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Miscibility behaviour of blends of poly(vinyl chloride) with poly(methyl methacrylate-*co*-styrene) copolymers

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Poly(vinyl chloride) (PVC) is shown to be completely miscible in the melt with a poly(methyl methacrylate-*co*-styrene) (P(MMA-*co*-St)) copolymer having a low styrene content (0–10 wt%). In blends of PVC with a low molecular weight P(MMA-*co*-St) copolymer containing 20 wt% of styrene, a lower critical solution temperature is found at approximately 170°C. For blends of PVC with P(MMA-*co*-St) copolymers containing 30 wt% of styrene, immiscibility is found over the whole temperature range (150–210°C) and independently of the molecular weight of the copolymer. These experimental results have been modelled using a mean-field binary interaction model of the Flory–Huggins theory. The binary interaction energy density for this blend system correctly predicts the homogeneous dispersion of methyl methacrylate/butadiene/styrene (MBS) graft copolymers in a PVC matrix. Copyright © 1996 Elsevier Science Ltd.

(Keywords: miscibility; PVC/PMMA blend; P(MMA-*co*-St) copolymers)

INTRODUCTION

The method of blend preparation is a very important factor determining the final homogeneity of the blends[1,2]. The preparation of blends from solution is an easy method but suffers from two main disadvantages. Firstly, the result in terms of the miscibility of the blend depends not only on their thermodynamic miscibility but also on whether the blends are prepared by solvent casting, coprecipitation or freeze drying, and moreover on the choice of the solvent, the casting temperature and the rate of solvent evaporation. For example, films of poly(vinyl chloride) (PVC)/poly(methyl methacrylate) (PMMA) blends cast from methyl ethyl ketone (MEK) appear to be more homogeneous than those cast from tetrahydrofuran (THF)[3,4]. Secondly, when polymer blends are made from solution, it is sometimes difficult to interpret a lower critical solution temperature (*LCST*) when it is located at a temperature where the diffusion of the chains is strongly hindered by the high viscosity of the blend. Heating to high temperatures can cause demixing because of kinetic reasons. Only when the demixing is followed by remixing after cooling, can one be certain of a true thermodynamic equilibrium *LCST*[5].

These two disadvantages are not encountered when preparing the blends in the molten state. However, this usually requires large amounts of both polymers to fill the processing equipment. With specific polymers and copolymers, synthesized on a laboratory scale, these large amounts are most often not available. The blends described in this paper were prepared in a recently developed mini-mixer/extruder having a volume of only 4–5 cm^3 that was designed with appropriate screws to obtain an intensive melt mixing.

Initially, this mini-extruder was used to study the miscibility of PVC/PMMA blends. The blends have been widely examined over recent years[3–18]. Most authors agree that the mixtures are miscible, but with an *LCST*[5,11,13,15,18] that depends on the molecular weight of the two components and on the tacticity of PMMA.

Next, blends of PVC with methyl methacrylate/styrene copolymers (P(MMA-*co*-St)) were investigated. These blends are of technological interest, because, as described elsewhere[19,20], methyl methacrylate/butadiene/styrene (MBS) impact modifiers for PVC consist of a shell of

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P(MMA-*co*-St) copolymers grafted onto a styrene/butadiene copolymer-based rubber latex. The miscibility of the copolymers in the shell of MBS with PVC will influence both the dispersion and adhesion of the modifier in the PVC matrix. In order to understand the reason for the good dispersion of MBS in the PVC matrix[21], the implications of the miscibility study with respect to the PVC/MBS blend system will be outlined in this paper.

EXPERIMENTAL

Materials

The PVC polymer used in this study was a commercial grade from the Kaneka Corporation, Japan with a *K*-value of 57. P(MMA-*co*-St) copolymers were synthesized with different molecular weights and different compositions. The molar masses of the different polymers were determined by gel permeation chromatography (Waters-590) relative to polystyrene standards, using THF as the eluent. The molar masses of the different homopolymers (PVC and PMMA) and copolymers used and the copolymer composition of P(MMA-*co*-St) are listed in *Table 1*. ^{1}H n.m.r. spectroscopy showed that both low and high molecular weight PMMA are atactic with about 57% syndiotactic sequences.

Blend preparation

Blends of PVC with PMMA or P(MMA-*co*-St) were prepared by melt mixing in a mini-extruder, developed by the DSM company. The mini-extruder is a conical co-rotating, fully intermeshing twin-screw extruder. It is especially suitable for compounding small batches, typically 4–5 g, of polymeric materials. The extruder consists of a lengthwise-split shell which contains a conical mixing chamber. The material can be repeatedly processed by using a recirculation channel. At the end of the mixing operation, the material flow is directed towards the die through a valve. A relative indication of the viscosity change during the mixing operation is given by the force-measuring device which is located under the housing. Recent observations[22] on incompatible nylon-6/PMMA blends revealed a blend morphology comparable to what would be obtained in a double-screw extruder; this demonstrates a high mixing intensity for this mini-extruder.

The mixing action of the mini-extruder is governed by the screw rotation speed and the residence time. A residence time of 3 min was chosen in this study at a relatively low screw speed of 30 r.p.m. To prevent degradation of the PVC, 2 wt% of octyl-tin-mercaptide was added as a heat stabilizer. Lubricants (0.8 wt% of glycerine ricinolate and 0.2 wt% of an ester of montanic acid) were also added to improve the gelation of the PVC matrix and to reduce the friction between powder particles and the extruder wall. The minimum processing temperature in this mini-extruder for the gelation of the primary particles of PVC[23–25] was found to be 150°C. At 220°C, severe degradation of the PVC was observed from the dark brown colour of the extruded material. For these reasons, the processing temperature (T_{extr}) was kept between 150 and 210°C. Unless otherwise stated, the blends were prepared at a 50/50 (wt%) PVC/copolymer ratio.

