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PII: S0032-3861(97)00489-8

*Polymer* Vol. 39 Nos. 8–9, pp. 1643–1645, 1998
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0032-3861/97/$17.00+0.00

# Persistent lamellar structure in binary blends of polyethylene and hydrogenated butadiene block copolymer

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*(Received 1 May 1997; revised 6 June 1997)*

A hydrogenated butadiene block copolymer (CEBC), polyethylene–poly(ethylene-co-butene)–polyethylene block copolymer, was found to be miscible with high density polyethylene (PE). We investigated the lamellar crystalline structure in the blends crystallized from the single-phase melt by TEM observation and DSC measurement. It is well known that crystal lamella of PE grows rather straight and the edge view of the lamella under TEM is a long stripe. Such lamellar structure was observed in 50/50 PE/CEBC blends crystallized at high temperatures (e.g., 110°C). On the other hand, when the blend was crystallized at low temperatures (e.g., 75°C), the lamella was not straight but zigzag. The difference of the lamellar structure was characterized by two morphological parameters: a persistent lamellar length PLL defined by the length of a straight lamellar segment formed by a persistent growth, and an angle $\alpha$ (between two persistent lamellae. The blend crystallized at lower angle $\alpha$ between temperatures had shorter PLL and wider $\alpha$. Differential scanning calorimetry melting peak of C (PE) block of CEBC was not detected in the blend crystallized at low $T_c$, suggesting an incorporation of C block chains in PE lamellae. The incorporation seems to force the zigzag growth of PE lamellae. The shorter the PLL and the wider the value of $\alpha$, the less ordered was the spherulite in radial direction. © 1997 Elsevier Science Ltd. All rights reserved.

**(Keywords: lamellar structure; block copolymers)**

It is well known that the morphology of a crystalline polymer is varied by blending with miscible impurity of dissimilar polymers[1–4]. By the exclusion of the miscible impurity from the crystalline lamellae, the interlamellar region becomes wider by blending. Such morphological change has been demonstrated in poly($\varepsilon$-caprolactone)/poly(vinyl chloride) blends[1,2] and poly(aryl ether ether ketone)/poly(ether imide) blends[3] by small angle X-ray scattering and the transmission electron microscopy (TEM); in terms of two morphological parameters: the lamellar thickness and the thickness of the amorphous region between lamellae. A fragmentation of crystal lamella was also pointed out in polypropylene/partially hydrogenated oligo(styrene-co-indene) blends[4]. In this paper, we discuss a new aspect for the change in lamellar structure with blending on the basis of TEM observation of crystalline morphology in the blends of high density polyethylene (PE) with a hydrogenated butadiene block copolymer (CEBC), polyethylene–poly(ethylene-co-butene)–polyethylene block copolymer.

The PE used was a commercial polymer supplied by Mitsui Toatsu Chemicals, Inc. (1300J; MFR(ASTM D1238) = 13 g/10 min). The CEBC was obtained from Japan Synthetic Rubber, Ltd. (Dynaron E6100P; $M_w = 3.0 \times 10^5$, ethylene content = 30 wt.%). PE and CEBC were melt-mixed at 210°C by using a Mini-Max moulder (CSI-183M MX, Custom Scientific Instruments, Inc.). The blend ratio was fixed at 50/50 weight ratio. The single-phase melt was excluded and chopped into pellets. A thin film specimen ( $\approx$ 15 $\mu$m thick) was prepared by pressing the pellets between two cover glasses at 210°C. After the specimen had been held at 210°C for 5 min, it was rapidly transferred into an another hot stage held at a desired crystallization temperature $T_c$. A quenched specimen was also prepared by dipping into an ice water bath.

For TEM analysis, ultrathin sections were cut with microtome from crystallized specimen and stained with ruthenium tetraoxide ($RuO_4$) in the gas phase. The lamellar morphology was observed under TEM with an accelerator voltage of 100 kV (JEM-100CX, JEOL Ltd.).

Light scattering measurement was carried out by using a highly sensitive CCD (charge-coupled device) camera system[4]. A polarized He-Ne gas laser of 632.8 nm wavelength was applied vertically to the film specimen. The scattered light was passed through an analyser. We employed the Hv geometry in which the optical axis of the analyser was set perpendicularly to that of the polarizer. The angular distribution of light scattering intensity was detected by a highly sensitive CCD camera with 576 × 382 data points.

