EUROPHYSICS LETTERS 1 April 2000

Europhys. Lett., **50** (1), pp. 35–40 (2000)

Wetting transition in a binary polymer blend

J. RYSZ[1], A. BUDKOWSKI[1](*), A. BERNASIK[2], J. KLEIN[3], K. KOWALSKI[2],
J. JEDLIŃSKI[2] and L. J. FETTERS[4]

[1] *Smoluchowski Institute of Physics, Jagellonian University*
Reymonta 4, 30-059 Kraków, Poland
[2] *Surface Spectroscopy Laboratory, University of Mining and Metallurgy and*
JCCASR Jagellonian University - Reymonta 23, 30-059 Kraków, Poland
[3] *Department of Materials and Interfaces, Weizmann Institute of Science*
76100 Rehovot, Israel
[4] *Exxon Research and Engineering Company - Annandale, NJ 08801, USA*

(received 15 November 1999; accepted 18 January 2000)

PACS. `36.20.-r` – Macromolecules and polymer molecules.
PACS. `68.10.-m` – Fluid surfaces and fluid-fluid interfaces.
PACS. `68.45.Gd` – Wetting.

Abstract. – We have used composition depth profiling, based on nuclear-reaction analysis and secondary ion mass spectroscopy, to study segregation at the free surface of a partly miscible binary mixture consisting of random olefinic copolymers. The equilibrium surface excess data, analysed within a mean-field Cahn approach, point to a wetting transition. The surface phase diagram obtained was confirmed by the observed dynamics of the segregation from a coexistence composition: the monotonic and halted growth of the surface layer was observed at temperatures above and below the predicted wetting point, respectively.

Wetting phenomena are classified primarily [1] in terms of the contact angle Θ, describing the geometrical arrangement of two coexisting phases ϕ_1 and ϕ_2 at the surface. An alternative approach (due to Cahn [2]) is provided by the picture of surface segregation described by the profile $\phi(z)$ of blend composition ϕ *vs.* distance z from the surface [2–5] (fig. 1a)): A surface composition $\phi_\mathrm{s} < \phi_2$ decaying smoothly to its bulk value ϕ_1 characterises partial wetting. In the case of complete wetting a macroscopically thick layer of the second phase ϕ_2 (say with thickness larger than the double width of the ϕ_1/ϕ_2 interface $2w$) resides at the surface and excludes the bulk phase ϕ_1 from the surface. In a *generic* situation, complete wetting occurs close to the critical temperature T_C (critical-point wetting) and the transition to partial wetting is observed [6,7] at T_W for a larger $|T_\mathrm{C} - T|$ value as predicted by the Cahn model assuming short-ranged, temperature-independent surface potential f_s [2,3,5]. Different scenarios, such as *reversal* wetting transition [8] or the sequence of two transitions [3, 9], were revealed in recent experiments. The discontinuous (first-order) [6, 9] and continuous (second-order or critical) [7–9] (generic) wetting transitions have been reported for small

---

(*) E-mail: `ufbudkow@cyf-kr.edu.pl`

molecule systems, where observations could be convoluted by the presence of gravitational and convective fields. These effects are negligible for thin films composed of polymer blends [10,11]. In addition, macromolecular length scales are large enough to facilitate the determination of the composition profiles $\phi(z)$ with modern profiling techniques [12,13]: the complete wetting behaviour [10,11,14] and the reversal wetting transition [8] have been observed for various polymer mixtures, mostly in spinodal demixing experiments [8,14]. The wetting transition in a polymer blend, despite its relevance to modern technological applications [15], huge theoretical attention [5] and very intensive research [10,11], so far eluded experimental observation.

