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Physical State of Radiation-Polymerized Polyethylene Blends

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Synopsis

The physical state of the blends of radiation-polymerized polyethylene with high-density polyethylene was studied. Only one peak was observed in DSC heating curves of the blends quenched from the melt regardless of the each polymer content. In addition, transparency of the high-density polyethylene was improved by melt blending with radiation-polymerized polyethylene. This is a characteristic of high-density polyethylene and radiation-polymerized polyethylene blends different from high-density and low-density polyethylene blends. A new peak and/or a new shoulder, however, appeared in DSC heating curves of the blends with heat treatment at 110°, 120°, and 125°C. These results suggest that the physical state of the blends quenched from the melt is one where the crystallization of the radiation-polymerized polyethylene is highly hindered by the presence of high-density polyethylene. The radiation-polymerized polyethylene may remain mainly in a physical state similar to the melt. The haze value of the blends increased with heat treatment. The increase in the haze is caused by change in physical states, such as growth of spherulites and formation of microcrystals and microvoids, by the heat treatment.

INTRODUCTION

Polymer blending is one of the important techniques for improving the physical properties of polymers. The physical properties of blends are much dependent not only on the blending ratio but also on the physical state of polymer blends. As for blends of crystalline polymers, the coagulations and dispersions of polymer molecules in the blends are much complicated by their physical states of crystalline and noncrystalline regions. A cocrystal peak in multiple peaked heating curves of linear and branched polyethylene blends has been reported,[1] but many workers have ascribed the peak to hybrid crystallites.[2-4]

A series of studies on radiation-induced polymerization of ethylene as well as the structures and properties of formed polyethylene have been carried out.[5-8] Radiation-polymerized polyethylene has been found to have several characteristics of structure and properties.[9-11]

In the course of the study, we found that the transparency of the high-density polyethylene is improved by melt blending with radiation-polymerized polyethylene. This is a characteristic of the radiation-polymerized polyethylene blends different from conventional polyethylene blends.

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TABLE I
Physical Properties of Polyethylenes

Sample	Mol. wt $\bar{M}_v \times 10^{-4}$	Density, g/ml	Melt index, g/10 min
HDPE	4.0	0.949	7.8
Radiation-polymerized PE	5.3	0.935	0.33
LDPE	4.2	0.930	0.33

In this paper, the physical states of the radiation-polymerized polyethylene blends are investigated on the basis of DSC curves, their change with heat treatment, and the improved transparency.

EXPERIMENTAL

High-density polyethylene (HDPE, Hizex 1000J of Mitsui Petrochemical Co.), low-density polyethylene (LDPE, Sumikathene F101 of Sumitomo Chemical Co.), and radiation-polymerized polyethylene (produced by Japan Atomic Energy Research Institute) were used as the blending materials.

Preparation of the radiation-polymerized polyethylene was carried out by use of a pilot plant with a 50-liter reactor, in which ethylene was polymerized in the presence of *tert*-butyl alcohol containing 25% distilled water under a pressure of 300 kg/cm^2 at 30°C and at a dose rate of 2.8×10^5 rad/hr with Co-60 gamma radiation.[12] The physical properties of the polyethylene are listed in Table I.

The two kinds of polyethylenes were blended in melt at 160°C for 30 min at 30 rpm mixing by use of a Brabender Plasticorder (Model PL-V-151). The blends were hot pressed to 0.5-mm-thick sheet at 160°C under a pressure of 150 kg/cm^2, followed by quenching to room temperature. The melting behavior of the blends was studied by differential scanning calorimetry by use of a Perkin-Elmer DSC 1B instrument at heating and cooling rates of 16°C/min. About 4 mg of sample was used for each measurement, and benzoic acid was used as a standard material.