Table 1 Molecular characteristics of the homopolymers and copolymers used

Polymer	Composition: MMA/St ratio (by weight)	$\bar{M}_w$ (g mol^{-1})	$\bar{M}_n$ (g mol^{-1})	$\bar{M}_w/\bar{M}_n$
PVC	–	96 000	51 000	1.9
PMMA	100/0	28 000	15 000	1.9
PMMA	100/0	81 000	37 000	2.2
P(MMA-*co*-St)	90/10	19 000	11 000	1.9
P(MMA-*co*-St)	90/10	80 000	33 000	2.4
P(MMA-*co*-St)	80/20	21 000	11 000	1.8
P(MMA-*co*-St)	80/20	84 000	37 000	2.3
P(MMA-*co*-St)	70/30	21 000	11 000	1.9
P(MMA-*co*-St)	70/30	84 000	41 000	2.1

Differential scanning calorimetry

The glass transition temperatures of the individual components and of the blends were measured using a Perkin-Elmer DSC-7 differential scanning calorimeter. However, since the T_g values of the individual blend components in this study are within 10–15°C of each other, it is almost impossible to decide for a mixture whether one or two transitions were being recorded. This problem can be solved by physical ageing of the polymer blend[26,27]. Physical ageing of polymers below the glass transition temperature results in a decrease in enthalpy that is recovered during heating. In the case of an immiscible polymer blend, two enthalpy recovery peaks are subsequently observed in a d.s.c. scan. If the polymer blend is miscible, then only one enthalpy recovery peak will be visible. This criterion can therefore be used to determine the miscibility of a blend when the T_gs of the two polymer components are close to each other.

The following ageing treatment was given to the samples. The individual components and the blends were first annealed at 130°C to erase the thermal history. Subsequently, they were quenched in liquid nitrogen (−196°C) and then aged during 46 h at a temperature of 60°C, which is approximately 20°C below the T_g of PVC and 30–35°C below the T_g of PMMA and P(MMA-*co*-St) copolymers. The samples were then scanned in the d.s.c. apparatus from 10 to 150°C at a scanning rate of 20°C min^{-1}, revealing one or two enthalpy recovery peaks, depending on the number of phases in the system. A conventional measurement of the T_g of the blend was also performed in a second scan.

Dynamic mechanical thermal analysis

Dynamic mechanical thermal analysis (d.m.t.a.) was performed as well to obtain information on the miscibility of the system. The viscoelastic behaviour of the samples was recorded on a DMTA MK-II of Polymer Laboratories. The scans were made in the bending mode from 0 to 150°C at a heating rate of 3°C min^{-1} and at frequencies of 1 and 10 Hz. The d.m.t.a. was restricted to the samples extruded at 190°C containing the high molecular weight PMMA or P(MMA-*co*-St) copolymers. Sample dimensions were $45 \times 12 \times 2$ mm^3; these bars were obtained by compression moulding of the extruded material at 180°C.

Infrared spectroscopy

The i.r. spectra were recorded with a Digilab FTS-40 *FT*i.r. spectrophotometer at a resolution of 2 cm^{-1} on films of PVC, PMMA and PVC/PMMA blends. The shift in the carbonyl peak of PMMA was investigated. The strong absorbance of the carbonyl group of PMMA requires very thin films (~1 μm) that could not be obtained by compression moulding. Therefore, the PMMA film was obtained by solvent casting of PMMA from a THF solution on a potassium bromide window. The spectrum of PMMA was compared with a spectrum of a PVC/PMMA blend, prepared at a 99/1 weight ratio. This blend was first extruded at 190°C with the mini-extruder and then compression moulded at 190°C into a 30 μm thick film. The low concentration of the PMMA in the blend avoids a too strong absorbance of the carbonyl group.

RESULTS AND DISCUSSION

Miscibility of blends of PVC with PMMA

The d.s.c. thermograms of 50/50 wt% PVC/PMMA blends extruded at temperatures between 150 and 210°C are shown in *Figure 1* for PVC blended with low molecular weight PMMA. The d.s.c. thermograms for PVC blended with high molecular weight PMMA were similar. The full line represents the enthalpy relaxation behaviour of the different systems. The dotted lines correspond to the conventional d.s.c. scans taken after the physical ageing history has been erased. The homopolymers PVC and PMMA are represented as well. The homopolymers shown here were extruded at 190°C. The extrusion temperature did not affect the enthalpy relaxation behaviour of the homopolymers.

In agreement with earlier findings, the blends exhibit only one T_g and one enthalpy recovery peak[26,27], which indicates miscibility between PVC and PMMA. The miscibility is independent of the extrusion temperature between 150 and 210°C. In other words, an *LCST* behaviour could not be discerned in this range of extrusion temperatures. As mentioned earlier, higher extrusion temperatures were not possible because of the severe degradation of PVC at temperatures higher than 210°C.

The viscoelastic behaviour of the blend of PVC with high molecular weight PMMA and of the individual components was examined by d.m.t.a. In *Figure 2*, the loss modulus (E'') is plotted as a function of temperature. The full lines with symbols correspond to the d.m.t.a. scans at 10 Hz; the dotted lines correspond to the d.m.t.a. scans at 1 Hz. The blend of PVC with high molecular weight PMMA exhibits only one peak in the $E''-T$ curve, confirming the miscibility of this system.

The d.s.c. and d.m.t.a. experiments demonstrate the miscibility between PVC and PMMA in agreement with data presented in literature, where, however, *LCST*s have been reported. The conditions of the *LCST*, in terms of the molecular weight of the two components, are summarized in *Table 2* (data from literature as indicated).

Since the molecular weights of the materials in the present study are not very different from the molecular weights given in *Table 2*, an *LCST* of 190°C or lower is estimated for the blend of PVC with high molecular weight PMMA. The *LCST* of the blend of PVC with low molecular weight PMMA is difficult to estimate from *Table 2*, but must be located at a higher temperature.

