

Blends of High Density Polyethylene and Ethylene/1-Octene Copolymers: Structure and Properties

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ABSTRACT: The morphology formation in the blends comprising a high density polyethylene (HDPE) and selected ethylene/1-octene copolymers (EOCs) was studied with variation of blend compositions using atomic force microscopy (AFM). The binary HDPE/EOC blends studied showed well phase-separated structures (macrophase separation) in consistence with individual melting and crystallization behavior of the blend components. For the blends comprising low 1-octene content copolymers, the lamellar stacks of one of the phases were found to exist side by side with that of the another phase giving rise to leaflet vein-like appearance. The formation of large HDPE lamellae particu-

larly longer than in the pure state has been explained by considering the different melting points of the blend components. The study of strain induced structural changes in an HDPE/EOC blend revealed that at large strains, the extensive stretching of the soft EOC phase is accompanied by buckling of HDPE lamellar stack along the strain axis and subsequent microfibrils formation. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1887–1893, 2007

Key words: polymer blends; semicrystalline polymer; α -olefin comonomers; deformation mechanism; atomic force microscopy; scanning electron microscopy

INTRODUCTION

Polyethylene (PE) and their copolymers form a part of commodity plastics, which cover a large part in the present days plastics consumption. A major area of practical application of these plastics is in the manufacture of packaging films and household containers. It has been demonstrated that the copolymerization of ethylene with α -olefins (such as 1-pentene, 1-hexene, 1-octene, etc.) using single-site metallocene catalysts leads to the formation of homogeneous ethylene/ α -olefin copolymers with uniform distribution of comonomers and a narrow molar mass distribution, which have a dramatic effect on their mechanical properties.^{1–6} Owing to their improved mechanical and thermal properties, the industrial application of metallocene-based ethylene copolymers is rapidly increasing.⁷

It is generally known that via copolymerization with higher α -olefin comonomers, the density and, hence, the melt flow index of these copolymers can be significantly lowered. These factors affect directly the polymer morphology in the melt as well as in the solid state leading finally to a drastic change in their mechanical

performance. Furthermore, high α -olefin copolymers, such as ethylene/1-octene copolymers (EOCs), which show predominantly elastomeric properties,^{4,8} can be used as impact modifiers for several polyolefins such as high density polyethylene (HDPE) and isotactic polypropylene.^{9–13} In such mixtures, it has been demonstrated that there exists a partial miscibility for a certain composition range and a significant improvement in processing as well as in mechanical properties. Recently, we studied the blends comprising an HDPE and a high 1-octene content ethylene/1-octene copolymer (EOC). It was shown that the blend components do phase-segregate and form crystalline entities corresponding to the blend components in the segregated regions. By changing the 1-octene content in the copolymers or by changing the copolymer content in the blends with HDPE, it was possible to tailor the mechanical properties of these multi-component systems over a wide range.¹⁴

The aim of the present work is to elaborate our recent works on HDPE/EOC blends by throwing more light on their solid state structure by means of atomic force microscopy (AFM). We will further analyze the micromechanical behavior of selected blends by means of scanning electron microscopy (SEM).

We dedicate this work to Prof. F. J. Baltá-Calleja on the occasion of his 70th birthday.

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EXPERIMENTAL

Materials and sample preparation

The characteristics of samples used to prepare the blends are presented in Table I. The ethylene/1-octene copolymers (EOCs) (named as EOC1, EOC2, and

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TABLE I
Characteristics of the Samples Used to Prepare Blends

sample code	HDPE	EOC1	EOC2	EOC3
commercial name	HDPE 53050 E	Affinity PL1845	Affinity PL1850	Affinity EG8150
Morphology ¹⁴	lamellae	lamellae	distorted lamellae	micellar domains
1-octene wt.-%	0	9.5	17.2	35.0
# density (g/cm ³)	0.953	0.910	0.902	0.868
* crystallinity degree	71	43	36	13
* melting point (K)	404	381	374	328

From manufacturer's data sheets.

