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Polycaprolactone-based block copolymers: 4. Interfacial activity in poly(vinyl chloride) containing polyblends

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The substantial difference in the T_g of poly(vinyl chloride) (PVC) and poly(ε-caprolactone) (PCL) offers a sensitive method of locating a polystyrene (PS)–PCL diblock in PVC or in PS/PVC polyblends. When mixed with PVC, these diblocks are dispersed as individual molecules in equilibrium with micelles. The equilibrium position depends on the composition of the diblock; when PCL is the major component, molecular dissolution in PVC is enhanced. A 50/50 PS–PCL diblock, each block of which is of a higher molecular weight than the related homopolymer, is located mainly at the PS/PVC interface, as shown by the essentially unchanged T_g of the PVC matrix and a sub-T_g assigned to the external layer of the PVC phases plasticized by the PCL blocks of the copolymer. Blocks longer than the associated homopolymer chain clearly enhance the mutual anchoring of the PS and PVC phases. Since PS and PVC are intrinsically brittle polymers, their melt blending in the presence of properly designed PS–PCL diblocks gives rise to fragile materials.

(Keywords: polyblends; emulsification; block copolymers; interfacial activity)

INTRODUCTION

Polymer blending is currently one of the most useful strategies to meet needs for new materials[1–3]. It has the advantage that it can be implemented with available polymers and existing processing equipment, thus resulting in substantial economy compared with the development of new chemistry. Although no simple rules are available to predict the property behaviour of polyblends, a nearly linear property dependence on composition is generally reported for amorphous, miscible binary blends[4–6]. In contrast, immiscible blends are multiphase systems and, interestingly, they are able to combine the properties of the constitutive polymers to an extent that depends on blend composition and degree of adhesion between the phases[7,8]. In this respect, emulsification of immiscible polymer blends is now recognized as an effective way to strengthen the interfacial region and to improve the overall mechanical behaviour. Numerous examples are available that illustrate the interfacial activity of diblock and graft copolymers comprising components of the same chemical nature as, or at least selectively miscible with, the blended polymers[1,3,9–13]. Immiscible blends of two very widespread commodity polymers, polyethylene (PE) and polystyrene (PS), have been successfully modified by various hydrogenated butadiene–styrene (hPBD–PS) diblock copolymers[11,13–17]. For instance, toughening of PS has been reported when ≈ 20 wt% low density PE is properly dispersed and stabilized in the PS matrix[14,18]. As far as

commodity polymers are concerned, poly(vinyl chloride) (PVC) must also be considered since PE, PS and PVC are the most consumed products and contribute predominantly to the polymer content of waste disposal in industrialized countries[19]. Recycling of PE, PVC and PS may be a solution to the ever increasing problem of pollution by non-biodegradable polymers. Although this paper does not address the question of what is the best strategy to be applied to such recycling for practical purposes, it will focus on a technique that may be useful, the emulsification of blends of PVC and PS, i.e. two immiscible, rigid polymers.

When the molecular architecture of amphipathic copolymers to be used as interfacial agents in immiscible polyblends is considered, the superiority of diblock structures over triblock and graft copolymers is unquestionable[14,18]. Since vinyl chloride can only be polymerized by a radical mechanism, production of PVC-containing diblocks is difficult, and a constitutive block miscible with PVC is the only alternative method. Syndiotactic poly(methylmethacrylate) (s.PMMA) and poly(ε-caprolactone) (PCL) are known to be miscible with PVC[20–24] and both MMA and ε-CL have been successfully block polymerized with styrene[25,26]. A preliminary paper has focused on the comparative efficiency of s.PMMA–PS and PCL–PS diblock copolymers in improving immiscible blends of PS and PVC[27]. Optical and scanning electron microscopy give evidence of the interfacial activity of both types of diblock: they provoke a substantial decrease in the mean size of the dispersed phases and strengthen the interfacial adhesion. Whatever the diblock used, the ultimate mechanical properties of PS-rich blends are depressed, resulting in 'allergic' effects, whereas some improvements are reported for the PVC-rich blends. As a rule, s.PMMA–PS

and PCL–PS diblocks of the same molecular weight and composition have the same qualitative effects on the ultimate tensile strength and elongation at break of PVC/PS blends. These observations address the question of the location of a PS–PX diblock copolymer in PS/PVC blends, where PX is the polar block miscible with PVC. The large difference in the T_g values of PVC and PCL provides the opportunity to investigate the penetration of PCL blocks into PVC phases. It is the purpose of this paper to determine if PCL blocks form a plasticized interfacial region in PVC when PS–PCL diblocks are added to PS/PVC blends. This approach may clarify the interfacial situation and tell us something about the interfacial activity of copolymers, one block of which is selectively miscible with the polar component of a polyblend.

EXPERIMENTAL

PCL and PS–PCL diblock copolymers were synthesized and characterized as described in detail elsewhere[26].

Two PVC samples were kindly supplied by Solvay Co. The Solvic 258 RD ($\bar{M}_n = 43\,000$ and $\bar{M}_w = 85\,000$) was a commercial product. A second sample, of a lower molecular weight, was synthesized by emulsion polymerization at 50°C ($\bar{M}_n = 20\,000$ and $\bar{M}_w = 36\,000$).

Polystyrene samples of $\bar{M}_n = 21\,000$, $40\,000$ and $160\,000$ were prepared by anionic polymerization in toluene at 0°C, using sec.BuLi as the initiator. A commercial polystyrene sample was also used as supplied by BASF (Polystyrol 158 K, $\bar{M}_n = 100\,000$, $\bar{M}_w/\bar{M}_n = 2.5$).

Polymers were melt-blended on a Camil laboratory two-roll mill at 175–180°C for 5 min. The powdery polymers were first blended at 25°C in the appropriate ratio and added with a PVC stabilizer (equimolar mixture of Zn and Ca stearate) at a level of 1 mol% of vinyl chloride. After mixing in the melt, blends were compression moulded into sheets at 180–185°C for 5 min.