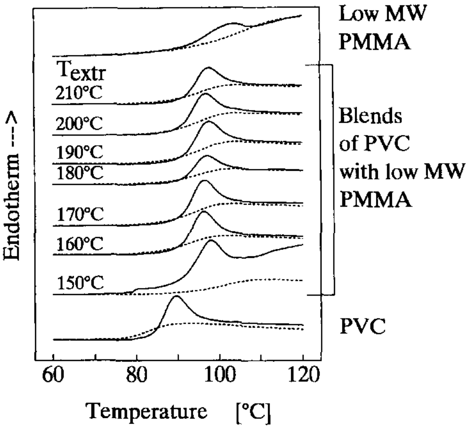

Figure 1 D.s.c. scans of PVC, low molecular weight PMMA, and the 50/50 (w/w) blend of PVC with low molecular weight PMMA extruded at different temperatures (T_{extr}). The full line is the enthalpy recovery behaviour; the dotted line is the conventional d.s.c. scan

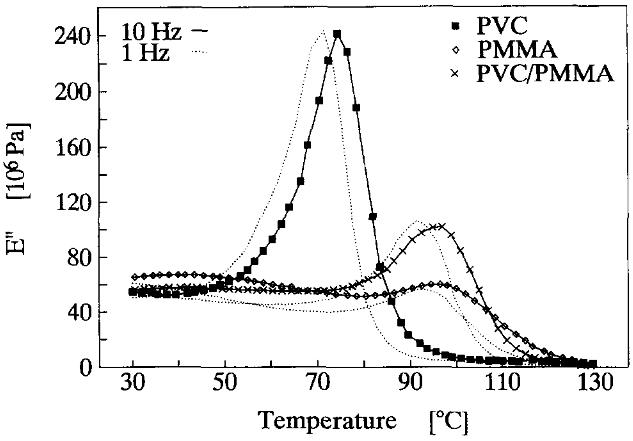

Figure 2 The loss modulus (E'') as a function of temperature (T) for PVC, high molecular weight PMMA, and the 50/50 (w/w) blend of PVC with high molecular weight PMMA extruded at a temperature of 190°C and subsequently compression moulded at the same temperature. The full line is the $E''-T$ curve at 10 Hz; the dotted line is the $E''-T$ curve at 1 Hz

Table 2 The *LCST* as a function of the molecular weights of the individual components. PMMA is atactic. ($D = \bar{M}_w/\bar{M}_n$)

PVC	PMMA	*LCST* (°C)	Ref.	B_{crit} (J cm^{-3})[a]
$\bar{M}_v = 55\,000$ $D = 1.4$	$\bar{M}_v = 60\,000$ $D = 2.1$	190	5	?
$\bar{M}_w = 80\,000$ $D = ?$	$\bar{M}_w = 84\,000$ $D = 1.8$	145	13	0.11
$\bar{M}_w = 62\,000$ $D = 1.1$	$\bar{M}_w = 102\,000$ $D = 1.1$	190	15	0.13
$\bar{M}_w = 83\,500$ $D = 2.2$	$\bar{M}_w = 75\,000$ $D = ?$	180	18	0.12
$\bar{M}_w = 75\,000$ $D = 2.1$	$\bar{M}_w = 100\,000$ $D = 2.2$	190	14	0.12
$\bar{M}_w = 75\,000$ $D = 2.1$	$\bar{M}_w = 80\,000$ $D = 2.1$	190	11	0.13

[a] For the calculation of B_{crit}, the weight-average molecular weights were used to determine the molar volume[28]

The fact that miscibility for the blend of PVC with high molecular weight PMMA is found over the whole temperature range of extrusion is therefore in contradiction to some of the results found in the literature. However, it cannot be ruled out that the

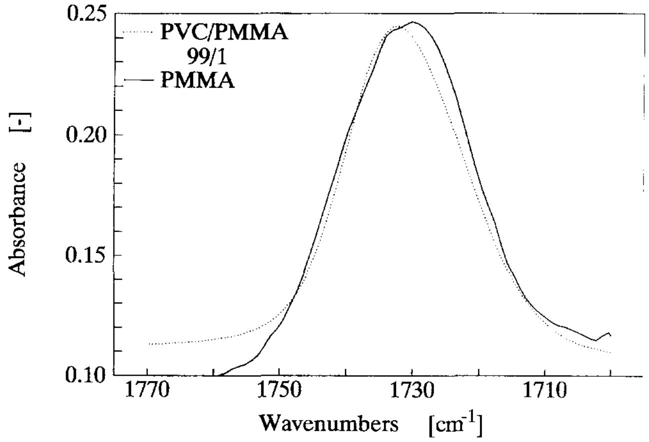

Figure 3 *FT*i.r. spectra in the carbonyl stretching region for unmodified PMMA and a 99/1 wt% blend of PVC/PMMA. The PMMA spectrum was recorded from a film obtained by solvent casting of PMMA on a KBr window. The spectrum of the blend was recorded from a $30\,\mu m$ thick compression moulded film of the extruded blend. Unmodified PVC does not absorb in this region

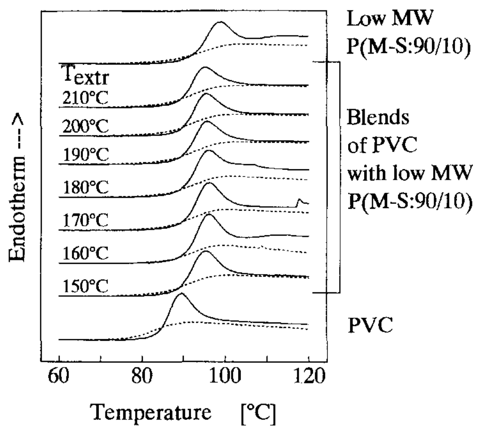

Figure 4 D.s.c. scans of PVC, low molecular weight P(MMA-*co*-St: 90/10), and the 50/50 (w/w) blend of PVC with low molecular weight P(MMA-*co*-St: 90/10) extruded at different temperatures (T_{extr})

intensive mixing in the extruder in combination with a possibly low interfacial tension between PVC and PMMA produces a microheterogeneous system, i.e. an immiscible blend but with a phase size too low to be detected by d.s.c. or by d.m.t.a. (detection limits ~20 nm). A study by Albert *et al.*[29] demonstrated that microphase separation can indeed occur in PVC/PMMA blends.

Phase separation with increasing temperature is generally explained by a variation of the thermodynamic interaction parameter χ with temperature (and concentration), which becomes positive above the *LCST*. χ can become positive when specific interactions that are responsible for the miscibility at relatively low temperatures dissociate at higher temperatures. Regarding such intermolecular interactions between PVC and PMMA, low molecular weight analogues have demonstrated that the interaction must involve the carbonyl group of PMMA and the α-H atom of PVC[10,14]. These interactions (Cl–C–H···O=C) are more likely to be attractive than repulsive, and can be described as hydrogen bonds[30]. The occurrence of these interactions explains the miscibility of PVC with a large variety of ester group-containing polymers[31,32].