* Determined by DSC.¹⁵

EOC3), synthesized by the INSITETM technology and the HDPE, were all provided by Dow Chemical (Terneuzen, The Netherlands). The binary mixtures with different HDPE/EOC weight ratios were prepared by melt blending using a twin-screw extruder. Approximately 1 mm thick plaques of each sample were compression-molded at 160°C and subsequent cooling under pressure at a rate of 1 K min⁻¹.

For the atomic force microscopic studies, ~ 40 µm thin films sliced from the compression-molded samples by means of a microtome were melted at a temperature of 150°C and allowed to cool down to room temperature at a rate of 10 K min⁻¹ using a special miniaturized heating device. The thermal treatment was performed between two freshly cleaved mica sheets as described by Godehardt et al.¹⁶ Selected blends were cryo-ultramicrotomed using diamond knife and the flat surface thus formed was directly imaged by the atomic force microscopy (AFM) operated at tapping mode. All the AFM experiments were performed under ambient conditions. The AFM tips used were microfabricated supersharp silicon cantilevers with a radius of curvature of about 10 nm, and the set point ratio (ratio of the cantilever amplitude relative to its free oscillation amplitude) was ~0.8.

RESULTS AND DISCUSSION

Morphological characterization

In our recent work, the morphology of EOCs as a function of comonomer content was analyzed. In particular, the correlation between morphology and deformation behavior of the HDPE/EOC3 blends (Table I) was investigated.¹⁴ Therefore, we will first summarize the results already published and mainly focus on the morphology formation in HDPE/EOC1 and HDPE/EOC2 blends. Finally, deformation micro-mechanisms of such blends will be discussed taking an HDPE/EOC2 blend as an example.

In contrast to the well-developed spherulitic morphology and parallel arrays of lamellar bundles with

each crystalline lamella being clearly separated by amorphous intercrystalline layers, with increasing 1-octene content, the spherulitic texture gradually disappeared and the lamellar structure is progressively destroyed. At lower 1-octene content, the morphology of the copolymer was found to be still similar to that of HDPE. For higher 1-octene content, worm-like crystals were observed, which resemble the crystalline *fringed micelles* discussed in the literature.¹⁷

In accordance with the earlier results by Bensason et al.,¹ with increasing comonomer content, a decrease of density (and crystallinity) was observed¹⁴ (Table I). The transition from the lamellar morphology to that comprising the bundled beaded-strings and worm-like micelles was attributed to the confinement effect imposed by the presence of side branches at regular intervals, which restrict the formation of well-defined lamellae via chain folding.¹

Figure 1 shows tapping mode AFM phase images of HDPE/EOC1 blends for two different asymmetric compositions (weight ratios 75/25 and 25/75). For both the compositions, two distinct regions consisting of lamellar crystals of different thicknesses are visible, which corresponds to the morphology of the constituent polymers. As depicted in Table I, both the polymers in the pure state possess lamellar morphologies, which are preserved in the blends.

Because of the similarity in chemical structure as well as in basic morphology of the polymer pairs, the segregation is different from that of the completely incompatible polymer pairs such as polypropylene/ethylene-propylene rubber systems. Irrespective of the blend composition, the lamellae collectively form a network similar to that of venal skeleton of a simple leaf—the thicker HDPE lamellae form the primary veins and the thinner EOC1 lamellae the secondary ones. It is to be noted that the blend components exist side by side; they are not segregated on the macroscopic scale.

The AFM phase images of the blends also represent the local mechanical heterogeneity of each sample. The regions having higher amount of mobile amorphous phase (such as EOC1 phase) appear

