Morphology of Polyethylene Blended with Thermotropic Hydroxyethyl Cellulose Acetate

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ABSTRACT: Morphology of low-density polyethylene (PE)/thermotropic hydroxyethyl cellulose acetate (HECA) blends, and the melting and crystallization behavior of PE in the blends were studied. The "sea island" morphology was observed in PE/HECA blends. The process of melting and crystallization of PE in blends was independent of the HECA fraction when the PE fraction was larger than 50 wt %. When the PE fraction is smaller than 20 wt %, however, multiple crystallization was observed in the low temperature region. HECA was incompatible with PE crystals in the blends, but partially compatible with the amorphous part of PE. HECA could exist between the PE lamellae in PE spherulites, and concentric ring morphology was observed in spherulites. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 1285–1291, 1998

Key words: polyethylene; thermotropic hydroxyethyl cellulose acetate; blend; morphology

INTRODUCTION

Research and development of liquid crystalline polymer (LCP)-based blends or composites with commercial polymers in the field of polymer material science and engineering are gaining intensive interest in the industrial and academic communities. The LCP-based blends and composites may exhibit high mechanical strength, excellent thermal and chemical resistance, easy processing, and rapid development. In the LCP/thermoplastics blends, the LCP can form microfibers or fibers in the matrix of thermoplastics by shear or extension flow during the process of extrusion or injection molding, and thermoplastics can be reinforced by LCP.[1]

Cellulose is one kind of natural polymer material, and the investigation of cellulose materials becomes more interesting because of their abundance in resource, fast regeneration, and biodegradability. Cellulose fibers have been extensively used as additive reinforcement to prepare composites with polymers.[2] The main drawback in the application of cellulose materials is that the length of cellulose fibers is limited in processing when cellulose materials are generally used in the form of fibers. Since 1976, it has been found that many cellulose derivatives and cellulose itself can form a cholesteric liquid crystalline phase in appropriate conditions.[3] He and colleagues[4] studied *in situ* fiber formation of ethyl cellulose in the polypropylene melt and reported that ethyl cellulose can be elongated into microfibers with the diameter of 1 μm and a ratio of the length to diameter above 30 in the process of injection molding.
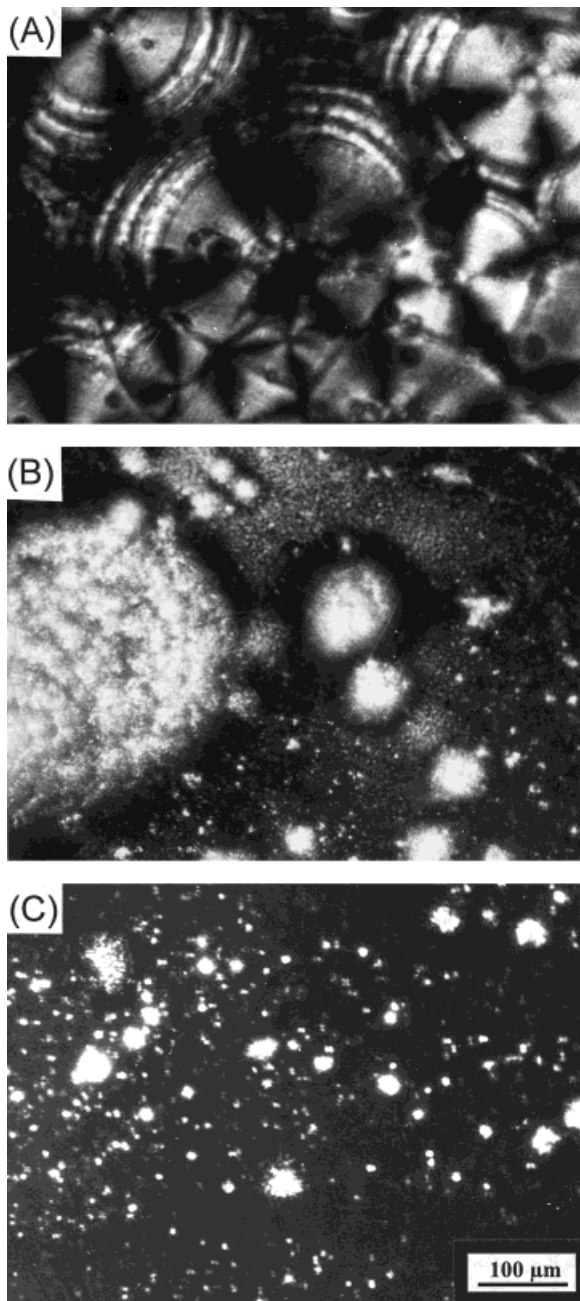
Figure 1 Polarized micrographs of HECA/PE blended films. HECA/PE: (A) 20/80, (B) 50/50, and (C) 80/20.