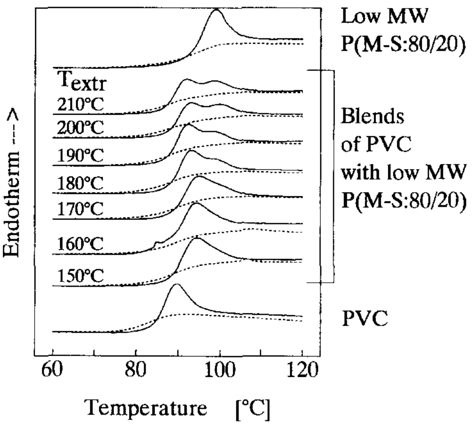

Figure 5 D.s.c. scans of PVC, low molecular weight P(MMA-*co*-St: 80/20), and the 50/50 (w/w) blend of PVC with low molecular weight P(MMA-*co*-St: 80/20) extruded at different temperatures (T_{extr})

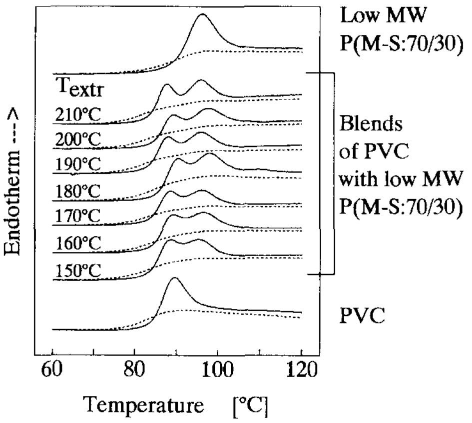

Figure 6 D.s.c. scans of PVC, low molecular weight P(MMA-*co*-St: 70/30), and the 50/50 (w/w) blend of PVC with low molecular weight P(MMA-*co*-St: 70/30) extruded at different temperatures (T_{extr})

The interaction between PVC and PMMA was investigated here by means of *FT*i.r. spectroscopy. A blend of PVC with low molecular weight PMMA was prepared in the extruder at a PVC/PMMA composition of 99/1 wt%. Besides reducing the carbonyl absorption due to the high dilution, the low molecular weight of the PMMA and the excess of PVC both favour a maximum number of intermolecular interactions of the carbonyl group of PMMA, so that these intermolecular interactions, if present, should be revealed.

The resulting *FT*i.r. spectra of the unmodified PMMA and the 99/1 PVC/PMMA blend in the carbonyl stretching region are shown in *Figure 3*. There is no significant shift in the carbonyl peak on blending with PVC. It must therefore be concluded that the interactions between both polymers are only minor in strength and/or number. The closeness between the solubility parameters of PVC ($\delta = 19.6\,J^{1/2}\,cm^{-3/2}$) and PMMA ($\delta = 19.4\,J^{1/2}\,cm^{-3/2}$)[6] in combination with the very weak intermolecular interactions is assumed to be the reason for their miscibility.

*Miscibility of blends of PVC with P(MMA-*co*-St) copolymers*

The d.s.c. thermograms of 50/50 wt% PVC/P(MMA-*co*-St) blends, extruded at temperatures between 150 and 210°C, are shown in *Figures 4–6*. Only the blends with the low molecular weight copolymers are shown. The copolymers differ in composition as indicated. In each figure, the full line represents the enthalpy relaxation behaviour of the different systems and the dotted lines correspond to the conventional d.s.c. scans taken after the physical ageing history has been erased. The thermal behaviour of the PVC homopolymer and the P(MMA-*co*-St) copolymer is represented as well.

The viscoelastic behaviour of the blends of PVC with the high molecular weight copolymers and of the individual components is represented in *Figures 7* and *8*. The loss modulus (E'') is plotted as a function of temperature in the region between 30 and 130°C. The full lines with symbols correspond to the d.m.t.a. scans at 10 Hz; the dotted lines correspond to the d.m.t.a. scans at 1 Hz. The blends and the individual components have been extruded at 190°C.

Since PVC is immiscible with polystyrene (PS)[33], it can be expected that increasing amounts of styrene in the P(MMA-*co*-St) copolymer will finally result in an immiscible blend.

At 10 wt% of styrene in the P(MMA-*co*-St) copolymer, only one enthalpy relaxation peak is observed after physical ageing of the blend, independent of the extrusion temperature and the molecular weight of the copolymer, and therefore this blend system is considered as miscible. The analysis of the viscoelastic response of the blend of PVC with high molecular weight P(MMA-*co*-St: 90/10), extruded at 190°C, is similar to the PVC/PMMA blend; it revealed also only one peak in the $E''-T$ curve, confirming the miscibility.

The transition from miscibility to immiscibility occurs at about 20 wt% of styrene in the P(MMA-*co*-St) copolymer. The blend of PVC with *high* molecular weight P(MMA-*co*-St: 80/20) (not shown here, but the results are summarized in *Table 3*) revealed two enthalpy relaxation peaks in the blends, independent of the extrusion temperature. This clearly indicates that this blend is not miscible. However, the temperatures at which the maxima in the enthalpy relaxation peaks occur (T_{max}) do not coincide with the maxima of the individual components. The second peak has a maximum at the position of the copolymer, but the T_{max} of the first peak is consistently higher than the T_{max} of PVC. This indicates that this system is partially miscible, and the two-phase system consists of a phase of P(MMA-*co*-St: 80/20) copolymer (the second peak) and a phase composed of a mixture of PVC with the P(MMA-*co*-St: 80/20) copolymer (first peak), which then must contain more than 50 wt% of PVC. It was beyond the scope of this work to further investigate this partial miscibility. The immiscibility of PVC with high molecular weight P(MMA-*co*-St: 80/20) was investigated by d.m.t.a. as well, and the data are presented in *Figure 7*. The occurrence of a shoulder in the $E''-T$ curve of the blend confirms the immiscibility of this system.

