

# The role of interfacial contact in immiscible binary polymer blends and its influence on mechanical properties

A. Leclair and B. D. Favis\*

*Department of Chemical Engineering, Ecole Polytechnique de Montréal, PO Box 6079, Stn. Centre-Ville, Montréal, Québec, Canada H3C 3A7*

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In this paper an immiscible blend comprised of a crystalline (polyethylene) and an amorphous (polycarbonate) component was studied. Depending on whether the crystalline material is the dispersed phase or matrix, high levels of voiding or good apparent contact, respectively, can be observed. It is shown that the system PC dispersed in HDPE displays a tensile modulus which mimics theoretical behaviour for perfect adhesion even in the absence of an interfacial modifier. The complementary blend of HDPE in PC with the voided interface displays all the characteristics of PC containing dispersed air. The transition from one behaviour to the other is closely related to the estimated region of phase inversion. The same pseudo-adhesion behaviour was not observed in a second amorphous/crystalline system (polystyrene and polyethylene). It is suggested that in order for this behaviour to occur a contraction of crystalline matrix must take place onto a rigid dispersed phase (below its glass transition). Copyright © 1996 Elsevier Science Ltd.

**(Keywords: blend; morphology; compression; voiding; properties)**

## INTRODUCTION

Significant work world-wide is being directed at improving the properties of polymer blends either by chemical modification of the interfacial region or through the addition of modifiers as a third component. In many cases, however, such interfacial agents are either unavailable or, in the case of recycling applications, too expensive. Other approaches must, therefore, be studied.

Kunori and Geil<sup>1,2</sup> studied the mechanical properties of HDPE (high density polyethylene)/PC (polycarbonate) blends. They considered the factors that influence the modulus and the stress as a function of composition and morphology. In that study, they reported that there is no adhesion between the HDPE and the PC and that the HDPE inclusions were loosely sitting in the holes in the PC matrix. They did not, however, suggest an explanation for this observation.

In previous work in this laboratory<sup>3</sup>, it was noted for unmodified polycarbonate (PC)/polypropylene (PP) blends, that significant voiding occurred around the PP phase when it was dispersed in polycarbonate. Interestingly, however, the complementary blend of PC dispersed in PP demonstrated what seemed to be a high degree of interfacial contact. In another study<sup>4</sup>, it was reported for injection moulded PP/PC blends (PP matrix) that the modulus increased with PC concentration despite the absence of an interfacial modifier. It was speculated that this effect was due to the crystalline nature of PP which resulted in a net contraction onto the dispersed PC phase. In this paper the mechanical properties of two

amorphous/crystalline polymer blend systems will be studied. The objective is to investigate in detail the role and influence of interfacial contact on mechanical properties.

## EXPERIMENTAL

### Materials

Two types of blend systems were studied: PS (polystyrene)/HDPE and PC/HDPE. The amorphous polymers used in this paper were the polycarbonate PC (M-2500) supplied by Mobay Corporation and the polystyrene PS (grade 204) from Polysar, while the semi-crystalline polymer, the polyethylene HDPE (Sclair 59C), was obtained from Dupont. The properties of these polymers are summarized in *Table 1*.

### Processing

Pellets of HDPE and PC, and of HDPE and PS were blended in volume concentrations of 0–100% PC or PS. *Table 1* gives the polymer densities at their compounding temperatures (200°C for HDPE/PS blends and 250°C for HDPE/PC blends). To minimize hydrolytic degradation of PC during processing, the blends were first dried at 95°C for about 12 h under vacuum. The polyethylene was stabilized with 0.2% antioxidant (Irganox 1010, Ciba Geigy). Compounding was then carried out in a Brabender mixing chamber under dry nitrogen at 200° or 250°C and 50 r.p.m. for about 5 min. The blends were removed, placed on rectangular plaques and compression moulded at 250°C. *Table 2* summarizes the moulding conditions.