The haze value of the specimens was measured with an integration sphere hazemeter (Nippon Seimitsu Kogaku, Model SEP-H-S) according to ASTM D-1003-61. The sample cell was filled with dimethylphthalic acid (n_d = 1.517) to prevent scattering on the surface of the specimen. The haze value is calculated by the following equation:

$$\text{haze}\ (\%) = \frac{T_d}{T_t} \times 100$$

where T_t and T_d are total and diffuse transmittances measured by the hazemeter. The haze value of the sample with approximately equal total transmittance can be used as a measure of the transparency. The lower haze value, then, implies higher transparency.

RESULTS AND DISCUSSION

The haze values of the blends of two kinds of polyethylene among radiation-polymerized polyethylene, high-density polyethylene, and low-density polyethylene quenched from the melt are shown in Figure 1. The haze value of the

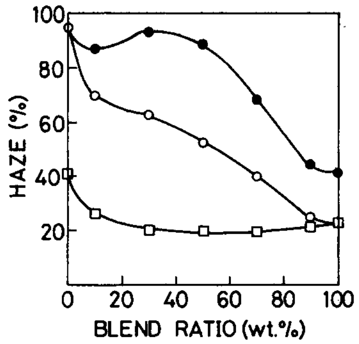
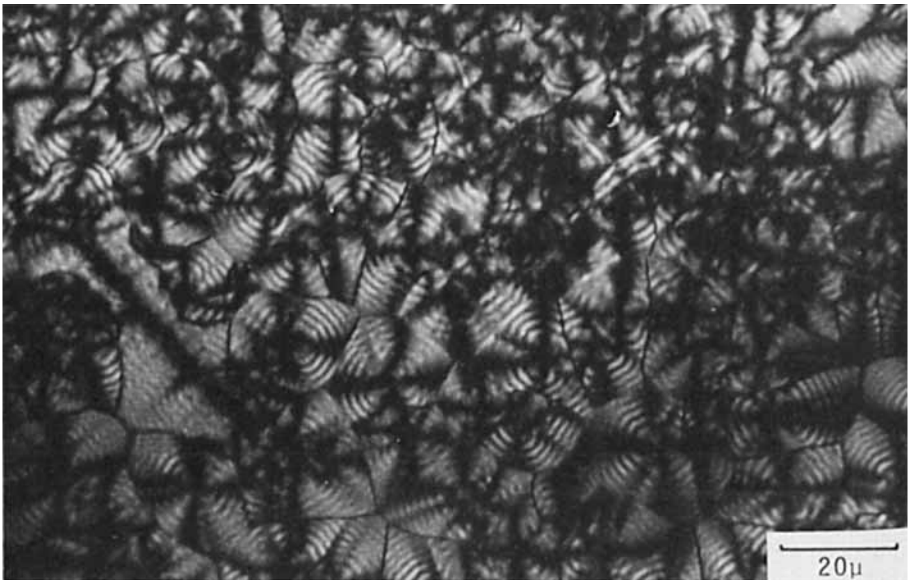


Fig. 1. Haze values of blends of various polyethylenes: (●) HDPE/LDPE; (○) HDPE/radiation-polymerized polyethylene; (□) LDPE/radiation-polymerized polyethylene.

