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Investigation of the melt interface between polyethylene and polystyrene using neutron reflectivity

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The characteristics of the interface between immiscible polymers, semicrystalline polyethylene (PE) and amorphous deuterated polystyrene (dPS), were determined in the melt state, using the neutron reflectivity technique. The neutron reflectivity profiles of PE–dPS bilayer samples were measured *in situ* at 150°C in the melt regime giving a melt interfacial roughness, σ_{12}, of 1.18 ± 0.33 nm. The measured interfacial width consists of a true interfacial width, l_t, convoluted with a width, l_0. The latter has been variously described by a number of authors as a capillary wave interfacial width or an initial width. From the true interfacial width the Flory–Huggins–Stavermann interaction parameter, χ, was calculated. The calculated values of χ were shown to differ by almost an order of magnitude from each other depending on the definition of l_0 used. These values are compared with other values of χ obtained via theoretical interpretations of interfacial tension measurements and solubility parameter determination. It is shown that neither definition of l_0 is totally satisfactory. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: Flory–Huggins χ parameter; polystyrene–polyethylene interface; neutron reflectivity)

Many common polymers such as polyethylene (PE) are semicrystalline. At room temperature this causes the surface of such films to be molecularly rough. Traditional room temperature neutron reflectivity measurements of such films therefore suffer from a drastic loss of specular reflectivity associated with the surface roughness, making such measurements at best very difficult or, more likely, impossible. Despite this the interfacial properties of such crystalline polymers are of immense interest. In order to overcome these experimental difficulties, and also to simulate the melt blend behaviour occurring in industrial processes, we have devised a simple cell which allows reflectivity measurements at elevated temperatures (< 200°C).

Previous experiments have demonstrated that merely heating a crystalline polymer film of, for example, PE supported on a silicon wafer, into the melt regime is insufficient to produce meaningful reflectivity profiles[1]. Although the molecular roughness associated with the polymer crystallinity is lost in the melt regime the surface still suffers from long-range waviness which adversely affects the reflectivity profile. The cell we have developed is based on the solid–liquid cells which are now being used routinely in neutron reflectivity measurements for investigation at the solid–liquid interface (*Figure 1*). By providing a molecularly smooth and flat surface to which the polymer moulds, both the molecular roughness and long-range waviness are successfully removed in the melt regime. This, therefore, is different from conventional reflectivity techniques applied to amorphous polymers where 'melt' behaviour is observed by freezing in the structure and measuring the sample at room temperature. It is clearly for use with immiscible or partially miscible systems for which an equilibrium melt interface exists.

Experimental

The cell consists of a brass trough which holds the PE against which a spin-coated silicon block is placed and held in position with a metal retaining plate (*Figure 1*). The cell is heated by means of thermostated cartridge heaters in the brass base. The cell is designed such that the neutron beam passes directly through the silicon with a transmissivity of the order of 90% for the size of block used. The silicon blocks used (supplied by Semi-Conductor Processing, Boston, USA) were used without stripping of their native oxide layer. Although there may be thermal loss for the top surfaces of the cell it was found that the polymer within the cell attains and holds the required cell temperature with approximately 10 min of heating, depending on the set point. During the experiment at the elevated temperatures the whole cell is housed inside an inert atmosphere box with neutron-transparent quartz windows front and back. No thermal degradation was observed at the temperatures used in these experiments. Alignment of the cell was achieved using the neutrons themselves, so there was always a delay of at least 45 min from the time of starting to heat up to the point where reflectivity data collection started. During this pre-data collection period the cell was allowed to heat to the desired set point and left for 10 min before proceeding with the alignment process. From other experiments and initial reflectivity measurements this temperature stabilization and alignment

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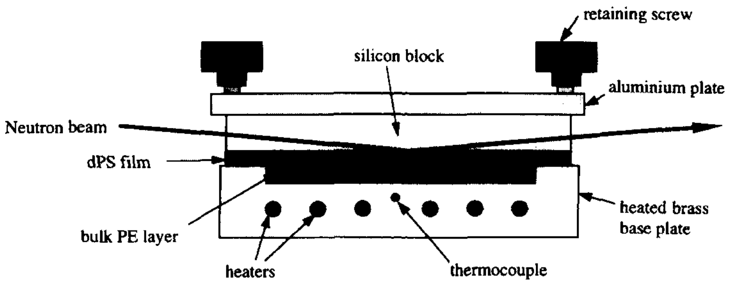