*Figure 1* shows the TEM micrographs for (a) neat PE quenched in ice–water, (b) the blend crystallized at $T_c$ = 110°C, (c) the blend crystallized at $T_c$ = 75°C and (d) the quenched blend. The crystalline lamellae appear as bright stripes since the staining agent ($RuO_4$) cannot penetrate into crystalline regions. In neat PE (*Figure 1*(a)), the crystalline

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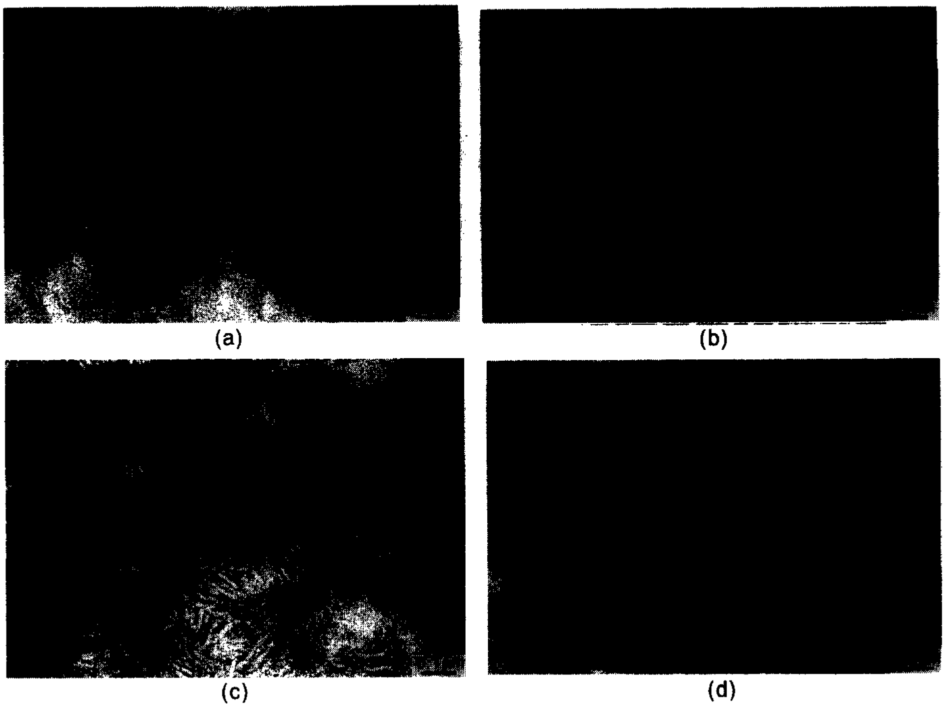

**Figure 1** TEM micrographs: (a) PE (quenched), (b) 50/50 PE/CEBC ($T_c$ = 110°C), (c) 50/50 PE/CEBC ($T_c$ = 75°C), (d) 50/50 PE/CEBC (quenched)

lamellae are straight and long. Such lamellar structure is also seen in the blend crystallized at high $T_c$ (*Figure 1*(b)). On the other hand, zigzag lamellae are seen in the blend crystallized at lower $T_c$ (*Figure 1*(c) and (d)). Note also that the interlamellar region in the blend is wider than that in neat PE. This could be ascribed to the exclusion of CEBC from PE lamellae. The interlamellar region becomes narrower as $T_c$ decreases. This may imply that the amount of the excluded CEBC decreases with decreasing $T_c$ and many C(PE) block chains are incorporated into PE lamellae. The exclusion of CEBC can be qualitatively discussed in terms of the parameter $\delta$ suggested by Keith and Padden[5,6]:

$$\delta = D/G \qquad (1)$$

where $\delta$ is the distance in which the non-crystalline component can be excluded from the crystalline front, $D$ is the diffusion coefficient of the non-crystalline component, $G$ is the growth rate of the crystalline polymer. In the case of PE crystallization below 110°C, it is expected that the lower the value of $T_c$, the smaller is $D$ and the larger is $G$, then the smaller could be $\delta$. This may explain the decrease in the amount of the excluded CEBC with decreasing $T_c$. The difference in the lamellar structure could be characterized by two morphological parameters: a persistent lamellar length (PLL), defined by the length of a straight lamellar segment formed by a persistent growth, and an angle $\alpha$ between two persistent lamellae. When the lamella is straight, PLL is large and $\alpha$ is small. The values of PLL and $\alpha$ were obtained form TEM micrographs and are mapped in *Figure 2*. The PLL is large and $\alpha$ is small in neat PE and the blend crystallized at high $T_c$. As $T_c$ decreases in the blends, the PLL is smaller, $\alpha$ is larger and the distribution of $\alpha$ is wider. The persistence in lamellar structure should affect the ordering in spherulite structure. The Hv scattering pattern from the PE/CEBC blends was a four-leaf clover type, characteristic of spherulite. To discuss the ordering in spherulite, it is convenient to employ the scattering profile at an azimuthal angle $\mu = 45°$ using a reduced scattering angle $w$[4,7]:

