Wetting transition in polyolefin blends studied by profiling techniques

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SUMMARY: Based on segregation data, determined with profiling techniques, we analyze surface phase diagram of binary liquid mixtures composed of random olefinic copolymers. Blends with extended- and small- critical point wetting regimes are discussed. First observation of wetting transition is presented. Surface enrichment-depletion duality, a phenomenon prerequisite to the 2nd order wetting transition, is described.

Introduction

Wetting phenomena were classified primarily[1)] in terms of the contact angle Θ, determining the geometrical arrangement of two coexisting phases ϕ_1 and ϕ_2 at the surface. An alternative approach is provided by the picture of surface segregation described by the profile $\phi(z)$ of blend composition ϕ vs. distance z from the surface[2-3)]: a surface composition $\phi_s<\phi_2$ decaying smoothly to its bulk value ϕ_1 characterizes *partial wetting*. In the case of *complete wetting* a macroscopically thick layer (i.e. with thickness larger than correlation lengths in the mixture) of the second phase ϕ_2 resides at the surface and excludes the bulk phase ϕ_1 from the surface (segregation changes into separation). Profiling techniques[4-5)], determining the profiles $\phi(z)$, can be used to study wetting phenomena: Complete wetting has been observed for various binary polymer blends[6-8)]. The most extensive study (and the only one free of spinodal demixing effects) concerns the model mixtures composed of random, nearly monodisperse ($M_w/M_n<1.08$), olefinic copolymers[7,9-15)] of the structure $(E_{1-x}EE_x)_N$ (N is the degree of polymerization). Here E and EE are the linear ethylene (C_4H_8) and branched ethyl-ethylene ($C_2H_3(C_2H_5)$) groups, respectively, distributed randomly in the ratio (1-x):x on the chains. The components in each binary mixture have different values x_1, x_2 of the EE fraction. While one blend component (hx_2) is hydrogenous, the other (dx_1) is deuterated to provide contrast, necessary for the ion beam methods of non-resonant ^{3}He Nuclear Reaction Analysis (NRA)[4)]

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and dynamic Secondary Ion Mass Spectroscopy (SIMS)$^{5)}$. Information about the profiles $\phi(z)$, with a depth resolution in the range of 7-20 nm, is provided by the energy spectrum of the nuclear reaction products (NRA) or by the intensity of the secondary ions (sputtered by low-energy (3-7 keV) primary ions) recorded in a function of the sputtering time (SIMS). Blend samples are stored at a temperature below the glass transition$^{14)}$ ($-70°C \leq T_g \leq -39°C$) until required for the experiments. Bulk and surface characteristics of all blends dx_l/hx_2 discussed here were determined previously with the profiling techniques$^{9-15)}$: Binodals (represented in Fig.1-3), yielded by the bilayers of coexisting phases monitored at various temperatures, were interpreted in terms of the bulk interaction parameter $\chi^{10,12,15)}$. Obtained χ values are in accord (see Ref.10) with small-angle neutron scattering data. Surface energy differences $\Delta\gamma$ between pure blend components (Fig.4) were evaluated$^{10,15)}$ by the mean field Cahn analysis$^{2)}$ of surface segregation data. The essential observable of these data is the surface excess z* of the deuterated (dx_l) component (shaded in Figs.1-2): $z^* = \int_0^{z(\phi_\infty)} [\phi(z) - \phi_\infty] dz$. Here $z(\phi_\infty)$ is the distance from the surface (z=0) to the plateau (ϕ_∞) in the profile $\phi(z)$.

Critical Point Wetting

In 1977 Cahn proposed$^{2)}$ that complete wetting characterizes temperatures close enough to the critical point T_C of the mixture, and the transition to partial wetting occurs for larger $|T_C-T|$ values. The original Cahn argument applies to polymer blends, which also are likely candidates$^{3,7,9,10)}$ to exhibit complete wetting even very far below T_C. Extended critical point wetting region has been concluded for the binary pair d66 (N=2030)/h52(N=1510) based on