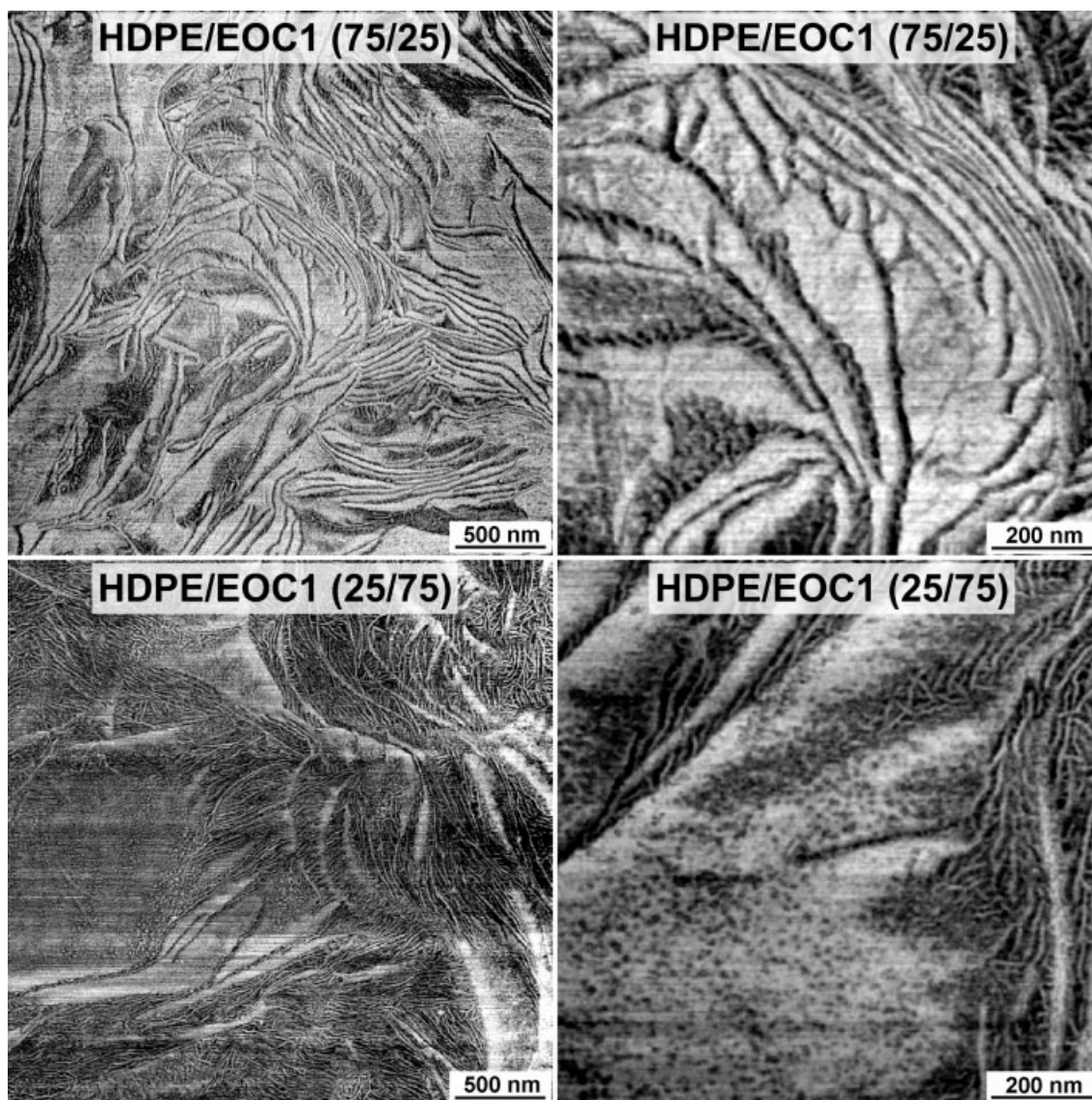


Figure 1 Lower (left) and higher (right) magnifications of AFM phase images showing the surface morphology of HDPE/EOC1 blends; the blend compositions are indicated.

darker than the one having lesser amount of amorphous component (such as HDPE phase).

It appears that the most influencing factor causing the segregation of the blend components is the different molecular architecture of the PE chains. Thus, it can be expected that the extent of segregation may become more dramatic if the architecture of the PE chains differ more significantly. Indeed, in the blends of HDPE and an ethylene/1-octene copolymer having higher amount of 1-octene (for instance EOC2, Table I), a stronger segregation of the blend components was observed (Fig. 2) than in the previous case. Now, the majority phase tends to form the matrix embedding the minority phase as inclusions. Nevertheless, the leaf-venation-like structure of the lamellae (with the HDPE lamellae forming the primary veins) does not vanish yet. As in the previous

case, the long extended HDPE lamellae are abundant independent of the blend composition.