A Gehman-type torsion pendulum was used according to ASTM 1053-58 T. The dimensions of the testing samples were: $3.5\,cm \times 0.8\,cm \times 0.2\,cm$. The temperature at which a transition occurs is assigned to the inflection point of that transition in the torsion modulus *versus* temperature curve.

Stress–strain curves were recorded according to ASTM D.638 V at 20°C, at an extension rate of 2 cm min⁻¹.

RESULTS AND DISCUSSION

PVC/PCL binary blends

In a preliminary step, blends of PVC ($20\,000$) and PCL ($36\,000$) were prepared by melt blending and the temperature dependence of their isochronous torsion modulus is shown in *Figure 1*. The experimental data are consistent with the well established miscibility of the two polymers[20,21]: a single T_g is observed for each blend and its value is in good agreement with that calculated using the Fox equation[28] (*Table 1*). *Figure 2* illustrates the corresponding behaviour when PCL is replaced by a diblock consisting of a block of PCL of about the same molecular weight ($40\,000$) and a block of PS, also with a molecular weight of $40\,000$ (diblock copolymer C1). The isochronous curves of torsion modulus *versus* temperature again show a significant decrease in the T_g of PVC. According to the experimental T_g values (*Table*
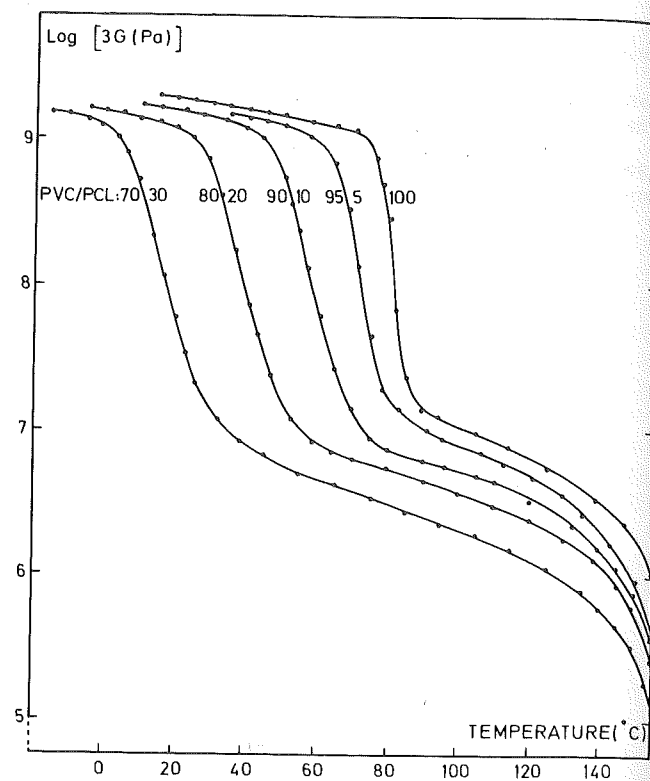

Figure 1 Isochronous (10 s) torsion modulus *versus* temperature curves of binary blends of PVC ($\bar{M}_n = 20\,000$) and PCL ($\bar{M}_n = 36\,000$) of various compositions

Table 1 Glass transition temperature of PVC/PCL blends of various compositions: comparison of experimental data and values calculated from the Fox equation[28]

Composition (wt%)		T_g (exp.)		T_g (calc.)	
PVC	PCL	(°C)	(K)	(°C)	(K)
1	0	81	(354)	–	
0.95	0.05	71	(344)	68	(341)
0.9	0.1	58	(331)	56	(329)
0.8	0.2	40	(313)	35	(308)
0.7	0.3	18	(291)	15	(288)
0	1	–71	(202)[21]	–	

Table 2 Glass transition temperatures of PVC/PS–PCL (C1) diblock blends of various compositions: comparison of experimental data and values calculated from the Fox equation[28]

Composition (wt%)		T_g (exp.)		T_g (calc.)		T_g (PS)
PVC	C1	(°C)	(K)	(°C)	(K)	(°C)
1.0	0	81	(354)	–		–
0.9	0.1	74	(347)	68	(341)	–
0.8	0.2	67	(340)	54	(327)	101
0.7	0.3	53	(326)	41	(314)	100
0.6	0.4	43	(316)	22	(295)	100

2), however, the ability of PCL to plasticize PVC has been significantly reduced by its covalent bonding to a block (PS) immiscible with PVC. This indicates that PCL has largely lost the opportunity to be randomly dissolved in PVC. Micellization of the diblock with formation of a PS core surrounded by a shell of PCL chains can account for this result. The moderate decrease in T_g of the PVC
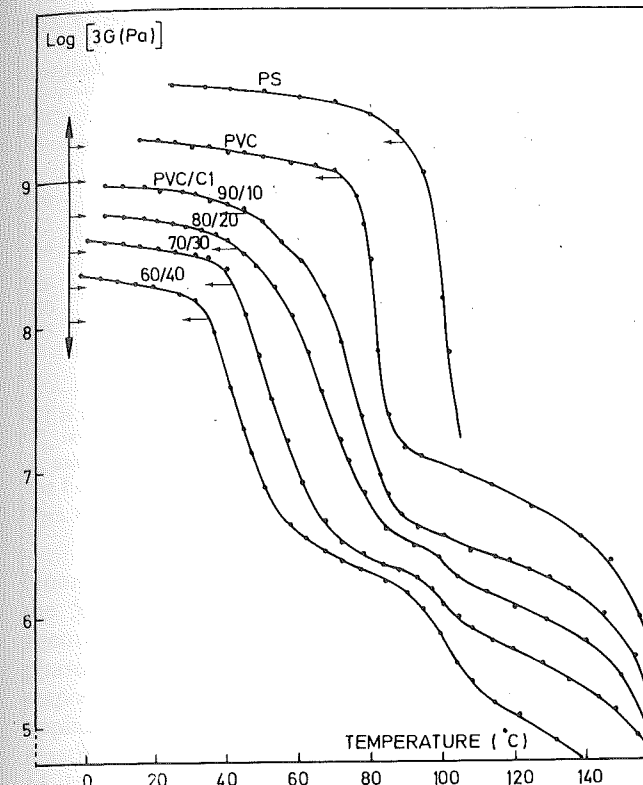