Figure 1 Schematic cut-away view of the neutron reflectivity cell used for investigation of polymer interfaces in the melt

Table 1 Polymer characteristics used in this study

Polymer	M_w	M_w/M_n	Supplier
Deuterated polystyrene (dPS)	190000	1.08	Professor R. W. Richard's group, Durham, UK
Polyethylene (PE)	43700	5.60	DSM Research, The Netherlands

procedure was found to be sufficient for the systems under investigation to reach equilibrium. All the data reported here were collected on the CRISP reflectometer at the ISIS pulsed neutron source at the Rutherford Appleton Laboratory. To achieve a large Q range ($Q = (4\pi \sin\theta)/\lambda$) three different angles were measured for each sample, with the pre-sample collimation slits varied such that at each angle a constant resolution and illuminated area was measured. The cell was calibrated by taking transmission measurements of the silicon block, giving the scaling factors essential for data normalization. Data fitting was carried out assuming PE and silicon as bulk media and deuterated polystyrene (dPS) as a single layer and using both non-linear least squares fitting routines[2,3] and maximum entropy methods[2,4]. No specific layer within the fitting model for the native silicon oxide was found to be necessary.

A series of samples was run, in order to evaluate the cell and obtain individually the scattering length densities of silicon dPS and PE at 150°C. The characteristics of the polymers used in this study are listed in *Table 1*. Reflectivity measurements of silicon against PE and silicon against dPS were both measured at 150°C in the melt cell. A combination of both these measurements allowed us to extract the necessary scattering length densities (ρ_z), from fits to the reflectivity curves, which gave $\rho_z(\mathrm{Si}) = 1.77 \times 10^{-6}\,\text{Å}^{-2}$, $\rho_z(\mathrm{dPS}) = 5.7 \times 10^{-6}\,\text{Å}^{-2}$ and $\rho_z(\mathrm{PE}) = -2.82 \times 10^{-7}\,\text{Å}^{-2}$ at 150°C. These are consistent with the calculated values derived from bulk room temperature values corrected for density differences at 150°C.

Determination of χ

Determination of the interfacial width is a direct route to obtaining the Flory–Huggins χ interaction parameter for immiscible blends[5,6]. When applied to these systems the χ parameter can be derived within the mean field approximation from the minimization of the free energy equation used to describe the interface of an incompatible blend. This method of the Flory–Huggins–Stavermann χ interaction parameter determination was applied to the PE–dPS system at 150°C. The deuterated PS (dPS) layer of approximately 70 nm thickness was spun directly onto the silicon block, which was placed against the PE press moulded directly into the brass cell base. The measurement procedure has been described above. A representative reflectivity profile obtained from one of the three separate samples measured is shown in *Figure 2*, where the points are the data and the line is calculated from the best fit model. The lack of damping in the Kiessig fringes at high Q demonstrates not only the quality of the data obtained from the CRISP neutron reflectometer but also that the cell works as well as expected in giving reflectivity interfaces without any long-range waviness.

For the general case of two homopolymers (1 and 2) with degree of polymerization N_1 and N_2, respectively, minimization of the free energy equation eventually gives, for χ[5],

$$\chi = \left(\frac{a}{l_t\sqrt{6}}\right)^2 + \frac{\pi^2}{6}(N_1^{-1} + N_2^{-1}) \tag{1}$$

