

THERMAL BEHAVIOR OF THERMOTROPIC HYDROXYETHYL CELLULOSE ACETATE/POLYETHYLENE BLENDS

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ABSTRACT

The thermal behavior of thermotropic hydroxyethyl cellulose acetate (HECA)/polyethylene (PE) blends has been studied by DSC. It is found that the blends of HECA and PE are immiscible but the crystallization of PE is affected by HECA chains in the blends with more than 50% HECA, which results in the subordinate crystallization of PE and the formation of imperfect structures in the PE crystals. The imperfection of PE crystals in the blends can be eliminated after annealing at 393K.

INTRODUCTION

In recent years, liquid crystalline polymers (LCPs) are used to blend with commercial polymers, because LCPs offer high level of thermal and mechanical performances. LCPs can provide outstanding strength, high thermal stability, excellent chemical resistance, high dimensional stability, low coefficient of expansion, low melt viscosity and easy orientation in flowing. Blending with LCPs can improve mechanical properties and the processability of the system^[1]. On the other hand, the crystallization and the orientation of the flexible polymer may also be influenced by LCPs in the blends^[2].

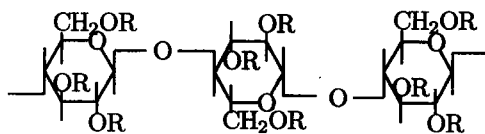
Cellulose and its derivatives are semirigid chain polymers and can form lyotropic liquid crystals in appropriate solvents. Some of cellulose derivatives can form both lyotropic and thermotropic liquid crystals^[3], such as hydroxyethyl cellulose acetate

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(HECA). HECA forms a thermotropic liquid crystalline phase in the temperature region between 410–458 K on heating and its thermotropic behavior is affected by its molecular weight^[4]. In the present work, we have studied the thermal behavior of thermotropic HECA/polyethylene (PE) blends. The influences of HECA and the thermal history on the crystallization of PE are discussed.

EXPERIMENTAL

HECA was prepared in our laboratory and the preparation was described elsewhere^[4]. The molecular formula of the HECA is as follows:



$R=H, CH_2CH_2OR', COCH_3$

$R'=H, COCH_3$

The degree of ether substitution of hydroxyethyl was 1.5–1.8 and ester substitution of acetyl was 2.8–3.0. The molecular weight of HECA, measured by a gel permeation chromatography (GPC), was 6.5×10^4 . High density polyethylene (PE) (GC7260) was produced by Liaoyang Petroleum and Chemical Fibre Co., China. The melting index of the PE was 20–26 (g/10 min).

Blending preparations were carried out by coprecipitations from common solutions of both HECA and PE in tetrachloroethane into a large amount of a mixture of petroleum ether/*n*-butyl alcohol/ethyl acetate (2/1/1) after the solutions were stirred at 120°C for 30 min. The blends were separated by high speed centrifugation and subsequently dried in vacuum at 60°C for 24h.

The thermal behavior of the blends was studied by differential scanning calorimetry (DSC) (Perkin-Elmer DSC-2C). In the measurement, the weight of blends was 17–18 mg and nitrogen was used to protect the specimen from oxidization. The scanning rate was 10 K/min on both heating and cooling. Temperature and energy were calibrated with a standard substance-indium at the same scanning rate with the measurement. The phase morphology of the blends was observed by a polarizing microscope (ORTHOPLAN-POL, Leitz). The crystalline structure of PE in the blends was studied by an X-ray spectrometer (D/max-1200, RIGAKU).

RESULTS AND DISCUSSION

1. General thermal behavior

Fig. 1 shows the DSC curves of HECA/PE blends with different composition on heating. The melting peak is clear and the phase transition peak from the liquid crystalline fluid to the isotropic melt of HECA appears in the temperature region between 415—455 K, when the content of HECA is more than 50% in the blends. The melting enthalpy ΔH_m of PE decreases with increasing HECA content in the blends and the characteristic temperatures T_p and T_0 also slightly decrease (Table 1).

Fig. 2 shows the DSC curves on cooling for HECA/PE blends. When HECA is more than 50% in the blends, the phase transition peak from the isotropic melt to the liquid crystalline fluid of HECA and the crystallization peak of PE appear with decreasing temperature. The temperature at which the crystallization of PE begins, T_i and the top temperature of the crystallization peak, T_c do not change with the composition of the blends (Table 1). When the content of PE in the blends is less than 20%, several crystallization peaks of PE appear in the PE crystallization temperature region. The total crystallization enthalpy of PE, ΔH_c also decreases with decreasing PE content in blends.