\* To whom correspondence should be addressed

**Table 1** Characteristics of polycarbonate, polystyrene and high density polyethylene resins

	Density 25°C (g cm <sup>-3</sup> ) <sup>a</sup>	Density 200°C (g cm <sup>-3</sup> ) <sup>a</sup>	Density 250°C (g cm <sup>-3</sup> ) <sup>a</sup>	Melting temperature (°C) <sup>b</sup>	Glass transition temperature (°C) <sup>b</sup>	Crystallinity (%) <sup>b</sup>
Polycarbonate (M-2500)	1.12	—	1.08	230–250	150	—
Polystyrene Polysar 204	1.04	0.98	—	190–274	90	—
Polyethylene Sclair 59C	0.95	0.74	0.73	120	-110	70–80

<sup>a</sup> Obtained from suppliers

<sup>b</sup> Measured

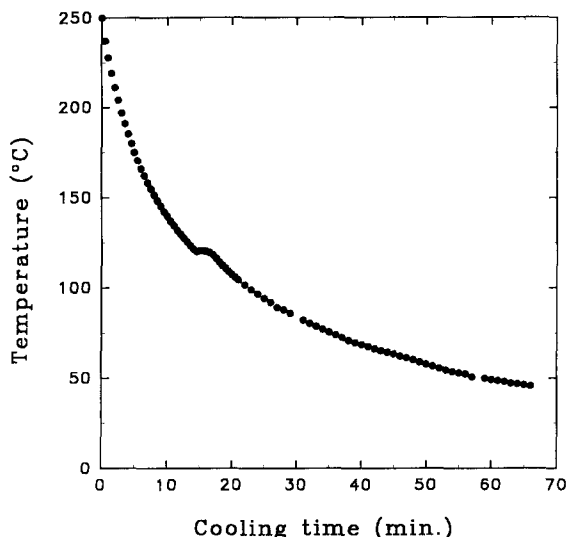
**Table 2** Moulding conditions

Time (min)	Pressure (metric ton)
0–5	0 (softening)
5–8	1
8–11	3
11–15	6 (including degassing)

liquid nitrogen and covered by a thin gold/palladium layer.

*Thermal analysis*

A DSC (model 910) from Dupont Instruments was used to evaluate the crystallinity of the HDPE in the blends. Tests were performed from 25 to 150°C at a heating rate of 20°C min<sup>-1</sup>.



**Figure 1** Cooling profile for HDPE/PC blends after compression moulding

The samples were then slowly cooled at room temperature (Figure 1).

*Mechanical properties*

Tensile samples were machined from the cooled moulds using the dimensions suggested by the ASTM D-638-M-III method. Tensile mechanical tests were performed with the tensiometer M30K from J.J. Instruments. An extensometer (model MTS 6302B) was used to obtain more precise values of the modulus. Tests were performed at 25°C and at a cross-head speed of 1 mm min<sup>-1</sup>. The tensile modulus (*E*), the stress at yield ( $\sigma$ ) and the deformation at yield ( $\epsilon$ ) were obtained in this manner.

*Morphological analysis*

A scanning electron microscope (JEOL JSM 820) was used to examine the shape of the dispersed phase and the interface with the matrix. Samples were fractured in