The AFM images of the blends presented in Figures 1 and 2 correspond to their surface morphology. Because of the presence of different interfaces (viz. the polymer/air interface), the latter may deviate from the bulk morphology. To ascertain whether the observed morphology corresponds to that of the bulk samples, we also investigated the bulk morphology of selected samples, which further confirmed the morphologies observed on the thin film surfaces.¹⁴

For the HDPE/EOC3 blends, irrespective of blend compositions, a strong tendency of phase separation was observed.¹⁴ As EOC3 contains the largest amount of 1-octene among the EOCs investigated (Table I), the HDPE/EOC3 system also inclines most robustly towards segregation. As an instance, Figure 3 illus-

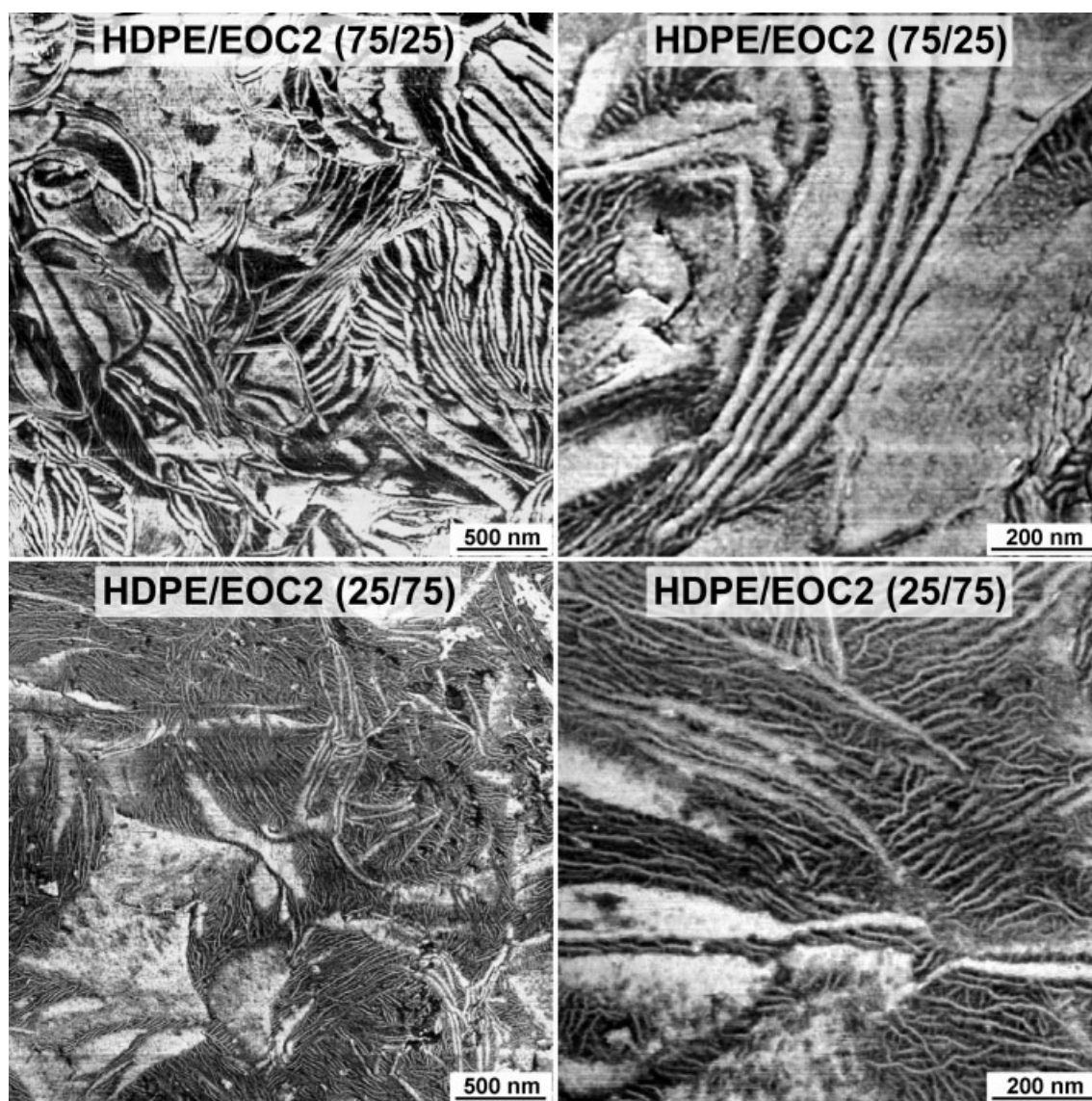


Figure 2 Lower (left) and higher (right) magnifications of AFM phase images showing the surface morphology of HDPE/EOC2 blends; the blend compositions are indicated.

trates the morphology of a blend containing 75 wt % EOC3. The sample surface for the SEM investigation was prepared according to the standard permanganic etching procedure described by Olley et al.¹⁸ and further developed in our group for specific multicomponent blends.¹⁹

The SEM micrographs show that the minority HDPE phase exists as isolated islands scattered in the matrix of EOC3. The HDPE lamellae appearing bright in the SEM images extend to a length of several hundred nanometers and act as filler for the matrix polymer.

