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Characterization of microstructure of polyethylenes by differential scanning calorimetry

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Abstract

The microstructures of polyethylenes (PEs) were investigated by differential scanning calorimetry (DSC). Homogeneous and inhomogeneous blends of three types of PEs, that is, low density polyethylene (LDPE), linear low density polyethylene (LLDPE), high density polyethylene (HDPE), were used for measurement. The thermal behavior of samples suggests that homogeneous blends of HDPE and LDPE or LLDPE have a metastable microstructure which is caused by the co-crystallization of two different types of PEs. The single endothermic peak, due to the fusion of the homogeneous blend, is observed in the first heating and is not completely split into the peaks of respective components PEs by the second heating. From the result, it is thought that the molecular chains of PEs are entangled during the co-crystallization and they are not completely loosened by the first melting. The relation between the microstructures and the thermal behavior revealed by DSC has been discussed.

Keywords: DSC; Microstructure; PE; Polymer blend; Thermal behavior

1. Introduction

Recently, new types of polyethylenes, such as ultra high molecular weight HDPE and LLDPE, have been manufactured. The physical properties of commercial products of PE depend, not only on the chemical structure, but also on the manufacturing process [1]. It is difficult to differentiate a variety of PEs from each other because of their simple structure and few indications for identification. The physical properties of PEs used as raw materials are of importance in the molding process of the products. Many methods, such as nuclear magnetic resonance (NMR), infrared spectroscopy (IR), pyrolysis-gas chromatography (Py-GC), size exclusion chromatography (SEC), fluorescent X-ray measurement, etc., have been reported for the characterization [2–6]. Nevertheless, they were not complete enough to characterize PEs, because these techniques required relatively large quantity of samples and the microstructures of PE chain – that is, short- and long-chain branches and structure of chain end – were not completely identified. Although numerous reports have dealt with the characterization of PEs, a few papers have presented the microstructure of blended PEs, that is, conformation, entanglement and higher order structures of PEs [7,8].

Since DSC is a useful method for studying the thermal property of polymeric materials, it has been used to characterize the natural or synthetic polymers. In this paper, we have investigated the characterization of the microstructure of several blends of PEs by DSC, because the thermal property of PEs may reflect

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sensitivity of their microstructure which is intimately correlated to branches and entanglement of PE chains.

2. Experimental

2.1. Materials

Three kinds of PEs, that is, HDPE, LLDPE and LDPE, were used. HDPE has a small number of short-chain branches, and LLDPE has a large number of short-chain branches induced by copolymerizing with 1-butene, 1-hexene or 1-octene. LDPE has many short-chain and long-chain branches. They were supplied by Iguchi Polyethylene Inc. and used as received.

Blending procedures for homogeneous ones are as follows: two kinds of PE pellets were added to xylene (approximate 0.1% w/w), and the mixture was heated at 135°C by stirring until they were dissolved completely. The solution was poured into excess methanol. The precipitate was filtered and dried under reduced pressure at room temperature for one day. Inhomogeneous blends were prepared by melt mixing. Two powdered PE samples were weighed in a DSC pan, held at 200°C for 20 min and then recrystallized at room temperature.

2.2. Measurement

The thermal analysis was performed using MAC Science Inc. model DSC 3110 differential scanning calorimeter. The calibration of temperature was carried out using indium. A scanning rate of 10°C/min was used in the range of 50–200°C. All samples (6.3 ± 0.5 mg) were sealed tightly in aluminum pans (5 mm i.d.). Microscopic examination was carried out by Nikon optical polarization microscope Model OPTI-PHOTO2-POL. Sample cutting was performed using the Leica Inc. model RM2155 rotary microtome.