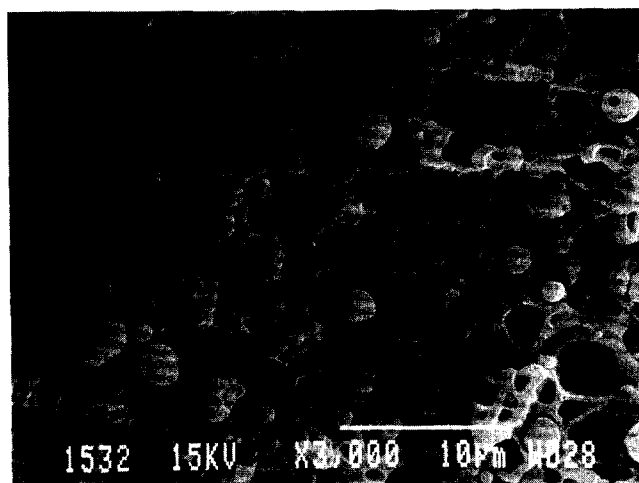
RESULTS AND DISCUSSION

*Morphology*

In Figures 2 and 3 micrographs of HDPE spheres dispersed in PC and PC in HDPE, respectively, are shown. For the purpose of illustrating the interfacial effects, the samples in Figures 2 and 3 were prepared by twin-screw extrusion. The slight tension applied on the strands as they exit the die serves to magnify even further the voiding effect. It is readily apparent that the HDPE dispersed in PC sample shows a significantly high level of voiding as compared to the sample in Figure 3. Similar observations were reported by Favis and Therrien<sup>3</sup> for polypropylene/polycarbonate systems.

*Mechanical properties*

The tensile modulus/composition curve of the PC/HDPE blend is shown in Figure 4. It can be seen that the modulus follows a sinusoidal-type relationship with



**Figure 2** Scanning electron micrographs of fracture surfaces of HDPE dispersed in PC (80% PC/20% HDPE)

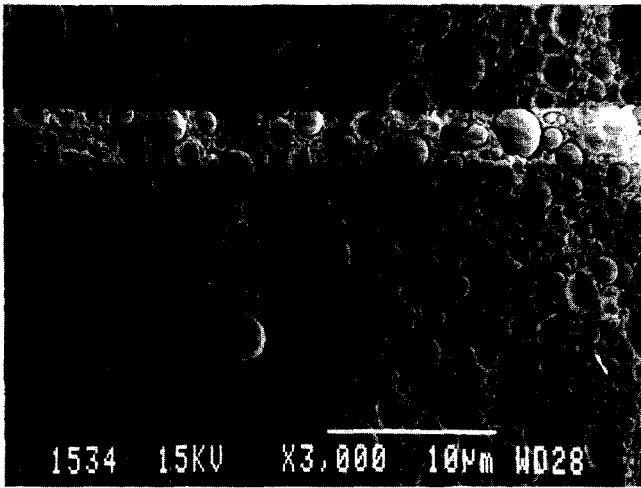


Figure 3 Scanning electron micrographs of fracture surfaces of PC dispersed in HDPE (20% PC/80% HDPE)

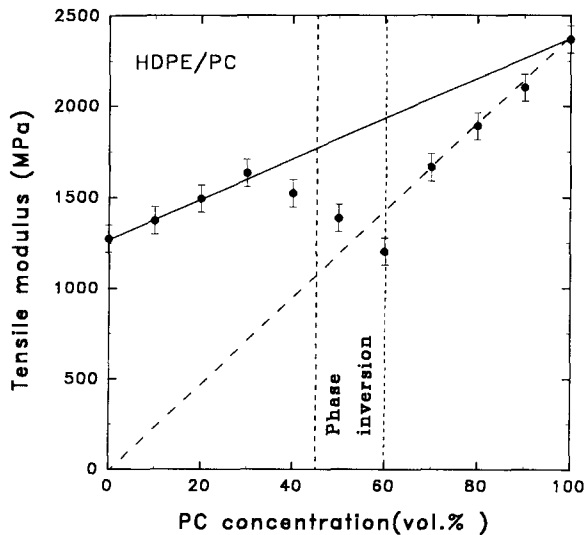


Figure 4 Tensile modulus ( $E$ ) in HDPE/PC blends as a function of composition

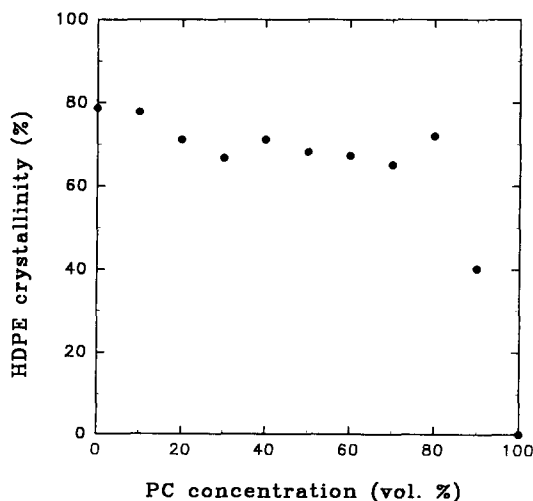


Figure 5 Crystallinity of the HDPE in PC/HDPE blends as a function of composition