It should be noted that the investigated blend partners are characterized by differences in their melting points (Table I), in general, the melting temperature lowering with increasing 1-octene content.¹⁵ The blends of HDPE with the copolymers showed two separate melting endotherms corresponding to

that of two pure components indicating that they crystallized as separate entities in all the blends.¹⁵ For example, regardless of the composition, two melting points were observed around 400 and 330 K in HDPE/EOC3 blends. The presence of multiple melting points in the blends supports strongly the notion of demixing of the blend components.

With the aid of transmission electron microscopy (TEM), the long individual lamellar crystals with very high aspect ratio could be revealed in EOC3-rich blends. The growth of lamellae to exceptionally long dimension can be correlated with a wide gap of the melting temperatures of polymers. On cooling the mixture from the melt, as the HDPE component solidifies due to crystallization, the surrounding EOC phase remains still mobile (molten state) due to much lower melting and crystallization tempera-

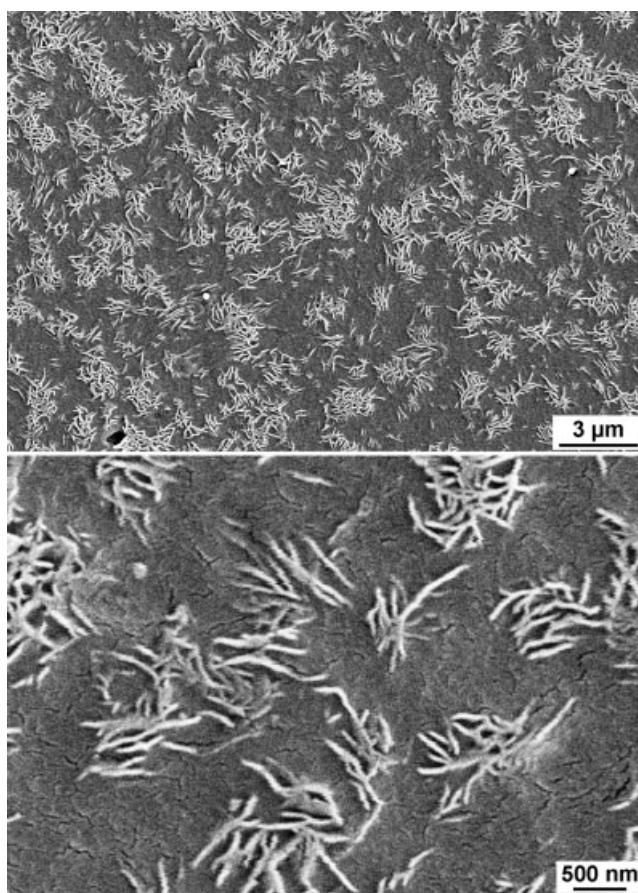


Figure 3 SEM images of different magnifications showing the typical matrix/dispersed phase bulk morphology of HDPE/EOC3 (25/75) blend.

