should be possible to tailor copolymer composition to create miscible polymer systems. The predictive value of $\chi_{\mathrm{i,j}}$'s has been demonstrated recently by Vukovic *et al*. [33] for halogenated polystyrene/sulfonated PPO systems. This technique provides a means by which miscibility can be induced without the introduction of specific interactions between the macromolecules.

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