

## 폴리스티렌 / 고밀도 폴리에틸렌 블렌드의 열적거동

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## Thermal Behavior of Polystyrene/High Density Polyethylene Blends

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요약 : 비상용성 PS / HDPE 블렌드의 열적성질을 DSC로 측정하였다. 블렌드의 결정화도와 용해열은 HDPE의 함량이 증가함에 따라 증가한다. PS의 유리전이온도와 HDPE의 녹는 온도가 서로 가깝게 중첩되어 onset 온도를 특성온도로 사용할 수 없다. 대신 onset 온도후 변곡점(열의 흐름이 온도에 대한 제2차 미분이 영이 되는 온도)과 최저온도를 PS / HDPE 블렌드의 열적거동을 조사하는데 사용하였다. 변곡점은 HDPE 함량의 증가에 따라 거의 직선적으로 증가한다. 그러나 최저온도는 PS / HDPE=30 / 70에서 완만한 최고값을 주고 있는데, 블렌드의 형태학과 연관성이 있다고 사료된다. 즉 주어진 10°C / min의 가열속도에서 분산상인 PS의 입자크기와 입자간의 간격, 그리고 연속상인 HDPE의 낮은 비열 등의 균형으로 PS / HDPE=30 / 70에서 최대가 나타난다고 판단된다. 70%이상의 HDPE를 포함한 블렌드의 최저온도에 대한 변화를 무시할 때, 이들 블렌드는 일정한 최저온도를 갖지만 변곡점은 PS함량과 직선적인 관계에 있다고도 할 수 있다.

**Abstract :** Thermal behavior of incompatible PS / HDPE blends is characterized by DSC thermogram. Crystallinity and heat of fusion of the blend are increased with the HDPE content. Overlapping of peaks by PS glass transition and HDPE melting prevents from using the onset point as characteristic temperature. Instead, the deflection point (temperature where the second derivative of energy flow against temperature becomes zero) after the onset and the peak temperature are used to examine the thermal behavior of PS / HDPE blends. The deflection temperature is linearly increased with the HDPE content. However, the peak temperature shows a mild maximum at PS / HDPE=30 / 70, which may be attributable to the phase morphology of the blend. That is, at a given heating rate of 10°C / min, particle size and spacing of the dispersed phase (PS), and the low heat capacity of HDPE medium could be balanced to yield a maximum at PS / HDPE=30 / 70. When one neglects the variation of peak temperature for the high HDPE content (70% or more), these HDPE-rich blends may have a constant peak temperature while the deflection point is varied linearly with PS content.

## INTRODUCTION

Physical blending of two or more polymers has been attracted much interest for commercial product development. Early work on blending was aimed almost exclusively at modifying polymer for impact strength with elastomeric materials. In recent years, however, blending is widely expanded to virtually all polymeric materials for various reasons.

It is a well-known fact that most of chemically different polymers give incompatible systems on blending. In other words, the macroscopic phase separation is inevitable in the incompatible blend. Therefore, there are many on-going efforts to improve properties of the incompatible polymer blend.

The thermodynamic criterion for a stable mixture of two polymers is that the second derivative of the free energy with respect to concentration is positive.<sup>1</sup> However, the actual determination of this condition is usually decided on vague definitions of compatibility based on experimentally measured properties of blends. Nevertheless, the thermal technique is one of most common methods to study and characterize polymer blends.

Blends of polystyrene (PS) and polyethylene (PE) are particularly interesting for several reasons. (1) They are two commodity polymers with large amounts of consumption in various application fields. (2) They are a typical pair of amorphous polymer (PS) and crystalline polymer (PE). (3) The blend of PS and PE represents an incompatible system with macrophase separation. (4) There are many commercial products available for possible compatibilizers for the blend. For example, block copolymers based on styrene and butadiene or isoprene are on the market. Ethylene-propylene rubber is another possible compatibilizer for PE phase with or without chemical reaction.