Figure 2 Isochronous (10 s) torsion modulus *versus* temperature curves of PS ($\bar{M}_n = 160\,000$), PVC ($\bar{M}_n = 20\,000$) and binary blends of PVC ($20\,000$) with increasing amounts of a PS–PCL diblock copolymer ($\bar{M}_n(PS) = 40\,000$ and $\bar{M}_n(PCL) = 38\,000$) designated as C1. For clarity, each curve has been shifted in the modulus scale except that for PVC. Arrows indicate the position of log $3G = 9$ for each curve

matrix may be attributed to diblock molecules being molecularly dissolved in the matrix and in equilibrium with the micelles. Furthermore, the protruding PCL component of the micelles may plasticize PVC locally, as supported by a lower ($\approx 56°C$), although little pronounced, T_g which can be detected in the 90/10 binary blend (*Figure 2*). When the PS–PCL copolymer content increases beyond 10%, the T_g of the PVC matrix decreases and rapidly overlaps the expected constant T_g of the PVC associated with the outer shell of the micelles. There is thus a change from two T_g values to a single glass transition of decreasing broadness. The T_g of PS is clearly observed when the diblock content is ≥ 20 wt%, i.e. when the percentage of PS is ≥ 10 wt%.

Instead of a 50/50 PS–PCL diblock, let us now consider a copolymer with 70% PCL, while maintaining the same length of PS ($40\,000$). Compared to the previous situation, the molecular weight of both the PCL block ($100\,000$) and PVC matrix ($43\,000$) have been increased by a factor of ≈ 2. To maintain the weight composition of the blends comparable to that of the previous PVC/PS–PCL system, homo PS ($40\,000$) was added to the $40\,000/100\,000$ PS–PCL copolymer such that the total PS content was 50% (A1). The isochronous curves of the torsion modulus are gathered in *Figure 3* and, at first glance, they exhibit the same pattern as in *Figure 2*. However, the T_g of the PVC matrix now decreases in good agreement with the Fox equation (*Table 3*), indicating that most of the PCL blocks are molecularly dispersed within the PVC. The sharpness of the transition is another indication of the homogeneous plasticization of PVC. In contrast to the 50/50 diblock of molecular

weight $78\,000$, the 30/70 PS–PCL copolymer of $140\,000$ molecular weight has little tendency to form micelles. However, a small part of the diblock contributes to the dispersion of the homo PS added. Very small PS particles must be formed: that this is so is supported by the transparency of the polyblends and the sub-T_g of $\approx 55°C$ ($\pm 3°C$) observed for blends containing $>85\%$ PVC.

The data reported so far suggest that PS–PCL diblocks are dispersed in PVC as individual molecules in equilibrium with micelles (and/or larger aggregates). The equilibrium position strongly depends on the composition of the diblock. It is shifted to molecularly dispersed species when the diblock is composed of $>50\%$ of the block doing the interactions, possibly by H bonding or charge transfer[20], with PVC. A tentative schematic view of this behaviour is given in *Figure 4a*. It is of the utmost importance when PS–PCL diblocks are to be used as
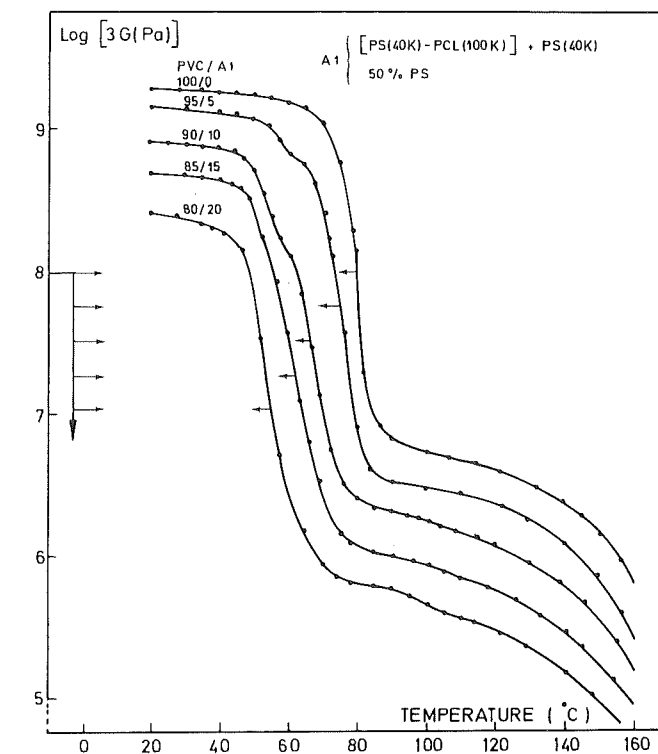

Figure 3 Isochronous (10 s) torsion modulus *versus* temperature curve of PVC ($\bar{M}_n = 43\,000$) and binary blends with increasing amounts of a 30/70 PS–PCL diblock copolymer ($\bar{M}_n(PS) = 40\,000$ and $\bar{M}_n(PCL) = 100\,000$) with homo PS ($\bar{M}_n = 40\,000$) previously added so that the PS content of the additive (A1) is 50%, as in *Figure 2*. For clarity, each curve has been shifted downwards relative to PVC. Arrows indicate the position of log $3G = 8$ for each curve

Table 3 Glass transition temperature of PVC/A1[a] blends of various compositions: comparison of experimental data and values calculated from the Fox equation[28]

