

Characterization of an Amorphous Surface Layer on Blown Polyolefin Film

A. C. Chang,¹ S. P. Chum,² A. Hiltner,¹ E. Baer¹

¹Department of Macromolecular Science and Center for Applied Polymer Research, Case Western Reserve University, Cleveland, Ohio 44106-7202

²Polyolefins and Elastomers R & D, The Dow Chemical Company, Freeport, Texas 77541

Received 22 January 2002; accepted 3 April 2002

ABSTRACT: This study concerned an amorphous surface layer on blown polyethylene film with a composition different from that of the bulk. The surface layer was characterized by gentle probing with an atomic force microscope. The demonstration of an amorphous layer uniformly covering the surface of a blown Ziegler–Natta-catalyzed polyethylene (znPE) film reproduced previous reports. Removing the surface layer by solvent washing confirmed the hypothesis that the layer consisted of lower molecular weight, higher branch content fractions. A blown film of znPE blended with up to 30 wt % impact-modified high-melt-strength polypropylene (hmsPP) also exhibited an amorphous surface layer. In thin films, it was advantageous for the mobile, amorphous fractions of ethylene–propylene rubber (EPR) to locate at the surface rather than at the phase interface. The amorphous EPR tended to segregate into pools on the film surface, and this pointed to a substantial difference between the amorphous surface layers on the znPE and hmsPP/znPE blend

films. Surface enrichment best described the compositional gradient that resulted from the concentration of lower molecular weight, higher branch content chains at the surface of the znPE film. Surface segregation was more appropriate for the emergence of EPR fractions as a separate phase on the surface of the hmsPP blend film. Films blown from a blend of a Ziegler–Natta-catalyzed polyethylene and a metallocene-catalyzed polyethylene (zn/mPE) and its blend with hmsPP reproduced the primary features of surface enrichment and surface segregation. Some differences between the znPE and zn/mPE films were attributed to the metallocene constituent of zn/mPE. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 3625–3635, 2002

Key words: polyolefins; films; surfaces; polyethylene (PE); poly(propylene) (PP); blends; atomic force microscopy (AFM)

INTRODUCTION

Recent studies have demonstrated the property enhancement that can be achieved from the blending of high-melt-strength polypropylene (hmsPP) with polyethylene for film applications.^{1–3} Higher stiffness and tensile strength are imparted to the inherently tough and tear-resistant polyethylene blown film. The specific balance of bulk properties derives from the oriented blend morphology achieved in the blown-film process.^{4,5}

Other key film properties, including blocking, hot tack, and heat seal, depend on surface characteristics. One result of chain heterogeneity is the possibility of the composition of chains near the surface differing from the average composition. In ethylene copolymers polymerized by Ziegler–Natta catalysts, heterogeneity takes the form of an excessive concentration of short-chain branches on chains of low molecular weight. Previous studies demonstrated the existence of an

amorphous surface layer on films of heterogeneous ethylene copolymers that was thought to originate from surface enrichment with highly mobile, lower molecular weight, higher branch content fractions.⁶ Films of a metallocene copolymer with a homogeneous comonomer distribution and a narrower molecular weight distribution did not possess a surface layer different from the bulk.

The surface layer has important implications for the development of self-adhesion above the melting temperature. Low molecular weight fractions cannot create good adhesion. In an experimental procedure for consecutively sealing and peeling a film at the same temperature, above the melting point, heterogeneous copolymers required longer time for resolution of the amorphous surface layer before achieving maximum adhesion strength.^{6,7} A significantly shorter time was required for copolymers with more homogeneous copolymer compositions.

The strength of the self-adhesion bond is of practical importance for the heat-seal and hot-tack performance of polymeric films. Recognizing that measurements of hot tack with a nonisothermal commercial tester include contributions from crystallization, we can nevertheless postulate that the amorphous surface layer

Correspondence to: A. Hiltner (pah6@po.cwru.edu).
Contract grant sponsor: The Dow Chemical Co.

contributes to lower hot tack of heterogeneous copolymers with respect to homogeneous copolymers.^{7,8}

Blending an ethylene copolymer with a second polymeric constituent increases the possibilities for surface compositions that are different from the bulk. This is particularly the case in blends with hmsPP, which is a modified impact resin containing an ethylene-propylene rubber (EPR). Typically, EPR made in a secondary step following propylene polymerization is chemically heterogeneous, containing high ethylene amorphous fractions in addition to low ethylene crystallizable fractions.⁹ This study was undertaken to examine the effect of blend constituents, especially amorphous EPR fractions, on the surface characteristics of blown films. Atomic force microscopy (AFM) was used to probe the surface of films blown from ethylene copolymers and their blends with hmsPP.

MATERIALS AND METHODS

Materials

An hmsPP, two linear low-density polyethylenes, and blends of each of the polyethylenes with 10, 20, and 30 wt % hmsPP were supplied by Dow Chemical Co. (Freeport, TX) in the form of 20- μm (0.8-mil) and 50- μm (2.0-mil) blown films. The polyethylenes and hmsPP were also supplied as pellets. As reported by the manufacturer, the hmsPP was a modified impact resin with 16 wt % EPR and a melt-flow index of 0.35 g/10 min. One polyethylene was a Ziegler-Natta-catalyzed ethylene-octene copolymer (znPE) with a density of 0.920 g cm⁻³ and a melt-flow index of 1.0 g/10 min. The other polyethylene, a blend of a Ziegler-Natta-catalyzed polyethylene and a metallocene-catalyzed polyethylene (zn/mPE), had a density of 0.916 g cm⁻³ and consisted of 63 wt % znPE (density = 0.925 g cm⁻³, weight-average molecular weight \cong 100 kg mol⁻¹) and 37 wt % metallocene-catalyzed ethylene-octene copolymer (density = 0.902 g cm⁻³, weight-average molecular weight \cong 145 kg mol⁻¹). The blend had a melt-flow index of 1.0 g/10 min. The melt-flow index was measured with a load of 2.16 kg at 190°C for polyethylene and at 230°C for polypropylene. Additional characterization of the films was reported previously.⁴ A conventional Ziegler-Natta-catalyzed polypropylene (znPP) was included in the study for comparison.

Methods

Dry blends were melted in a Haake (Karlsruhe, Germany) Rheodrive 5000 fitted with a counter-rotating intermeshing twin-screw extruder. The screw speed was 33 rpm. The extrudate temperature was kept below 230°C to avoid degradation of the hmsPP. The

extrudate was quenched in a water bath and pelletized.

For the preparation of plaques, pellets were melted in the press at 225°C under minimal pressure for 5 min. The pressure was cycled for the removal of air bubbles, and this was followed by 5 min at 0.5 MPa and by 1 min at 1 MPa. The plaques were quenched in water. Specimens for microscopy were prepared by cryomicrotoming of the molded plaques in the cross section.