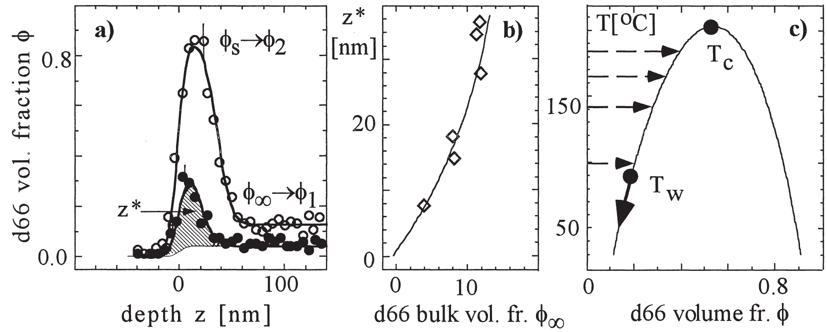

Fig.1: **(a)** Surface enriched profiles $\phi(z)$ of the d66/h52 blend$^{9)}$ following 2h of annealing at 99°C and **(b)** the corresponding surface excess z* isotherm. The isotherms were determined for composition ranges marked as dashed arrows on the phase diagram **(c)**. Wetting transition temperature T_W is located below 99°C.

the analysis of surface segregation data$^{9)}$ (Fig.1). A divergence of the surface excess z* was observed as the binodal of the mixture was approached from the one-phase region, even at a temperature 105 deg below T_C (Fig.1.b), and interpreted as the advent of complete wetting behavior$^{7)}$. This also is revealed by the shape of the surface enriched profiles (Fig.1.a)): the surface concentration ϕ_S of the enriched layer attains (at z=0) the upper coexistence composition ϕ_2, as bulk volume fraction ϕ_∞ approaches (at z > 100 nm) the lower coexistence value ϕ_1. A large difference between critical and wetting points (T_C-T_W >75 deg) was also concluded$^{9)}$ for the blend d86(N=1520)/h75(N=1625).

Surface Enrichment-Depletion Duality

According to a common viewpoint the free surface of a binary mixture A/B is enriched in one component, say A, regardless of the value of bulk composition ϕ_∞. From recent theoretical analyses$^{16)}$ and Monte Carlo simulations$^{17)}$ one expects however that some mixtures can exhibit surface enrichment in the component A, when the bulk volume fraction ϕ_∞ is below certain value Q, and a depletion in A for $\phi_\infty > Q$. The duality phenomenon plays an important role in the reduction of the miscibility gap expected for polymer blends confined in thin films between symmetric walls$^{17)}$. It also is a prerequisite$^{16)}$ for the 2nd order wetting transition (critical wetting). The first experimental study of the duality, reported$^{13)}$ for the olefinic mixture h66(N=2030)/d52(N=1510) annealed at T=71°C, is depicted in Fig.2. The enrichment in d52 is observed for $\phi_\infty \leq \phi_1$, while the depletion in the d52 component is detected for $\phi_\infty \geq \phi_2$

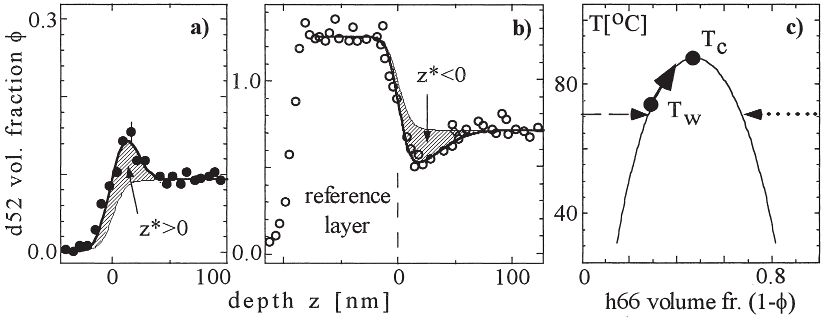

Fig.2: Composition-depth profiles $\phi(z)$ of the h66/d52 blend$^{13)}$ indicating: an enrichment (z*>0) **(a)** and a depletion (z*<0) **(b)** in the d52 component, obtained for samples annealed to equilibrium at 71°C. The surface (z=0) position is yielded by: the profile itself **(a)**; an interface created by a reference layer positioned on top of the annealed sample **(b)**. Positive and negative surface excess z* values were obtained for composition ranges marked by dotted and dashed arrow on phase diagram **(c)**. The wetting point T_W is located above 71°C.

($\phi_1 < Q < \phi_2$). This suggests[13,16] that wetting point T_W is located above 71°C, i.e. close to the critical point of the blend T_C= 88°C. Both, the reduced critical point wetting regime (T_C-T_W <17 deg) and the duality effect itself[10,13,16], point on a very small $\Delta\gamma$ value.