Thermal behavior of PS blends is studied by many researchers. In particular, PS with poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) represents a compatible blend system.<sup>2-5</sup> Poly(vinyl-methyl ether)<sup>6,7</sup> and poly(methylmethacrylate)<sup>8</sup>

are also studied with PS thermally. Other styrenic copolymers are also tested by many others.

In this study, thermal behavior of PS / HDPE blends is characterized by DSC thermogram. It is obvious that incompatible PS / HDPE blends will show each characteristic peak for PS and HDPE separately. One of the objectives is how these characteristic peaks are varying with the composition ratio of blends.

## EXPERIMENTS

### Materials

Blends of two commercial polymers are examined. They are polystyrene (PS, Styron 666D, Dow Chemical Co.,  $\bar{M}_n=166,000$ ,  $\bar{M}_w=260,000$ , density=1.05) and high-density polyethylene (HDPE, Alathon 7050, Du Pont,  $\bar{M}_n=19,000$ ,  $\bar{M}_w=59,000$ , density=0.96). Binary blends of PS and HDPE are prepared by weight ratio.

### Apparatus

For the thermal property, a DSC (differential scanning calorimeter, Du Pont 1090) is used. Temperature span has been from -160°C to 280°C although the result is given in the range of 0°C to 240°C. Heating rate is 10°C/min under 20 cm<sup>3</sup>/min nitrogen flow with about 10mg sample.

The scanning electron micrograph (Hitachi Model S-510) is taken with samples prepared by etching PS phase in toluene for 3 minutes at 20°C.

## RESULTS AND DISCUSSION

Fig. 1 represents DSC thermograms for PS / HDPE blends. PS, curve(a), shows a very weak transition : onset at 89.6°C, deflection point at 93.5°C, and peak temperature at 96.7°C. Fig. 2 is a blow-up of PS thermogram near transition temperature showing transition points. Normally,  $T_g$  of PS is known to be around 100°C, but polydispersity ( $\bar{M}_w/\bar{M}_n=2.1$ ) of commercial PS seems to give a slightly lower  $T_g$  than the monodispersed PS. HDPE, curve(g) of Fig. 1, requires a large heat flow for melting of crystals;

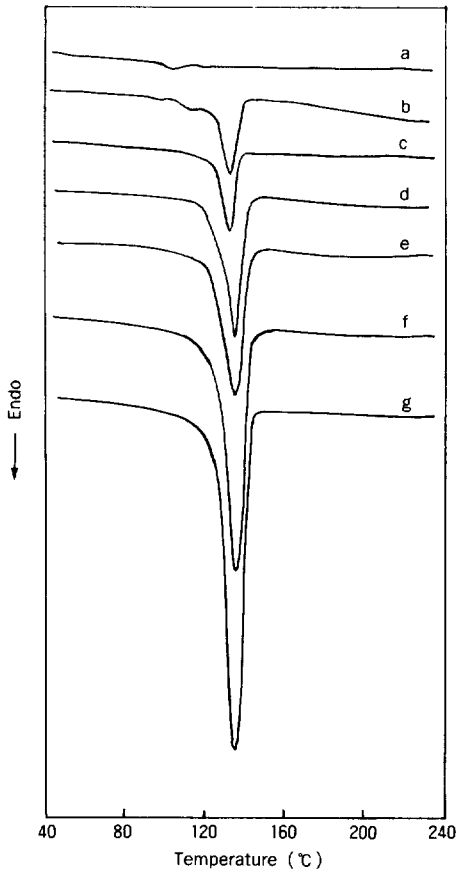


Fig. 1. DSC thermograms of PS/HDPE blends: (a)PS, (b)PS/HDPE=85/15, (c)70/30, (d)50/50, (e)30/70, (f)15/85, (g)HDPE.