The blend of PVC with *low* molecular weight P(MMA-*co*-St: 80/20) copolymer is even more on the edge of miscibility, as indicated by *Figure 5*. Mixtures of PVC with low molecular weight P(MMA-*co*-St: 80/20), extruded at a temperature of 150 or 160°C, are miscible, as is evidenced by only one enthalpy relaxation peak in the blend. The enthalpy relaxation peak enlarges at an extrusion temperature of 170°C. A shoulder appears at

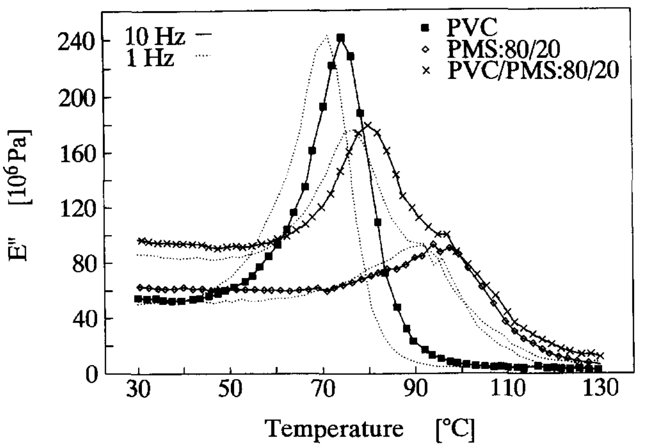

Figure 7 $E''-T$ curves for PVC, high molecular weight P(MMA-*co*-St:80/20), and the 50/50 (w/w) blend of PVC with high molecular weight P(MMA-*co*-St:80/20) processed at 190°C

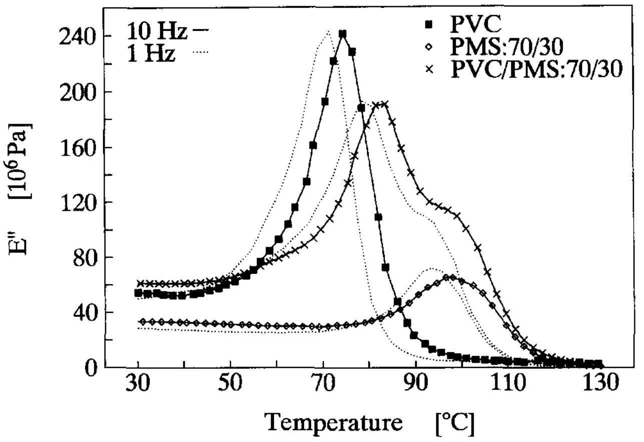

Figure 8 $E''-T$ curves for PVC, high molecular weight P(MMA-*co*-St:70/30), and the 50/50 (w/w) blend of PVC with high molecular weight P(MMA-*co*-St:70/30) processed at 190°C

Table 3 T_g and T_{max} values of the individual components and of the blends by d.s.c. analysis

Polymer	T_g (°C)	T_g in the blend with PVC (°C)	T_{max} (°C)	T_{max} in the blend with PVC (°C)
PVC, $\bar{M}_w = 96\,000$	83		89	
PMMA, $\bar{M}_w = 28\,000$	97	89	99	97
PMMA, $\bar{M}_w = 81\,000$	101	91	97	98
P(MMA-*co*-St: 90/10), $\bar{M}_w = 19\,000$	95	89	99	96
P(MMA-*co*-St: 90/10), $\bar{M}_w = 80\,000$	103	92	101	98
P(MMA-*co*-St: 80/20), $\bar{M}_w = 21\,000$	93	–	98	94 or 93/99[a]
P(MMA-*co*-St: 80/20), $\bar{M}_w = 84\,000$	102	–	101	95/104
P(MMA-*co*-St: 70/30), $\bar{M}_w = 21\,000$	90	–	96	88/96
P(MMA-*co*-St: 70/30), $\bar{M}_w = 84\,000$	101	–	101	90/102

[a] T_{max} is 94°C in the miscible system (below the *LCST* of 170°C), and T_{max} is 93°C for the first peak and 99°C for the second peak in the partially miscible system (above the *LCST* of 170°C)

180°C, which increases in intensity with increasing extrusion temperature. This behaviour points to an *LCST* located at 170°C. For the immiscible systems (for extrusion temperatures higher than 180°C), the T_{max} of the second peak is again located at the T_{max} of the pure copolymer. The T_{max} of the first peak is situated between the T_{max} of the two polymers, which points to partial miscibility. From the examination of the curves in *Figure 5*, it seems that the degree of phase separation increases with increasing extrusion temperature. A possible interpretation of the *LCST* behaviour is that the weak hydrogen interactions at low temperatures are dissociated at higher temperatures due to the increased Brownian motion of the molecules. In that way, the interaction parameter becomes (more) positive, leading to an immiscible blend.

Since PVC/P(MMA-*co*-St: 80/20) blends are on the edge of miscibility, it is expected that a P(MMA-*co*-St) copolymer with 30 wt% of styrene exhibits complete immiscibility with PVC. Two enthalpy relaxation peaks are indeed observed in *Figure 6* for the blends of PVC with low molecular weight P(MMA-*co*-St: 70/30) copolymer. The blends of PVC with high molecular weight P(MMA-*co*-St: 70/30) copolymer showed an analogous behaviour. In addition, the positions of the two peaks coincide with those of the individual components, indicating that even partial miscibility does not occur. The immiscibility is confirmed by the viscoelastic experiment on the blend of PVC with high molecular weight P(MMA-*co*-St: 70/30) represented in *Figure 8*, showing the occurrence of a pronounced shoulder in the $E''-T$ curve. Due to the nearness of the T_gs of the two components, a shoulder in the peak with the highest intensity is observed instead of two clearly separated peaks.

It should be mentioned here that the T_gs of PVC and the low molecular weight P(MMA-*co*-St: 70/30) are only separated by 7°C. On a conventional d.s.c. scan their immiscibility could nearly not be demonstrated. However, with the use of physical ageing, two enthalpy relaxation peaks can be made visible. The usefulness of this technique is also demonstrated by the observation of the *LST* behaviour (see *Figure 5*), which cannot be detected in conventional d.s.c. runs.