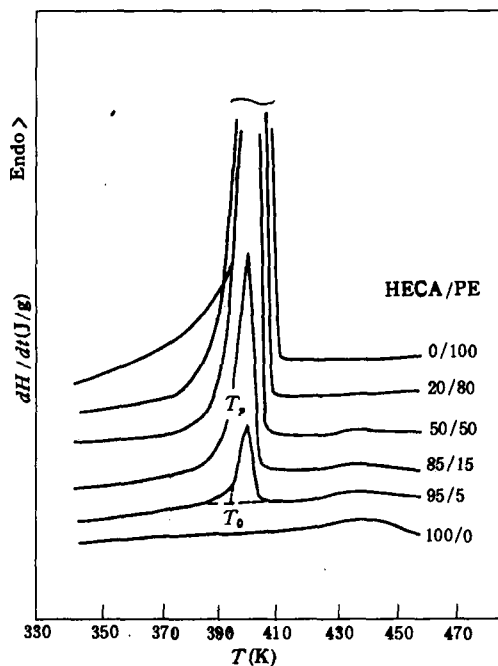


Fig. 1 DSC curves on heating of HECA/PE blends with different compositions

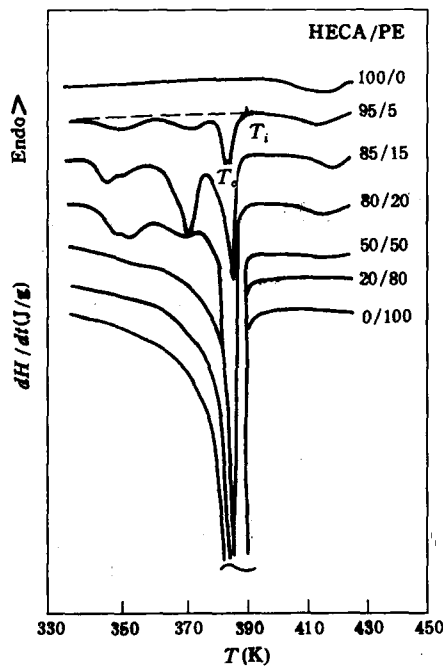


Fig. 2. DSC curves on cooling of HECA/PE blends with different compositions

These results indicate that the temperature of the phase transitions of PE and HECA in the blends is nearly unchanged with the variation of the composition. It

can be concluded that HECA and PE are immiscible. When the blend is cooled from the isotropic melt, HECA is firstly transformed from isotropic fluid to a liquid crystalline phase. The domains of the liquid crystalline phase, however, can not act as the nuclei for PE crystallization and PE is crystallized in the same temperature region as individual PE is crystallized. The plot of total crystallization enthalpy ΔH_c against the composition is linear (Fig. 3), which confirms that HECA and PE are immiscible in the blends. The results of the measurement of T_g s for both HECA

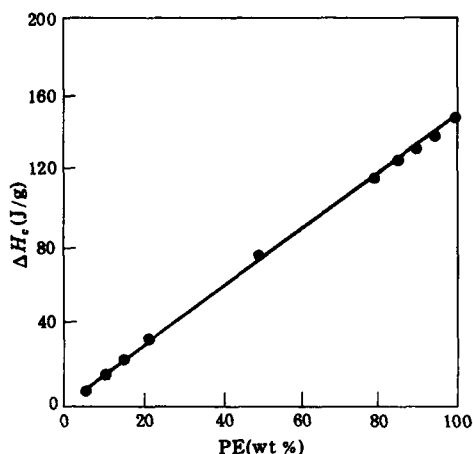


Fig. 3 Plot of total crystallization of PE in blends against the composition

and PE in the blends by DSC^[5] and the observations with a polarizing microscope also confirm the phase separation in the HECA/PE blends (Fig. 4). When the content of HECA in the blends is larger than 50%, however, the process of PE crystallization is obviously influenced by the existence of HECA polymer chains in the blends, and "multi-peak" crystallization appears in DSC curves.

