Studies of polyester/chlorinated poly(vinyl chloride) blends

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Chlorinated poly(vinyl chloride) (CPVC) was solution blended with poly(caprolactone) (PCL), poly(hexamethylene sebacate) (PHMS), poly(α-methyl-α-n-propyl-β-propiolactone) (PMPPL), poly(valerolactone) (PVL), poly(ethylene adipate), poly(ethylene succinate) and poly(β-propiolactone). From calorimetric glass transition temperature (T_g) measurements, it is concluded that CPVC is miscible with polyesters having a CH_2/COO ratio larger than three (PCL, PHMS, PMPPL and PVL). The Gordon–Taylor k parameter was also calculated and found equal to 1.0 and 0.56 for PCL/CPVC and PHMS/CPVC blends, respectively. From these values, it is concluded that CPVC gives a stronger interaction with polyesters than poly(vinyl chloride) due to its larger chlorine content.

Keywords Polyester blend; chlorinated poly(vinyl chloride); calorimetry; miscibility; glass transition

INTRODUCTION

It is now well established that several polyesters are miscible with poly(vinyl chloride)[1–16] (PVC). Miscibility is however not found if the CH_2/COO ratio of the polyester is smaller than four[8–11,17,18] since a high degree of chain mobility is required in order to have miscibility.

Recently, it has been shown that a high chlorine concentration is necessary for obtaining miscible polyester/chlorinated polymer blends. For example, polycaprolactone (PCL) is miscible with PVC[1,2] and with chlorinated polyethylenes (CPE) containing 48, 42 and 36 wt% Cl[19], but it is not miscible with polyethylene[20] and with a CPE containing 25 wt% Cl[19]. Similarly, poly(valerolactone) (PVL) and poly(α-methyl-α-n-propyl-β-propiolactone) (PMPPL) are miscible with PVC[3–5] but they are not miscible with any of the CPE mentioned above[19]. It is then expected that several polyesters, including PCL, PVL and PMPPL, will be miscible with chlorinated polymers having a Cl concentration higher than that of PVC. It is the first objective of this paper to investigate the miscibility of several polyesters with chlorinated PVC (CPVC).

It has also been suggested that the Gordon–Taylor equation[21],

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

where T_g is the glass transition temperature of the blend, T_{g1} and T_{g2} those of components 1 and 2, w_1 and w_2 the corresponding weight fractions and k an adjusting parameter, can express the T_g–composition dependence of polymer/polymer blends and that k, expressing its degree of curvature, can be semi-quantitatively related to the strength of the interaction between the two polymers. For example, in PCL/CPE blends[19], where the CPE contains 36% Cl, k equals 0.25 while $k=0.51$ in PCL/PVC blends[19,22], the interaction being stronger in the latter case. It is then expected to find even higher values of k in PCL/CPVC blends and it is the second objective of this paper to check this point.

EXPERIMENTAL

Table 1 gives the list of the polymers used in the present study, along with their acronym, their weight average molecular weight, $\bar{M}_w$, their glass transition temperature, T_g, their melting point, T_m, and their intrinsic viscosity, $[\eta]$. Several polyesters (PCL, PHMS, PEA and PES) were obtained from Aldrich Chemicals whereas others were prepared in our laboratories (PMPPL[23], PVL[4,5] and PβL). The CPVC sample was kindly supplied by Dr M. Roha from the BF Goodrich Chemical Division. It was prepared by suspension polymerization. Elemental analysis indicates that it contains 67.2 wt% Cl. The Cl atoms are believed to form mainly 1,2 substituted repeat units with a fair amount of vinyl chloride and a lesser amount of vinylidene chloride units[24].

Blends were prepared by slowly casting films from tetrahydrofuran (THF) solutions. The resulting films were dried under vacuum until they reached constant weight. Film thicknesses were ~40 μm.

Differential scanning calorimetry (d.s.c.) was conducted using a Perkin–Elmer DSC-2 apparatus calibrated with mercury, gallium and indium. Reported T_g's were recorded at half-height of the heat capacity jump. Reported T_m's were recorded at the end of the melting curve. A heating rate of 20 K min^{-1} was used in all cases.