composition. From 0 to 30% the modulus displays additive type behaviour. From 40 to 60% PC a major departure from this behaviour is observed and a minimum in the properties is observed at 60% PC. Although the modulus increases from 60 to 100% PC, negative deviation from additivity is observed throughout this final composition region. It is important to note that the region of additive behaviour corresponds to PC dispersed in HDPE while the region of negative deviation corresponds to HDPE in PC. In fact the extrapolation of modulus results at high % PC intersects the origin. This is not unexpected for a system displaying voiding. The intermediate range of 40–60% PC represents the region of phase inversion and co-continuity. Phase inversion has been studied extensively in this laboratory for a variety of systems<sup>5</sup>. The estimated region of co-continuity based on a similar system of the same viscosity ratio is shown in *Figure 4* illustrating a good correlation. The modulus in the additive region at 30% PC is almost 40% greater than that observed at 60% PC. This is a large difference for a tensile modulus, a property which is not as sensitive to the state of the interface as a high strain type property such as elongation at break or impact strength.

A possible explanation for the increasing modulus could be increased crystallinity of the systems. In order to verify this point the crystallinities of the PC/HDPE blends were determined. *Figure 5* shows that there is no major change in the crystallinity of HDPE from 0 to 80% PC. Consequently, the observed increases in the tensile modulus are not caused by an increase in crystallinity with the PC concentration. It is likely that the contraction at the interface caused by the shrinkage of the crystalline HDPE is responsible for the increased modulus. This contraction apparently promotes the stress transfer at the interface and thus increases the mechanical properties of the blend. This is in agreement with the morphology observed in the HDPE/PC blends when the HDPE is the matrix (*Figure 3*). In the following section it will be shown that the sinusoidal-type dependence observed in *Figure 4* can be predicted by theoretical expressions concerning the behaviour of composite materials displaying perfect and poor adhesion.

#### Theoretical considerations

The theoretical estimation of the elastic properties of a two-phase composite system from the properties of their constituent phases has been known for some time. Nielson<sup>6</sup> and more recently Manson and Sperling<sup>7</sup> have presented extensive reviews on these theories and equations. Most of the proposed models assume that perfect adhesion exists between the matrix and the dispersed phase. The inclusions are considered to be spherical in shape and are embedded in an isotropic matrix.

In all of the following equations, subscript 1 refers to the matrix and 2 refers to the dispersed phase,  $E$  is the Young's modulus of the blend,  $\phi$  is the volume fraction and  $\nu_1$  is the Poisson's ratio for the matrix.

One of the first equations developed was that of Einstein<sup>8</sup> (equation (1)). It is valid only at low concentrations of filler (<5%) and assumes the filler is much more rigid than the matrix. This equation is not really applicable to polymer blends. For the case of no adhesion between the phases equation (1) is:

$$E = E_1 * (1 + 2.5 * \phi_2) \quad (1)$$

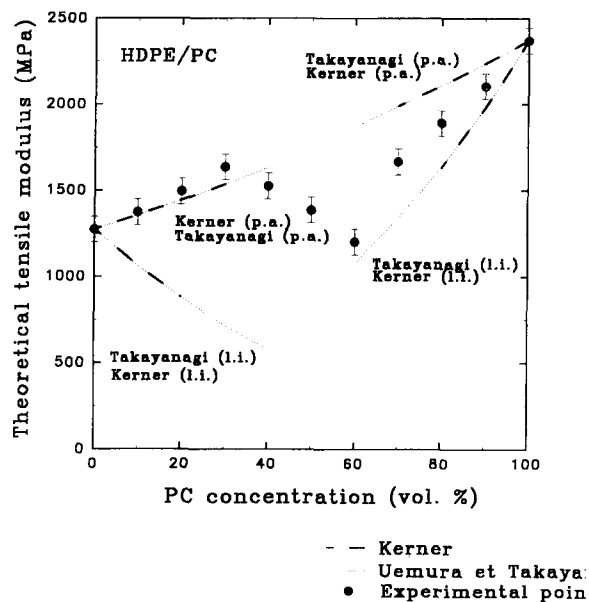


Figure 6 Comparison of the theoretical and experimental tensile moduli of PC/HDPE blends as a function of composition. In the models p.a. refers to perfect adhesion and l.i. refers to loose inclusions