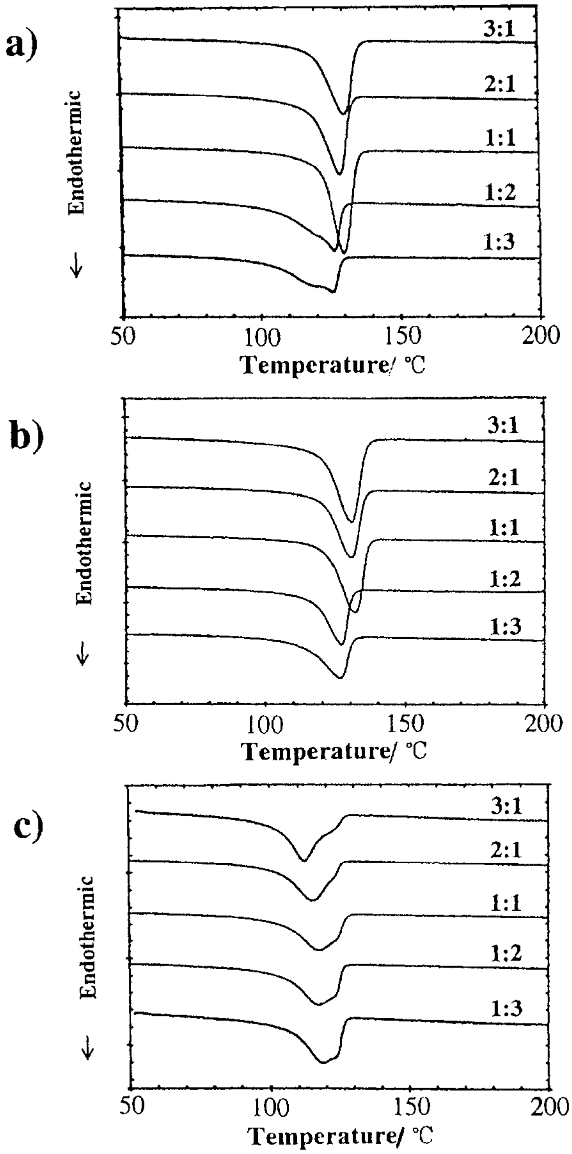

Fig. 1. The DSC first-heating curves of homogeneous blends: (a) HDPE and LDPE, (b) HDPE and LLDPE, and (c) LDPE and LLDPE.

3. Results and discussion

In highly crystalline polymeric materials, the melting temperature almost agrees with the endothermic peak temperatures on the DSC curves. However, when multiple melting temperature appears, it is difficult to obtain the melting temperature of the polymer sample, because it has a gradually changing or unresolved peak. In this study, we therefore used the endothermic peak temperatures in the DSC curves for a constant sample mass to examine the thermal behavior of PEs.

Fig. 1(a–c) show the endothermic DSC curves for the first heating of homogeneous blends of (a) HDPE:

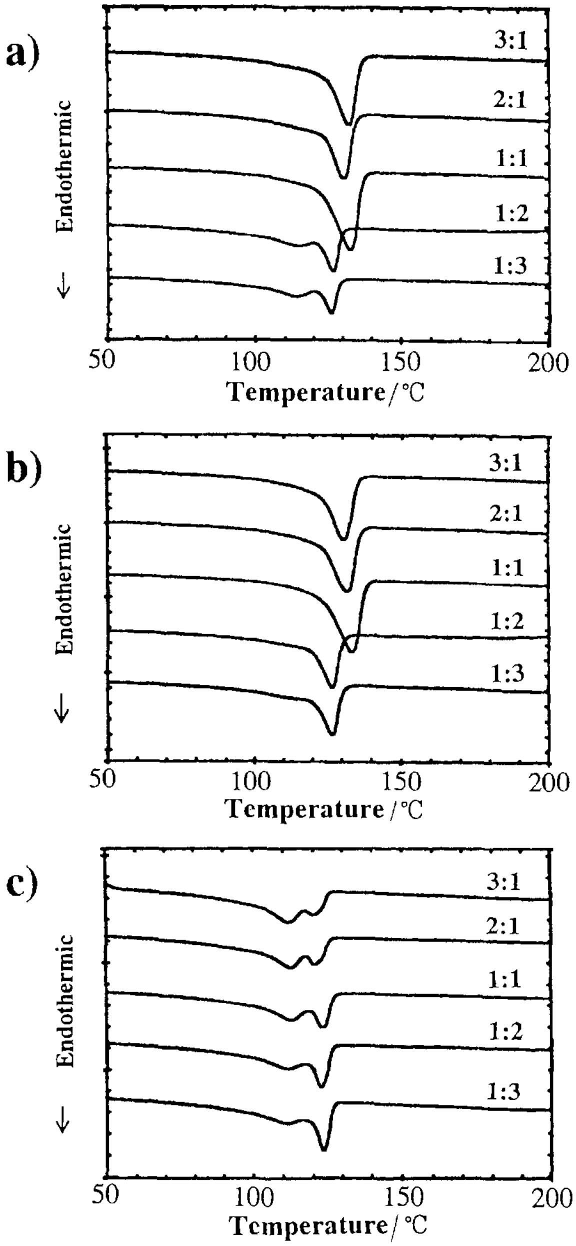

Fig. 2. The DSC second heating curves of homogeneous blends: (a) HDPE and LDPE , (b) HDPE and LLDPE, and (c) LDPE and LLDPE.