In the d.s.c. apparatus, the samples were first cooled to 150 K and maintained at that temperature for 30 min. They were then brought to 370 K (first fusion) and kept at that temperature for 5 min before being quenched to 150 K. The samples were then reheated a certain number of

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Table 1 Characterization of the polymers used in this study

Polymer	Acronym	$\bar{M}_w$[a]	T_g (K)	T_m (K)	$[\eta]$[b] (dl g^{-1})
Chlorinated poly(vinyl chloride)	CPVC	119 000	352	–	0.7[c]
Poly(caprolactone)	PCL	20 000	210	343, 335[d]	0.26
Poly(hexamethylene sebacate)	PHMS	30 000	215	341	–
Poly(α-methyl-α-n-propyl-β-propiolactone)	PMPPL	131 000	275	353	0.48
Poly(valerolactone)	PVL	33 000	216	332	0.53
Poly(β-propiolactone)	PβL	6000	241	345	–
Poly(ethylene adipate)	PEA	2600	215	320	–
Poly(ethylene succinate)	PES	–	255	384	–

[a] Determined by gel permeation chromatography in tetrahydrofuran at 298 K
[b] Determined in tetrahydrofuran at 298 K
[c] Determined in cyclohexanone at 298 K
[d] See Table 2

Table 2 Glass transition temperature, melting temperatures and enthalpies of fusion of poly(caprolactone)/chlorinated poly(vinyl chloride) blends (d.s.c. measurements)

CPVC Wt. %	T_g(K)	T_{m1} (K)	T_{m2} (K)	ΔH_{m1} (J g^{-1})	ΔH_{m2} (J g^{-1})
0	210	343	335	107	81
10	225	340.5	331	99	78
20	242	339	331	95	75
30	251	335	331	89	63
40	274.5	332	–	62	–
50	272	330.5	–	16	–
60	292	–	–	–	–
70	316	–	–	–	–
80	330	–	–	–	–
90	346	–	–	–	–
100	352	–	–	–	–

T_{m1} and ΔH_{m1}: first fusion
T_{m2} and ΔH_{m2}: subsequent fusions

times (subsequent fusions) under the same thermal regime. No difference in T_g was observed between the first and subsequent fusions. Small differences in T_m and in enthalpy of fusion, ΔH, were observed between the first and the following fusions. Some annealing experiments were also conducted on PCL/CPVC blends: after melting and quenching as indicated above, the samples were heated up to 310 K at 20 K min^{-1} and maintained at that temperature for the desired period of time; they were then quenched to 150 K and reheated as above.

Small-angle light scattering (SALS) experiments were carried out on an apparatus made of a He/Ne laser (2 m W), a polarizer, an analyser, a shutter and a Polaroid camera (type 545, with type 57 films of 3000 ASA)[25]. The reported photographs were recorded under the Hv mode of polarization where the incident light is polarized vertically and the scattered light is polarized horizontally. Under these conditions (crossed polars), only orientation fluctuations are observed[26].

For SALS experiments, blends were prepared from THF solutions. They were melted 5 min at 360 K, kept 45 min at 313 K and left at room temperature for at least 2 weeks before observation, except for those reported in *Figure 6* which were observed after the period of time indicated.

Dynamic mechanical measurements were conducted using a Rheovibron DDV-II instrument at frequencies of 3.5, 11 and 110 Hz. These measurements were carried on the THF cast films.