The thermotropic cellulose derivatives are one kind of important LCPs in LCP/thermoplastic blending and in preparing *in situ* composites because of their high tendency to form fibers.

Hydroxyethyl cellulose acetate (HECA) is a thermotropic material and can form a cholesteric liquid crystalline phase in the temperature region between 135 to 185°C.[5] In this article, morphology of polyethylene (PE)/HECA blends by solution blending is studied, and melting and crystallization of PE in the blends are discussed.

EXPERIMENTAL

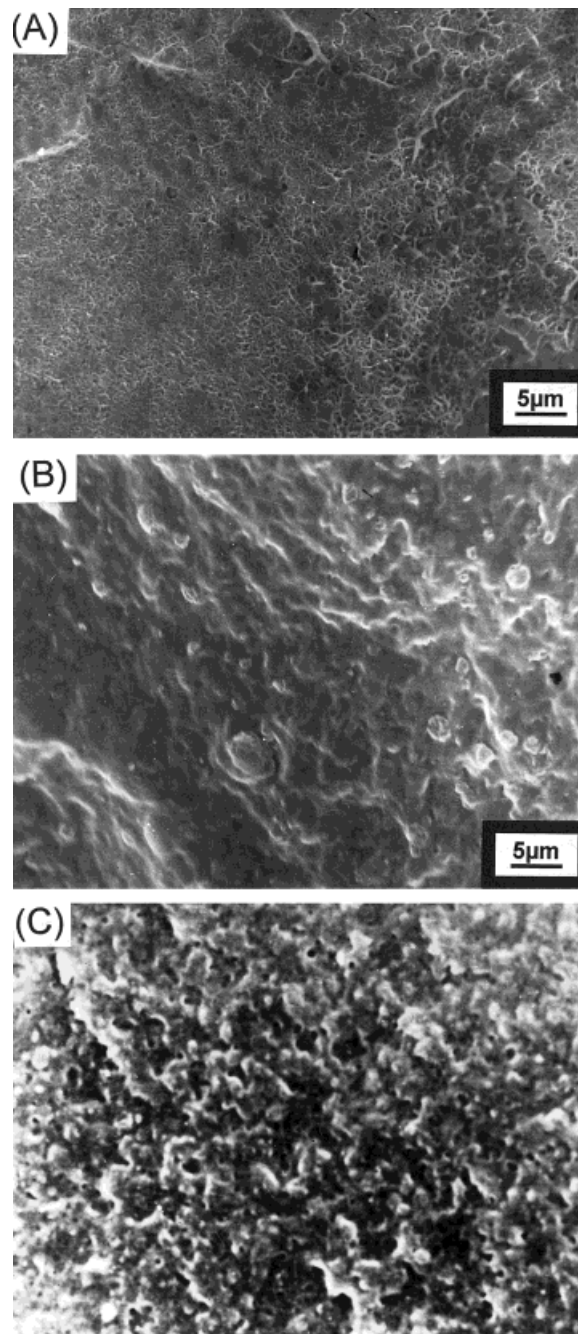HECA was prepared by esterification of hydroxyethyl cellulose (the degree of substitution for hy-