In this letter we present results of two types of studies on the surface segregation, free of the spinodal decomposition effects, indicating the wetting transition at the free surface of a model binary polymer blend. First, the *equilibrium* properties of the segregation from the one-phase region of phase diagram are analysed within the Cahn approach [2], pointing to the transition [16]. This is confirmed by experiments focused on the *dynamics* of the segregation

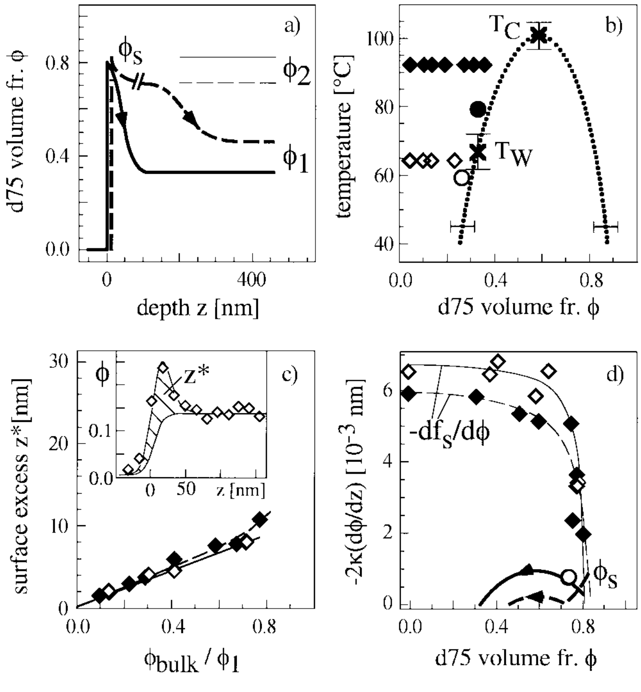

Fig. 1 – Segregation and wetting characteristics of the $d75/h66$ mixture. Different symbols (data points) and line types (calculated from a mean-field model [2,5]) correspond to various temperatures: ○ $T = 59\,^\circ\mathrm{C}$; ◇ and — $T = 64\,^\circ\mathrm{C}$; • $T = 79\,^\circ\mathrm{C}$; ◆ and - - - $T = 92\,^\circ\mathrm{C}$. a) Composition-depth profiles $\phi(z)$ corresponding to the free surface ($z = 0$) partially ($T = 64\,^\circ\mathrm{C}$, $w = 30.1\,\mathrm{nm}$) and completely ($T = 92\,^\circ\mathrm{C}$, $w = 59.8\,\mathrm{nm}$) wetted from the blend at coexistence. b) Temperature variation of coexistence compositions ϕ_1 and ϕ_2 denoted by binodal [17] (dotted line). Bulk compositions ϕ_{bulk} are marked for which the segregation from the one-phase region and from the coexistence composition was studied. Solid bars represent the evaluated uncertainty of T_{C}, T_{W}, ϕ_1 and ϕ_2. c) Variation of the equilibrium surface excess z^* as a function of $\phi_{\mathrm{bulk}}/\phi_1$. The inset shows a typical NRA profile with z^* marked by the shaded area. d) The Cahn construction [2] predicting $T_{\mathrm{W}} = 67 \pm 5\,^\circ\mathrm{C}$: The trajectories $-2\kappa(\mathrm{d}\phi/\mathrm{d}z)$ *vs.* ϕ, marked by thick lines, correspond to the profiles of fig. 1a). The "bare" surface energy derivative $(-\mathrm{d}f_{\mathrm{s}}/\mathrm{d}\phi)$, derived from the z^* data (panels c) and b)), determines the starting points (at the surface composition ϕ_{s}) of the trajectories.

from the coexistence composition.

We used the mixture composed of two random poly(ethylene-ethylethylene) copolymers of mean microstructure $(C_4H_8)_{1-x}(C_2H_3(C_2H_5))_x$. Such blends, where the two components have different ethylethylene fractions x_1 and x_2, create an attractive model system, as bulk [17–19] and surface [10, 11, 18, 20–22] interactions may be tailored by a suitable choice of x-values. The molecular characteristics of the pair used in this study, $d75$ ($x = 0.75$), which is partially deuterated, and $h66$ ($x = 0.66$), are as follows: for $d75$: degree of polymerisation $N = 1625$; statistical segment length $a = 0.64\,\text{nm}$; degree of deuteration $= 0.40$; glass transition temperature $T_g = -46\,°\text{C}$; for $h66$: $N = 2030$; $a = 0.68\,\text{nm}$; $T_g = -54\,°\text{C}$. Both polymers had polydispersity index < 1.08. The $d75/h66$ mixture displays a phase equilibrium with $T_C = 101 \pm 4\,°\text{C}$ and the binodal (see fig. 1b)) described within the Flory-Huggins model by the interaction parameter $\chi = (0.371/T - 2.7 \times 10^{-5})\ (1 + 0.212\phi)$, dependent on the $d75$ volume fraction ϕ [17].