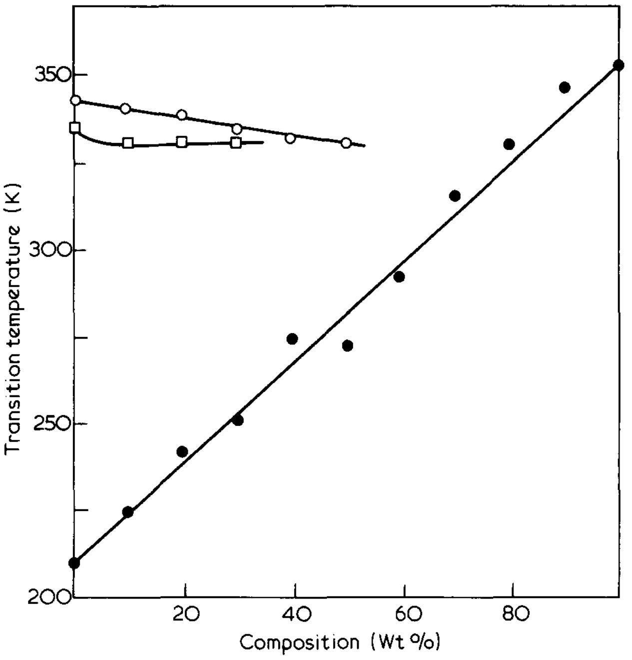

Figure 1 Phase diagram of poly(caprolactone)/chlorinated poly(vinyl chloride) blends. (○) = T_{m1}; (□) = T_{m2}; (●) = T_g

In this paper, the following terminology is adopted: a sample is declared miscible when it gives for all compositions a single T_g intermediate between those of its pure components even if crystals of components 1 and/or 2 form. A sample exhibiting two T_g's at a given composition is declared immiscible. According to this terminology, it suffices to observe two T_g's at one composition in order to conclude that the sample is immiscible, even if the possibility of observing a single T_g at other compositions is not excluded.

RESULTS AND DISCUSSION

PCL/CPVC blends

D.s.c. measurements were conducted on a large number of PCL/CPVC blends. T_g, T_m and ΔH_m values are reported in *Table 2*. A single glass transition temperature was observed at each composition indicating miscibility, i.e. extensive mixing between the two polymer components.

As shown in *Figure 1*, despite some scatter of the results due to experimental uncertainty, a linear relationship is found when T_g is plotted against composition. This result

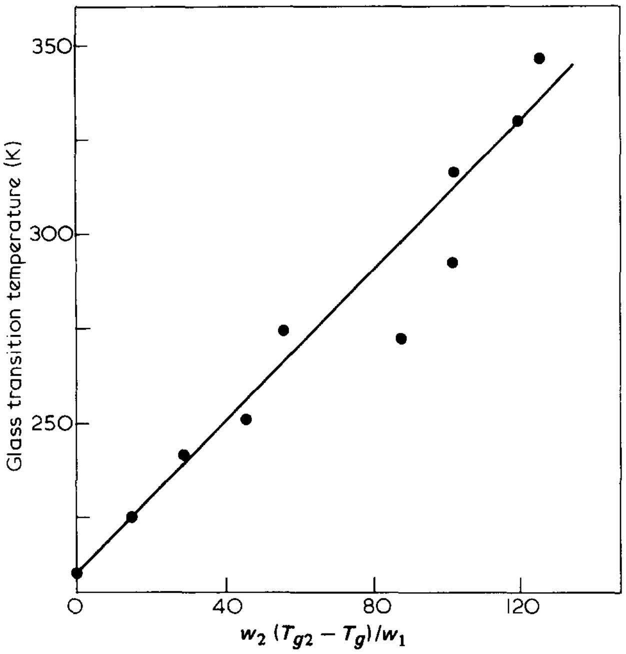

Figure 2 Plot of the Gordon–Taylor equation for poly(caprolactone)/chlorinated poly(vinyl chloride) blends. The slope of the line equals *k*

is in contrast with those reported for other PCL/chlorinated polymer blends where a pronounced curvature was observed. If equation (1) is rewritten as follows:

$$T_g = T_{g1} + kw_2(T_{g2} - T_g)/w_1 \qquad (2)$$

and if T_g is plotted as a function of $w_2(T_{g2} - T_g/w_1$ (*Figure 2*), a straight line is obtained and its slope *k* equals 1.0. The data used in *Figure 2* were not corrected for degree of crystallinity but the same value of *k* is obtained when considering uniquely high CPVC composition blends which are amorphous.