Figure 2 SEM micrographs of the fracture surface of HECA/PE blended films. HECA/PE: (A) 20/80, (B) 50/50, and (C) 80/20.
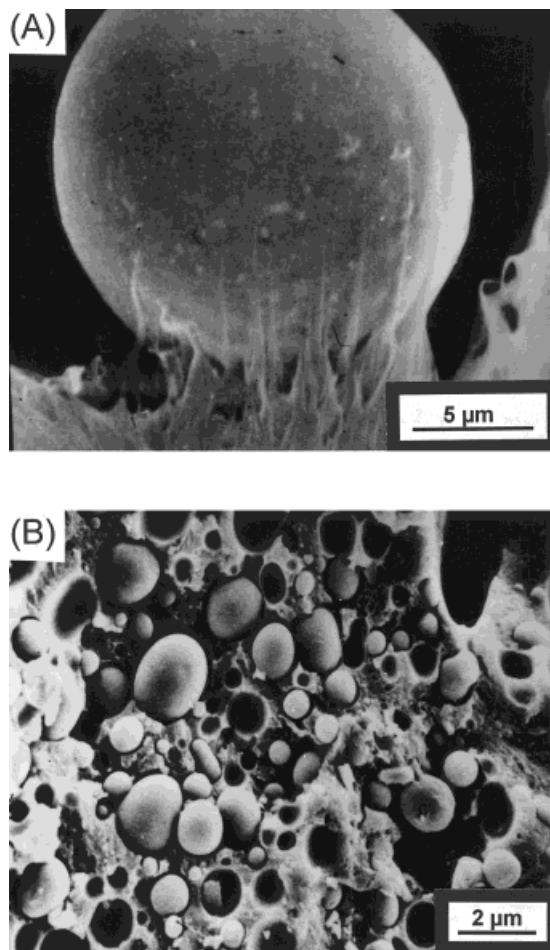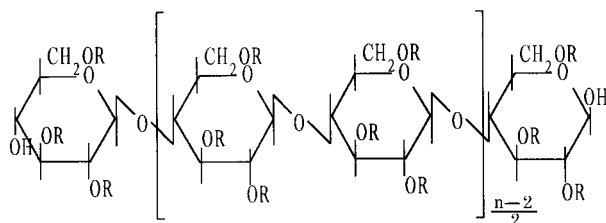
Figure 3 SEM micrographs of the fracture surface of HECA/PE films. The temperature at which the films are cast is below 383 K. HECA/PE: (A) 20/80 and (B) 80/20.

droxyethyl was 1.5–1.8) with acetic anhydride.[5] The molecular formula of HECA is as follows:

R=H, CH$_2$CH$_3$, CH$_2$CH$_2$CN

The degree of substitution for acetyl was 2.8–3.0. The molecular weight of HECA was measured by GPC (Waters ALC/244/GPC) and calibrated by standard polystyrene, M_n was 6.5×10^4, and M_w was 15×10^4. Distribution of molecular weight M_w/M_n was 2.34. The melt index of low-density PE (GC7260, Liaoyang Petrochemical Fiber Co.,

China) was 20–26. All other reagents were chemically pure.

HECA and PE were dissolved in 1,1,2,2-tetrachloroethane at 120°C and stirred for 30 min. The mixture solution was poured onto a glass plate that was heated to 403 K or 383 K, and blended films were prepared. The mixing solution was also poured into a mixture nonsolvent system of petroleum ether/n-butyl alcohol/ethyl acetate (2/1/1, v/v), and the precipitate was separated by centrifugal separation. Blended powder was dried in a vacuum oven at ∼ 323 K.