The results of the d.s.c. analysis in terms of T_g and T_{max} values of the individual components and of the blends are summarized in *Table 3*. This table demonstrates again that:

(i) The enthalpy relaxation method is useful in making a distinction between a miscible and an immiscible system, if the T_gs are separated from each other by less than 20°C.

(ii) In a miscible system (PVC/PMMA and PVC/P(MMA-*co*-St: 90/10)), the T_g of the blend is located between the T_gs of the individual components.

(iii) In a completely phase-separated system (PVC/P(MMA-*co*-St: 70/30)), the maxima of the enthalpy recovery peaks are located at the same positions as the maxima of the individual components.

(iv) In the partially miscible systems (PVC/P(MMA-*co*-St: 80/20)), the T_{max} of the second peak is located at the T_{max} of the P(MMA-*co*-St: 80/20) copolymer; the T_{max} of the first peak is located between the T_{max} values of the individual components.

*Theoretical modelling of the miscibility behaviour of PVC/P(MMA-*co*-St) blends*

With such a variety of data, it seems worthwhile to model the results of the miscibility study using a simple mean-field binary interaction model of the Flory–Huggins theory for miscibility.

According to this theory, the state of miscibility of any mixture is governed by the free energy of mixing ΔG_m, which is defined as[31]

$$\Delta G_m = \Delta H_m - T\Delta S_m \qquad (1)$$

where ΔH_m is the enthalpy change on mixing, ΔS_m the entropy change on mixing and T the absolute temperature. A miscible system is characterized by a negative free energy of mixing ΔG_m. The Flory–Huggins theory assumes that the heat of mixing ΔH_m follows a quadratic dependence on composition, i.e. a van Laar expression,

$$\Delta H_m = B_{blend} V \Phi_1 \Phi_2 \qquad (2)$$

where V is the volume of the mixture and B_{blend} is the interaction energy density characteristic of polymer–polymer segmental interactions. For non-polar systems, B_{blend} can be estimated from solubility parameters as

$$B_{blend} = (\delta_1 - \delta_2)^2 \qquad (3)$$

$$\Delta H_m = (\delta_1 - \delta_2)^2 V \Phi_1 \Phi_2 \qquad (4)$$

The Flory–Huggins theory estimates the entropy of mixing ΔS_m as the combinatorial contribution computed from the lattice model of the mixture. This results in a convenient expression which may be written as

$$\Delta S_m = -\frac{RV}{V_r}\left(\frac{\Phi_1 \ln \Phi_1}{x_1} + \frac{\Phi_2 \ln \Phi_2}{x_2}\right) \qquad (5)$$

where R is the gas constant, V_r is a reference volume and x_i is the degree of polymerization of component i relative to the reference volume and is of the same order as the degree of polymerization expressed in terms of the number of monomer units in the chain. The combinatorial entropy of mixing of two polymers is dramatically less than that for two low molecular weight compounds and tends to zero as the molecular weight of the two components and consequently x_i goes to infinity. From equation (1), it can then be understood that $\Delta H_m \leq 0$ in miscible polymer blends with an infinite molecular weight. For a given molecular weight the criterion for miscibility is that B_{blend} must be lower than a critical value which depends on the molar volumes of the two polymer components (V_i) through

$$B_{crit} = (RT/2)(V_1^{-1/2} + V_2^{-1/2})^2 \qquad (6)$$

Equation (3) is useful for estimating ΔH_m between two homopolymers which interact only via dispersive or van der Waals-type bonding between their segments. However, the miscibility windows for the blends of PVC with P(MMA-*co*-St) may be driven by intramolecular repulsion effects between the copolymer units. This is explained by a simple mean-field binary interaction model[34–36]:

$$B_{blend} = B_{13}\Phi_1' + B_{23}\Phi_2' - B_{12}\Phi_1'\Phi_2' \qquad (7)$$

where Φ_1' and Φ_2' are respectively the segment volume fractions of monomers 1 and 2 in the copolymer and the B_{ij}s are the interaction energy densities between the various monomer units comprising the blend and the composition of the copolymer. Based on this model, it is clear that B_{blend} may become negative for a certain range of copolymer compositions even though all B_{ij}s are positive. A well-known example of this behaviour is the miscibility of PMMA with styrene/acrylonitrile (SAN) copolymers[37].

Applying relation (7) to the PVC/P(MMA-*co*-St) system studied in this paper, the miscibility will depend on the interaction parameter $B_{\mathrm{PVC/P(MMA}\text{-}co\text{-}\mathrm{St)}}$ as

$$B_{\mathrm{PVC/P(MMA}\text{-}co\text{-}\mathrm{St)}} = B_{\mathrm{MMA/VC}}\Phi'_{\mathrm{MMA}} + B_{\mathrm{St/VC}}\Phi'_{\mathrm{St}} - B_{\mathrm{MMA/St}}\Phi'_{\mathrm{MMA}}\Phi'_{\mathrm{St}} \qquad (8)$$

where

$$\Phi'_{\mathrm{MMA}} + \Phi'_{\mathrm{St}} = 1 \qquad (9)$$

The major problem is to obtain reliable estimations of the different monomer pair interaction energy densities (B_{ij}). Most of these quantities are not directly available from the literature. An exception to this rule is the PS/PMMA interaction that has been widely studied. Estimations of the interaction energy density ($B_{\mathrm{MMA/St}}$) range from 0.2 to $1.4\,\mathrm{J\,cm^{-3}}$[38,39], with an average of $0.70\,\mathrm{J\,cm^{-3}}$[40,41]. This indicates that PMMA and PS are immiscible, consistent with experiment[42].