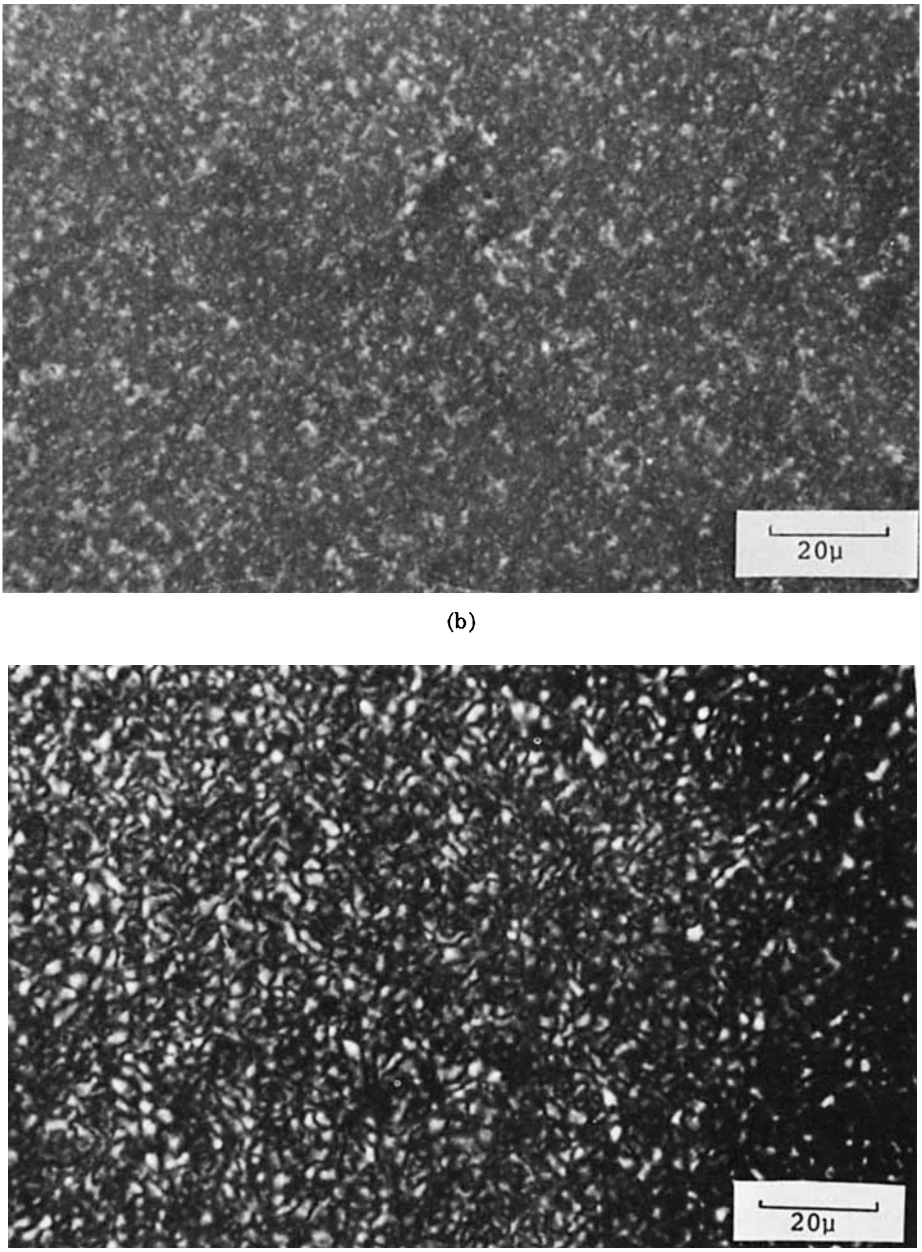
blends was found to decrease considerably upon increasing the radiation-polymerized polyethylene contents. On the other hand, that of the blends of high-density polyethylene with low-density polyethylene was not changed up to 50 wt-% content of low-density polyethylene. As the total transmittance of the blends was approximately same in spite of the decrease of the haze value, the decrease of the haze value is caused by the decrease of diffuse transmittance of the blends. The transparency, therefore, of the high-density polyethylene and low-density polyethylene was found to be improved by blending with radiation-polymerized polyethylene. These results seem to indicate that the physical states, such as size of spherulites, microcrystals, and density fluctuation caused by their primary structures, influence the optical properties of the blends.