Composition (wt%)		T_g (exp.)		T_g (calc.)	
PVC	A1	°C	(K)	°C	(K)
1	0	81	(354)	–	
0.95	0.05	76	(349)	75	(348)
0.90	0.10	67	(340)	68	(341)
0.85	0.15	62	(335)	61	(334)
0.80	0.20	55	(328)	54	(327)

[a] A1 results from the addition of PS ($40\,000$) to the PS ($40\,000$)–PCL ($100\,000$) diblock to such an extent that the PS content is 50%
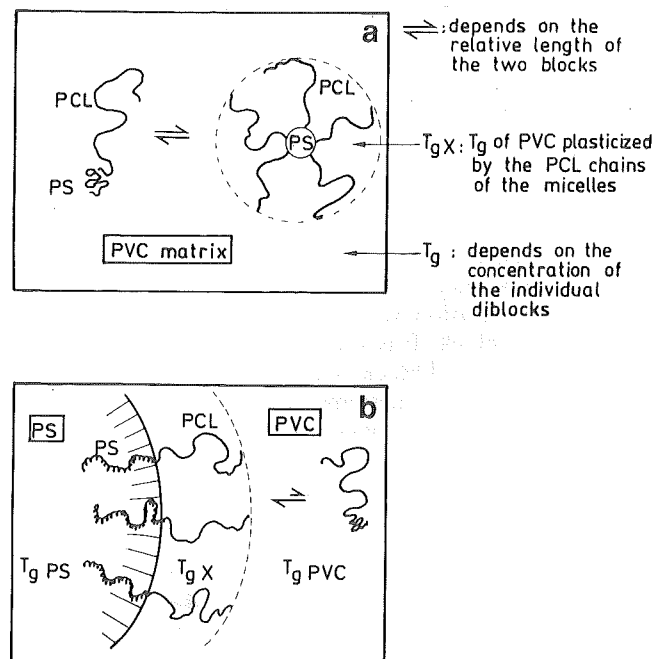
Figure 4 Schematic view of the distribution of a PS–PCL diblock copolymer in binary and ternary blends: (a) PVC + PS–PCL; (b) PS + PVC + PS–PCL

Figure 5 Isochronous (10 s) torsion modulus *versus* temperature curves of PVC ($\bar{M}_n = 20\,000$), PS ($\bar{M}_n = 21\,000$) and PS (40 000)–PCL (38 000) diblock (C1) polyblends of various weight compositions: A, 80/20/0; B, 72/18/10; C, 64/16/20

Figure 6 Isochronous (10 s) torsion modulus *versus* temperature curves of PVC ($\bar{M}_n = 20\,000$), PS ($\bar{M}_n = 21\,000$) and PS (40 000)–PCL (38 000) diblock (C1) polyblends of various weight compositions: A, 66/34/0; B, 60/30/10; C, 53/27/20. Note that the initial composition of the PVC/PS binary blend has been changed from 80/20 in *Figure 5* to 66/34 here

Table 4 Some characteristics of PVC ($\bar{M}_n = 20\,000$), PS ($\bar{M}_n = 21\,000$) and C1 diblock[a] ternary blends

Composition (wt%)			T_g PVC (°C)		T_g (PS) (°C)	PCL (wt%)		Torsion modulus at 90°C ($\times 10^{-7}$ Pa)
PVC	PS	C1	T_{g_x}[b]	T_g		$1 - w_x$[c]	w_{PCL}[d]	
1	0	0	–	81	–	–	–	1.4
0.80	0.20	0	–	80	102	–	–	3.8
0.72	0.18	0.10	55	77	101	0.11	0.064	7.9
0.64	0.16	0.20	48	76	101	0.14	0.13	19
0.66	0.34	0	–	80	100	–	–	13
0.60	0.30	0.10	47	76	100	0.14	0.075	20
0.53	0.27	0.20	42	75	100	0.16	0.15	29
0	1	0	–	–	101	–	–	100

[a]C1 is the PS (40 000)–PCL (38 000) diblock
[b]T_{g_x} is the T_g of PVC plasticized by PCL diblocks
[c]w_x and $(1 - w_x)$ are the weight compositions of PVC and PCL, respectively, in the shell layers of PVC around the PS phases. w_x is calculated from the Fox equation[28] in which $T_g(PVC) = 354$ K and $T_g(PCL) = 202$ K
[d]w_{PCL} is the theoretical weight composition of PCL in PVC

surface active agents in PS–PVC blends. To behave as a surfactant, a molecule must indeed be amphipathic and have as small a tendency as possible to dissolve (or to be dispersed) selectively in one phase of the system. With this in mind, a preliminary requirement is the well known immiscibility of the two blocks[29,30] and the ultimate key parameter is the composition of the diblock copolymer.