The segregation equilibrium studies were performed for monolayer samples of various overall $d75$ concentration (and thickness D ca. 500 nm), prepared by spin coating from a toluene solution onto polished silicon wafers. The segregation dynamics observations were made for bilayers of a pure $h66$ film ($D = 220 \pm 50\,\text{nm}$) on top of a pure $d75$ layer ($D = 170$–$800\,\text{nm}$): the $h66$ film was spin coated onto freshly cleaved mica and then float-mounted onto the $d75$ layer. The samples were annealed in a vacuum oven ($\leq 10^{-2}$ Torr) at temperatures T (stable to $\pm 1\,°\text{C}$) for different times t, and stored at $T < T_g$ until required for the experiments. The profiles $\phi(z)$ of the deuterated $d75$ blend component normal to the sample surface were determined either by nuclear reaction analysis (NRA) [12] or by secondary ion mass spectroscopy (SIMS) [13] with a depth resolution in the range of 9 to 20 nm, as described earlier [12, 13].

The segregation from the one-phase region of the phase diagram is described in terms of the (integrated) surface excess z^* of $d75$, represented in the inset to fig. 1c) by the shaded area. z^* was measured from the profiles of the monolayer samples annealed at $T = 64$ and $92\,°\text{C}$ for $t > 1$ day. The times used were sufficient to reach the equilibrium, due to a large molecular mobility of the polyolefines [19]. In contrast to the situation at the free surface, no segregation was observed at the blend interface with the substrate [20]. The equilibrium z^* values were determined for bulk compositions ϕ_{bulk} marked by diamonds in the phase diagram of fig. 1b). Figure 1c) shows the corresponding segregation isotherms with z^* plotted as a function of the normalised bulk composition $\phi_{\text{bulk}}/\phi_1$.

To analyse the segregation data of fig. 1c) we follow the standard Cahn procedure [2], reviewed recently [5] and used previously [18, 20–22]. The excess free energy functional $F[\phi]$ is represented as a sum of the bulk and "bare" surface f_s free energies, dependent on $\phi(z)$ and its surface value ϕ_s, respectively [2, 23]:

$$\frac{F[\phi]}{k_B T} = \int_0^\infty \mathrm{d}z[\Delta f(\phi) + \kappa(\mathrm{d}\phi/\mathrm{d}z)^2] + f_s(\phi_s)\,. \tag{1}$$

Here κ is the ϕ-dependent coefficient [24] and $\Delta f(\phi)$ is the energy needed to create a unit volume with composition ϕ from a bulk region with ϕ_{bulk} [24].

To minimise $F[\phi]$ we analyse the Cahn construction (fig. 1d)), that is, the ϕ-dependence of two quantities: the trajectory $-2\kappa(\mathrm{d}\phi/\mathrm{d}z)$ (equal to $2(\kappa\Delta f)^{1/2}$ and specified entirely by bulk parameters [24]) and the derivative $(-\mathrm{d}f_s)/\mathrm{d}\phi)$ driving the segregation. While each equilibrium profile $\phi(z)$ [25] is determined by its own trajectory, the starting point of the latter (at ϕ_s) is given by the intersection of both, $-2\kappa(\mathrm{d}\phi/\mathrm{d}z)$ and $(-\mathrm{d}f_s/\mathrm{d}\phi)$, relations. The reversal procedure [18, 20–22] allows us to determine the $(-\mathrm{d}f_s/\mathrm{d}\phi)$ relation, whenever the profiles $\phi(z)$ with the ϕ_s values, or equivalently the segregation data, are known. Diamonds