tures. This situation enables a rapid growth of the HDPE lamellae penetrating through the EOC phase. This assumption is supported by the presence of pointed tip-like appearance of each lamella at the interface with the copolymer matrix.^{14,16}

Micromechanical properties of HDPE/EOC2 blends

The understanding of different micromechanical deformation processes, which form a bridge between the nanostructural diversities of the polymeric materials on one side and their macroscopic mechanical properties on the other, is of practical significance. However, compared to the structural characterization and the study of mechanical properties of multicomponent PEs, there are only limited investigations available, which systematically deal with the correlation between their macroscopic mechanical properties and the underlying mechanisms of deformation. One of the objectives of this work is to explore the micromechanisms operating in selected multicomponent PEs subjected to uniaxial tensile deformation. Here, we present the preliminary results obtained in the HDPE/EOC2 blends. The detailed analyses of the deformation

processes as a function of copolymer composition as well as the applied strain are to follow in future.²⁰

For the characterization of deformation behavior of polymers, one of the best methods comprises the acquisition of changes in structural details of the polymers subjected to an *in situ* test.¹⁶ Such tests allow a direct visualization of the micromechanical properties of heterogeneous polymers, albeit mainly con-

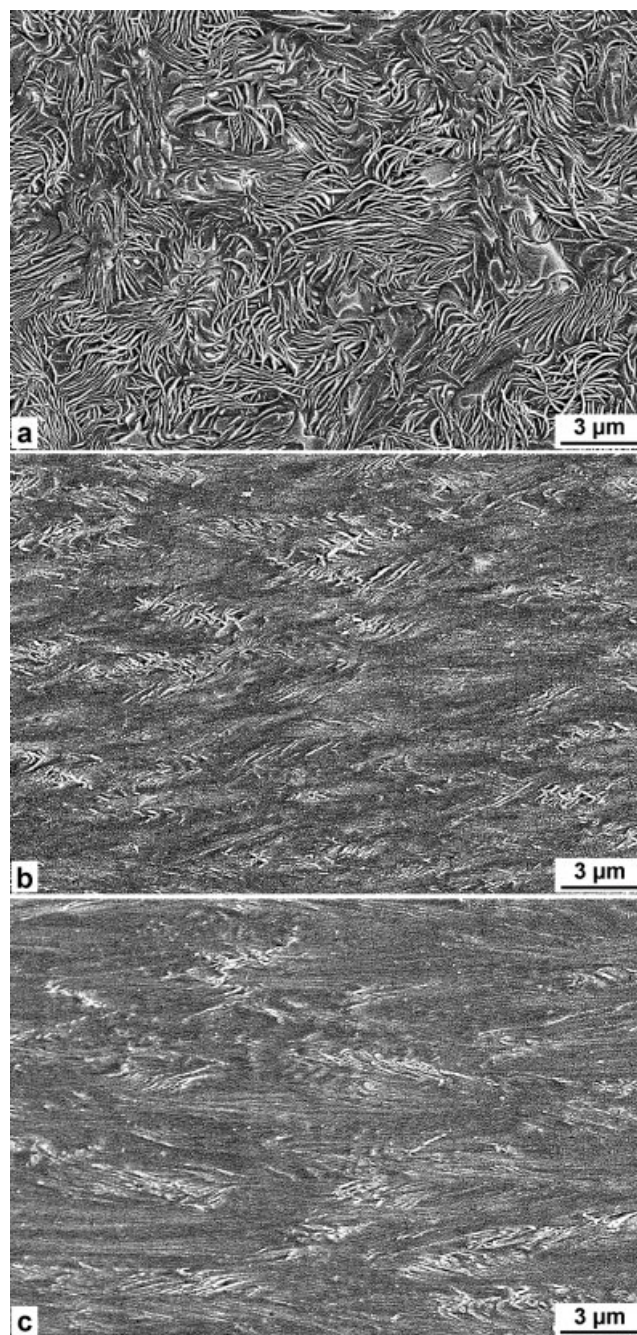


Figure 4 SEM micrographs showing strain-induced structural changes in a blend comprising HDPE and 75% EOC2; (a) undeformed region, (b) location at the necking zone, and (c) highly deformed area far away from the neck; deformation direction is horizontal.

fined to the sample surface. Alternatively, if one is also interested to study the deformation processes occurring in the bulk polymers, which deform via necking and drawing, the deformation structures in a tensile bar along the necking region beginning from the undeformed area can be studied with the aid of scanning and TEM.