For the exposure of the crystalline morphology, films and compression-molded plaques were etched with a 0.7 wt % solution of potassium permanganate in a 2:1 (v/v) mixture of concentrated sulfuric acid and 85% orthophosphoric acid.¹⁰ Films were etched 2–4 h to reduce the film to 40–60% of the original thickness; plaques were etched 24 h. Etched specimens were rinsed with methanol and blown dry with compressed air.

For the removal of the amorphous fractions, the microtomed melt blend or the films were placed in 1,1,2,2-tetrachloroethane (TCE) at 80°C for 3–5 h¹¹ and dried in a vacuum oven at 70°C for 1–2 h. Specimens were rinsed with methanol and were blown dry with compressed air.

For scanning electron microscopy (SEM), specimens were sputter-coated with a 100-Å-thick layer of gold and were examined with a scanning electron microscope.

AFM images were obtained in air with a Digital Instruments (Santa Barbara, CA) Nanoscope IIIa in the tapping mode. Moderately hard tapping at 50% of the free oscillation amplitude (A_o) with driving amplitudes of 100–175 mV was used to bring out differences in the moduli of polypropylene and polyethylene but retain topographic information. The unetched inner surface of the film was probed for an amorphous surface layer. The sample-to-tip distance was set nominally at $A_o = 36$ nm. After the driving amplitude was adjusted for minimal contact, the surface was scanned with increasingly hard tapping by progressive lowering of the ratio of the sample-to-average-tip distance ($R = A/A_o$) while a constant driving amplitude was maintained. Phase and height images were recorded simultaneously.

RESULTS AND DISCUSSION

Bulk morphology

An AFM image of the 35/65 znPP/znPE melt blend is shown in Figure 1(a). The phase image shows relative differences in the moduli, with lighter shades indicating higher modulus and darker shades representing lower modulus. The lighter (i.e., harder) znPP phase is dispersed in the darker (i.e., softer) znPE matrix. The znPP domains are large, and the interface between the

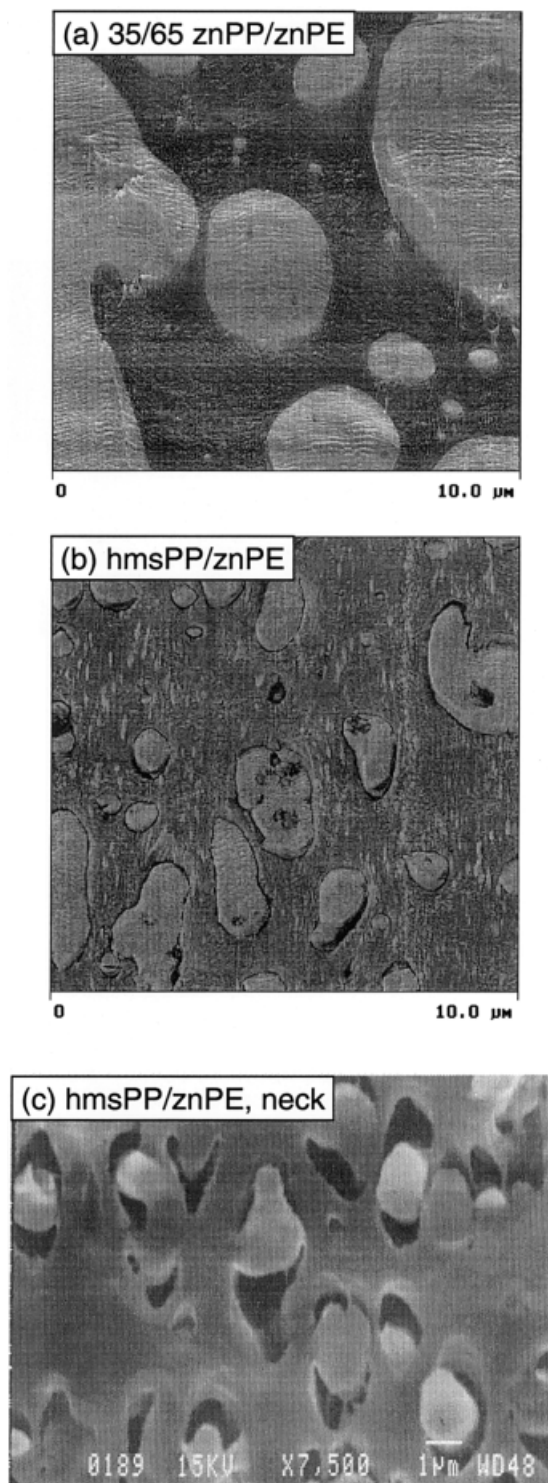


Figure 1 Melt blends of polypropylene and znPE: (a) AFM phase image of 35/65 znPP/znPE, (b) AFM phase image of 35/65 hmsPP/znPE, and (c) scanning electron micrograph of the necked region of 35/65 hmsPP/znPE. The extension direction was vertical.

phases is sharp. The image shows no evidence of the amorphous interfacial layer of low molecular weight, highly branched PE fractions that exists in injection-molded polypropylene/polyethylene blends.¹² The

layer is probably too thin to be resolved at the scale of the AFM image. Occasional vertical streaks and horizontal lines are artifacts of microtoming.

A comparison was made with another blend in which hmsPP replaced znPP. The hmsPP used in this study contained about 16 wt % EPR synthesized in a secondary step after propylene polymerization. Typically, EPR made in this manner contains chains of various compositions with a distribution of ethylene and propylene sequence lengths.^{13,14} The sequence lengths can include noncrystallizable short blocks and runs that are long enough to crystallize as lamellae. As a result, the heterogeneous solid-state structure may be complex.^{9,15}

In the AFM phase image of the 35/65 hmsPP/znPE melt blend in Figure 1(b), the hmsPP phase is dispersed as 1–2- μm domains in the znPE matrix. The light vertical streaks in the znPE matrix are artifacts of microtoming. Many of the hmsPP domains contain small particles of a darker (i.e., softer) material. These particles are crystallizable EPR fractions. They may be anchored to isotactic polypropylene by cocrystallization.⁴ In addition, a very dark (i.e., very soft) interfacial layer separates the hmsPP domains from the znPE matrix. This layer is not evident in the znPP/znPE blend. It is identified as the amorphous EPR fractions. In the process of blending, mobile, amorphous EPR fractions separated from the hmsPP phase and redistributed at the interface. The interfacial layer functioned to reduce interfacial tension and decrease domain size relative to the znPP/znPE blend, which did not contain EPR. The rubbery interfacial layer did not impart good adhesion. An SEM image of the necked region from a uniaxially extended specimen revealed extensive interfacial failure and cavitation [Fig. 1(c)]. Melt blends of hmsPP and zn/mPE were not significantly different from hmsPP/znPE blends in either AFM images of the undeformed blend or SEM images of the necked region.