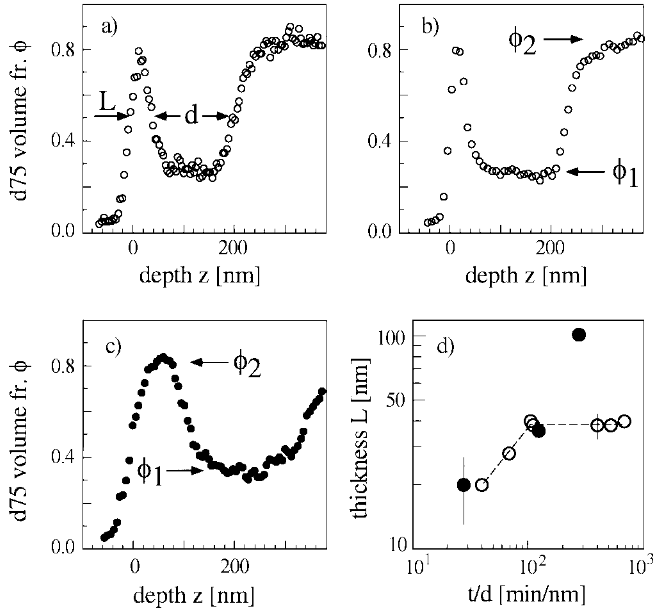

Fig. 2 – Dynamics of surface enrichment from a coexistence phase ϕ_1: ○ $T = 59\,°\mathrm{C} < T_{\mathrm{W}}$ ($w = 28.3\,\mathrm{nm}$); • $T = 79\,°\mathrm{C} > T_{\mathrm{W}}$ ($w = 38.6\,\mathrm{nm}$). SIMS composition-depth profiles $\phi(z)$ of the surface layer (of thickness L) growing from the bulk phase ϕ_1 (of width d), a) after 12.6 days at 59 °C, b) after 73.2 days at 59 °C ($z^* = 19.2 \pm 1.5\,\mathrm{nm}$), c) after 3.4 days at 79 °C corresponding [19] to 18.8 days at 59 °C. An additional film, rich in $d75$ (at $z > 200$–$300\,\mathrm{nm}$), acted as a material reservoir. d) Variation of L with the parameter (t/d) reduced to 59 °C [11]. Dashed lines are a guide to eye.

in fig. 1d) represent the $(-\mathrm{d}f_{\mathrm{s}}/\mathrm{d}\phi)$ *vs.* ϕ relation derived from the experimental input of fig. 1c). An additional point (○) corresponds to the final stage of the segregation dynamics detected at 59 °C (fig. 2b)), where the equilibrium surface excess is attained for the bulk composition ϕ_1. A non-linear shape of the $(-\mathrm{d}f_{\mathrm{s}}/\mathrm{d}\phi)$ function was observed and examined previously [18, 20–22] for the other dx_1/hx_2 mixtures. Figure 1d) shows that the $(-\mathrm{d}f_{\mathrm{s}}/\mathrm{d}\phi)$ *vs.* ϕ relation is, for the values $< 4 \times 10^{-3}\,\mathrm{nm}$, hardly temperature dependent. This result enables us to evaluate the wetting point $T_{\mathrm{W}} = 67 \pm 5\,°\mathrm{C}$. Typical computed trajectories (fig. 1d)) and profiles (fig. 1a)) correspond to partial (solid lines) and complete (dashed lines) wetting at $T = 64$ and 92 °C, respectively. The Cahn analysis suggests the critical wetting transition. This model also predicts a phenomenon prerequisite to the continuous transition (an enrichment-depletion duality), which was observed recently in the $d52/h66$ blend [22].

To study the dynamics of the segregation from the coexistence composition we followed the idea of Steiner *et al.* [10, 11] and measured the bilayer samples annealed at $T = 59$ and 79 °C for times from 5 h to 2.4 months. Such long annealing times (10 times longer than used previously [10, 11]) were necessary to distinguish the partial from the complete wetting behaviour. Typical profiles corresponding to two temperatures are shown in figs. 2a)-b) and c), respectively. They reflect the structure of the sample after the transient initial stage, characterised by interdiffusion leading to coexisting compositions, is completed. The profiles $\phi(z)$ may be divided into three regions: i) the surface layer of thickness L; ii) the bulk phase ϕ_1 of width d [26]; iii) the $d75$-rich layer acting as a material reservoir. At the late stage of the annealing a different shape of the surface layer was observed at both temperatures:

While the profile characteristic of complete wetting was measured at $T = 79\,^\circ\mathrm{C}$ (fig. 2c)), it was never observed at $T = 59\,^\circ\mathrm{C}$ for equivalent and even much longer annealing times. Instead the profile typical of partial wetting was monitored persistently (figs. 2a) and b)).