Increasing values of *k* are then obtained with an increase in chlorine concentration of the chlorinated polymer: $k_{\text{CPE}} = 0.26$[19], $k_{\text{PVC}} = 0.51$[19,22] and $k_{\text{CPVC}} = 1.0$. CPE, PVC and CPVC have, respectively, chlorine concentrations of 36, 56 and 67.2%. This result is in agreement with the suggestion made earlier that, in a given series of polymers, *k* can be taken as a semi-quantitative measure of the strength of the interaction between PCL and the chlorinated polymer[19]. If the interaction between PCL and CPE, PVC and CPVC involves the α-hydrogens of the chlorinated polymer as it has been suggested[1,2], it is expected that the number of interactions will increase with the number of CHCl groups on the polymer chain, following the same trend as *k*.

Dynamic mechanical measurements can also be used to study the miscibility of polymer/polymer blends and it has been reported that they are more sensitive than the d.s.c. measurements[27]. Generally dynamic mechanical and d.s.c. measurements lead to the same conclusion even if one exception is known[28]. *Figure 3* shows the storage modulus, *E*′, and the loss modulus, *E*″, values of four PCL/CPVC blends as a function of temperature, in the T_g region. Other blends were too brittle to be accurately studied by this technique. A shift of T_g with decreasing CPVC composition is clearly seen, T_g being closely related to the maximum of the *E*″ curve. These results confirm the miscibility of the PCL/CPVC blends.

Figure 1 and *Table 2* also indicate that the T_{m1}'s (first fusion) and the T_{m2}'s (subsequent fusions) behave differently. A regular decrease of T_{m1} is observed with blend composition. However, the T_{m2}'s of the blends are, within experimental error, constant and lower than T_{m1} of PCL.

For a given composition, T_{m2} is always lower than T_{m1}, but the difference becomes smaller with increasing CPVC. ΔH_{m2} is also always smaller than ΔH_{m1} indicating that the d.s.c. crystallization, under the chosen conditions, leads to a lower degree of crystallinity and to less perfect crystals than the solvent casting crystallization.

Depression in melting point measurements as a function of composition have often been used to calculate the thermodynamic interaction parameter χ between two polymers in the solid state[27]. Such measurements are however inaccurate since decreases of T_m of a few degrees may be the result of changes in lamellar thickness with composition[29], or changes in environment[30,31], and since recent measurements indicate that χ varies with blend composition[32–34], thus invalidating the use of the polymer–diluent theory which assumes a unique value of χ for all compositions. *Figure 1* and *Table 2* indicate that depression in melting point values also depend upon the conditions of preparation of the sample. Annealing experiments were therefore conducted on PCL/CPVC blends, at 310 K, and the change in melting point as a function of annealing time is given in *Figure 4* for two blends. Withoug annealing, the 90/10 blend shows a T_{m2} equal to 331 K. As a function of annealing time, T_m increases rapidly and for long annealing times, T_{m1} is found again. Without annealing, the 80/20 blend also shows a T_m equal to 331 K. As a function of time, T_m increases but less rapidly than in the previous case. At long annealing times, T_{m1} is also found, T_{m1}(80/20) being however lower than T_{m1}(90/10). Other blends show the same tendency. The changes are however smaller at

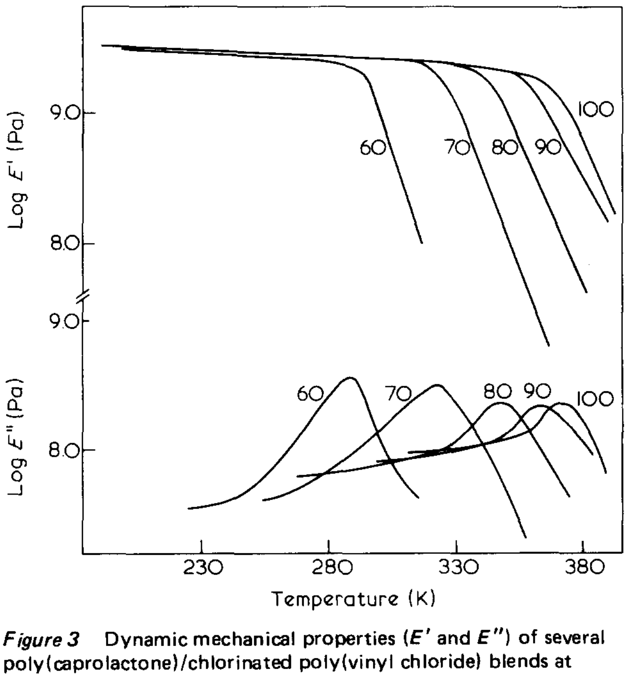

Figure 3 Dynamic mechanical properties (*E*′ and *E*″) of several poly(caprolactone)/chlorinated poly(vinyl chloride) blends at 110 Hz

higher CPVC compositions as expected from *Table 2* and *Figure 1* and the changes become slower. ΔH values follow exactly the same trend as the T_m values.