Etching the 35/65 hmsPP/znPE melt blend with TCE removed the amorphous EPR fractions, leaving a distinct depression at the interface [Fig. 2(a)]. The moderately hard tapping condition also revealed the individual lamellae of the phases. Epitaxial crystallization of polyethylene on polypropylene is well documented.^{16,17} A near lattice match of the unit cells results in the growth of polyethylene lamellae at a characteristic 42° angle to the polypropylene lamellar long axis. The absence of oriented lamellar growth of znPE at the interface with hmsPP indicated that the amorphous interfacial layer prevented intimate contact of the crystallizable hmsPP and znPE constituents.

An AFM image of an hmsPP/znPE blown film is shown in Figure 2(b). Acid etching into the interior revealed the morphology in the plane of the oriented film. A lighter hmsPP domain, surrounded by a darker znPE matrix, extends in the extrusion direction.

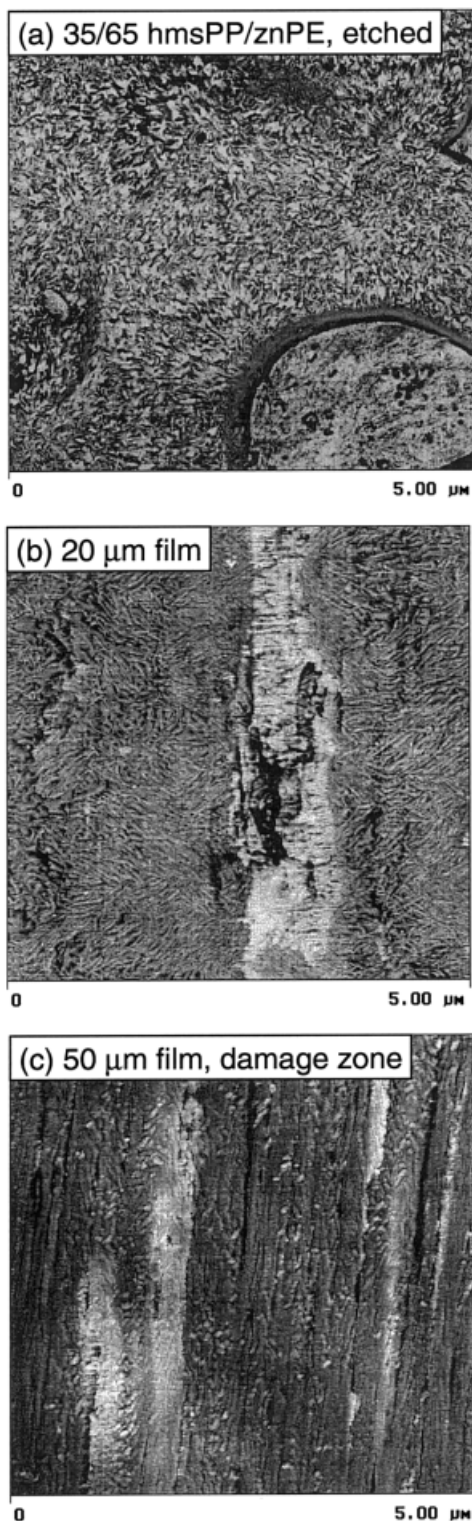


Figure 2 Blends of hmsPP and znPE: (a) AFM phase image of the 35/65 hmsPP/znPE melt blend after etching with TCE, (b) AFM phase image of the 20- μm 10/90 hmsPP/znPE film after acid etching, and (c) AFM phase image of the 50- μm 10/90 hmsPP/znPE film stretched to about 800% and acid-etched.

The hmsPP lamellae are stacked in a column, with lamellar long axes perpendicular to the extrusion direction. Near the hmsPP domain, znPE lamellae are

oriented with long axes $\pm 40\text{--}50^\circ$ to the extrusion direction. These lamellae produce the herringbone pattern characteristic of epitaxially crystallized polyethylene. The blend in Figure 2(b) had the composition 10/90 hmsPP/znPE. In films with higher hmsPP contents approaching that of the melt blend in Figure 1(b), virtually the entire znPE matrix exhibited the herringbone texture of epitaxial crystallization.⁴ The image in Figure 2(b) shows no evidence of the amorphous interfacial layer that was present in the melt blend. Cross-sectional views of the films, which permitted a better evaluation of the phase interface, substantially confirmed this observation.⁴

The hmsPP/znPE film in Figure 2(c) was stretched about 800% in the machine direction. Despite the high extension, epitaxially crystallized znPE remained well adhered to the hmsPP domains. The darker znPE matrix was drawn into fibrillar structures, except in some areas close to the lighter hmsPP domains. Remains of the herringbone texture were seen in which good adhesion to hmsPP constrained large deformation of the matrix. Stress transfer to the hmsPP domains was evident from the shear displacement of the stacked lamellae.

Films with znPE

The interesting question is what happened to the amorphous EPR fractions that constituted an interfacial layer in the melt blend but disappeared from the interface when the blend was blown into a film. One result of molecular heterogeneity is the possibility for the composition of chains near the film surface to differ from the average composition. Segregation of low molecular weight species is well known and exists even for linear homopolymers.¹⁸ Recently, we demonstrated the presence of an amorphous surface layer on blown films of conventional ethylene copolymers, synthesized with Ziegler–Natta catalysts, similar to the znPE used in this study.⁶ The amorphous layer was thought to originate from surface segregation of the lower molecular weight, higher branch content fractions of the heterogeneous copolymer.

The driving force for surface segregation is both energetic and entropic. The entropic reason is halving in the conformational freedom of polymer chains on the surface with respect to chains in the bulk. Therefore, locating chains on the surface is not advantageous in terms of free energy. However, the shorter the chain is, the less freedom it has and the less entropy is lost if the chain is located on the surface. The enthalpic reason for segregation is the decrease in surface energy due to the interaction of chain ends. Shorter chains have a higher concentration of chain ends. The enthalpic advantage for surface segregation can be considerably enhanced if the chain topology is

changed to increase the number of chain ends, for example, by short-chain branching.

The linear low-density polyethylene produced by conventional Ziegler–Natta catalysts is characterized by a wide molecular weight distribution and considerable nonuniformity in comonomer distribution. The chains with the highest concentration of short-chain branches are also those in the low molecular weight tail of the molecular weight distribution. Consequently, short chains that are driven to the surface by the entropic contribution to the chemical potential also have an enthalpic advantage in moving to the surface.