Here l_t is the true interfacial width between polymers 1 and 2, and a is the mean segment length. It can be seen that as N tends towards infinite molecular weight, equation (1) becomes very sensitive to the values of l_t and a. It should also be noted that in the derivation of equation (1), Schubert *et al.*[5] have used a hyperbolic tangent function interfacial profile. Although the fitting routines mentioned above typically use a Gaussian interfacial profile, for these immiscible blend systems the interfacial width is small enough that a hyperbolic tangent and a Gaussian interfacial profile become indistinguishable. The roughness, σ_{12}, is defined as one standard deviation of a half-Gaussian interfacial profile, so that the interfacial width, l, is defined as $l = \sqrt{(2\pi)}\sigma_{12}$. From the model fits to the reflectivity data plots for the three samples an interfacial roughness, σ_{12}, between the dPS and PE at 150°C equal to 1.18 ± 0.33 nm was obtained. This translates into a measured interfacial width, l, of 2.96 ± 0.84 nm. This compares to a theoretically calculated interfacial width of 1.5 nm obtained from the theory of Helfand and Sapse[7], for a PS–PE system at 140°C. This theory uses Gaussian random walk statistics to describe the interface between two immiscible polymers. It has the advantage over previous theories since it is more generally applicable

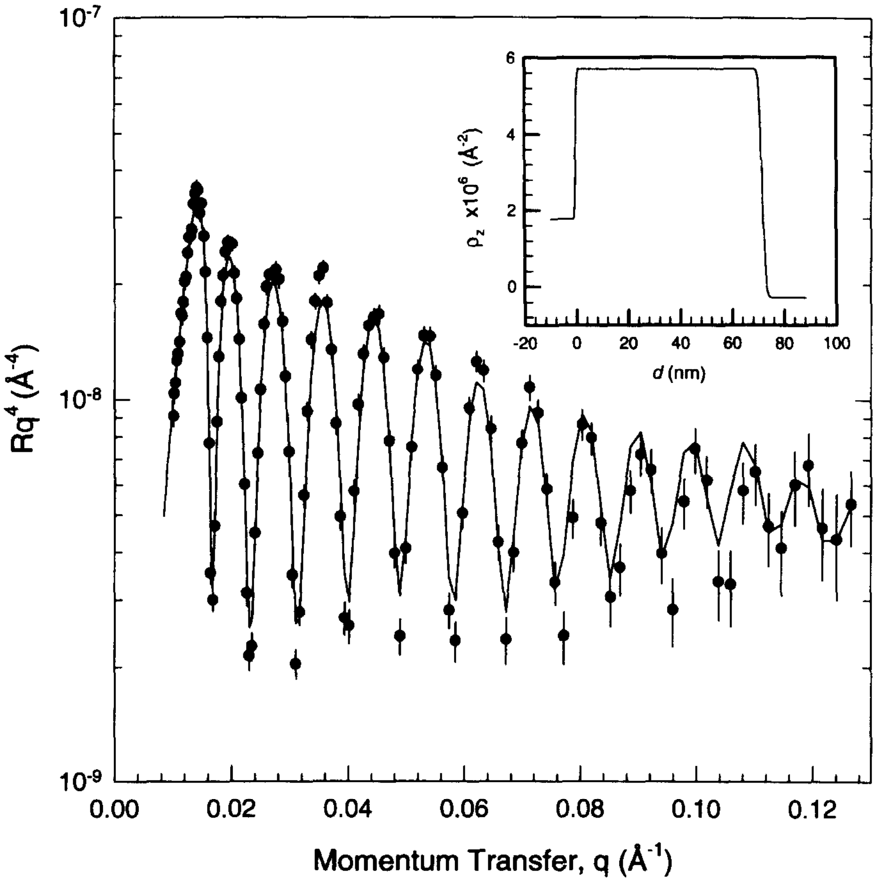

Figure 2 Reflectivity profile plotted as Rq^4 obtained from one of the samples of Si/dPS/PE at 150°C. The experimental data points are plotted as closed circles, and the best fit model over-plotted with a line assuming a σ_{12} of 1.18 nm. Inset is the scattering length density profile of the model used to produce the best fit

and removes the assumption that the properties of the polymers are not identical. The discrepancy between our measured interfacial width and the Helfand and Sapse theory derives from the measured interfacial width, l, being a convolution of the true interfacial width, l_t, and a secondary width, l_0, such that

$$l = (l_0^2 + l_t^2)^{1/2} \qquad (2)$$

The value of l_0 has variously been interpreted in the literature by Shull *et al.*[8] and Müller *et al.*[9] as a capillary wave interfacial width, and by Stamm *et al.*[5,10] as a width equal to the interfacial width in the as made state before any annealing.