The fracture surface of blended films, which were broken in liquid nitrogen, and the etched surface of blended films, which were etched by acetone (in which the HECA could be dissolved), were examined by a scanning electron microscope (S-430, Hitachi, Japan). The surface of the specimen was coated with a thin layer of gold before examination by scanning electron microscopy. Phase transitions (melting and crystallization) of
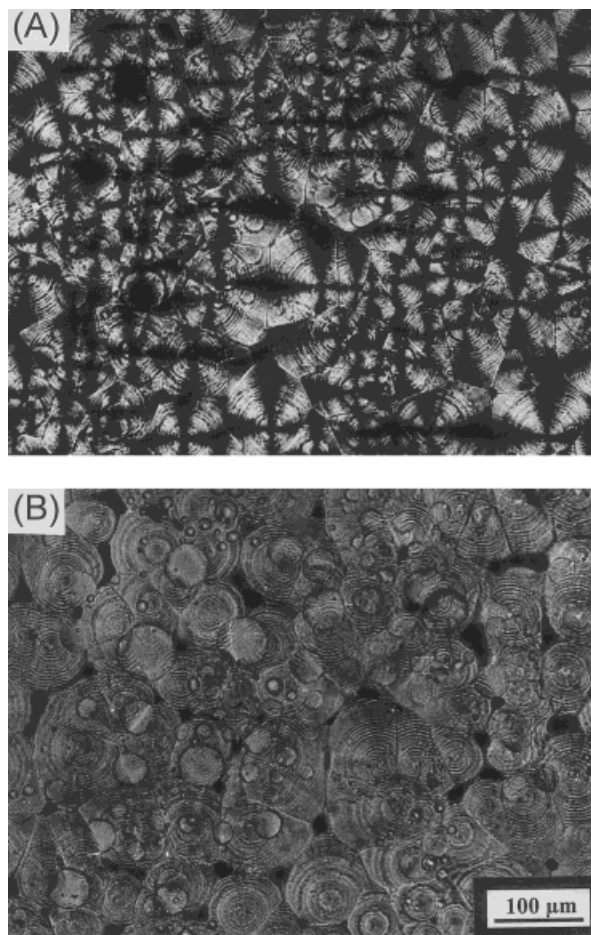

Figure 4 Optical micrographs of HECA/PE (15/85) film observed in (A) cross-polarizing light and (B) normal light.
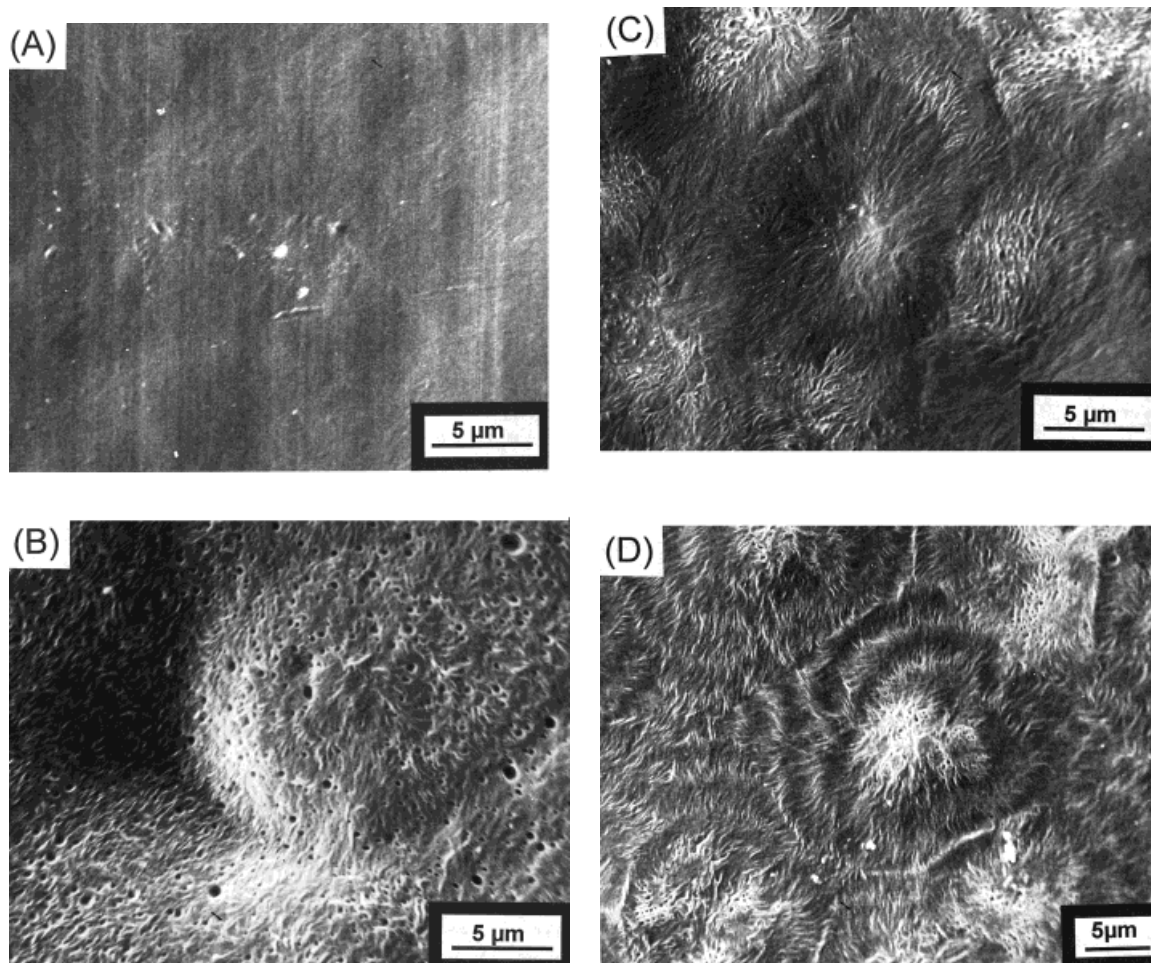
Figure 5 SEM micrographs of HECA/PE (20/80) blending film that is etched in acetone for (A) 0 h, (B) 2 h, (C) 12 h, and (D) 24 h.