Factors favoring surface segregation are offset by a bulk term that resists creating a volume of material different from the bulk. The connectivity of the polymer chain imposes a constraint that penalizes concentration gradients that are too steep in comparison with the chain dimension. As a heterogeneous polymer mixture comes closer to the point of phase separation, segregation at the surface becomes more favorable as the energetic cost of maintaining a layer at a different composition from the bulk becomes smaller. Biphasic blends of two homogeneous metallocene copolymers with different comonomer contents readily form a surface layer consisting of the more highly branched constituent.⁶

The phase separation of amorphous EPR fractions in impact polypropylene resins is extensively documented.^{9,15} In blends of these resins with polyethylene, it is energetically advantageous for amorphous EPR to distribute as an interfacial layer between domains of the crystallizable polypropylene and polyethylene constituents. However, in blown films, surface segregation is an attractive alternative. The high ethylene content of amorphous EPR fractions, roughly 50% on a molar basis,⁹ creates the additional possibility that lower molecular weight, higher branch content znPE chains are miscible with amorphous EPR.

An amorphous surface layer formed in the melt during blown-film processing should be preserved during subsequent solidification. A very thin and soft layer should be detectable if the surface is probed very gently. Moreover, it should be possible to remove a layer that differs in chemical composition from the bulk through washing with an appropriate solvent. The inner surface of the znPE blown film was imaged with gradually increasing tapping force in the sequence of AFM phase images shown in Figure 3(a–c). The image obtained with the lightest tapping was featureless, except where a few lamellar segments appeared as bright spots. Increasing the contrast brought out the surface topography [Fig. 3(a)]. Slightly harder tapping with normal contrast revealed more lamellar features [Fig. 3(b)]. Normal tapping conditions exposed the lamellar texture, but dark, featureless areas remained, for example, in the center of the image [Fig. 3(c)]. Taken in sequence, the images suggested a sur-

face enriched in amorphous fractions. These fractions constituted a soft layer through which the AFM tip had to probe to detect underlying crystalline lamellae. By detecting the presence of some crystalline lamellae with the lightest tapping condition, the phase images suggested a gradient of increasing lamellar density.

A second sequence of images was obtained with the same tapping conditions after the surface was washed with TCE [Fig. 3(d–f)]. Instead of being almost featureless, the image obtained with the lightest tapping conditions and shown with normal contrast contained numerous bright lamellar segments [Fig. 3(d)]. With slightly harder tapping, the lamellar morphology became apparent [Fig. 3(e)]. Normal tapping revealed more of the lamellar texture [Fig. 3(f)]. The sequence of images demonstrated that washing removed much of the amorphous surface layer. However, the fact that light tapping did not fully reveal the lamellar morphology probably indicated that some insoluble amorphous material remained on the surface. This suggested that a compositional gradient was thermodynamically favored over a sharp interface. The gradient located the most highly branched, lowest molecular weight fractions at the surface with the gradually increasing concentration of crystallizable chains approaching that of the bulk composition. Washing removed the most soluble chains, which were the lower molecular weight, higher branch content fractions at the surface. By removing these fractions, washing revealed crystallizable chains in addition to amorphous chains of somewhat higher molecular weight and lower branch content. These amorphous chains were possibly anchored to crystals, which further discouraged their dissolution.

Although the amorphous surface layer uniformly covered the znPE film, the surface of the hmsPP/znPE blend film appeared heterogeneous when large areas (10 μm^2) were imaged with light tapping conditions [Fig. 4(a)]. Featureless regions alternated with textured regions in the blend film. The possibility that the loss of tip tracking due to surface waviness caused the changes in texture was precluded by good height tracking and the absence of correspondence between the AFM phase and height images [Fig. 4(b)].

A region that contained both textures was imaged with gradually increasing tapping force in the sequence of higher resolution AFM phase images shown in Figure 5 (a–c). With minimal tip penetration, the phase image obtained with the lightest tapping showed primarily surface topology of the featureless regions [Fig. 5(a)]. In contrast, the lightest tapping revealed a crystalline morphology in the textured regions. The area on the left side of Figure 5(a) shows polyethylene lamellae surrounding a dense light area that is a polypropylene domain. That much longer polyethylene lamellae were present at the surface rather than in the bulk [cf. Fig. 2(c)] was consistent