The spherulites of the polyethylene blends observed under a polarizing microscope are illustrated in Figure 2. The spherulites are obviously found in the



(a)

Fig. 2 (*continued*)



(b)

(c)

Fig. 2. Spherulites of polyethylene blends quenched from the melt: (a) 100% HDPE; (b) HDPE blended with radiation-polymerized polyethylene by 50 wt-%; (c) HDPE blended with LDPE by 50 wt-%.

blends by 50 wt-% of high-density polyethylene with low-density polyethylene (Fig. 2c). On the other hand, the spherulites in the blends of high-density polyethylene with radiation-polymerized polyethylene are remarkably collapsed in shape with increase in radiation-polymerized polyethylene content. The clear spherulites are no longer observed in the blends by 50 wt-% of radiation-

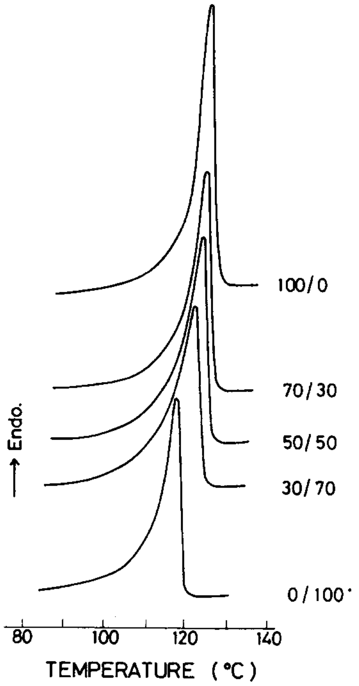


Fig. 3. DSC heating curves of blends of radiation-polymerized polyethylene with HDPE quenched from the melt. Numerals of each curve are the blend ratios of HDPE to radiation-polymerized polyethylene.

polymerized polyethylene (Fig. 2b). These results may indicate that the growth of the spherulites of high-density polyethylene in the blends must be prevented by the presence of radiation-polymerized polyethylene. The crystallinity of the radiation-polymerized polyethylene is about 65% by x-ray analysis, but a clear spherulite was not observed. This may be due to the primary structure of the radiation-polymerized polyethylene, such as long-chain branching and molecular weight distribution.[6]

Figure 3 shows DSC heating curves of the blends of radiation-polymerized polyethylene with high-density polyethylene quenched from the melt. The peak temperatures of radiation-polymerized polyethylene and high-density polyethylene were about 117° and 125°C, respectively. Only one peak was, however, observed in DSC heating curves of the blends of radiation-polymerized polyethylene with high-density polyethylene regardless of the polymer content. On the other hand, the blends of high-density polyethylene with low-density polyethylene gave a multiple endothermic peak near their melting points. This indicates that the physical state of the blends of high-density polyethylene with radiation-polymerized polyethylene is different from that of high-density polyethylene with low-density polyethylene.

The endothermic peak temperatures T_p and end temperatures T_e were obtained from DSC heating curves. The crystallization peak temperatures T_c were obtained from DSC cooling curves. Heats of fusion ΔH_f were calculated from their areas of endothermic thermogram using benzoic acid as standard compound (33.9 cal/g). Degrees of crystallinity X were estimated from the heats of fusion and the value for crystalline polyethylene of 66 cal/g. The

TABLE II
Results of DSC Study of Blends Quenched from the Melt

Composition (HDPE/radiation-polymerized PE)	T_p, °C	T_e, °C	T_c, °C	Heat of fusion ΔH_f, cal/g	Crystallinity X, %
100/0	124.7	129.1	104.0	37.3	56.5
90/10	124.4	128.8	104.8	34.1	51.7
70/30	123.7	127.8	104.7	32.5	49.3
50/50	123.0	126.5	104.0	31.5	47.7
30/70	121.2	124.3	103.5	28.5	43.2
10/90	119.3	122.9	101.4	28.4	43.0
0/100	116.7	120.8	99.5	28.4	43.0

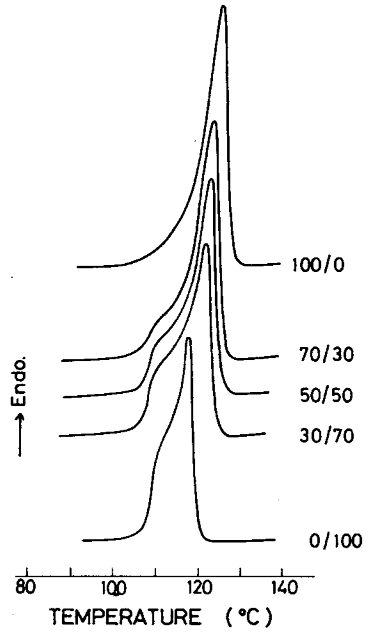


Fig. 4. DSC heating curves of blends of radiation-polymerized polyethylene with HDPE heat treated at 110°C. Numerals indicate blend ratio as in Fig. 3.