PS/PVC/diblock ternary blends

With regard to the possible interfacial activity of PS–PCL diblocks in PS/PVC blends, the 50/50 diblock copolymer is undoubtedly much more suitable than the 30/70 one. *Figures 5* and *6* illustrate the effect that the already mentioned 50/50 diblock (C1) has on the thermal dependence of the isochronous torsion modulus of 80/20 and 66/34 PVC/PS blends, respectively. Three transitions can clearly be identified, i.e. the T_g of each homopolymer, in close agreement with the values exhibited by the unmodified polyblends, and a third T_g (T_{g_x}) due to the addition of the diblock. The last transition must be attributed to plasticization of PVC by the miscible PCL block of the copolymer at the interface, a situation which is reminiscent of that observed in the binary PVC/diblock mixtures. Experimental T_g values are reported in *Table 4*. Clearly, the effect of the diblock on the T_g of PVC strongly depends on the presence of PS. Recall that in the absence of homo PS, the bulk PVC is plasticized to some extent by molecularly dissolved PCL blocks; furthermore, the T_g of PVC is locally decreased as shown by a sub-T_g of ≈ 55°C which is apparently independent of diblock content (*Figures 2* and *3*). In the ternary blend, the sub-T_g (T_{g_x}) is observed to decrease by a few degrees when the diblock content is increased from 10 to 20%, whereas the T_g of PVC is little modified by the diblock whatever its content up to 20%. As a whole, these observations suggest that the diblock copolymer is located mainly at the PVC/PS interface and no longer dispersed in PVC as it is in the
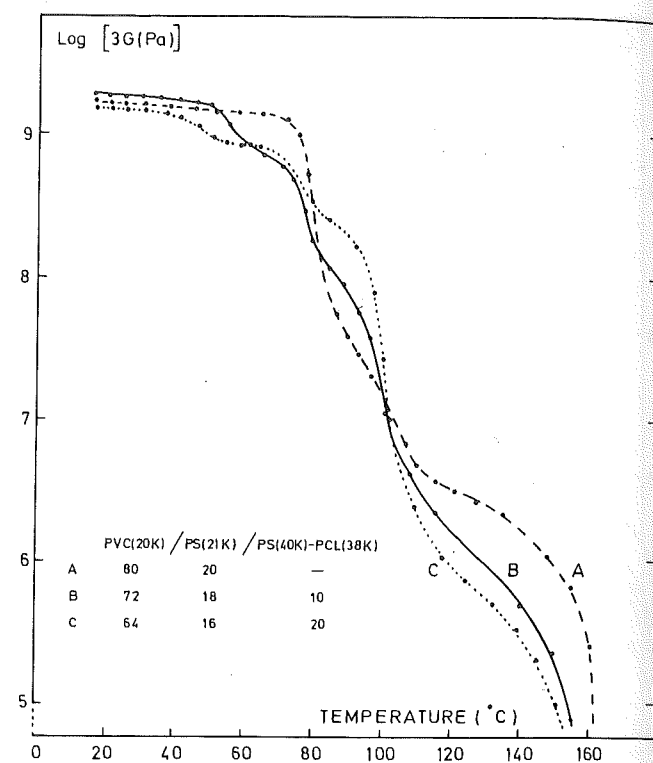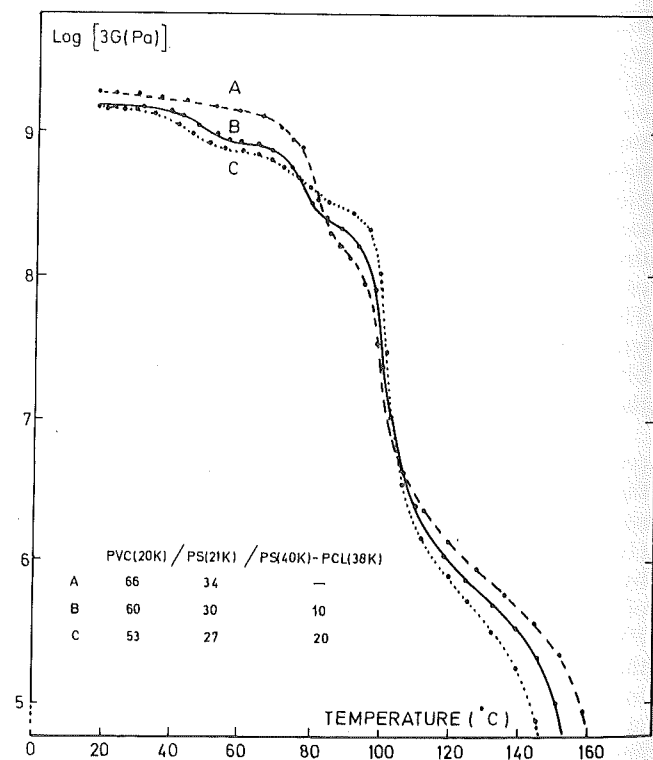
binary blends. Thus, when PVC and PS are melt blended, the 50/50 PS–PCL diblock behaves as an interfacial agent and the PCL blocks attached to the surface of PS phases are confined as an external layer in PVC and are responsible for the occurrence of T_{g_x} (*Figure 4b*). By application of the Fox equation, the composition of the plasticized shell layer can be calculated ($(1 - w_x)$: 11–16%; *Table 4*) and it is found to be largely independent of both the PS and the diblock content. Thus, in the composition range investigated in this study, the average area occupied by one diblock at the surface of the dispersed PS phases is nearly constant, and the mean size of these phases must change in relation to the percentage of PS and diblock in the ternary blends. This is qualitatively illustrated by an increase in opacity of the blends induced by an increasing PS content from 18 to 30% and 16 to 27% at a constant diblock percentage of 10 and 20, respectively (*Table 4*). Furthermore, *Table 4* shows that the PVC/PCL composition of the shell layer around the PS phases is close to the value calculated from the actual amounts of PVC and diblock in the polyblend when 20% diblock is used. Within the limits of accuracy of the T_g data and the applicability of the Fox equation, it might be proposed that the population of PS phases dispersed within PVC is large enough for the PCL shells to contact one another. However, this is not absolutely true since the T_g of the unaffected PVC is still visible, even though significantly reduced compared with the blends containing half the amount of diblock (i.e. 10%). In the particular case of the 66/34 PVC/PS blend, the T_g is so broad that a very diffuse transition from the PVC outside and inside the PCL shell of the stabilized PS particles may be suspected. Note, however, that the modulus range over which the glass transition is observed does not reflect the volume percentage of the related material but strongly depends on the phase morphology itself.

With regard to the mechanical behaviour, the torsion modulus is particularly influenced by the diblock in the temperature range between the T_g values of PVC and PS. For instance, the modulus at 90°C increases with diblock content. This modification is dramatic when the initial PS content is only 20%. A fivefold increase in modulus is then observed upon the addition of 20% diblock compared with a twofold increase for the blend initially containing 34% PS (*Table 4*). The comparison is not, however, straightforward since the relative

position of the plateaus of the glassy PVC and PS phases in the modulus scale depends on the composition of the (unmodified) polyblends. Nevertheless, it can be argued that the increase in modulus at 90°C induced by the diblock reflects the efficiency of the latter to anchor PVC and PS phases to each other. Even when the major PVC phase has become rubbery, the glassy PS domains are still able to impart rigidity to the material, due to an intimate connection to PVC through the diblock. Lastly, it is amazing that, beyond the T_g of PS, viscous flow is improved as the diblock percentage is increased. Thus, in the melt, the diblock copolymer would no longer be a bridging agent between PS and PVC but rather a 'fluidifying' agent. This suggests a profound change in the mutual interaction of each component, for which no explanation is currently available.