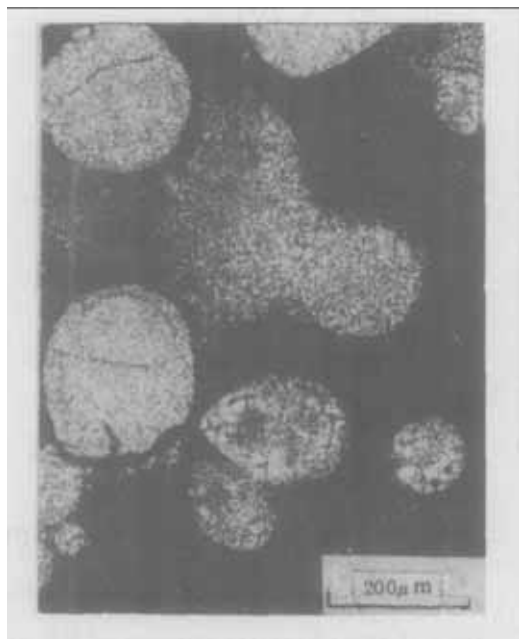


Fig. 4 Polarized light micrograph of HECA/PE (50/50) blend

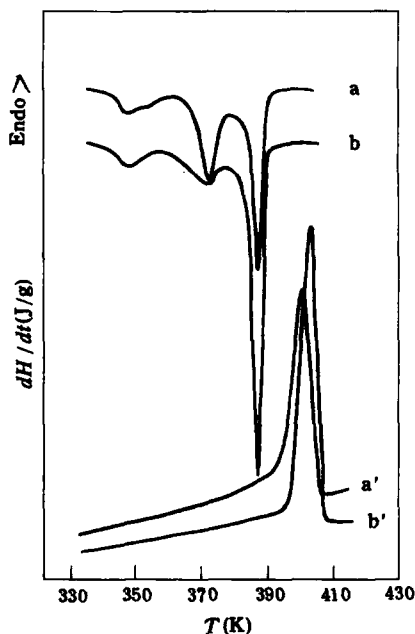


Fig. 5 DSC curves on (a), (b) cooling and (a'), (b') heating of HECA/PE (85/15) blend (a), (a') before and (b), (b') after annealing

Table 1 Temperatures and enthalpies of PE phase transitions in HECA/PE blends

No.	HECA/PE	T_p (K)	T_0 (K)	ΔH_m (J/g)	T_c (K)	T_i (K)	ΔH_c (J/g)
PE	0/100	404	397	165	386	393	150
1	5/95	402	395	143	386	392	138
2	10/90	403	395	138	386	392	131
3	15/85	402	394	131	386	393	127
4	20/80	403	393	122	387	392	119
7	50/50	402	393	85	386	392	78
10	80/20	400	392	38	386	393	38
11	85/15	400	393	27	386	392	24
12	90/10	399	393	17	387	393	15
13	95/5	399	393	8	386	393	7

2. *Characteristics of multi-peaks of PE crystallization*

The multi-peak of PE crystallization appears only when HECA is more than 50% in the blends. The blend with 85% HECA is cooled from 473 K (Fig. 5a) and then, heated again, in which only one melting peak appears in DSC heating curve (Fig. 5a'). No melting peak at the lower temperature in heating curve, which corresponds to the subordinate crystallization peak in cooling curve, is observed and therefore, the subordinate peaks are also attributed to PE crystallization. When the sample is cooled from 410 K to room temperature (Fig. 5b) and subsequently heated to 473 K (Fig. 5b') after an annealing treatment at 393 K for 3.5 h, it can be found that the principal crystallization peak of PE is enlarged and the subordinate peaks are decreased. From Fig. 5a' and b', it is clear that the melting peak is sharpened and the top temperature of peak T_p also shifts to higher temperature after annealing. The results indicate that the subordinate peaks in the cooling curve show the formation of PE crystals with imperfect structures in the blends. In HECA/PE blends, the hindrance of HECA polymer chains to ordering of PE in the crystallization increases with increasing HECA content and for some of PE chains, higher undercooling is required for crystallization. After the principal crystallization, the subordinate crystallization occurs and the crystalline structure formed in this period is more imperfect. In annealing, the phase separation of HECA and PE increases and PE crystals are reorganized. The crystalline structure of PE appears to be more perfect and the degree of crystallinity is higher than before. Consequently, the PE melting peak is sharper and shifts to higher temperature after the sample is annealed.

The results of X-ray diffraction can also confirm the conclusions mentioned above. The spectra of X-ray diffraction are shown in Fig. 6. Sample I is a blend without thermal treatment, sample II is a blend which has been heated to 458 K and subse-

quently cooled to room temperature and sample III is one which has been annealed at 393 K for 3.5 h. The data of X-ray diffraction are listed in Table 2. It is shown that the PE diffraction peaks are sharpened, their intensity is increased, the half-width of the peak is decreased and the correspondent sizes of PE crystalline particles indicate an increase after the sample annealing at 393 K. This confirms that the imperfection in PE crystals decreases after annealing and is agreed with the results of DSC experiments.