results of DSC measurements are summarized in Table II. T_p and T_e of the blends of radiation-polymerized polyethylene with high-density polyethylene shifted toward lower temperature, and the heat of fusion of the blends decreased with increasing radiation-polymerized polyethylene content, while T_c was not changed markedly. This suggests that the crystallization from the melt of high-density polyethylene is affected by the blending of radiation-polymerized polyethylene.

The blends of radiation-polymerized polyethylene with high-density polyethylene were heat treated at temperatures of 110°, 120°, and 125°C for 2 hr. The DSC heating curves of the blends after heat treatment are shown in Figures 4, 5, and 6. Data of the DSC measurements are summarized in Tables III, IV, and V. With heat treatment, a new peak and/or a new shoulder appeared in the DSC heating curves. For the samples heat treated at 110°C, new shoulders were found in the DSC heating curves at about 110°C for the blends and radia-

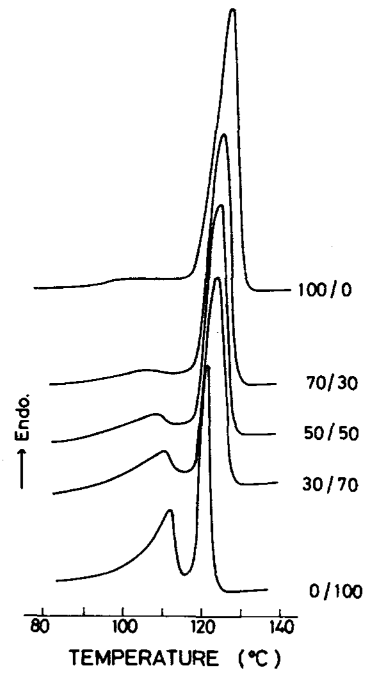


Fig. 5. DSC heating curves of blends of radiation-polymerized polyethylene with HDPE heat treated at 120°C. Numerals indicate blend ratio as in Fig. 3.

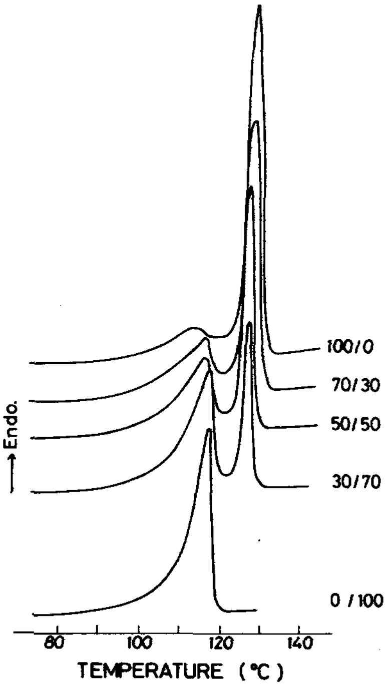


Fig. 6. DSC heating curves of blends of radiation-polymerized polyethylene with HDPE heat treated at 125°C. Numerals indicate blend ratio as in Fig. 3.