Sato and Furukawa<sup>9</sup> developed a theory for the case in which the adhesion between two phases is weak. The matrix is assumed to deform, forming elliptical cavities around each inclusion.

Kerner<sup>10</sup> developed a model for the shear modulus of a composite that can be applied to the Young's modulus of a blend assuming that the matrix and the dispersed phase Poisson ratios are the same and equal to 0.5. Similar equations have been obtained by Uemura and Takayanagi<sup>11</sup>.

For a system having perfect adhesion (p.a.) at the boundary, the Takayanagi model may be written as:

$$E = E_1 \frac{(7 - 5\nu_1)E_1 + (8 - 10\nu_1)E_2 - (7 - 5\nu_1)(E_1 - E_2)\phi_2}{(7 - 5\nu_1)E_1 + (8 - 10\nu_1)E_2 + (8 - 10\nu_1)(E_1 - E_2)\phi_2} \quad (2)$$

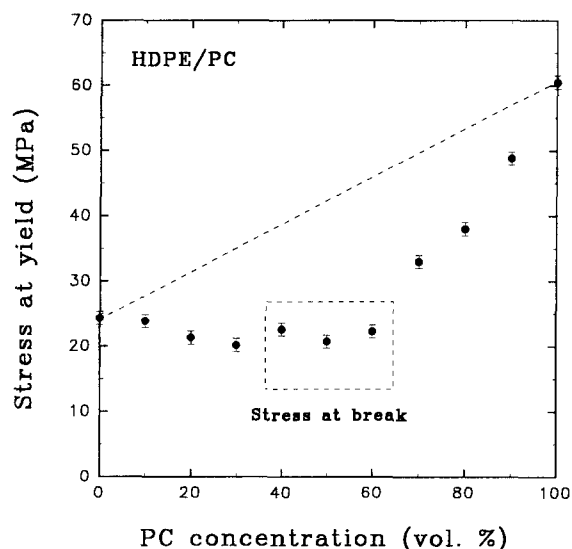
For a system with no adhesion (voids at the interface), equation (2) is reduced by extrapolating  $E_2$  to zero to:

$$E = E_1 \frac{(7 - 5\nu_1)E_1 - (7 - 5\nu_1)E_1\phi_2}{(7 - 5\nu_1)E_1 + (8 - 10\nu_1)E_1\phi_2} \quad (3)$$

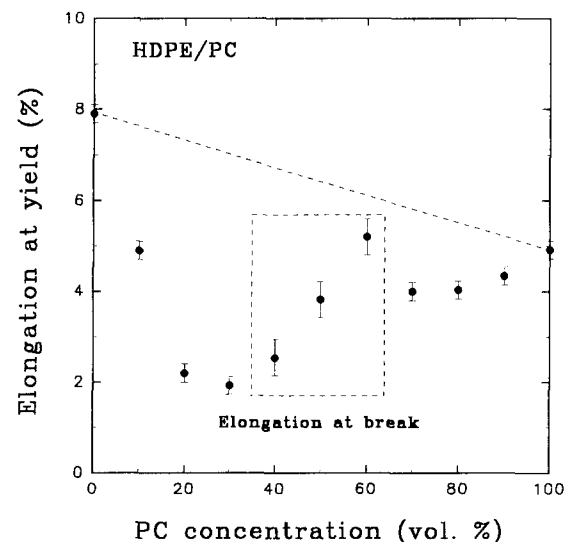
The applicability of both the Kerner and Takayanagi equations is explained by the fact that these equations are based on an analysis of the effect of uniform hydrostatic compression and uniform tension acting on a particle. These equations also take the Poisson's ratio into consideration. The Einstein and Furukawa equations, which are less elaborate, are only based on the composition and matrix modulus.