It is clear that T_{m2} values are non-equilibrium values and that they cannot be used in the polymer–diluent Flory–Huggins theory in order to calculate χ after having assumed that the factors mentioned in the preceding paragraph can be neglected. It can be tempting to use the T_{m1} values to calculate χ. However, it has not been proved that the T_{m1} values are near-equilibrium values. Annealing at higher temperatures may change the T_m–composition dependence and casting films from a different solvent may lead to completely different results since it is now recognized that the thermodynamic quality of the solvent has a pronounced influence on the properties of the blend[35,36].

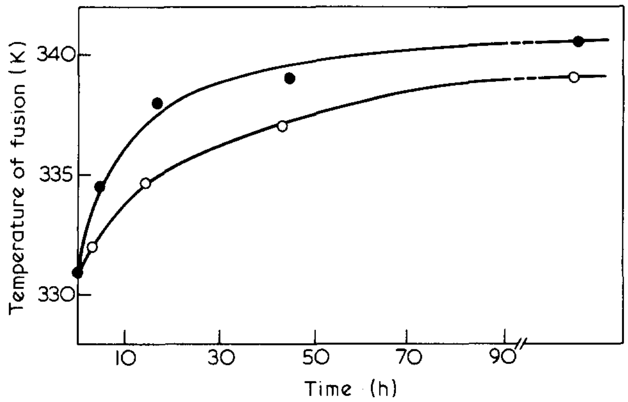

Figure 4 Melting point of poly(caprolactone)/chlorinated poly(vinyl chloride) blends as a function of time. (●) 90/10 blend; (○) 80/20 blend

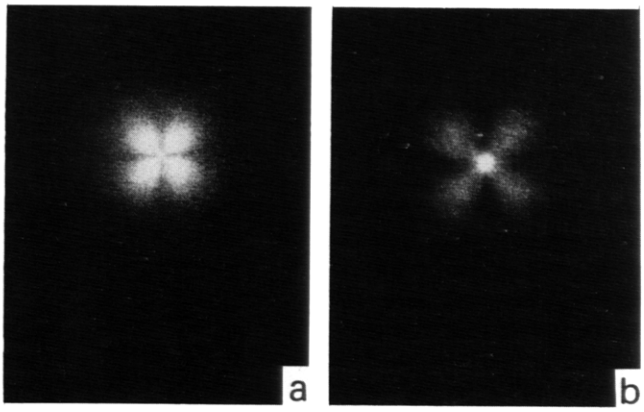

Figure 5 Small-angle Hv light scattering patterns of poly(caprolactone)/chlorinated poly(vinyl chloride) blends. Blend content in CPVC: (a) 40% and (b) 50%

SALS Hv patterns have been observed for PCL/CPVC blends. All samples in the 0–40% composition range have clearly a spherulitic morphology as exemplified by *Figure 5a*. Large spherulites of the order of 100 μm are observed for PCL and the size of the spherulites decreases with increasing CPVC composition. *Figure 5a* corresponds to a spherulite radius of 10 μm. CPVC then acts as a better nucleating agent than pure PCL, as most chlorinated polymers seem to do[4,18,19,29]. For higher CPVC compositions, a rod-like morphology is observed[37] (*Figure 5b*).

PCL crystallization in PCL/CPVC blends is not very rapid. For example, in a 60/40 blend, the final spherulite dimensions are reached after one day (*Figures 5a* and *6c*). Spherulites having radii of 3.7, 6.1 and 9.2 μm are found in *Figures 6a*, *b* and *c* after 1, 2 and 24 h. For a 70/30 composition blend, changes in spherulite radii can be followed by SALS for a period of about 30 min. This period is reduced to 5 min for the 80/20 blend. These higher crystallization rates in PCL rich blends were also observed in PCL/PVC blends[38,39].