TABLE III
Results of DSC Study of Blends Heat Treated at 110°C

Composition (HDPE/radiation-polymerized PE)	T_p, °C		T_e, °C	T_c, °C	Heat of fusion ΔH_f, cal/g	Crystallinity X, %
100/0	125.4		130.9	103.8	38.9	58.9
90/10	123.0	107.4	128.0	103.7	37.9	57.4
70/30	123.5	109.0	128.0	103.9	35.7	54.2
50/50	123.0	110.3	127.7	103.5	35.1	53.2
30/70	122.0	110.0	125.5	103.0	32.7	49.6
10/90	119.5	110.7	123.4	101.0	21.8	33.1
0/100	117.7	110.3	122.0	99.5	28.3	42.9

TABLE IV
Results of DSC Study of Blends Heat Treated at 120°C

Composition (HDPE/radiation polymerized PE)	T_p, °C		T_e, °C	T_c, °C	Heat of fusion ΔH_f, cal/g	Crystallinity X, %
100/0	127.4		132.2	103.2	41.6	63.1
90/10	127.0	104.5	132.8	104.0	40.9	61.9
70/30	125.6	106.3	130.9	104.1	38.8	58.8
50/50	124.7	108.0	129.8	103.7	36.3	55.0
30/70	124.0	110.9	129.2	103.0	33.8	51.3
10/90	122.1	111.5	126.0	101.0	30.7	46.5
0/100	121.2	111.9	125.4	98.9	30.2	45.8

TABLE V
Results of DSC Study of Blends Heat Treated at 125°C

Composition (HDPE/radiation-polymerized PE)	T_p, °C		T_e, °C	T_c, °C	Heat of fusion ΔH_f, cal/g	Crystallinity X, %
100/0	129.0	114.0	134.5	103.7	43.2	65.4
90/10	128.0	115.0	133.0	104.4	42.4	64.2
70/30	128.2	116.0	133.0	104.5	38.8	58.8
50/50	126.8	115.7	131.8	104.3	35.5	53.8
30/70	127.0	116.8	131.2	103.1	32.0	48.5
10/90	126.0	117.7	129.3	101.2	26.9	40.7
0/100	117.0		121.0	99.4	27.8	42.2

tion-polymerized polyethylene alone, but were not found in high-density polyethylene. For the samples heat treated at 120°C, new double-peaked heating curves were found in the blends and radiation-polymerized polyethylene alone. Appearance of a new peak or shoulder is ascribed to the effect of the heat treatment on radiation-polymerized polyethylene, since that for high-density polyethylene is small at this heat treatment condition on the DSC curves. For 125°C heat treatment, the results are similar to 120°C treatment, except that high-density polyethylene crystallizes to give double-peaked heating curves. The high-temperature peak in the blends heat treated at 120°C was broader than that for heat treatment at 125°C. This was due to insufficient separation of the peak of radiation-polymerized polyethylene from high-density polyethylene.

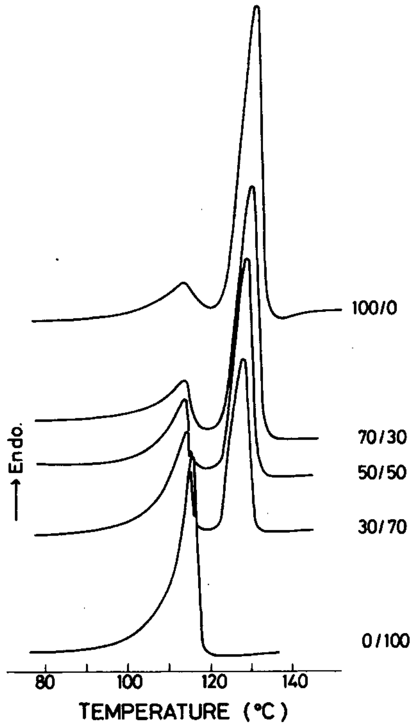


Fig. 7. DSC heating curves of blends of radiation-polymerized polyethylene with HDPE crystallized at 123°C. Numerals indicate blend ratio as in Fig. 3.