the blends were studied by a differential scanning calorimeter (DSC) (DSC-2C, Perkin-Elmer, Norwalk, CT), with a heat rate of 10 K/min and a cooling rate of 1.25 K/min. Phase transitions were also observed by a polarizing microscope (Leitz, ORTHOPLAN-POL, Germany) with a hot stage. Glass transition temperatures of blends were measured by dynamic thermal analysis. Wide angle X-ray diffraction of the blends was conducted by an X-ray diffractometer (D/Max-1200, Rigaku, Japan).

RESULTS AND DISCUSSION

PE is a nonpolar polymer, and HECA is a polar polymer. Consequently, the compatibility of the HECA with PE is rather poor. Figure 1 shows the polarized micrographs of the HECA/PE blends with different compositions. It can be observed

that PE in blends exists as spherulites, and HECA is amorphous or liquid crystalline glass and the blends exhibit "sea island" morphology. The PE phase changes from a dispersed phase to a continuous phase, with an increasing PE fraction.

Figure 2 shows the scanning electron microscopic (SEM) micrographs of the fracture surface of the blends. The two-phase morphology cannot be observed from the fracture surface by scanning electron microscopy, which means that the mixture state of HECA and PE in blends is very well and the blended films are nearly homogeneous when the blended films are prepared in the conditions described previously. The morphology of the blended films, however, is strongly influenced by the rate of solvent evaporation during casting films. Two-phase morphology cannot be observed in the blended films when the solvent is evaporated quickly enough. When the temperature at which the blended films are cast is decreased to
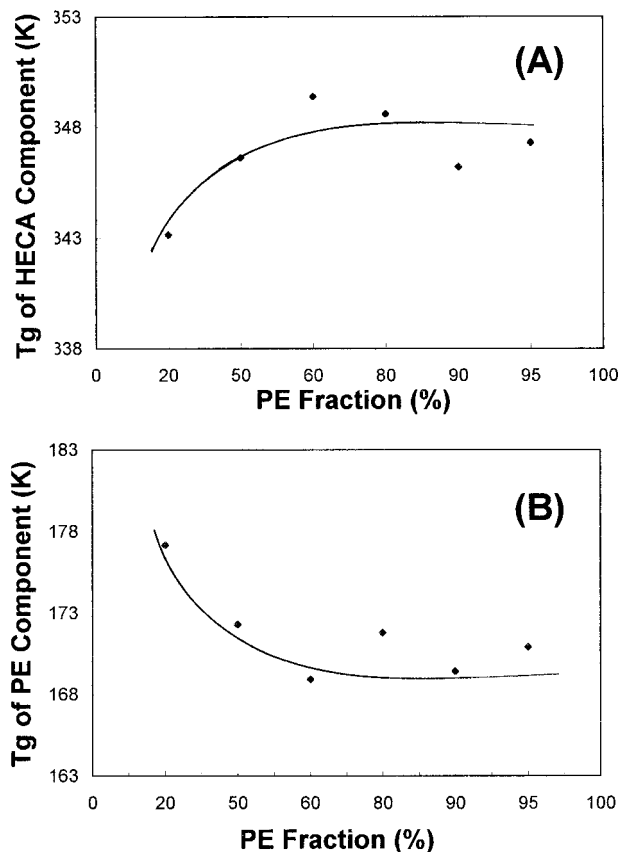
Figure 6 The glass transition temperatures of (A) HECA and (B) PE of blended films.