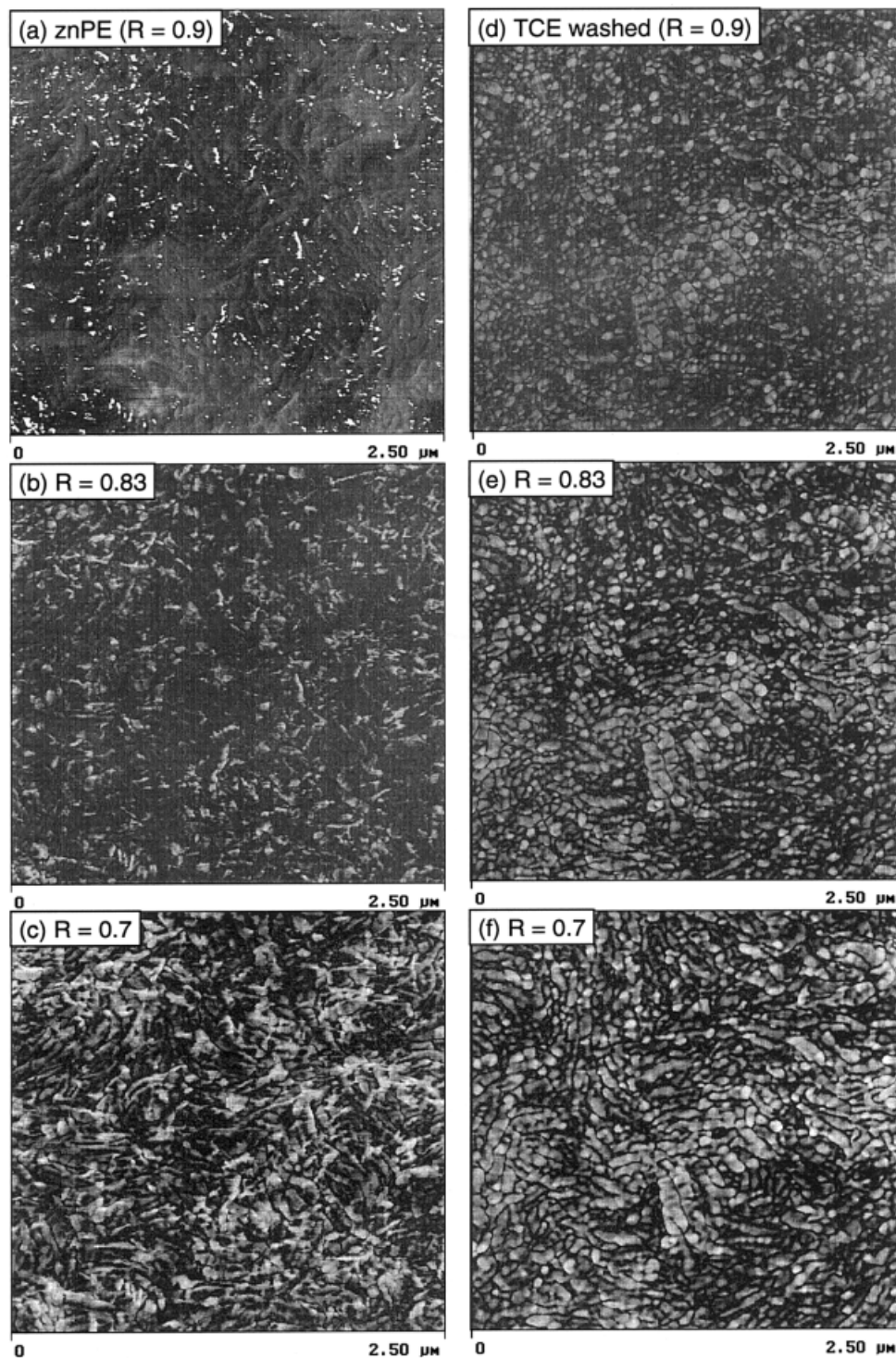


Figure 3 AFM phase images of the 50- μm znPE film surface: (a–c) imaged with increasingly hard tapping and (d–f) washed with TCE and imaged with increasingly hard tapping.

with the higher temperature inside the bubble and, therefore, a somewhat slower crystallization rate at the inner surface. Harder tapping revealed more polyethylene lamellae and another polypropylene domain underlying the featureless region [Fig. 5(b,c)]. The herringbone texture, characteristic of epitaxially crystallized polyethylene,^{16,17} was evident in several places.

Washing with TCE completely removed the featureless regions [Fig. 5(d–f)]. Even the lightest tapping condition fully revealed the crystalline morphology on the entire surface [Fig. 5(d)]. Harder tapping did not expose any additional features [Fig. 5(e,f)].

The absence of an interfacial layer in the blend film can now be understood. In thin films, most of the

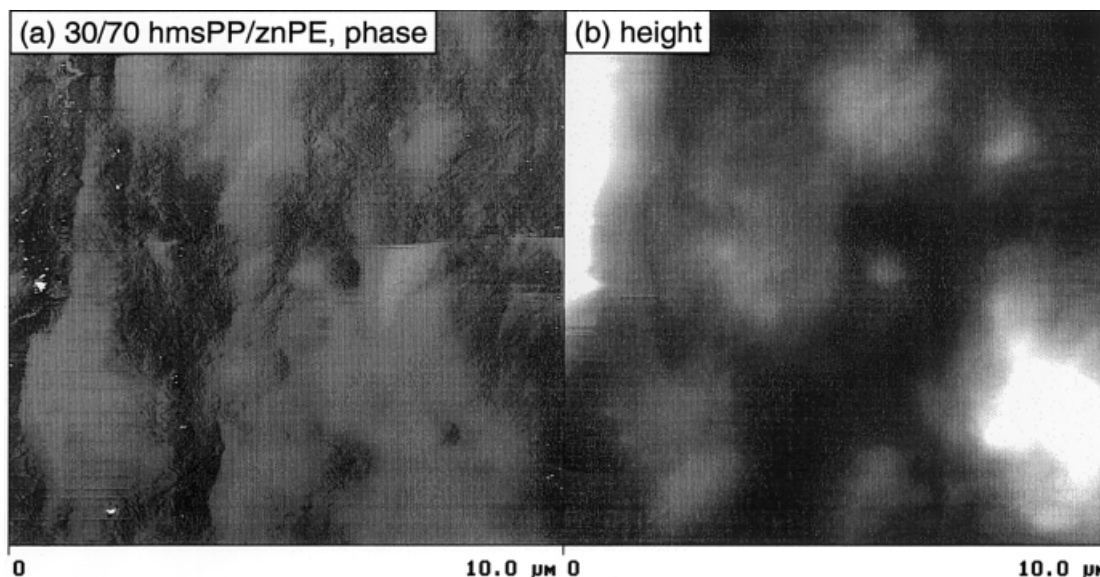


Figure 4 AFM images of the 50- μm 30/70 hmsPP/znPE film surface obtained with very light tapping: (a) phase image and (b) height image.

mobile, amorphous EPR fractions locate at the surface rather than at the interface between hmsPP and polyethylene domains. The tendency for the amorphous surface layer to segregate into pools is characteristic of an immiscible substance. This contrasts with the continuity of the amorphous surface layer on the znPE film and points to a substantial difference between the amorphous surface layers on the znPE and hmsPP/znPE films. Surface enrichment best describes the compositional gradient that results from the concentration of lower molecular weight, higher branch content chains at the surface of the znPE film. Surface segregation is more appropriate for the emergence of EPR fractions as a separate phase at the surface of the blend film.

Even though znPE was the major constituent of the blend film, there were regions of the film surface in which even the lightest tapping fully revealed the crystalline morphology. These regions did not possess a detectable amorphous layer comparable to that on the znPE film. It was likely that the amorphous EPR pools also contained lower molecular weight, higher branch content znPE fractions that otherwise would have constituted a surface-enriched layer.

Films with zn/mPE

The inner surface of the zn/mPE blown film was imaged with gradually increasing tapping force in the sequence of AFM phase images in Figure 6(a–c). The image obtained with the lightest tapping was essentially featureless if the image was viewed with normal contrast. The very high contrast used for Figure 6(a) revealed the surface topology, which resembled arrays of curving lamellae, and a few bright spots, which were lamellar segments. The lamellar texture was confirmed

by the correspondence between the surface topology and the bright lamellar fragments revealed by slightly harder tapping [Fig. 6(b)]. Normal tapping conditions exposed more of the lamellar texture [Fig. 6(c)]. The sequence of images of the zn/mPE film closely resembled images of the znPE film [cf. Fig. 3(a–c)] obtained with the same tapping conditions, which suggested that the zn/mPE film had approximately the same degree of surface enrichment in amorphous fractions.

A second sequence of images obtained after the zn/mPE film was washed with TCE showed essentially no change from the unwashed surface [Fig. 6(d–f)]. With the lightest tapping, the surface appeared featureless until increasing contrast brought out the surface topography [Fig. 6(d)]. Images in Figure 6(e,f) obtained with harder tapping revealed about the same amount of lamellar detail as comparable images of the unwashed zn/mPE film [Fig. 6(b,c)].