$$w = (2\pi/\lambda)R_{\mathrm{Hv}}\sin\theta \qquad (2)$$

where $\lambda$ is the wavelength, $\theta$ is the scattering angle, $R_{\mathrm{Hv}}$ is the radius of the spherulite given by $4.1 = 4\pi(R_{\mathrm{Hv}}/\lambda)\sin(\theta_m/2)$, $\Theta_m$ being the scattering angle for the intensity maximum in the scattering profile at $\mu = 45\int$. The profile of the blend crystallized at high temperature (e.g., $T_c$ = 110°C) was sharp. The profile became broader with decreasing crystallization temperature. According to the model calculation of scattering profiles by Yoon and Stein[7], the broadening of the scattering profiles is ascribed to the orientation-angle fluctuation of the optic axis within a spherulite. The relative intensity in the wide angle region ($w > 4$) increases as the ordering of the optic axis in the radial direction decreases. Hence, as a measure of the ordering of the optic axis in the radial direction, we employ a ratio Pr of the intensity $I$ at $w = 4$ to that at $w = 10$:

$$\mathrm{Pr} = I(w = 4)/I(w = 10) \qquad (3)$$

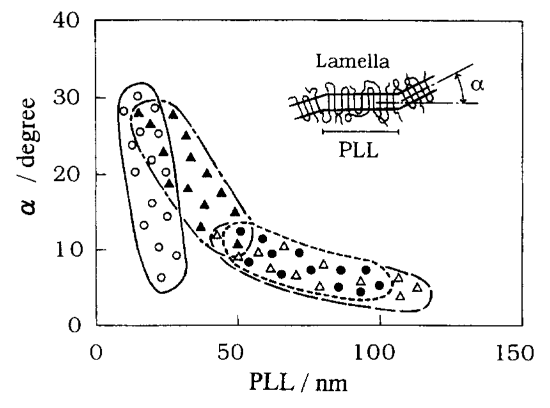

**Figure 2** Persistence of crystal lamella: (△) PE (quenched), (●) 50/50 PE/CEBC ($T_c$ = 110°C), (▲) 50/50 PE/CEBC ($T_c$ = 75°C), (○) 50/50 PE/CEBC (quenched)

**Table 1** Order parameter of spherulite in radial direction, Pr

| PE | Blend | | |
|---|---|---|---|
| quenched | $T_c = 110°C$ | $T_c = 75°C$ | quenched |
| 4.5 | 4.7 | 2.0 | 1.2 |

The observed values of the order parameter Pr of equation (3) are shown in *Table 1*. The values of Pr of neat PE and the blend crystallized at high $T_c$ are almost the same. The Pr of the blends is smaller for lower $T_c$. These are as expected: the shorter PLL and wider $\alpha$ should lead to the smaller Pr.

Thus, TEM analysis showed the a new morphology in PE crystals is available by adding miscible impurity and controlling $T_c$. The zigzag lamellar structure was quantitatively characterized by two parameters: the persistent lamellar length and the angle between two persistent lamellae. The zigzag lamellae lead to the less ordered spherulite.

## REFERENCES

1. Warner, F. P., MacKnight, W. J. and Stein, R. S., *J. Polym. Sci., Polym. Phys. Ed.*, 1977, **15**, 2113.
2. Stein, R. S., Khambatta, F. B., Warner, F. P., Russell, T., Escala, A. and Balizer, E. J., *Polym. Sci., Polym. Symp.*, 1978, **63**, 313.
3. Hudson, S. D., Davis, D. D. and Lovinger, A. J., *Macromolecules*, 1992, **25**, 1759.
4. Lee, C. H., Saito, H. and Inoue, T., *Macromolecules*, 1995, **28**, 8096.
5. Keith, H. D. and Padden, F. J. Jr., *J. Appl. Phys.*, 1963, **34**, 2409.
6. Keith, H. D. and Padden, F. J. Jr., *J. Appl. Phys.*, 1964, **35**, 1270.
7. Yoon, D. Y. and Stein, R. S., *J. Polym. Sci., Polym. Phys. Ed.*, 1974, **12**, 753.