3. Effects of thermal treatment on the HECA phase

It has been found^[6] that when HECA is annealed in the temperature region of the existence of liquid crystalline phase, the temperature of the phase transition shifts to higher temperature and its enthalpy increases with increasing time of annealing. This indicates that the defects in the liquid crystalline phases decrease and the degree of ordering increases after HECA is annealed, similar to the behavior of the nematic phase^[7].

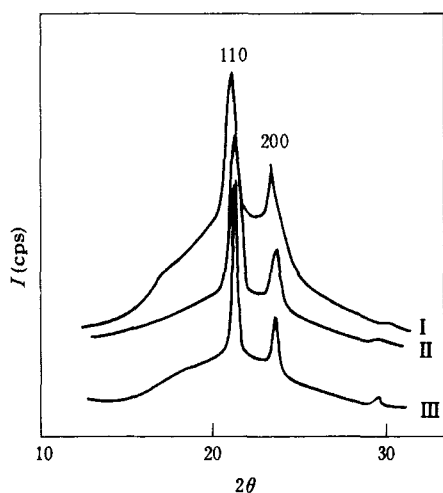


Fig. 6 Spectra of X-ray diffraction of HECA/PE (85/15) blend (I) without thermal treatment, (II) with eliminating thermal history and (III) with annealing at 393 K for 3.5 h

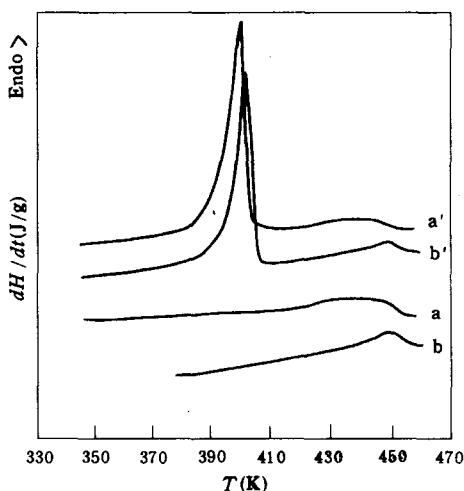


Fig. 7 DSC curves of HECA (a and b) and HECA/PE (85/15) blend (a' and b') before (a and a') and after (b and b') annealing at 425 K for 3.5 h

In Fig. 7, curve a and a' are the heating curves of HECA and a HECA/PE blend (85/15) and curve b and b' are the reheating curves of HECA and a HECA/PE blend (85/15) after they are annealed at 425 K for 3.5 h. The variation of the HECA phase transition in the blends is similar to that of individual HECA. After annealing, the

temperature of the phase transition from the liquid crystalline phase to the isotropic melt shifts to higher temperature and the phase transition enthalpy increases for both pure HECA and that in the blends. The phase transformation temperature region is also narrowed after annealing. It is suggested that the degree of ordering in the HECA liquid crystalline phase increases and the liquid crystalline structure is more homogeneous. The existence of PE in blends cannot influence the structure of HECA liquid crystalline phase and the phase transformation, which confirms again that HECA and PE are immiscible in the blends.

Table 2 Data of X-ray diffraction of HECA/PE (85/15) blend

No	Miller Index	2θ	I (cps)	β	$L_{h.k.l}$ (nm)
I	110	21.4	4541	1.050	10.7
	200	23.8	3254	1.050	10.7
II	110	21.6	7392	1.050	25.2
	200	24.0	3691	1.050	25.4
III	110	21.4	7735	0.900	26.5
	200	23.8	3751	0.900	26.2

θ =diffraction angle, I =intensity of diffraction, β =width of half-height of peak,

$L_{h.k.l}$ =the size of crystal particles according to the Scherrer equation

CONCLUSIONS

HECA and PE are immiscible in blends. The crystallization temperature of PE in the blends do not change with the variation of composition and the total crystallization enthalpy is linearly decreasing with decreasing PE content. When HECA is more than 50% in the blends, the crystallization of PE is affected by the existence of HECA chains and the multi-peak of PE crystallization appears, when the blends is cooled from melt. The imperfection of PE crystals is decreased and the degree of crystallinity is increased after the blend is annealed at 393 K. The HECA mesophase structure is more homogeneous after the blend is annealed at 425 K.

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Keywords:

Hydroxyethyl cellulose acetate/Polyethylene blends; Thermal behavior; Polyethylene; Blends

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