TCE washing possibly did not alter the surface of the zn/mPE film because an amorphous surface layer was not present. However, it is more likely that the surface layer existed but was insoluble in TCE. Support for this conclusion comes from the tapping conditions that were used to image the zn/mPE film. A correspondence of the phase images of the unwashed zn/mPE film with the phase images of the unwashed znPE film obtained with the same tapping conditions [cf. Fig. 6(a–c) and Fig. 3(a–c)] indicated that the AFM tip had to penetrate through an amorphous surface layer to reveal the underlying lamellar morphology of the zn/mPE film. Otherwise, a much smaller tapping force would have sufficed. At least two examples demonstrate that the light tapping condition used here would have revealed the lamellar morphology if an amorphous surface layer were not present. As this

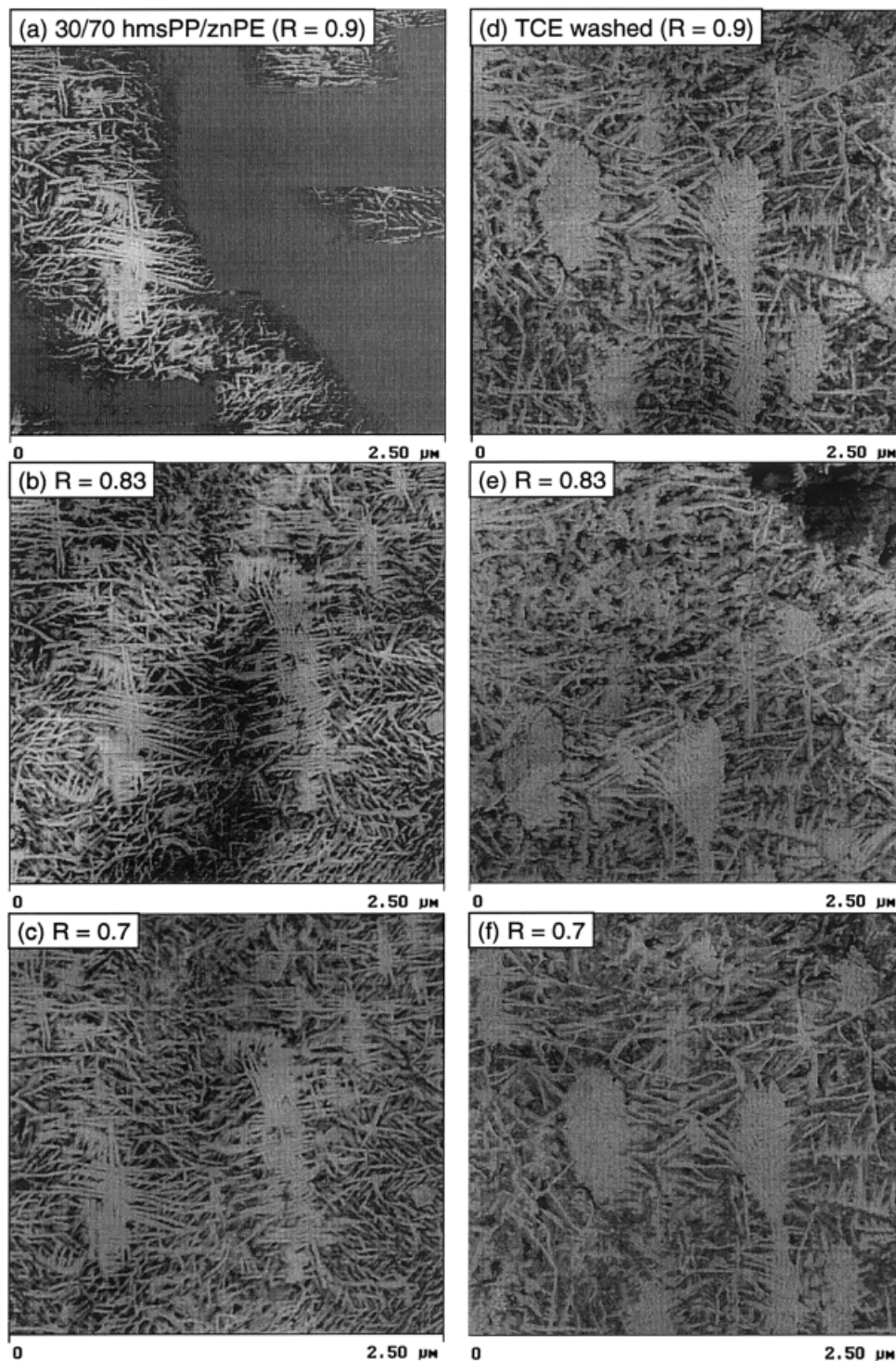


Figure 5 AFM phase images of the 50- μm 30/70 hmsPP/znPE film surface: (a–c) imaged with increasingly hard tapping and (d–f) washed with TCE and imaged with increasingly hard tapping.

study demonstrated, light tapping revealed the lamellar morphology of the znPE film after a solvent removed the amorphous layer and exposed the underlying lamellae [cf. Fig. 3(d–f)]. In a previous study,⁶ a homogeneous metallocene copolymer film, which did not possess a surface layer that differed from the bulk, required much lighter tapping to fully reveal the la-

mellar morphology than a Ziegler–Natta copolymer film, which did have an amorphous surface layer. Therefore, if a surface layer were not present on the znPE film, the light tapping conditions used to obtain Figure 6(a) should have revealed the lamellar morphology. This was not the case. Rather, the zn/mPE film appears to possess an amorphous surface layer