383 K, however, the solvent evaporation is slow and two-phase morphology is clearly observed in the films (Fig. 3). The boundary between the PE phase and the HECA phase is distinct. Morphology of the HECA/PE films, therefore, is dependent on the conditions of casting films. HECA and PE mix well in the solution, but phase separation between HECA and PE occurs during evaporation of the solvent. If solvent evaporation is quick enough, the system is solidified before phase separation occurs. This means that there is competition between solidification and phase separation. The homogeneous-blended films can be prepared only when solvent evaporation is fast.

In general, PE exists as spherulites in blended films, and concentric ring morphology is observed in the spherulites by using optical microscopy. Figure 4 shows the morphology of the blended films (HECA/PE = 15/85) examined by an optical microscope, in which the concentric rings are very distinct. It has been found that the concentric ring morphology can be observed with cross-polarizing light [Fig. 4(A)] and normal light [Fig. 4(B)]. It is suggested, according to Fig. 4(A), that two

kinds of microstructures exist in the spherulites. Figure 4(B) suggests that the composition is periodically varied along radius directions in spherulites. Therefore, Figure 4(B) implies that HECA may exist in spherulites.

HECA dissolves in acetone, but PE does not. The blended films are etched in acetone, and HECA in the blended films can be dissolved. If HECA exists in the spherulites, the lamellae of the PE can be totally exposed after HECA is partially dissolved in acetone. Figure 5 gives the SEM micrographs of blended films that are etched in acetone in different periods. It can be found that no spherulites are observed by scanning electron microscopy before the blended films are etched in acetone [Fig. 5(A)]. Spherulites are revealed after the films are etched, and the lamellae of the PE can be observed after the blended films are etched for 12 h. When the etching time is 24 h, both the lamellae and concentric ring morphology are clearly observed in spherulites. It is obvious that the amorphous part between the PE lamellae in the spherulites is dissolved in acetone during etching. It is suggested, therefore, that the
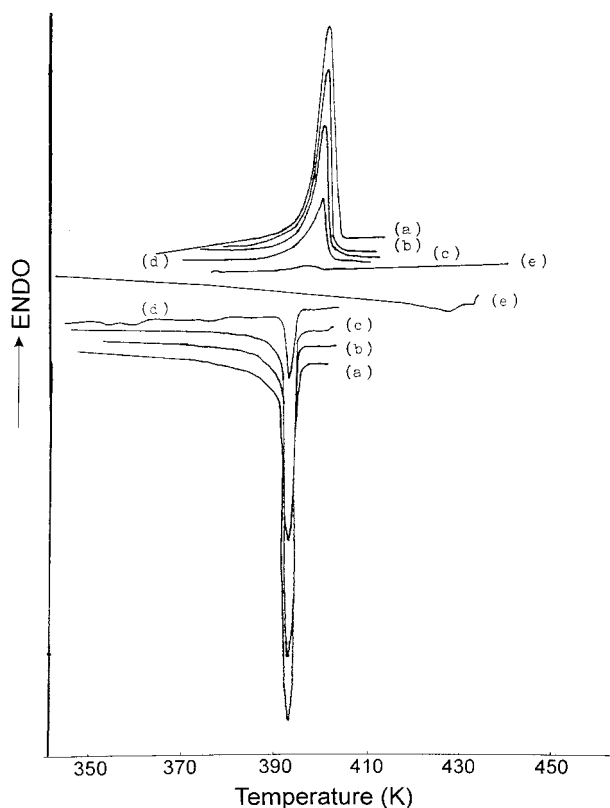