Using experimental data and Poisson ratios of 0.5 for PC and PS, and 0.4 for HDPE, these theoretical equations can be used to predict the modulus as a function of  $\phi_2$ . The results for the HDPE/PC blends are shown in Figure 6.

For the HDPE/PC blend, even though there is no adhesion between the two phases<sup>1</sup>, the Takayanagi and



a



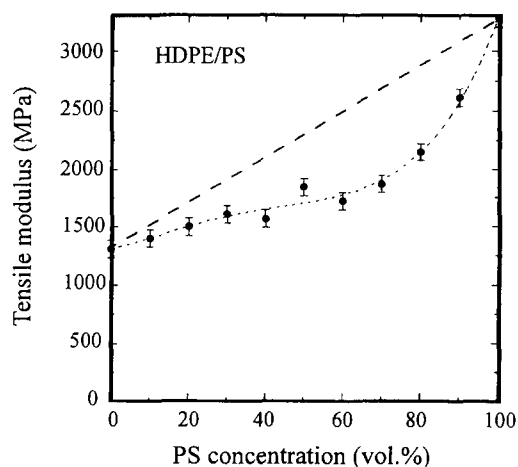
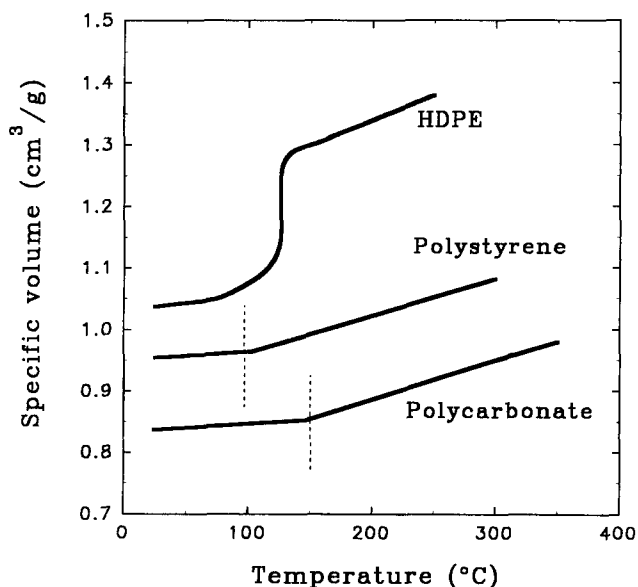
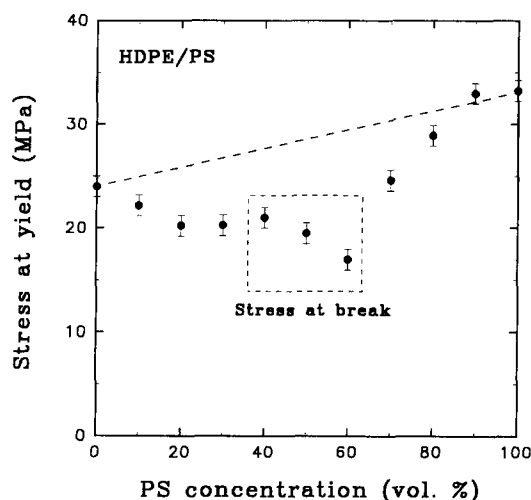
b

Figure 7 (a) Stress at yield in HDPE/PC blends; (b) elongation at yield in HDPE/PC blends