LDPE, (b) HDPE: LLDPE, and (c) LDPE:LLDPE with the ratio 1 : 3 to 3 : 1, and Fig. 2(a–c) show the DSC curves for the second heating of the same blends. When HDPE content was 50% and more in a series of the blend of HDPE and LDPE or LLDPE (Fig. 1(a) and (b)), the peak temperatures of the first heating agreed well with that of the HDPE (130°C). The peaks in the first heating were almost unchanged and unresolved in the second heating (Fig. 2(a) and (b)). On the other hand, when HDPE content was less than 50% in the blends of HDPE and LDPE, the peaks in the first heating (Fig. 1(a)) appeared at a lower temperature and had a shoulder. As shown in Fig. 2(a), these peaks were separated into two peaks in the second heating. Although, in the blends of HDPE and LLDPE, these peaks in the first heating (Fig. 1(b)) were lower in temperature, the shoulder was not obviously seen in the peaks and they were sharpened and not separated in the second heating (Fig. 2(b)).

In the first-heating curves for a series of the blend of LDPE and LLDPE (Fig. 1(c)), all the peaks had a shoulder irrespective of the blend ratio, and their peak temperatures were raised with increasing LLDPE content. The peaks of the first heating were separated into two peaks in the second heating (Fig. 2(c)), and the separated peaks became broader with the increase in LLDPE content.

Successively, measurements with a series of LDPE and LLDPE blends were carried out to distinguish inhomogeneous blends from homogeneous ones. The typical endothermic DSC curves in the first and second heatings of the inhomogeneous 1 : 1 blend are shown in Fig. 3. There appeared two peaks on each curve. The higher and lower peaks agreed with that of LDPE (113°C) and LLDPE (123°C), respectively. Similar DSC curves were obtained for other blends from LDPE and LLDPE.

The peak temperatures of each of the blend samples are plotted against blend ratio in Fig. 4. It is obvious from Fig. 4(a,b) that an abrupt lowering of the peak temperature occurs between the blend ratios 1 : 1 and 1 : 2. This suggests that the contribution of LDPE or LLDPE to the melting behavior is hidden in the blends with a HDPE whose content is higher than 50%. On the contrary, the peak temperature in the first heating of the blend of LDPE and LLDPE (Fig. 4(c)) increased monotonously with increasing LDPE content. The higher temperature peak of the second heating was also raised, but the lower temperature peak was slightly decreased. Furthermore, the peak temperatures in the first heating always appear between the two peaks in the second heating.

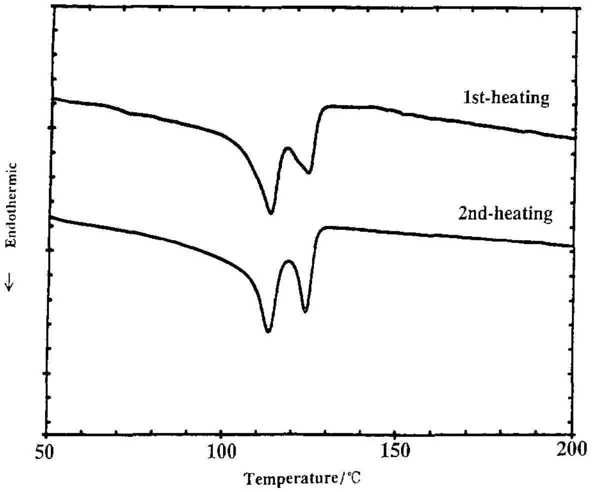

Fig. 3. The DSC first and second heating curves of inhomogeneous blends (1 : 1) of LDPE and LLDPE.