Effect of the relative length of homopolymers and of the parent constitutive blocks of diblocks

It can be safely concluded that a 50/50 PS–PCL diblock, the constitutive blocks of which are longer than the related homopolymer chains, is an effective interfacial agent when melt-blended with immiscible PVC and PS. To answer the question of the possible effect of the relative length of block and parent homopolymer on the emulsification process, the same PS/PVC blends as above were modified by a diblock, each constitutive component of which is approximately twice as long (C2 instead of C1), i.e. PCL of molecular weight 90 000 and PS of molecular weight 70 000. *Figure 7* shows that the emulsification capability of C2 is greater than C1. Indeed the torsion modulus at 90°C has increased from 7.9×10^7 Pa (C1) to 18×10^7 Pa (C2), making the glass transition of the unaffected PVC much less pronounced. At a constant diblock content of 10%, a twofold increase of the diblock molecular weight results in a twofold decrease of the number of amphipathic molecules. That reduction does not affect adversely the emulsification of the PVC/PS blends. Rather, longer diblocks enhance the mutual anchoring of the two phases, because of more important chain entanglements between each block of the interfacial agent and the related homopolymer.

To evaluate the situation when the blocks are shorter than the blended homopolymers, copolymer C1 was melt blended with homopolymers of molecular weight higher than the related blocks (PVC, 43 000; PS, 58 000).
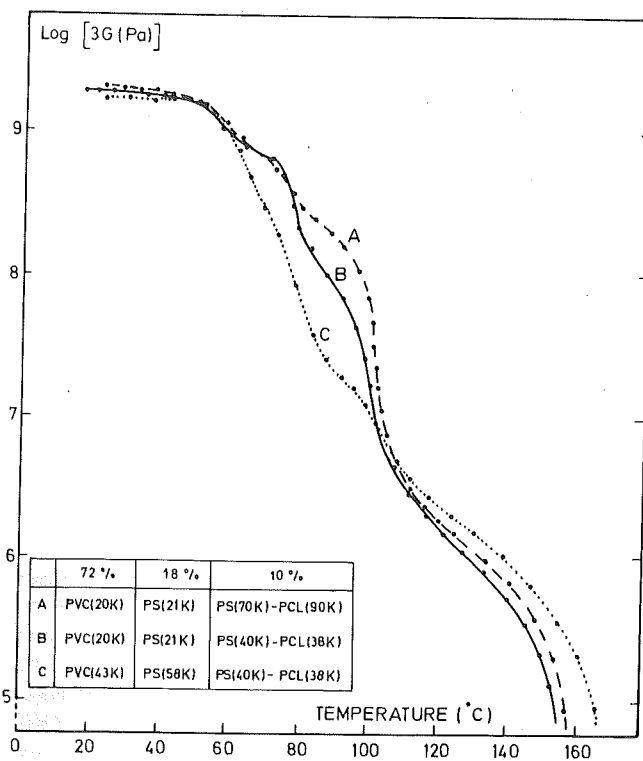
Figure 7 Effect of the relative molecular weight of homopolymers and diblock on the isochronous (10 s) torsion modulus *versus* temperature curves of PVC(72%)/PS(18%)/PS–PCL diblock (10%) ternary blends: A, PVC (20 000)/PS (21 000)/PS (70 000)–PCL (90 000) diblock (C2); B, PVC (20 000)/PS (21 000)/PS (40 000)–PCL (38 000) diblock (C1); C, PVC (43 000)/PS (58 000)/PS (40 000)–PCL (38 000) diblock (C1)

According to *Figure 7*, PS and PVC are still phase separated: the T_g of PS is observed at the usual temperature, but that of PVC extends over a very broad temperature range. In fact, the latter transition appears to result from the overlap of two transitions, the glass transition of the unmodified PVC ($\approx 78°C$) and a lower transition to $\approx 63°C$. Whatever the detailed structure of that broad transition, it indicates a complex situation and most likely a very heterogeneous plasticization of the PVC phase. Note that the modulus at 90°C is now very low (1.9×10^7 Pa) and close to the value reported for the unmodified polyblend (3.8×10^7 Pa).

Undoubtedly, morphological features of PVC/PS blends are largely governed by the length of homopolymers compared with the blocks of the copolymer used as an interfacial agent. When the homopolymers are longer, the situation is worse. This is in apparent contrast to the observations reported for PS/PE blends using h.PBD–PS diblock copolymers[14,18], i.e. when hydrophobic partners interact weakly by Van der Waals type forces. Recall that in the presence of PVC and under shearing conditions, the 50/50 PS–PCL diblock (C1) preferentially forms micelles rather than molecularly dissolved species. When PS is the minor component of the polyblend, as it is in this study, it can be incorporated into the PS core of the micelles as long as its molecular weight is smaller than the related PS block; otherwise it would be rejected from the micelles[31,32]. This excluded PS is not expected to form macrophases in PVC because of the presence of molecularly dissolved diblocks. These initially unassociated diblocks might be adsorbed onto the surface of PS particles and stabilize them against coalescence. Thus, homo PS could be dispersed into PVC

by two distinct mechanisms, resulting in a difference of coverage of the PS phases by PCL blocks and accounting for a heterogeneous plasticization of PVC by the diblock present at the interface. To account for the low modulus at 90°C, and thus an expectedly poor interfacial adhesion, when PS cannot be accommodated into diblock micelles (curve C, *Figure 7*), it has to be assumed that PS rejected from the diblock micelles is not as strongly bridged to PVC as PS dissolved into the micelles. It might be tentatively suggested that not enough diblock molecules are initially available to anchor the PS rejected from the diblock micelles firmly to the matrix. If this is so, one might expect that the final equilibrium situation has not yet been reached.