Figure 7 DSC curves of HECA/PE blends. The heating rate is 10 K/min, and the cooling rate is 1.25 K/min. HECA/PE: (a) 0/100, (b) 20/80, (c) 50/50, (d) 95/5, and (e) 100/0.
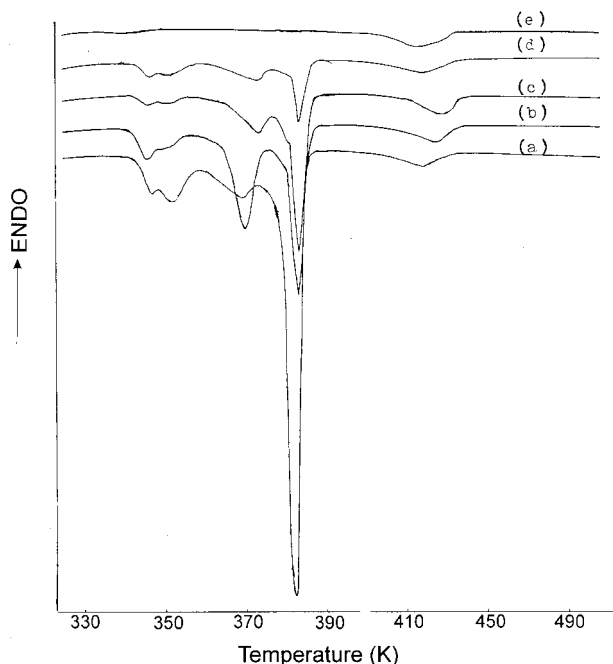
Figure 8 DSC curves of HECA/PE blends, with the PE fraction smaller than 20 wt %. Cooling rate is 10 K/min. HECA/PE: (a) 80/20, (b) 85/15, (c) 90/10, (d) 95/5, and (e) 100/0.

HECA does exist in the amorphous part between the PE lamellae in the spherulites, which means that amorphous HECA and PE are partially compatible.

It has also been found from Figure 5(D) that the concentric rings are clearly revealed after the specimen is etched for a long period, and there exist two morphologies of the ring bands in the spherulites. Half of the ring bands consist of lamellae that are ordered, others are mainly amorphous, and some lamellae are disordered. In the ordered parts, the lamellae are arranged in radial directions. In the disordered parts, the lamellae, dispersed in amorphous PE and HECA, are packed without certain directions. Therefore, ordering and orientation of the PE lamellae in spherulites are periodically varied along radial di-

rections, which forms the concentric ring morphology when the film is observed with cross-polarizing light. Half of the ring bands consist mainly of amorphous PE and HECA, and others consist of PE lamellae. Therefore, the composition in half of the ring bands is different from that in the other half of the ring bands. This results in the appearance of the concentric ring morphology when the film is observed with normal light, because the density and the refractive index in the parts with mainly amorphous PE and HECA are different from those in the parts with PE lamellae.

The HECA/PE blends show two glass transition temperatures (T_g) that vary with composition. Figure 6 shows variation of T_g of HECA and PE in blends with the composition. T_g of the HECA component in blends increases and the PE component decreases with increasing PE fraction until the PE fraction is $\sim$ 50 wt %. T_g of both components in blends is nearly independent of the variation of the composition when the PE fraction is larger than 50 wt %. Variation of T_g with the composition confirms that HECA and the PE amorphous part are partially compatible when the PE component is smaller than 50 wt %. They are incompatible when PE is > 50 wt % in blends.

The DSC curves of HECA/PE blends are shown in Figure 7. In heating and cooling, the melting and crystallization of PE in blends are not influenced by the existence of HECA when the PE fraction is larger than 50 wt %, which suggests that the process of crystallization and crystalline structure of the PE in blends are independent of the existence of HECA. Therefore, it can be concluded that HECA and the PE crystalline phase are totally incompatible. When the HECA fraction is equal to or larger than 80 wt %, some small exothermic peaks appear in the low temperature region beside the liquid crystal transition peak of HECA and the normal crystallization peak of PE in the DSC curves when the blend is cooled from an isotropic melt (Fig. 8). This means that the crystallization process of PE is influenced some-

Table I Enthalpy of Melting and Crystallization of PE in HECA/PE Blends[a]