The profiles resembling fig. 2c) were observed previously [10, 11] for the $d88/h78$ and $d66/h52$ mixtures: It was established that the surface layer thickness L grows at the expense of the material reservoir, while the thickness d of the bulk phase ϕ_1 remains unchanged. This process is limited by the diffusion of the dx_1 blend component across the bulk phase and therefore L depends on the parameter (t/d) rather than time t. The surface layer thickness L, growing with (t/d), attained macroscopic dimensions ($L/(2w) \geq 1.2$ [10]) indicating a complete wetting regime.

To examine the segregation dynamics data of this study we represent them in fig. 2d) as a plot of L *vs.* the parameter (t/d) reduced to $59\,^\circ\mathrm{C}$ [11]. The data set corresponding to $79\,^\circ\mathrm{C}$ (●) reproduces the monotonic evolution of the surface layer to a macroscopic surface phase ϕ_2 (here with $L/(2w) = 1.3$) reported previously for critical-point wetting [10, 11]. On the contrary, the data points of $T = 59\,^\circ\mathrm{C}$ (○) after an initial increase level off (compare figs. 2a) and b)) at the value $L = 38 \pm 2\,\mathrm{nm}$, smaller than the double interfacial width ($2w = 56.6\,\mathrm{nm}$). This observation clearly indicates a completed build-up of the surface enriched layer corresponding to a partial wetting regime.

There are two conclusions. First, we have demonstrated for the first time the wetting transition for a polymer blend: the dynamics of the segregation from the coexistence composition characteristic of complete and partial wetting was observed in the $d75/h66$ mixture at $T = 79$ and $59\,^\circ\mathrm{C}$, respectively (fig. 2d)). Second, this observation is in accord with the prediction, $T_\mathrm{W} = 67 \pm 5\,^\circ\mathrm{C}$, of the Cahn approach based on the surface excess data (fig. 1). Previously this model has been used to describe other wetting-related phenomena, such as the enrichment-depletion duality [22] or the extended critical-point wetting regime [21]. The present results show that for polymer mixtures the Cahn theory can provide reasonable predictions of the surface phase diagram. Further experimental studies are needed to explain how this diagram is altered by the long-ranged surface forces [3, 4, 7, 9].

* * *

We thank Profs. K. BINDER and U. STEINER for useful discussions. Partial support from the Reserve for Individual Research of the Rector of Jagellonian University, the German-Israel Foundation (GIF) and the Ministry of Science and Arts (Israel) is gratefully acknowledged.

REFERENCES

[1] YOUNG T., *Philos. Trans. R. Soc. London*, **95** (1805) 65.

[2] CAHN J. W., *J. Chem. Phys.*, **66** (1977) 3667; SCHMIDT I. and BINDER K., *J. Phys.* (*Paris*), **46** (1985) 1631.

[3] DE GENNES P.-G., *Rev. Mod. Phys.*, **57** (1985) 827.

[4] DIETRICH S., in *Phase Transitions and Critical Phenomena*, edited by C. DOMB and J. L. LEBOWITZ, Vol. **II** (Academic, New York) 1988, pp. 1-218.

[5] BINDER K., *Acta Polym.*, **46** (1995) 204; *Adv. Polym. Sci.*, **138** (1999) 1 and references therein.

[6] MOLDOVER M. R. and SCHMIDT J. W., *J. Chem. Phys.*, **79** (1983) 379; BONN D., KELLAY H. and WEGDAM G. H., *Phys. Rev. Lett.*, **69** (1992) 1975.

[7] RAGIL K. *et al.*, *Phys. Rev. Lett.*, **77** (1996) 1532.