Ultimate mechanical properties of modified PS/PVC blends

Taking advantage of the availability of a nearly 50/50 diblock copolymer of a high molecular weight (190 000), commercial PVC ($\bar{M}_n = 40\,000$) and PS ($\bar{M}_n = 100\,000$) were melt blended in various proportions, and the blends characterized by stress–strain testing (*Figure 8*). The unmodified polyblends containing up to 80% PVC exhibit the usual brittleness of PS. This implies that, over the major composition range, PS tends to form a continuous phase due to a lower melt viscosity and to impart its poor mechanical resistance to the blends.
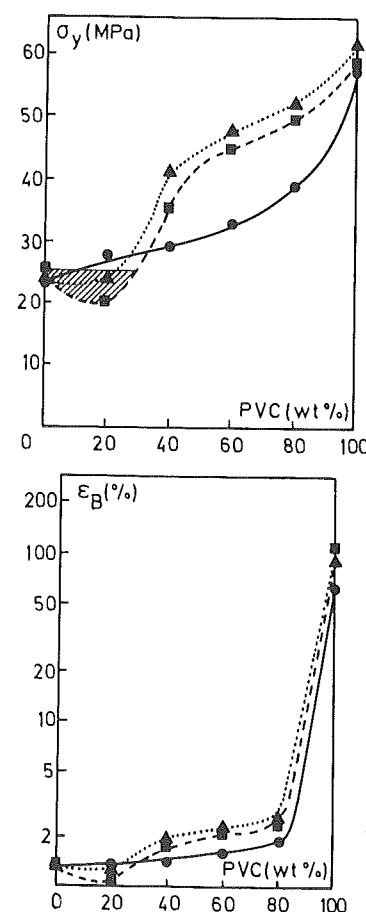

Figure 8 Tensile strength at yield point (σ_y) and elongation at break (ε_B) of PVC ($\bar{M}_n = 40\,000$) and PS ($\bar{M}_n = 100\,000$) blends: ●, without diblock; ▲, with 10% PS (90 000)–PCL (100 000) diblock (C3); ■, with 10% PS (90 000)–Pester (110 000) diblock (C4). The Pester block is a random copolymer of 40% ε-caprolactone and 60% β,δ-methyl-ε-caprolactone

Addition of 10% diblock to blends containing 40% PVC or more has a beneficial effect on the ultimate tensile strength and the elongation at break. All of these blends, however, remain fragile. Similarly, upon the addition of the diblock, the mechanical properties of pure PVC are improved slightly, especially the elongation at break and, to a lesser extent, the ultimate tensile strength and Young's modulus, which increases from 2600 to 2900 MPa. The moderate improvement of PVC and of polyblends containing 40% PVC and more is not consistent with plasticization of PVC by PCL blocks; otherwise, the ultimate tensile strength should decrease as the elongation at break increases. It is most likely due to a stabilized dispersion of rigid PS particles within PVC and to the mutual anchoring of the phases. PS particles might be responsible for crazes that interact favourably
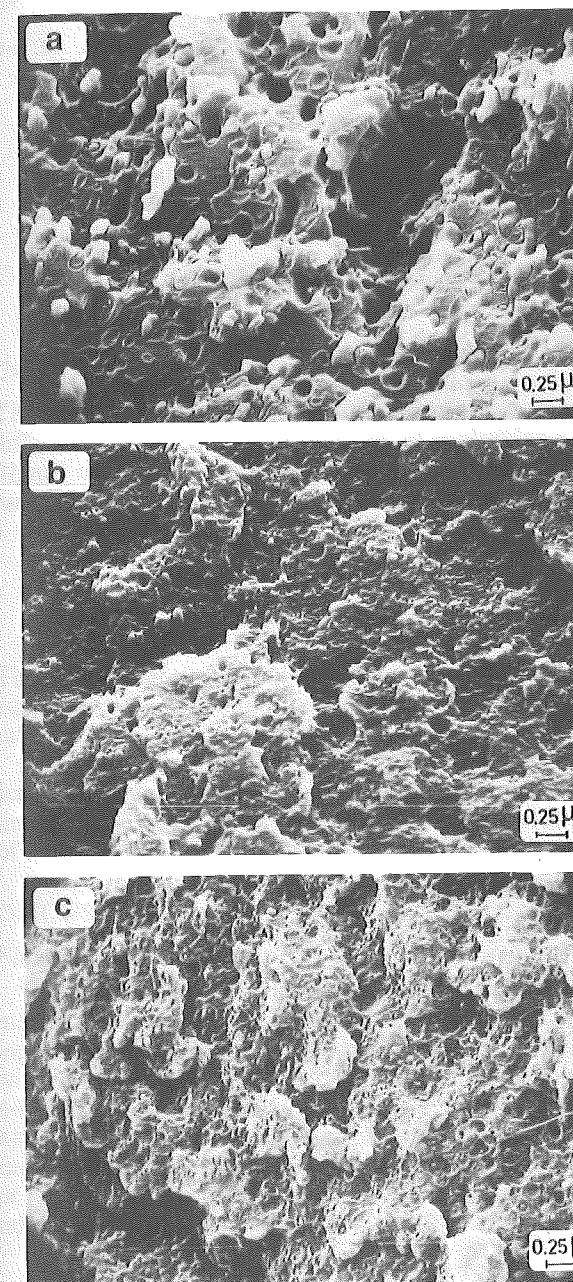