Interaction energy densities for the PVC/PMMA and the PVC/PS systems are not available from the literature but can be estimated from experimental data. For the PVC/PMMA system, an *LCST* has been reported of around 190°C. On the basis of equation (6), the interaction energy density can be estimated at the equilibrium temperature (190°C), where B_{blend} equals B_{crit}, and the calculation is reported in the last column of *Table 2*; the average value of $B_{\mathrm{MMA/VC}}$ is $0.13\,\mathrm{J\,cm^{-3}}$. It is assumed that this value is temperature-independent, which by itself cannot explain the *LCST* behaviour. The small but positive value agrees with a system with a small difference in solubility parameter and where hydrogen bond-type interactions are very weak. The value is also in agreement with a recent publication giving a value for the Flory–Huggins parameter $\chi_{\mathrm{MMA/VC}}$ of 0.0031[43]. At a temperature of 190°C and a reference volume of $64\,\mathrm{cm^3\,mol^{-1}}$, this converts into an interaction energy density $B_{\mathrm{MMA/VC}}$ of $0.19\,\mathrm{J\,cm^{-3}}$.

The explanation above relies on the observation of an *LCST* behaviour at 190°C, which was not observed experimentally here. However, the *LCST* behaviour reported in the literature refers to blends prepared by solution casting, a method which differs from the blend preparation used in this work. As pointed out earlier, it cannot be ruled out that the intensive mixing in the extruder in combination with the low interfacial tension between PVC and PMMA produces a microheterogeneous system, with a phase size too low to be detected by d.s.c. or d.m.t.a.[29]. This could explain the differences between the literature and our own experimental data. On the other hand, it should be possible to compare the miscibility behaviour of PVC/PMMA and PVC/P(MMA-*co*-St) systems by considering only the literature data for $B_{\mathrm{MMA/St}}$ and $B_{\mathrm{St/VC}}$ and the *LCST* observed for the low molecular weight PVC/P(MMA-*co*-St: 80/20) blends without referring to the literature data for PVC/PMMA. Undoubtedly, one would get a better fit of the results, because one then calculates the third parameter $B_{\mathrm{MMA/VC}}$ so that it exactly fits the experimental results. We did not use this approach, because the aim of this study was to see how good the experimental results fit the theory when using only literature data.

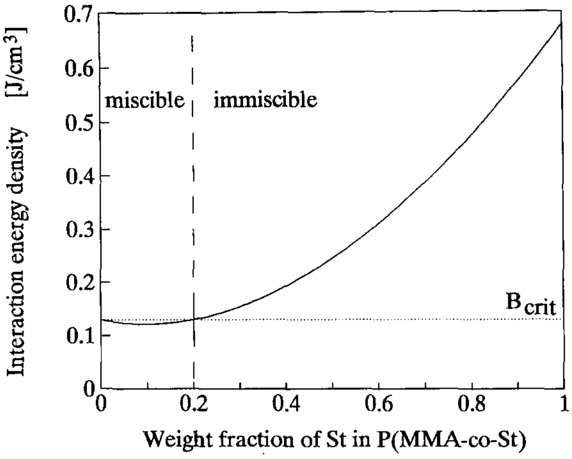

Figure 9 Interaction energy density ($B_{\mathrm{PVC/P(MMA}\text{-}co\text{-}\mathrm{St)}}$) as a function of the weight per cent of styrene in the copolymer using equation (8) and the interaction energy density parameters mentioned in the text. Although the horizontal axis is labelled '*weight* fraction of styrene in P(MMA-*co*-St)', the reader should be aware that for the calculations of the interaction energy density, the segment *volume* fraction of styrene was used

Finally, as far as we know, the interaction energy density between PVC and PS has not been experimentally verified and these blends have not been widely studied. Again, there are some experimental data that can provide us with an estimate of $B_{\mathrm{St/VC}}$. Firstly, the interaction energy density can be estimated from the heats of mixing of low molecular weight analogues. From the heat of mixing of 1,3-dichlorobutane with styrene oligomers, the interaction energy density $B_{\mathrm{St/VC}}$ was estimated to be $0.80\,\mathrm{J\,cm^{-3}}$[32]. Secondly, PVC is known to be miscible with SAN copolymers when the acrylonitrile (AN) content in the copolymer is between 11.5 and 26 wt%[2], i.e. between 10.3 and 24 vol%. Taking $B_{\mathrm{St/AN}} = 22.8\,\mathrm{J\,cm^{-3}}$[41], and using equation (7), the interaction energy density between PS and PVC can be calculated, and one finds $B_{\mathrm{St/VC}} = 0.56\,\mathrm{J\,cm^{-3}}$. On average, we therefore have $B_{\mathrm{St/VC}} = 0.68\,\mathrm{J\,cm^{-3}}$. The small but positive value of the interaction energy density agrees with the immiscibility between PS and PVC[33].

Summarizing our estimations of the interaction energy densities of the different segments in the PVC/P(MMA-*co*-St) system, we have

$$B_{\mathrm{MMA/VC}} = 0.13\,\mathrm{J\,cm^{-3}}$$

$$B_{\mathrm{St/VC}} = 0.68\,\mathrm{J\,cm^{-3}}$$

$$B_{\mathrm{MMA/St}} = 0.70\,\mathrm{J\,cm^{-3}}$$

Using equation (8), the interaction energy density for the blend of PVC with P(MMA-*co*-St) copolymers can be calculated as a function of the styrene content in the copolymer, and the result is shown in *Figure 9*.

According to *Figure 9*, miscibility between PVC and P(MMA-*co*-St) occurs ($B_{\mathrm{blend}} < B_{\mathrm{crit}} \sim 0.13$) for copolymers with a styrene content of less than 20 wt%. This theoretical prediction is in agreement with the earlier experimental observations, where it was found that PVC is miscible with P(MMA-*co*-St) copolymers containing less than 20 wt% of styrene and not miscible for styrene contents higher than or equal to 20 wt%. The binary interaction model is thus a powerful tool for understanding the miscibility behaviour of blends of PVC with P(MMA-*co*-St) copolymers.

Moreover, the agreement between theory and experiment is excellent if one considers the relatively low absolute values of the interaction parameters B_{ij}: a small variation in one of the B_{ij} estimations can cause a dramatic change in the homopolymer/copolymer phase behaviour. In particular, if the value of $B_{\mathrm{St/VC}}$ is higher than $0.68\,\mathrm{J\,cm^{-3}}$, then the miscibility window would shift to lower styrene contents in the copolymer, and eventually explain the effect of the molecular weight on the miscibility of PVC/P(MMA-*co*-St:80/20) blends. However, in view of the assumptions used for the estimations of the B_{ij} values, it seems unreasonable to further adjust the $B_{\mathrm{St/VC}}$ interaction parameter so that theoretical prediction and experimental observation finally coincide.