[8] GENZER J. and KRAMER E. J., *Phys. Rev. Lett.*, **78** (1997) 4946; *Europhys. Lett.*, **44** (1998) 180.

[9] Shahidzadeh N. *et al.*, *Phys. Rev. Lett.*, **80** (1998) 3992.

[10] Steiner U., Klein J., Eiser E., Budkowski A. and Fetters L. J., *Science*, **258** (1992) 1126.

[11] Steiner U. and Klein J., *Phys. Rev. Lett.*, **77** (1996) 2526; *Mater. Res. Soc. Symp. Proc.*, **464** (1997) 121.

[12] Kerle T. *et al.*, *Acta Polymer.*, **48** (1997) 548.

[13] Bernasik A. *et al.*, in *ECASIA '97*, edited by I. Olefjord, L. Nyborg and D. Bryggs (John Wiley & Sons, Chichester) 1997, pp. 775-778; Schwarz S. A. *et al.*, *Mol. Phys.*, **76** (1992) 937.

[14] Bruder F. and Brenn R., *Phys. Rev. Lett.*, **69** (1992) 624; Krausch G. *et al.*, *Macromolecules*, **26** (1993) 5566; Straub W. *et al.*, *Europhys. Lett.*, **29** (1995) 353.

[15] Mayes A. M. and Kumar S. K., *MRS Bulletin*, January issue (1997) 43; Service R. F., *Science*, **278** (1997) 383; Böltau M. *et al.*, *Nature*, **391** (1998) 877.

[16] Such a conclusion, valid for the short-ranged surface potential f_s, might not be true if the long-range interfacial interactions are also present [11]. To check this conclusion we have performed the dynamics experiments.

[17] Scheffold F. *et al.*, *J. Chem. Phys.*, **104** (1996) 8786.

[18] Budkowski A., *Adv. Polym. Sci.*, **148** (1999) 1; Budkowski A. *et al.*, *J. Polym. Sci. Polym. Phys. Ed.*, **36** (1998) 2691.

[19] Losch A. *et al.*, *J. Polym. Sci. Polym. Phys. Ed.*, **33** (1995) 1821.

[20] Scheffold F. *et al.*, *J. Chem. Phys.*, **104** (1996) 8795.

[21] Budkowski A., Scheffold F., Klein J. and Fetters L. J., *J. Chem. Phys.*, **106** (1997) 719.

[22] Budkowski A., Rysz J., Scheffold F. and Klein J., *Europhys. Lett.*, **43** (1998) 404; Budkowski A. *et al.*, *Vacuum*, **54** (1999) 273.

[23] Equation (1) corresponds to the long-wavelength limit: $R < 1$, where $R = a(N/6)^{1/2}(\mathrm{d}\phi/\mathrm{d}z)_\mathrm{max}$. $R = 0.1$ at $T = 64\,^\circ\mathrm{C}$ for $\phi_\mathrm{bulk} = \phi_1$, $N = N_{h66}$ and $a = a_{h66}$.

[24] $\kappa = ((1-\phi)a_{d75}^2 + \phi a_{h66}^2)/(36\phi(1-\phi))$, $\Delta f(\phi) = f(\phi) - f(\phi_\mathrm{bulk}) - (\phi - \phi_\mathrm{bulk})(\partial f/\partial\phi)\phi_\mathrm{bulk}$, $f(\phi) = \phi \ln\phi/N_{d75} + (1-\phi)\ln(1-\phi)/N_{h66} + \chi\phi(1-\phi)$.

[25] The replacement of the short- [18, 20–22] by long- [11] ranged f_s term in eq. (1) leads to no experimentally detectable changes in the equilibrium profile $\phi(z)$ corresponding to the one-phase region of the phase diagram; Jones R. A. L., *Phys. Rev. E*, **47** (1993) 1437; Genzer J., Faldi A., Oslanec R. and Composto R. J., *Macromolecules*, **20** (1996) 5438.

[26] A depletion region of the bulk phase ϕ_1, adjacent to the surface layer, with local concentration $\phi_\mathrm{d} \approx \phi_1$ was also detected [11].