Other polyester/CPVC blends

For comparison, several PHMS/CPVC blends were studied and the pertinent data are given in *Table 3*.

The single value of T_g at any composition indicates miscibility between PHMS and CPVC. However, despite some scatter of the data, *Figure 7* shows that the T_g–composition curve is concave. Equation (2) leads to $k = 0.56$ for this system. It is interesting to compare this value with the one that we calculated from the data of

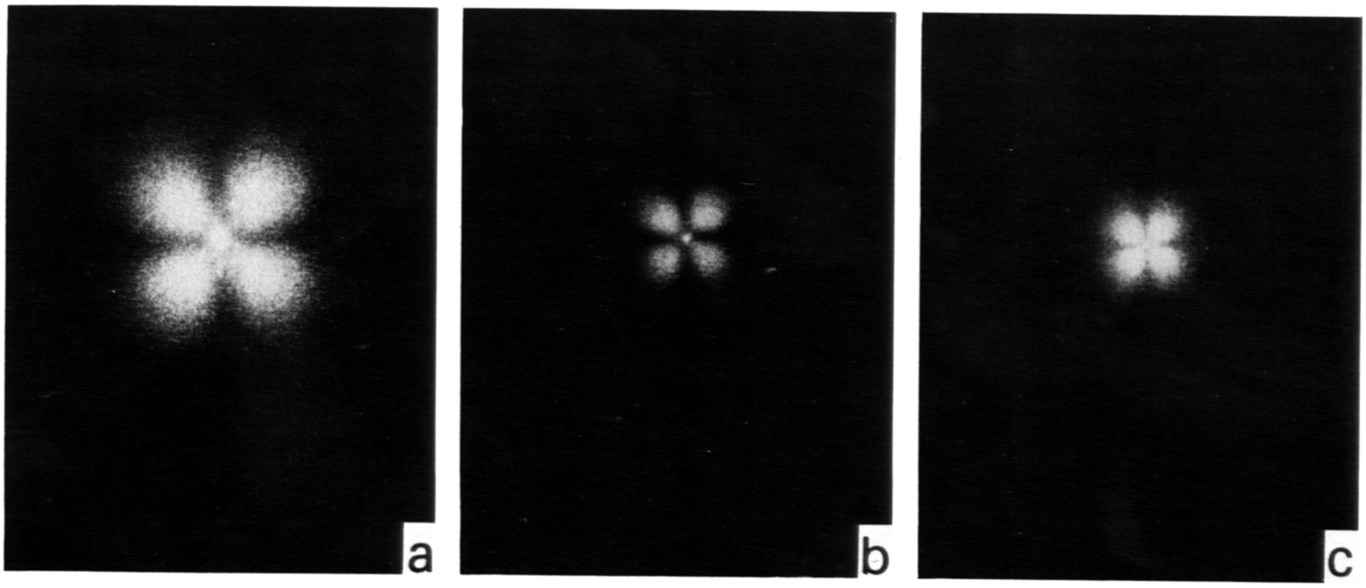

Figure 6 Small-angle Hv light scattering patterns of 40/60 poly(caprolactone)/chlorinated poly(vinyl chloride) blends recorded as a function of time: (a) 1 h, (b) 2 h and (c) 24 h

Table 3 Glass transition temperature, melting temperatures and enthalpies of fusion of poly(hexamethylene sebacate)/chlorinated poly(vinyl chloride) blends

CPVC Wt. %	T_g (K)	T_{m1} (K)	T_{m2} (K)	ΔH_{m1} (J g^{-1})	ΔH_{m2} (J g^{-1})
0	215	340.5	341	133	111
20	238	341	340.5	117	90
40	241	338	337	91	63
50	260	336	–	59	–
60	288	–	–	–	–
80	330	–	–	–	–
100	352	–	–	–	–

T_{m1} and ΔH_{m1}: first fusion
T_{m2} and ΔH_{m2}: subsequent fusions

Table 4 List of polyesters forming miscible and immiscible blends with chlorinated poly(vinyl chloride) (CPVC)