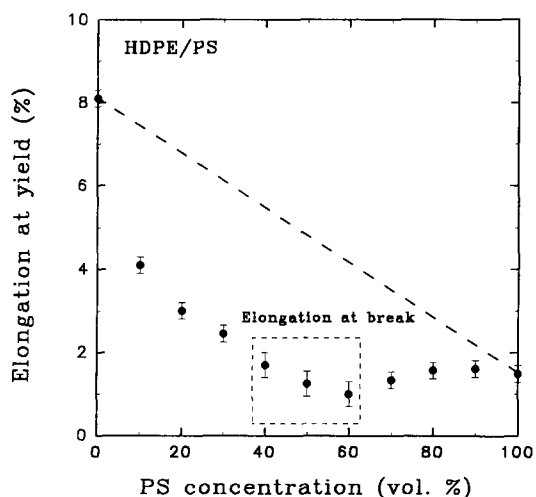
Kerner equation for perfect adhesion shows the best fit. The experimental data closely follow the Kerner (p.a.) equation up to 0.3 volume fraction in agreement with what was expected from our morphological investigation. The contraction of the HDPE on the PC would explain the applicability of equations demonstrating perfect adhesion. The observed interfacial contact apparently facilitates stress transfer in mechanical tension.

For the complementary blend (>70% PC), the modulus does not follow the Kerner (p.a.) equation but approaches that for loose inclusions (l.i.). The system of HDPE/PC can be regarded to be mechanically equivalent to PC containing holes<sup>1,2</sup>. For a system with p.a. followed by l.i. behaviour, it should be noted that the Kerner and Takayanagi equations would predict a sinusoidal dependence of the modulus with the composition as was demonstrated experimentally for PC/HDPE. Indeed, the observed additivity and negativity are well predicted by these models as well as the inflexion point observed at phase inversion.

Evaluation of the other mechanical properties such as stress ( $\sigma$ ) and elongation at yield ( $\epsilon$ ) do not show the same behaviour as the modulus. Figure 7 (a and b)


 Figure 8 Tensile modulus ( $E$ ) in HDPE/PS blends

 Figure 10 Dependence of specific volume of various polymers on temperature<sup>15</sup>


a



b

Figure 9 (a) Stress at yield in HDPE/PS blends; (b) elongation at yield in HDPE/PS blends

displays a negative deviation for the whole range of composition. Note that samples with 40, 50 and 60% PC show brittle behaviour and no yield was observed. In those cases, the yield properties tend to be the ultimate properties. These poor results at yield as compared to the modulus results are not unexpected. The compression of the matrix onto the dispersed phase allows for good

stress transfer under conditions of very low deformation. As soon as higher deformation is applied to the sample this contact will be disrupted since there is no actual chemical bonding or chain entanglement present at the interface.

A second system was also studied in order to gain a greater understanding of the compression behaviour. The system chosen was HDPE/PS since it also represents a crystalline/amorphous material. The modulus is shown as a function of composition in *Figure 8*. In light of the PC/HDPE results, the variation of the PS/HDPE modulus is surprising. None of the main features of the modulus/composition dependence observed for PC/HDPE such as a sinusoidal dependence, additivity and correlation to phase inversion are evident.

*Figure 9 (a and b)* shows the stress at yield and the elongation at yield/composition curves for the HDPE/PS blend. As in the HDPE/PC blends, properties at yield show a negative deviation for the whole range of composition. These results are in agreement with the literature. Indeed it has been demonstrated many times that HDPE/PS blends give invariably poor mechanical properties<sup>12-14</sup>.

#### Specific volume/temperature effects

The specific volume as a function of temperature for the pure components considered in this study are shown in *Figure 10*<sup>15</sup>. It is interesting to note from this figure that during the slow cooling, the PC becomes a solid glass well before the crystallization of the HDPE. A HDPE contraction would then occur on the dispersed PC which is already in solid form, thereby concentrating the stresses at the interface. *Figure 11 (a and b)* shows idealized diagrams of HDPE in PC and PC in HDPE, respectively. These figures illustrate the mechanisms related to voiding and the high degree of interfacial contact, respectively. In the case of the HDPE/PS blend, the PS is still in a deformable state during the crystallization of the HDPE phase. Indeed, during the crystallization of the HDPE at 120°C, PS is above its glass transition (90°C). While the crystallization of the HDPE