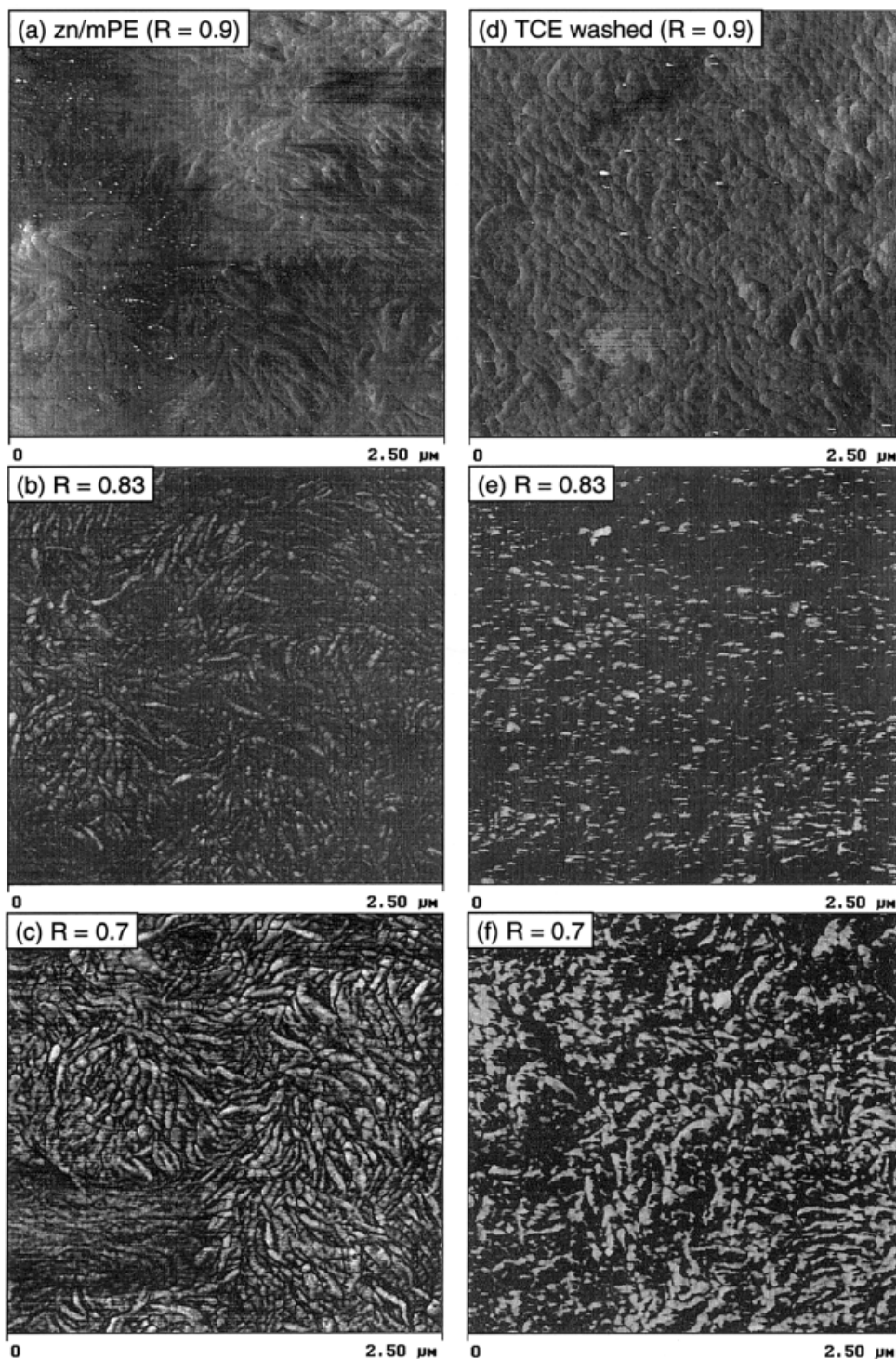


Figure 6 AFM phase images of the 50- μm zn/mPE film surface: (a–c) imaged with increasingly hard tapping and (d–f) washed with TCE and imaged with increasingly hard tapping.

that is not removed by TCE washing. Differences in the effect of TCE washing on znPE and zn/mPE surfaces must lie in the composition of the chains that constitute the amorphous layer.

Although znPE and zn/mPE have approximately the same density and, therefore, the same overall level of crystallinity, they differ in chain composition. The

heterogeneous Ziegler–Natta constituent of zn/mPE has a somewhat higher density and, therefore, a lower overall branch content than the heterogeneous copolymer of the znPE film. In zn/mPE, short-chain branching resides primarily with high molecular weight chains of the homogeneous metallocene constituent. The driving force for the surface segregation

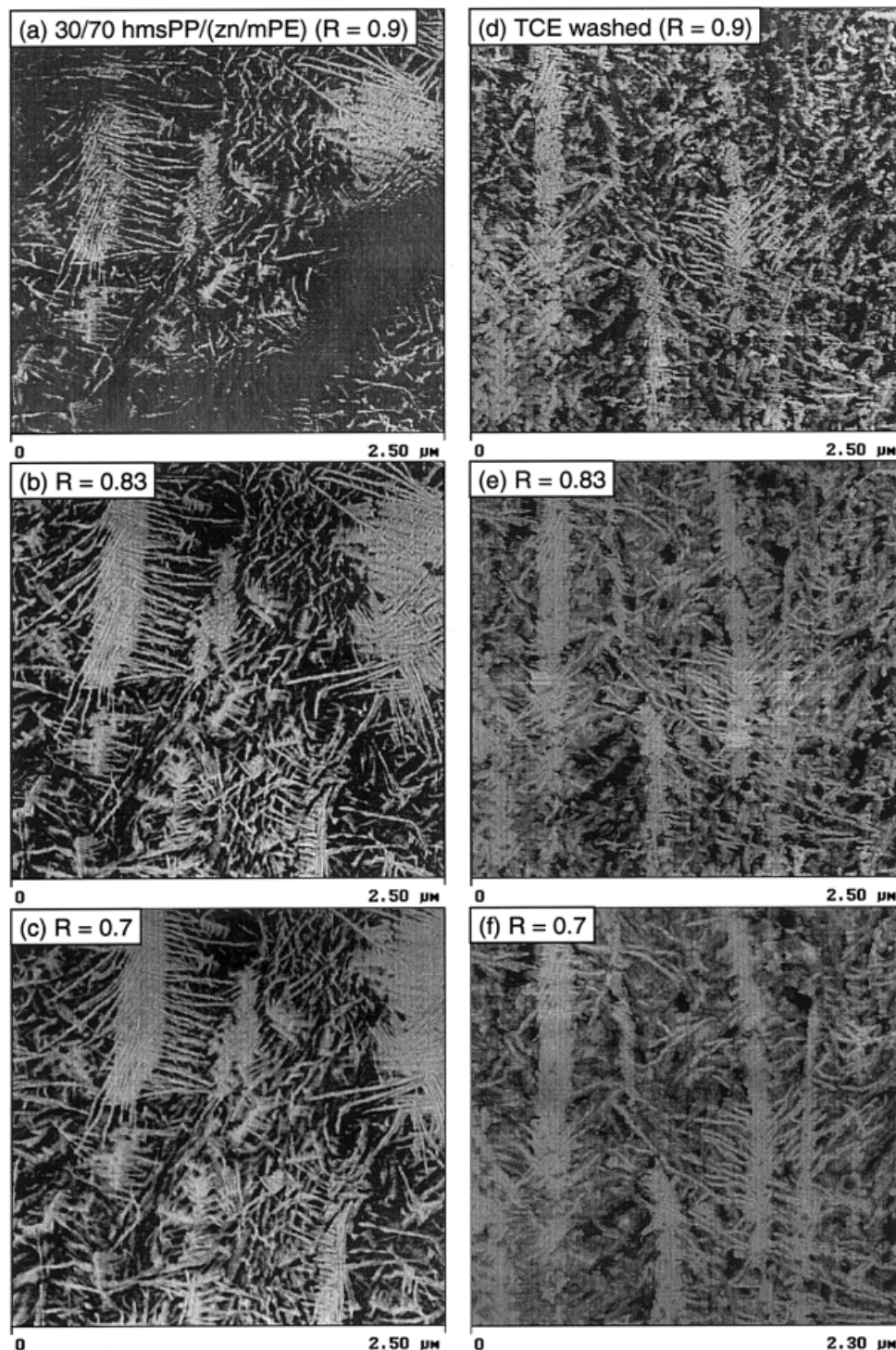


Figure 7 AFM phase images of the 50- μm 30/70 hmsPP/(zn/m) PE film surface: (a–c) imaged with increasingly hard tapping and (d–f) washed with TCE and imaged with increasingly hard tapping.

of branched metallocene chains is only enthalpic; there is an entropic disadvantage for higher molecular weight chains to segregate at the surface. Furthermore, the metallocene constituent may compatibilize the lower molecular weight, higher branch content Ziegler–Natta chains, making surface segregation of these fractions less favorable. Speculation regarding

the composition of the surface layer is complicated by the very heterogeneous chain composition of zn/mPE. However, it can be hypothesized that metallocene chains constitute a significant component of the surface layer. The anchoring of these high molecular weight chains by cocrystallization and entanglement with crystallizable fractions of the Ziegler–Natta con-

stituent could make them resistant to dissolution by TCE.