Miscible blends		Immiscible blends	
Poly(caprolactone)	(5)	Poly(ethylene adipate)	(3)
Poly(α-methyl-α-n-propyl-β-propiolactone)	(6)	Poly(ethylene succinate)	(2)
Poly(valerolactone)	(4)	Poly(β-propiolactone)	(2)
Poly(hexamethylene sebacate)	(6)		

Numbers in parentheses indicate the CH_2/COO ratio of each polyester

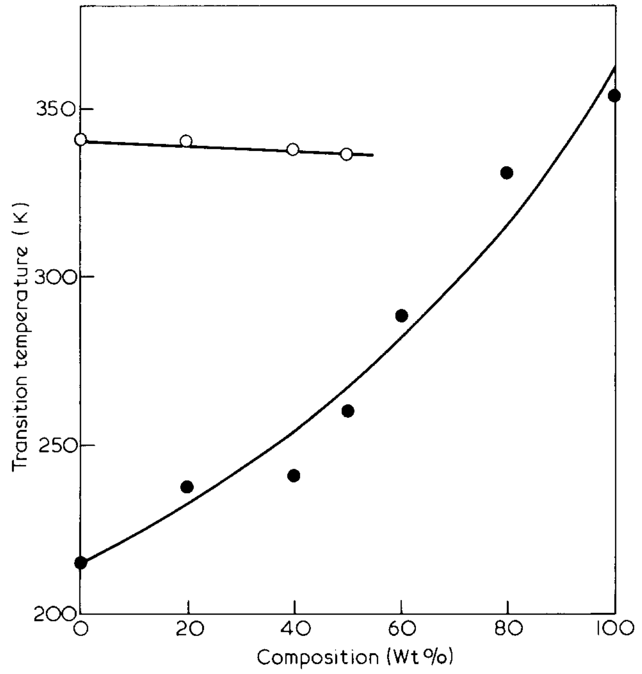

Figure 7 Phase diagram of poly(hexamethylene sebacate)/chlorinated poly(vinyl chloride) blends. (○) = T_m; (●) = T_g, k = 0.56

Ziska, Barlow and Paul for PHMS/PVC blends[8]: $k = 0.4$. It is then found in two cases that the k's determined by using PHMS are smaller than the k's calculated by using PCL:

$$k_{\mathrm{PHMS/PVC}} < k_{\mathrm{PCL/PVC}}$$
$$k_{\mathrm{PHMS/CPVC}} < k_{\mathrm{PCL/CPVC}}$$

This result indicates that PCL has a greater tendency to blend with chlorinated polymers than PHMS. The same data also indicate that the k's calculated by using PVC are smaller than those obtained by using CPVC:

$$k_{\mathrm{PHMS/PVC}} < k_{\mathrm{PHMS/CPVC}}$$
$$k_{\mathrm{PCL/PVC}} < k_{\mathrm{PCL/CPVC}}$$

This result indicates that CPVC has a greater tendency to blend with polyesters than PVC due to its higher chlorine content.

Table 3 also shows that the crystallization of PHMS occurs in a composition range of 0–50%. The decrease of T_m as a function of composition is much smaller than that observed in PCL/CPVC blends and consequently the detailed behaviour of this parameter cannot be assessed from the present results. It however appears that the difference between T_{m1} and T_{m2} is negligible.

Other polyester/CPVC blends have been studied by d.s.c. and it is shown in *Table 4* that all blends made with polyesters having a CH_2/COO ratio of 4, 5 and 6 are miscible while those made with polyesters having a CH_2/COO ratio of 2 and 3 are immiscible. These results support previous suggestions that a CH_2/COO ratio larger than 3 is required for having miscibility in polyester/chlorinated polymer blends[8–11,17,18].

CONCLUSIONS

The results presented in this paper clearly indicate that several polyesters are miscible with CPVC when their CH_2/COO ratio is larger than 3.

The Gordon–Taylor k parameter found for PCL/CPVC blends is larger than that previously reported for PCL/PVC blends suggesting a stronger interaction between PCL and CPVC than between PCL and PVC.

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