The high-temperature peak originated mainly in the high-density polyethylene and shifted toward higher temperature with heat-treatment temperature and with high-density polyethylene content. The low-temperature peak of the blends originated mainly in the radiation-polymerized polyethylene. This indicates that the effects of heat treatment on radiation-polymerized polyethylene and high-density polyethylene were independent. Multiple-peaked heating curves in the high-density polyethylene and in the radiation-polymerized polyethylene alone resulted from partial melting and partial crystallization during heat treatment of the polymers.[13]

The blends of radiation-polymerized polyethylene with high-density polyethylene were isothermally crystallized at 123°C for 46 hr from the molten state. Since the temperature is higher than the peak temperature of the radiation-polymerized polyethylene and lower than that of the high-density polyethylene, only the latter isothermally crystallized and the former is in a molten state at the temperature. The DSC heating curves of the blends isothermally crystallized are shown in Figure 7. Data of the DSC measurement are summarized in Table VI. Each endothermic peak appearing at higher temperature originated from high-density polyethylene, and that appearing at lower temperature originated from radiation-polymerized polyethylene, respectively. The peak temperature originating from high-density polyethylene is higher (129.0° → 131.5°C) and heat of fusion ΔH_f is larger (43.2 → 44.4 cal/g) than those heat treated at 125°C. This indicates that the high-density polyethylene crystallizes separately from the radiation-polymerized polyethylene.

TABLE VI
Results of DSC Study of Blends Crystallized Isothermally at 123°C

Composition (HDPE/radiation-polymerized PE)	T_p, °C		T_e, °C	T_c, °C	Heat of fusion ΔH_f, cal/g	Crystallinity X, %
100/0	131.5	113.7	137.0	104.0	44.4	67.3
90/10	131.5	114.5	136.9	104.2	40.9	61.9
70/30	130.5	114.0	135.3	104.7	38.6	58.5
50/50	129.7	114.1	134.4	104.3	35.7	54.1
30/70	128.5	114.7	132.6	103.0	32.5	49.3
10/90	126.8	115.8	131.0	101.5	27.1	41.4
0/100	115.0		120.0	99.4	29.6	44.8

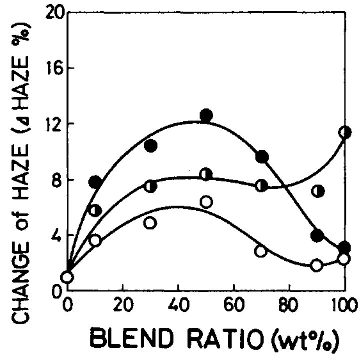


Fig. 8. Change in haze value of blends of radiation-polymerized polyethylene with HDPE by heat treatment at various temperatures: (○) 110°C; (◑) 120°C; (●) 125°C.

The above-mentioned results suggest that the physical state of the blends quenched from the melt is inferred to be one where the crystallization of the radiation-polymerized polyethylene is highly hindered by the presence of high-density polyethylene. The radiation-polymerized polyethylene may mainly remain in a physical state similar to the melt condition.

The high-density polyethylene in the blends crystallizes in small crystallite, since the migration of polymer molecule is slow because of the presence of radiation-polymerized polyethylene. Though the profiles of the heating curves of the blends quenched from the melt show a single peak, the physical state of the blends is neither cocrystals nor hybrid crystallites.

The haze values of the blends changed by the heat treatment at various temperatures are shown in Figure 8. The change in haze value is maximum at about 50 wt-% of radiation-polymerized polyethylene content, and the higher the heat treatment temperature, the more markedly the haze value increases. As the total transmittance was not, however, markedly changed by heat treatment, the increase in haze was due to the increase in the diffuse transmittance, which was caused by the change in physical state, such as growth of spherulites and formation of microcrystals and microvoids, by the heat treatment. The change in haze value agrees with the results of the melting behavior of the blends by heat treatment.

It is assumed that the radiation-polymerized polyethylene in the blends is similar to its molten state condition and occupies the region between the crystallites of high-density polyethylene and covered the surface of the crystallites in the blends. Therefore, the density fluctuation (refractive index fluctuation) in the blends is smaller than that in high-density polyethylene alone. Consequently, the diffuse transmittance of the blends of high-density polyethylene with radiation-polymerized polyethylene is decreased, and hence the transparency is improved.

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