Following the technique discussed by Henning et al.,²¹ the bar close to the necking region was cryoultramicrotomed and subjected to permanganic etching to reveal the deformation structures at different stages of deformation. The representative SEM images are presented in Figure 4. Because of more intense chemical degradation (etching) of the less densely packed EOC2 phase, the bundle of HDPE lamellae [appearing bright patches in the SEM micrograph, Fig. 4(a)] appear more abundant on the SEM micrographs recorded from undeformed region. Therefore, the SEM micrographs to follow [i.e., Fig. 4(b,c)] represent essentially the deformation structures of the HDPE lamellae. There are still dark regions between the lamellar bundles, which can be assigned to the EOC2 phase. In agreement with the conclusions drawn from the morphological features observed on thin film surface by AFM studies, strips of the HDPE lamellae extend to several microns in length.

During tensile deformation, the sample formed a sharp neck, which was extended by drawing the undeformed materials towards itself. The morphology of the sample at the vicinity of the necking region is illustrated by SEM micrograph in Figure 4(b). Upon necking, the morphology of the sample changes dramatically. The original isotropic arrangement of lamellae is destroyed and an anisotropic structure evolves with a majority of lamellae aligned along the strain direction in the form of microfibrils. A part of lamellar bundles, presumably aligned perpendicular to the strain direction form so-called chevron-pattern (buckling process) as also observed in other lamellae-forming systems.^{22,23} Similar results were reported recently by Li et al.¹⁰ and Lee et al.²⁴ in PE-based materials.

In addition, indicative of lamellar separation processes, one can see the formation of dark gaps between the lamellar strips [see the bright strips in Fig. 4(b) and 4(c)]. In the meantime, the darker regions, which were found between the lamellar bundles, do not appear in the SEM micrograph, implying that a large plastic deformation of the EOC2 phase has taken place. In other words, the deformation of the sample is, as expected, mainly controlled by the deformation of the EOC2 matrix.

Figure 4(c) shows the electron micrographs of the sample far beyond the neck close to fracture surface, i.e., the region with much higher degree of deformation. The deformation structures similar to that of the necking region are observed. At high deformation, the amount

of the individual islands of relatively less deformed HDPE lamellar bundles become significantly low; and the microfibrils extend much to longer dimension.

The detailed structure of the microfibrils and role of EOC2 lamellae cannot be precisely discussed on the basis of the SEM results so far obtained. In future, the results from the TEM investigations will be reported to elucidate precisely the lamellar nanostructures in both the blend components.²⁰

CONCLUDING REMARKS

We have studied the morphology formation in the blends of commercially available HDPE and metallocene EOCs with the aid of AFM and SEM. The multi-component PEs studies showed, depending on the comonomer content, a variety of crystalline structures ranging from lamellae to micellar fragments. Consequently, it was possible to tailor the mechanical properties over wide range. It was found that, the blend components in HDPE/EOC blends possess a strong tendency towards segregation in agreement with the calorimetric studies. Generally speaking, the higher the amount of 1-octene in given EOC, the stronger is the inclination towards phase segregation.

The analysis of strain-induced structural changes in a binary HDPE/EOC blend demonstrated that the deformation behavior of the blend is predominantly controlled by the matrix phase. The lamellar structure of the blends was successively destroyed with increasing strain. At high deformation, the buckling of HDPE lamellae and microfibrils formation was observed. It should be anticipated that the proposed deformation micromechanisms based on the limited experiments so far performed is still rather incomplete. Detailed study of deformation processes with the aid of different high-resolution microscopic techniques is underway and will be the object of future publication.

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