Implications for the PVC/MBS blend system

Having conducted the miscibility study on the blends of PVC with P(MMA-*co*-St) copolymers, we were interested in translating the results to blends of PVC with MBS containing 50 wt% styrene in the copolymer of the shell[20]. Clearly, from the above experimental data and concepts, it is evident that the blends of PVC with P(MMA-*co*-St:50/50) copolymers are immiscible with PVC. Nevertheless, from *Figure 9*, the binary interaction energy density of PVC/P(MMA-*co*-St:50/50) blends is predicted to be only $0.25\,\mathrm{J\,cm^{-3}}$.

Helfand has developed a theory which relates the characteristics of the polymer–polymer interface to the Flory–Huggins interaction parameter (χ)[44]. This theory uses the assumption that the polymer–polymer interface is diffuse and that it can be characterized by a thickness (d) where the segments of the two polymers are mixed. As the polymer–polymer interaction, reflected by the χ parameter, is more unfavourable for mixing, the interfacial tension between the two components will be high and the interfacial composition gradient will be sharper. As a consequence, a relatively low value of B, such as for the PVC/P(MMA-*co*-St) blend system, will result in a relatively large interphase thickness (d) and a low interfacial tension (γ). These quantities can be calculated from Helfand's theory using

$$d = (2b)/(6\chi)^{1/2} \tag{10}$$

$$\gamma = bRT(\chi/6)^{1/2}/V_{\mathrm{r}} \tag{11}$$

$$\chi = (B_{\mathrm{blend}}V_{\mathrm{r}})/(RT) \tag{12}$$

where R is the gas constant, T the absolute temperature, V_{r} the reference volume, χ the Flory–Huggins interaction parameter and b the effective length of a monomer unit ($b = C_{\infty}^{1/2}b_0$). With d being proportional to $\chi^{-1/2}$ and γ proportional to $\chi^{1/2}$, it is clear that the interfacial tension (γ) is inversely proportional to the interphase thickness (d).

Helfand's theory requires common values for V_{r} and b, which are taken as the geometric means of both polymers[44]. Using Ref. 45, $C_{\infty,\mathrm{PVC}} = 7.6$, $C_{\infty,\mathrm{P(MMA\text{-}co\text{-}St:50/50)}} = 9.3$, $b_0 = 0.204\,\mathrm{nm}$, $V_{0,\mathrm{PVC}} = 45\,\mathrm{cm^3\,mol^{-1}}$ and $V_{0,\mathrm{P(MMA\text{-}co\text{-}St:50/50)}} = 90\,\mathrm{cm^3\,mol^{-1}}$, one gets $b = 0.59\,\mathrm{nm}$ and $V_{\mathrm{r}} = 64\,\mathrm{cm^3\,mol^{-1}}$. Taking $T = 463\,\mathrm{K}$ (190°C), one finds an interphase thickness (d) of 7.5 nm and an interfacial tension (γ) of $0.9 \times 10^{-3}\,\mathrm{J\,m^{-2}}$.

In order to get more feeling for these values, they have to be compared with systems which have a 100-fold higher interaction parameter (e.g. PS/PAN (poly(acrylonitrile) blends). According to equations (10) and (11), a decrease in interphase thickness and an increase in the interfacial tension by a factor of 10 is expected for those systems. The obtained values for γ and d are very reasonable, when experimental data from the literature are compared. For instance, in a blend of polyethylene (PE) with polypropylene, two polymers of similar polarity, the interfacial tension at 180°C equals $0.8 \times 10^{-3}\,\mathrm{J\,m^{-2}}$; on the other hand, in a blend of PE with PMMA, two polymers with a large difference in polarity, the interfacial tension at 180°C was found to be $9.0 \times 10^{-3}\,\mathrm{J\,m^{-2}}$[46].

The theoretical calculations reveal that although PVC and P(MMA-*co*-St:50/50) are immiscible their blends have a low interfacial tension. This explains the good dispersion of the MBS particles in the PVC matrix[21]. On the other hand, the interphase thickness in PVC/MBS blends might differ from the estimated value because the interpenetration of the two phases is restricted by the fact that the P(MMA-*co*-St) copolymers are grafted onto the styrene/butadiene rubber core. The value of $d = 7.5\,\mathrm{nm}$ can therefore be considered as an upper limit and the actual value of the interphase thickness will be determined by the length (molecular weight) of the grafted chains and the grafting density.

CONCLUSIONS

The miscibility of PVC/P(MMA-*co*-St) blends was investigated in this paper. The use of a mini-extruder made it possible to examine the miscibility of these systems in the melt, with the following advantages of melt mixing over solution blending:

(i) True thermodynamic *LCST* behaviours can be observed because intensive mixing overcomes the diffusion problems sometimes encountered in the conventional detection of the *LCST* in blends.
(ii) The miscibility will not depend on the solvent, or solvent preparation method (solvent casting *versus* coprecipitation) but on the thermodynamic miscibility of the two polymers.
(iii) The results obtained by this method can more readily be translated to industrial situations, since polymer blends are usually prepared by melt mixing. This is certainly the case for the PVC/MBS blend system for which this miscibility study was performed.

With the use of the enthalpy relaxation method for the evaluation of miscibility, this study revealed that PVC is miscible with P(MMA-*co*-St) copolymers as long as the styrene content is less than 20 wt%. Blends of PVC with low molecular weight P(MMA-*co*-St:80/20) show an *LCST* behaviour and are partially miscible above the *LCST* temperature. At higher styrene contents in the copolymer, complete immiscibility is observed. These results have been modelled using the mean-field binary interaction model of the Flory–Huggins theory; it was shown that the predictions from this theory agree with the experimental observations.

Finally, application of the above-mentioned results to the PVC/MBS blend system predicts immiscibility between the shell of MBS and the PVC matrix.

Nevertheless, the interfacial tension is low ($\gamma = 0.9 \times 10^{-3}\,\mathrm{J\,m^{-2}}$), and this explains the good dispersion of the MBS particles in the PVC matrix.

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