These phenomena suggest that the homogeneous blend of PEs may exist in the intermediate state caused by co-crystallization which is pronounced in the blend of LDPE and LLDPE. This intermediate state should be a metastable one, because it was converted toward inherent states in respective PE components by heating, but it was not completely segregated. In addition, these results indicate that the molecular chains composed of PE blends are well entangled with each other in the homogeneous blends as reported for ultra-high molecular weight PE blends [9] and the entangled chains may not be loosened entirely by the first heating. These entangled states may also be reflected by the microstructures in the various homogeneously blended polymers. However, the inhomogeneous blends of LDPE and LLDPE, such phenomena as the homogeneous blends could not be observed. The inhomogeneous blend seems unlikely to contain an intermediate state even partly, since the melt-mixing cannot mix two PEs homogeneously and cause co-crystallization in the following cooling process.

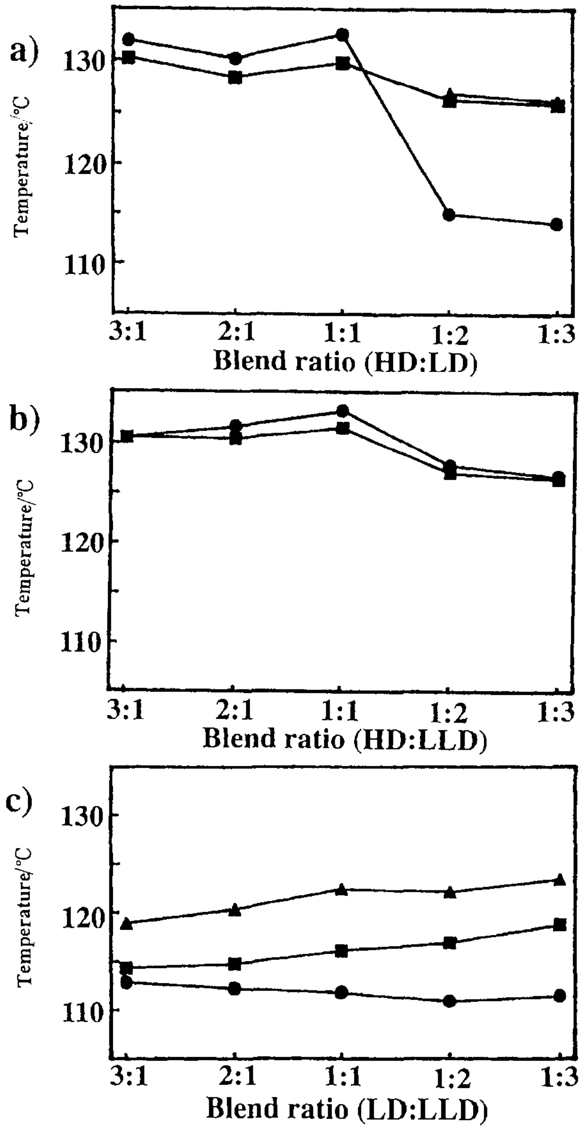

Fig. 4. Change of peak temperature with blend ratio homogeneous blends of (a) HDPE and LDPE, (b) HDPE and LLDPE , (c) LDPE and LLDPE blends: (■) first heating, (●,▲) second heating.

Finally, the sliced samples were observed with a polarization microscope. The typical photomicrographs of LLDPE and the inhomogeneous blend of HDPE and LLDPE (1 : 3) are shown in Fig. 5(a,b) respectively. In these pictures, the crystalline region is easily distinguishable from the amorphous one and one can see the difference in the size and dispersion of the crystalline region. This microscopic observation supports the DSC data described above; that is, the crystalline state has been changed by the blend, even though a further detailed study should be made on the correlation of thermal behavior with microscopic observation.