The surface of the hmsPP/(zn/mPE) blend film had the same heterogeneous appearance as the hmsPP/znPE film (cf. Fig. 5) when areas $10 \mu\text{m}^2$ were imaged with light tapping conditions. A region that contained both textures was imaged with gradually increasing tapping force in the sequence of higher resolution AFM phase images shown in Figure 7(a–c). With minimal tip penetration, the phase image obtained with the lightest tapping showed the surface topography of the featureless regions and a crystalline morphology in the textured regions [Fig. 7(a)]. However, a comparison with the unwashed surface of the hmsPP/znPE blend film [cf. Fig. 4(a)] suggested that the boundary between the featureless and textured regions was less distinct in the hmsPP/(zn/mPE) blend, as if phase separation of the mobile, amorphous EPR fractions were poorer than in the hmsPP/znPE blend. In addition, the separation of lamellae by dark, featureless areas was more noticeable in the hmsPP/(zn/mPE) blend, as if the crystalline regions contained more amorphous material. It is possible that the mobile EPR fractions were more compatible with zn/mPE than with znPE. Harder tapping revealed more of the lamellar blend morphology [Fig. 7(b,c)]. Washing with TCE removed the featureless regions and exposed an overall lamellar blend morphology [Fig. 7(d–f)]. Even with normal tapping [Fig. 7(f)], the image of washed hmsPP/(zn/mPE) revealed less inner detail than the corresponding image of the washed hmsPP/znPE film [cf. Fig. 5(f)]. It was possible that the separation of the amorphous zn/mPE fractions with amorphous EPR was less complete in the hmsPP/(zn/mPE) film. Some chains might have remained in the polyethylene phase, in which anchoring to polyethylene lamellae made them insoluble to TCE, much as the amorphous surface layer on the zn/mPE film was insoluble to TCE.

CONCLUSIONS

This study concerned the nature of certain blown-film surfaces. It was stimulated by the observation that although melt blends of polyethylene with impact-modified polypropylene possessed an interfacial layer of mobile, amorphous EPR fractions, this layer was not detected in a film blown from the blend. In the absence of an interfacial EPR layer in the blend film, intimate contact of the phases resulted in epitaxial crystallization of polyethylene. Good adhesion between the phases ensured effective stress transfer during deformation. The existence of a surface layer with a composition different from that of the bulk on the blown film of Ziegler–Natta ethylene copolymers, previously demonstrated by gentle probing of the surface with AFM, was the basis for examining the surfaces of

blend films with the same methodology. The demonstration of an amorphous layer on the surface of the blown znPE film reproduced previous reports. Removing the surface layer by solvent washing confirmed the hypothesis that the layer consisted of lower molecular weight, higher branch content fractions. Films of the hmsPP/znPE blend also exhibited an amorphous surface layer.

The absence of an interfacial EPR layer in the hmsPP/znPE blend film was now understood. In thin films, most of the amorphous EPR fractions located at the surface rather than at the phase interface. The tendency for the amorphous surface layer to segregate into pools was characteristic of an immiscible substance. This pointed to a substantial difference between the amorphous surface layers on the znPE and hmsPP/znPE films. Surface enrichment best described the compositional gradient that resulted from the concentration of lower molecular weight, higher branch content chains at the surface of the znPE film. Surface segregation was more appropriate for the emergence of EPR fractions as a separate phase at the surface of the blend film. Films containing zn/mPE reproduced the primary features of surface enrichment (zn/mPE) and surface segregation [hmsPP/(zn/mPE)]. Some differences were attributable to the metallocene constituent of zn/mPE.

The generous technical and financial support of The Dow Chemical Co. is gratefully acknowledged.

References

1. Hoenig, W. D.; Bosnyak, C. P.; Sehanobish, K.; Van Volkenburgh, W.; Ruiz, C.; Tau, L. M. *Proc Soc Plast Eng Annu Tech Conf* 2000, 46, 1843.
2. Wu, S.; Bosnyak, C.; Faul, D.; Tau, L.; Huang, Y. *Proc Soc Plast Eng Annu Tech Conf* 2001, 47, 2828.
3. Chang, A. C.; Tau, L.; Hiltner, A.; Baer, E. *Polym Eng Sci*, to appear.
4. Chang, A. C.; Tau, L.; Hiltner, A.; Baer, E. *Polymer* 2002, 43, 4923.
5. Chang, A. C.; Chum, S. P.; Hiltner, A.; Baer, E. *Polymer*, to appear.
6. Qureshi, N. Z.; Rogunova, M.; Stepanov, E. V.; Capaccio, G.; Hiltner, A.; Baer, E. *Macromolecules* 2001, 34, 3007.
7. Qureshi, N. Z.; Stepanov, E. V.; Capaccio, G.; Hiltner, A.; Baer, E. *Macromolecules* 2001, 34, 1358.
8. Shih, H.-H.; Wong, C.-M.; Wang, Y.-C.; Huang, C.-J.; Wu, C.-C. *J Appl Polym Sci* 1999, 73, 1769.
9. Zacur, R.; Goizueta, G.; Capiati, N. *Polym Eng Sci* 2000, 40, 1921.
10. Olley, R. H.; Bassett, D. C. *Polymer* 1982, 23, 1707.
11. Kolbert, A. C.; Didier, J. G. *J Appl Polym Sci* 1999, 71, 523.
12. Chaffin, K. A.; Bates, F. S.; Brant, P.; Brown, G. M. *J Polym Sci Part B: Polym Phys* 2000, 38, 108.
13. Lehtinen, A.; Paukkeri, R. *Macromol Chem Phys* 1994, 195, 1539.
14. Hongjun, C.; Xiaolie, L.; Dezhu, M.; Jiamin, W.; Hongsheng, T. *J Appl Polym Sci* 1999, 74, 93.
15. D'Orazio, L.; Mancarella, C.; Martuscelli, E.; Cecchin, G.; Corriero, R. *Polymer* 1999, 40, 2745.
16. Lotz, B.; Wittman, J. C. *J Polym Sci Part B: Polym Phys* 1987, 25, 1079.
17. Wittman, J. C.; Lotz, B. *Prog Polym Sci* 1990, 15, 909.
18. Jones, R. A.; Richards, R. W. *Polymers at Surfaces and Interfaces*; Cambridge University Press: New York, 1999.