Stamm *et al.* defines l_0 as an empirical constant, which is clearly dependent on the polymer pairs and method of sample preparation. Shull *et al.* directly extend ideas derived from theories of capillary waves at the liquid–vapour interface to polymeric interfaces. The mean square displacement of the interface from its average position is obtained from the interfacial tension, such that

$$l_0^2 = \left[a\rho_0(\chi/6)^{0.5}\right]^{-1} \ln(\lambda_{\max}/\lambda_{\min}) \qquad (3)$$

where ρ_0 is the segment density and $\lambda_{\min}$ and $\lambda_{\max}$ are, respectively, the minimum and maximum wavelengths of the capillary fluctuations. The value of $\lambda_{\min}$ depends most significantly on the interfacial tension between the polymers, and therefore a good approximation is provided by the intrinsic interfacial width. Although Shull *et al.*[8] estimate $\lambda_{\min} = 3.0$ nm for a PS–PMMA (polymethyl methacrylate) system, this value is used in the following calculations as a reasonable approximation for the current system because the logarithmic term in equation (3) is insensitive to variations in $\lambda_{\min}$. The value of $\lambda_{\max}$ of the capillary wave for an interface between two semi-infinite media is related to the neutron lateral coherence length. Ignoring the possible complication of a finitely thin layer, a good approximation of $\lambda_{\max} \approx 1\ \mu$m is related to the characteristics of the neutron beam. Müller *et al.*[9] using Monte Carlo simulations have shown that interfacial broadening from long-range capillary wave fluctuations leads to logarithmic divergence of the interfacial width, such that $l = \{l_t^2[1 + c\ \ln(L/s)]\}^{0.5}$. Here L is the lateral dimension of the system, and c and s are parameters which are system dependent. Although the validity of this equation has been confirmed with Monte Carlo simulations on models of binary alloys, the exact form of c and s has yet to be determined satisfactorily[9], and therefore this approach cannot be applied directly.

For the current dPS–PE melt system, it is not possible to measure l_0 defined by Stamm *et al.* Before annealing, the crystallinity of the PE makes the interface macroscopically rough[1]. Estimates for l_0 have been made by comparison to values obtained from immiscible amorphous polymers prepared in a similar method. This gives l_0 in the range 1.2–2.5 nm, which corresponds to $1.57 \leq l_t\ (\mathrm{nm}) \leq 2.68$. Average segment lengths obtained from the literature give for PS $a = 0.68\ \mathrm{nm}$[11,12] and for PE $a = 0.88\ \mathrm{nm}$[13]. Inputting the values for N(PE) = 1560

Table 2 Comparison between measured and calculated values of interaction parameter, χ, listed according to their source

		γ (mN m^{-1})		
Interaction parameter, χ		4.1–4.9[a]	4.6[b]	5.9[c]
Current work (l_0 = 1.2–2.5 nm)	0.016–0.043	–	–	–
Current work (l_0 = equation (3))	0.141 ± 0.086	–	–	–
Equation (4)	0.026	–	–	–
Helfand *et al.*[19]	–	0.035–0.049	0.043	0.071
Broseta *et al.*[20]	–	0.036–0.050	0.045	0.072
Tang and Freed[21]	–	0.037–0.051	0.073	0.073

[a] From Elemans *et al.*[22]
[b] From Helfand and Sapse[7]
[c] From Wu[23]

and N(PS) = 1696, l_t and an average value for a = 0.78 nm into equation (1), gives a value of χ in the range 0.016–0.043 at 150°C. Using the method of Shull *et al.* by rearranging equation (2) in terms of equations (1) and (3) and inputting the measured value of l, N(PE), N(PS), a and $\rho_0 = 6.06 \times 10^{-3}$ Å^{-3}[8], gives a value of $\chi = 0.141 \pm 0.086$ at 150°C. Clearly then there is a large discrepancy between these methods of calculating χ and below follows an attempt to reconcile these data to values of χ derived indirectly from other experimental methods.