HECA/PE	ΔH (J g^{-1})	ΔH^* (J g^{-1})	$\overline{\Delta H}$ (J g^{-1})	$\overline{\Delta H^*}$ (J g^{-1})
0/100	152.4	-156.2	152.4	-156.2
20/80	123.6	-124.9	154.5	-156.1
50/50	76.8	-77.8	153.6	-155.6
80/20	39.8	-20.5	199.0	-122.5

[a] ΔH and ΔH^* are enthalpy of melting and crystallization of PE respectively. $\overline{\Delta H}$ leq lgDH/(PE composition in blends); $\overline{\Delta H^*}$ = ΔH^*/(PE composition in blends).
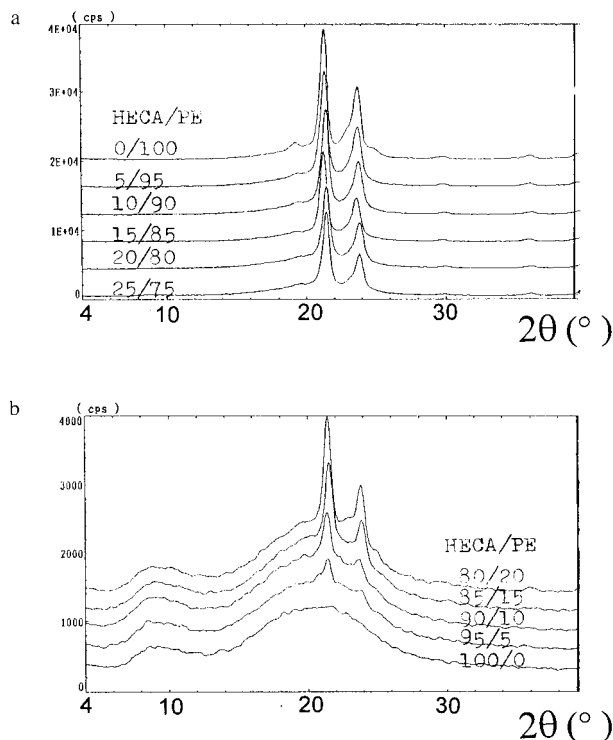
Figure 9 X-ray diffraction of HECA/PE-blended films. The PE fraction is (a) equal and above 75 wt % and (b) equal and below 20 wt %.

how by HECA when the HECA fraction is larger than 80 wt %. The enthalpy of the phase transitions of the PE in blends is shown in Table I. It is demonstrated, from the data in Table 1, that the enthalpy of the phase transitions of the PE in blends is independent of the composition of the blends when the PE fraction is larger than 20 wt %. Therefore, it can be concluded that the phase transitions (melting and crystallization) of the PE in blends is not affected by the existence of HECA, and crystallinity of PE in blends is independent of the HECA content when the PE fraction is high enough.

The conclusions described previously are also confirmed by the results of X-ray diffraction. Figure 9 gives the X-ray diffraction spectra of HECA/ PE blends. It has been found that the X-ray diffraction spectra of the blends are a combination of the diffraction patterns of HECA and the PE. The position and the shape of the diffraction peaks of the PE are not changed with the variation of composition, which means that the crystalline structure of the PE in blends is independent of the existence of HECA, and HECA does not exist in PE crystals. This is consistent with the results in DSC measurements. It can be concluded, consequently, that HECA is totally incompatible with PE crystals in the HECA/PE blends, and the crystalline structure and melting point (T_m) of PE are not influenced by the variation of the HECA fraction in blends.

CONCLUSIONS

The mixture state of HECA and PE in HECA/PE blends is dependent on the blending process and conditions. PE usually exists as a spherulite in the HECA/PE blends, and HECA is totally incompatible with PE crystals. Melting and crystallization behavior and crystallinity of PE in blends are independent of the existence of HECA when the PE fraction is larger than 50 wt %. HECA, however, is partially compatible with the amorphous part of PE in blends and can exist in the amorphous region between PE lamellae in spherulites. Orientation and arrangement of PE lamellae and distribution of the amorphous part are varied along the radial directions in spherulites, which result in the existence of the concentric ring morphology. Existence of HECA in the blends with the PE fraction lower than 20 wt % may influence the crystallization process of PE. Multiple crystallization of the PE appears in the lower temperature region when the blends are cooled from the isotropic fluid.

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