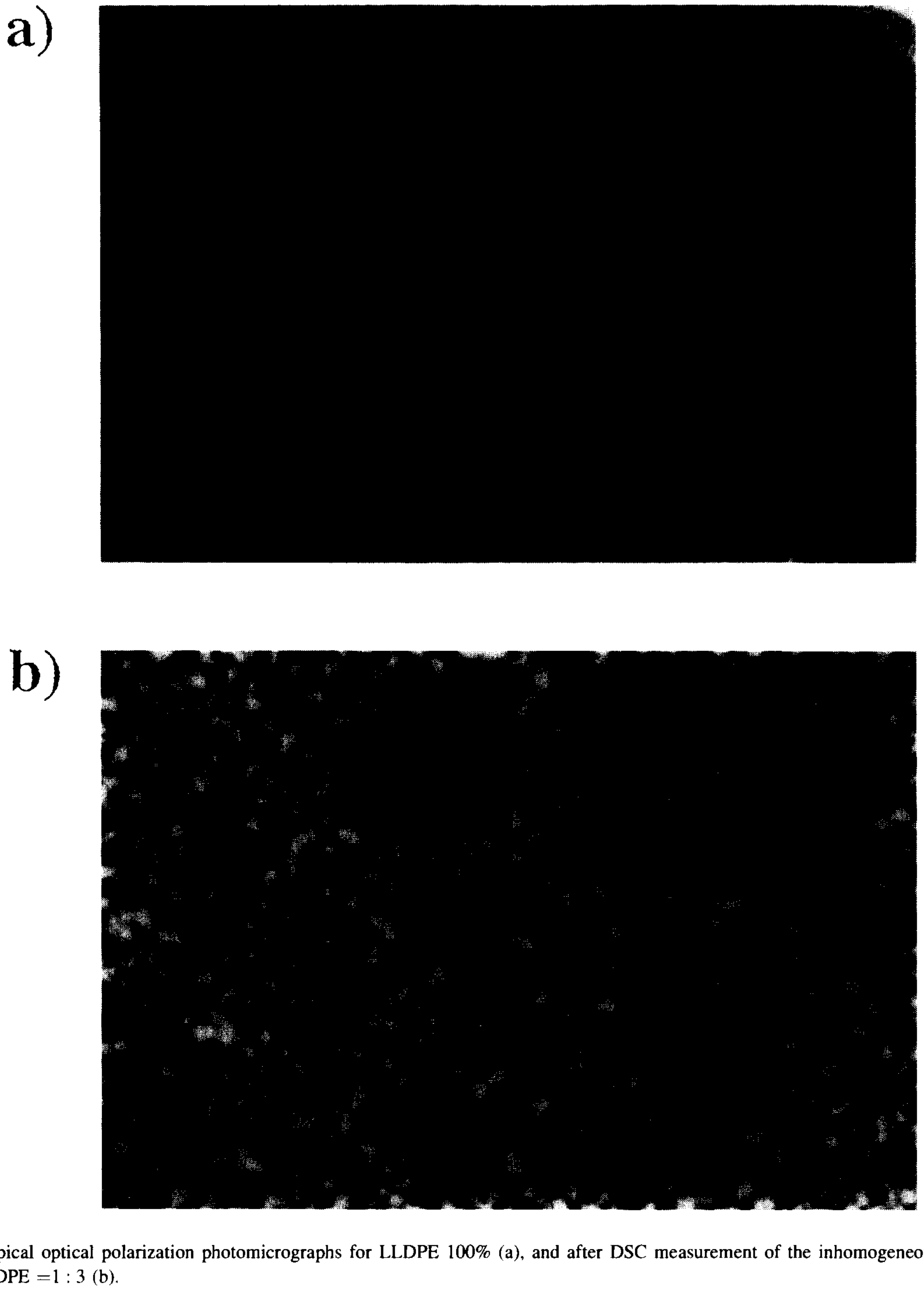

Fig. 5. Typical optical polarization photomicrographs for LLDPE 100% (a), and after DSC measurement of the inhomogeneous blend of HDPE:LLDPE =1 : 3 (b).

4. Conclusion

The homogeneous blends of two types of PEs from HDPE, LDPE and LLDPE exhibit the intermediate thermal behavior of the original PEs. The metastable intermediate state of a series of blends containing HDPE revert to those inherent for the component PEs by heating. On the other hand, the blends of LDPE and LLDPE do not revert to the thermal behavior of LDPE and LLDPE by heating. It seems that the molecular chains of LDPE and LLDPE are entangled and the entanglement cannot be loosened by heating.

Different crystalline states were observed for the blends with different blend ratios with a polarization microscope. It suggests that there is a relation between crystalline state of blended PEs and thermal behavior measured by DSC.

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