Figure 9 Scanning electron micrograph of the fracture surface of (a) 40% PVC ($\bar{M}_n = 40\,000$) and 60% PS ($\bar{M}_n = 100\,000$) blends with (b) 10% C3 (PS (90 000)–PCL (100 000) diblock) and (c) 10% C4 (PS (90 000)–Pester (110 000) diblock) added, respectively. Composition of the Pester block is given in *Figure 8*

with shear bands, promoted by the deformation of the PVC matrix. The beneficial effect that each type of deformation (crazing of PS and shear bands in PVC) might have on each other no longer occurs when PVC is the minor component (<40%). The reverse situation should occur since the mechanical properties of the blends deteriorate because of the presence of the diblock: an 'allergic' effect emerges. In that case, dispersed PVC particles containing PS–PCL micelles (and thus expected to be plasticized) are not effective in preventing craze propagation and catastrophic failure of the PS matrix. The propensity of PCL to crystallize when mixed with <60 wt% PVC[21] has no effect on the mechanical properties of the emulsified polyblends. Whatever the composition range and particularly one comprising PVC phases rich in PCL blocks (zone of allergy), there is no qualitative difference when crystallizable PCL blocks are replaced by amorphous poly(CL–co-XCL) ones, all the other molecular features remaining constant (*Figure 8*). Crystallinity and miscibility of random copolymers of ε-caprolactone (CL) and β,δ-methyl-ε-caprolactone (XCL) have been discussed elsewhere[33]. Scanning electron microscopy of fracture surfaces of 60/40 PS/PVC blends clearly illustrates the very poor interfacial adhesion of the partners (*Figure 9*): loose dispersed particles (expected to be PVC) and their cavities in the matrix are easily observed. However, upon the addition of the diblock, dispersion of the phases is very much improved whatever the nature of the diblock used.

CONCLUSION

Although interfacial adhesion is a key parameter in alleviating the generally poor mechanical performance of immiscible polymer blends, intrinsic properties of the components must also be considered. These properties must be compatible, i.e. complement each other in such a way that the deficiency of one component can be compensated by the superiority of the second.

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Representation of hydrodynamic data as a function of molecular weight for semi-rigid and rigid-chain polymers*

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Analytical expressions for the molecular-weight dependences of intrinsic viscosity $[\eta]$, sedimentation constant s_0 and diffusion coefficient D are suggested:

$$[\eta] = M^2 (K_1 + K_2 M^{1/2})^{-3}$$

$$s_0 = K_3 + K_4 M^{1/2}$$

$$D = M^{-1}(K_5 + K_6 M^{1/2})$$

As employed for semi-rigid and rigid-chain polymers, the coefficients K_i in these equations are non-sensitive to molecular-weight variation over a wider M range than the numerical coefficients in the well known empirical Mark–Kuhn–Houwink equations: $[\eta] = K_\eta M^a$, $s_0 = K_s M^{1-b}$ and $D = K_D M^{-b}$.

(Keywords: intrinsic viscosity; sedimentation; diffusion; molecular weight; analytical representation)

INTRODUCTION

The intrinsic viscosity $[\eta]$, sedimentation constant s_0 and diffusion coefficient D as functions of molecular weight M are usually represented by well known and widely used Mark–Kuhn–Houwink (MKH) empirical equations:

$$[\eta] = K_\eta M^a \tag{1}$$

$$s_0 = K_s M^{1-b} \tag{2}$$

$$D = K_D M^{-b} \tag{3}$$

The numerical values of coefficients a, b and K_i in equations (1)–(3) have been collected in numerous tables[1].

According to equations (1)–(3), in double-logarithmic scales the dependence of $[\eta]$, D and s_0 on M must be linear. The experimental data obtained over a wide range of M, however, do not always satisfy this requirement.

DISCUSSION

Flexible-chain polymers

For flexible-chain polymers the excluded-volume effects increase the slope of the plots of $\log[\eta]$ and $\log D$ versus $\log M$, i.e. they increase the scaling exponents a and b with increasing M. For polymer–solvent systems with non-linear dependence of $\log[\eta]$ on $\log M$, a few attempts have been made to compose more universal expressions than equation (1) to describe adequately the dependence of $[\eta]$ on M. For this purpose Palit[2] has proposed the relation:

$$100\rho_0[\eta] + \ln M = K'M^{2/3} + K'' \tag{4}$$

where ρ_0 is the polymer density at solute concentration $c \to 0$, and K' and K'' are numerical coefficients.

A more convenient analytical expression has been suggested by Dondos and Benoit[3]:

$$1/[\eta] = -A_2 + A_1 M^{-1/2} \tag{5}$$

The linearity of $1/[\eta]$ plotted against $M^{-1/2}$ confirmed by experimental data[4,5] over a wide M range allows the dependence of $[\eta]$ on M for a flexible-chain polymer to be described by relation (5) with two numerical coefficients A_1 and A_2.

Rigid-chain polymers

For semi-rigid and rigid-chain polymers over a wide M interval, the experimental dependences of $\log[\eta]$ (*Figure 1*) and, to a lesser degree, $\log D$ and $\log s_0$ on $\log M$ are more non-linear functions. The data in *Figure 1* are consistent with the hydrodynamic theory for worm-like chains[11,12]. In particular, Kolomiets and Tsvetkov have shown[13] that the scaling exponent a in equation (1) is a function of the length L and diameter d of the macromolecule and its equilibrium rigidity, which may be characterized by the Kuhn segment length A of the equivalent chain (*Figure 2*). In good agreement with this conclusion are the experimental double-logarithmic plots of $[\eta]$ versus M for the most rigid-chain polymers represented by S-shaped curves, which may be approximated by a straight line only in a narrow M range.

A similar conclusion is also valid for the diffusion–sedimentation data. We have used the theory for translational friction of worm-like sphero-cylinders developed by Yamakawa[11,15] and Fujita et al.[16], which yields expressions (6) and (7) for high and low M values. For $L/A \geqslant 2.278$:

$$D = (kT/3\pi\eta_0 L)\left(B_1(L/A)^{1/2} + B_2 + \sum_{i=3}^{\infty} B_i(A/L)^{(i-2)/2} \right) \tag{6}$$