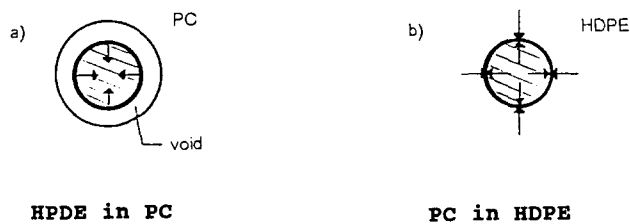


Figure 11 Idealized diagram showing the (a) voiding and (b) compression effects for HDPE/PC blends

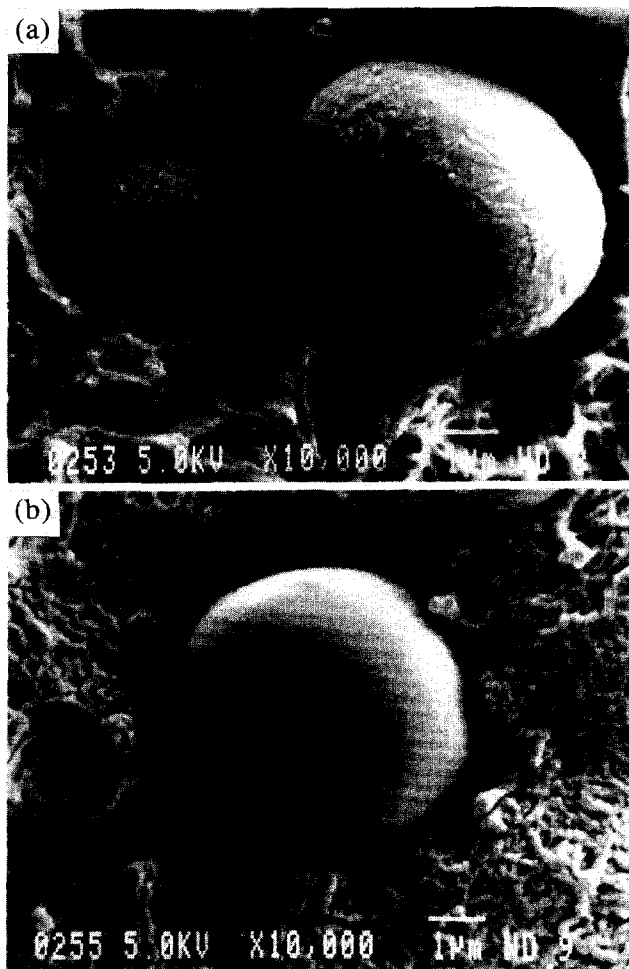


Figure 12 Scanning electron micrographs of blend fracture surfaces at high magnification ( $\times 10\,000$ ): (a) 20% PS/80% HDPE—rough surface; (b) 20% PC/80% HDPE—mirror-like surface

is taking place, it would be expected to result in local deformations of the rubbery PS material with a likely possibility of microvoiding occurring due to the high immiscibility of these two components. It is interesting to note that micrographs (Figure 12) of the dispersed PC in

PC/HDPE blends illustrate a very smooth surface, whereas the surface of dispersed PS in the PS/HDPE blends is very rough. These observations would support the above explanation.

### CONCLUSION

It is shown that the modulus of slowly cooled polycarbonate/high density polyethylene blends can be dramatically influenced by composition and follows a sinusoidal dependence. The modulus shows alternately additive behaviour at low %PC and high negative deviation from additivity at high %PC. These results are explained by a mechanism based on high pseudo adhesion due to the contraction of the crystalline HDPE matrix onto an amorphous PC dispersed phase and high voiding for the complementary blend. The results obtained correlate closely with the expected region of phase inversion and are supported by known theoretical expressions for composite materials. Scanning electron micrographs illustrate good apparent contact for PC dispersed in HDPE and high levels of voiding for HDPE dispersed in PC. Parallel experiments on polystyrene/high density polyethylene blends indicate that in order to obtain an increased modulus in these immiscible blends, the contraction should take place on a non-deformable surface. This study has shown that it is possible to significantly influence the modulus in immiscible polymer blends based on the specific volume/temperature relationship of the pure base polymers.

### ACKNOWLEDGEMENT

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