Wetting Transition

In spite of intensive research[6-8] the observations of wetting transition in polymer blends are still very scarce. Only a *reversal* wetting transition has been reported[8b] so far for the mixture of poly(ethylene-propylene) and its deuterated counterpart: while complete wetting at low- and partial wetting at higher- temperatures was observed in the experiment[8b], it is not clear if complete wetting behavior could be attained again at temperatures close enough to T_C. The first experimental observation of *standard* wetting transition, determined[11] for the olefinic blend d75(N=1625)/h66(N=2030), is represented in Fig.3. Surface layers growing from the bulk phase ϕ_1 were studied as a function of the annealing time. The bulk composition ϕ_1 was not altered during annealing as an additional layer, rich in the d75 component (located at z > 200-300 nm and for the sake of clearness not shown in Fig.3.a)), acted as a material reservoir[7]. The profiles $\phi(z)$ characteristic of complete wetting were observed at T=79°C (marked as ○ in Fig.3.a)). Monotonous growth of the surface layer is halted when temperature is changed to T=59°C. For instance the profile $\phi(z)$ marked as ● in Fig.3.a) is identical to that measured for much shorter annealing times. This is a sign of a partial wetting regime. A reduced critical point wetting region (37°>T_C-T_W >22°) is indicated.

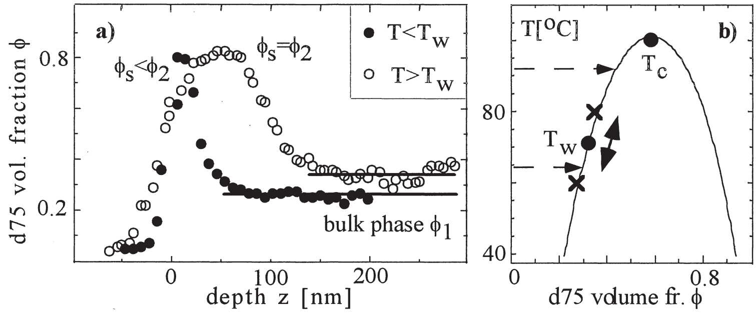

Fig.3: **(a)** Surface layers[11] of the blend d75/h66 growing from the bulk phase ϕ_1. The profiles[11]: ● and ○ correspond to samples annealed at 59 and 79°C for 73.2 and 3.4 days, respectively. The second annealing time is equivalent[14] to 18.8 days at 59°C. No change in the shape of the profile ● is observed[11] already after 12.6 days of annealing. **(b)** The phase diagram with marked regions corresponding to determined segregation isotherms (dashed arrows) and to studied dynamics (see **(a)**) of the enrichment from coexistence phase (**×**). The wetting point: 64°C < T_W < 79°C.

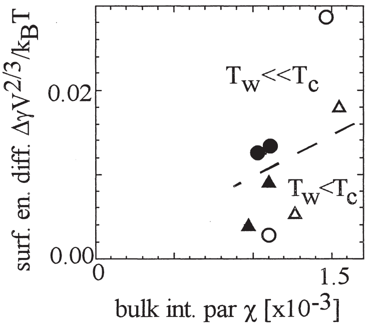

Fig.4: Surface energy difference $\Delta\gamma V^{2/3}/k_BT$ plotted as a function of bulk interaction parameter χ for blend pairs: ○ - (d66/h52, h66/d52), △ - (d86/h75,h86/d75), ▲ - (d75/h66, h75/d66), ●-(d52/h38,h52/d38) at T = 100°C[10] (V-is the segmental volume). For each blend pair a point with higher both χ and $\Delta\gamma V^{2/3}/k_BT$ values corresponds to the mixture, where the component with higher EE fraction x is deuterated.

Conclusions

A wetting transition[11] and enrichment-depletion duality[13], suggesting critical wetting, was observed at the free surface of polyolefine mixtures with a small critical point wetting regime. For such mixtures their components are characterised[10,15] (Fig.4) by a *small* difference $\Delta\gamma$ and a *substantial* disparity in cohesive energy, manifested by non-zero χ values. This suggests destructive superposition of enthalpic and entropic forces driving the segregation[15]. A considerable change in $\Delta\gamma$ and in the extent of critical point wetting (T_C-T_W) is often caused (Fig.4) by the swap of the blend component labeled by deuterium[15], e.g. for blends d66/h52 and h66/d52 (compare Figs.1 and 2).

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