Comparison to indirectly derived values of χ

Unfortunately, no directly measured literature values for χ have been found for this PE–dPS system. To compare the current measured value a number of indirect methods have been used. χ values can be determined from the solubility parameters, δ_i, of the two components, i = 1 or 2[14,15]:

$$\chi = \frac{V_1}{RT}(\delta_1 - \delta_2)^2 \tag{4}$$

where V_1 is the molar volume of the smallest species and obtained by the parachor group contribution method described by van Krevelen[16]. Polyethylene has the smaller molar volume, $V_{\mathrm{PE}} = 32.8\,\mathrm{cm^3\,mol^{-1}}$. Average values of δ_i taken from literature are 16.5 (J cm^{-3})$^{0.5}$ for PE and 18.2 (J cm^{-3})$^{0.5}$ for PS[17,18]. This gives a calculated $\chi = 0.026$ from substitution of the appropriate parameters into equation (4). An alternative but rather indirect method of evaluating the measured χ if the data are available is from interfacial tension, γ, measurements. A number of slightly differing theoretical approaches have derived expressions relating γ in terms of χ[19–21]. The equation used to derive the values of χ from literature values of γ, are

$$\gamma = \left(\frac{\chi}{6}\right)^{1/2} a\rho_0 k_{\mathrm{B}} T\left(1 - \frac{2\log 2}{\chi N}\right)$$

(Helfand *et al.*[19])

$$\gamma = a\left(\frac{\chi}{6}\right)^{1/2} \rho_0 A k_{\mathrm{B}} T\left[1 - \frac{\pi^2}{12\chi}\left(\frac{1}{N_1 + N_2}\right)\right]$$

(Broseta *et al.*[20])

$$\gamma = a\left(\frac{\chi}{6}\right)^{1/2} \rho_0 A k_{\mathrm{B}} T\left[1 - 1.35\left(\frac{2}{\chi N}\right)\right]$$

(Tang and Freed *et al.*[21])

(The notation has been modified from the original references to be consistent with equations (1)–(4)). Here $N = 1/2(N_1 + N_2)$ and A is the interfacial area; all the other notation is given above. The interfacial tension between high-density PE and PS has been measured by Elemans *et al.* using a breaking thread method, giving values of γ in the range 4.1×10^{-3}–$4.9 \times 10^{-3}\,\mathrm{N\,m^{-1}}$ at 200°C[22]. These values agree well with the calculated values from the theory of Helfand and Sapse, who obtained $\gamma = 4.6 \times 10^{-3}\,\mathrm{N\,m^{-1}}$ and l = 1.5 nm for a PS–PE system assuming a temperature of 140°C[7]. A slightly larger value of $\chi = 5.9 \times 10^{-3}\,\mathrm{N\,m^{-1}}$ was obtained experimentally by Wu[23] from contact angle measurements. If these values of γ together with the appropriate parameters are substituted into the equations above relating to γ to χ then the values of χ listed in *Table 2* are obtained. Using the definition of l_0 from Stamm *et al.*, the experimentally determined values of χ = 0.016–0.043 generally underestimate the value expected from those calculated from theoretically derived values. Clearly, though, the choice of l_0 is very important since, as it increases to its upper limit, the value of χ compares extremely well with the derived values. By comparison, $\chi = 0.141 \pm 0.086$ (assuming l_0 is defined by equation (3)) drastically overestimates the theoretically calculated values. This suggests that the definition of the capillary wave interfacial width used by Shull *et al.*[8] to explain their reflectivity data is perhaps not the most appropriate form, and appears to give a capillary interfacial width that is too large. This is in general agreement with the discrepancies revealed by Müller *et al.* in their Monte Carlo simulations, where the exact description of the fluctuations is not well described at present.

Conclusions

There are few experimental methods for the accurate determination of χ between two immiscible homopolymers. It has been demonstrated that neutron reflectivity is a simple and reliable technique for determining interfacial widths between two immiscible polymers. The method is, however, limited by the discrepancy in the literature of the specific form of the components (l_0) of the measured interfacial width. This clearly has dramatic implications on the value of χ which is calculated from the measured interfacial width. If this problem can be overcome, then this method of determining χ would have great advantages over other techniques, for example calorimetry[24], small-angle neutron scattering[25], solubility parameter determination[14,15], or evaluation of interfacial tension measurements, since it is applicable to all polymer systems, and is equally adaptable to crystalline and amorphous systems.

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