Table 1. Results of DSC for PS/HDPE Blends

PS/HDPE (wt. ratio)	Crystal- linity(%)	Heat of Fu- sion(J/g)	Melting Temperature <sup>a</sup> T <sub>md</sub> (°C)	T <sub>mp</sub> (°C)
100/0	0	-	-	-
85/15	8.67	21.2	122.9	129.5
70/30	19.3	47.3	124.2	131.9
50/50	35.5	87.0	124.6	135.0
30/70	45.3	129	125.8	136.2
15/85	60.3	171	126.5	136.1
0/100	88.8	252	127.7	135.7

<sup>a</sup> T<sub>md</sub> is the deflection temperature after onset, T<sub>mp</sub> is the peak melting temperature.

deflection point at 127.7°C and peak temperature at 135.7°C. Various PS/HDPE blends, curves

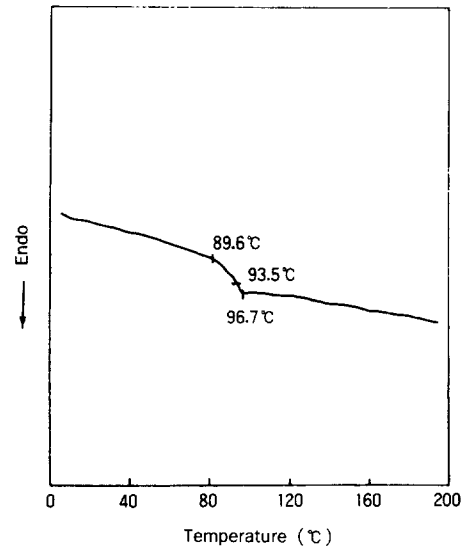


Fig. 2. DSC thermogram of PS showing a glass transition temperature.

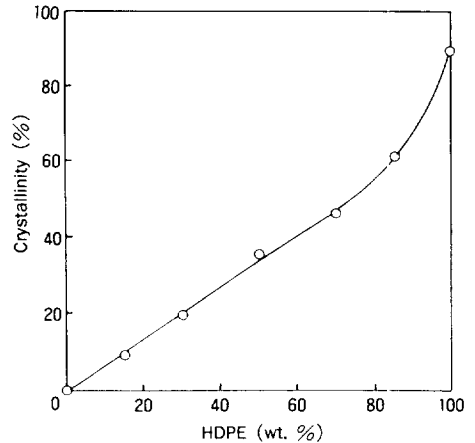


Fig. 3. Variation in crystallinity of PS/HDPE blends.

(b) to (f) in Fig. 1, show intermediate thermal behavior between PS and HDPE.

As may be seen in Fig.1, T<sub>g</sub> of PS and T<sub>m</sub> of HDPE are close enough to give overlapped region for the blend. Thus, it is almost impossible to determine the onset point for PS/HDPE blends.

Table 1 summarizes the result of DSC experiment. As expected, the crystallinity of PS/HDPE blends is increased with HDPE content. This

## Thermal Behavior of PS / HDPE Blends

can also be seen in Fig. 3. HDPE homopolymer exhibits a very high crystallinity, almost 90%. However, 15wt% addition of PS lowers the crystallinity of the blend to 60% level. Further addition of PS decreases the crystallinity almost linearly. Similar behavior can be observed in heat of fusion of the blend as seen in Fig. 4.

Fig. 5 shows variation of two transition temperatures,  $T_{md}$  and  $T_{mp}$ . The deflection temperature  $T_{md}$  is a transition temperature measured at halfway point of melting peak after the onset temperature. In other words,  $T_{md}$  is the temperature where

the second derivative of heat flow against temperature becomes zero. That is a breaking point of heat capacity gradient. The other transition temperature  $T_{mp}$  is the peak point of the melting range.

It is interesting to see that  $T_{md}$  varies linearly with HDPE content while  $T_{mp}$  appears to give a mild maximum at PS / HDPE = 30 / 70. This somewhat different behavior of two transition temperatures may be related to the phase morphology of the blend. In other words, PS as the dispersed phase in PS / HDPE blends exhibit a rather large particle size in HDPE medium,<sup>9</sup> in particular with PS-rich blends. Fig. 6 demonstrates the

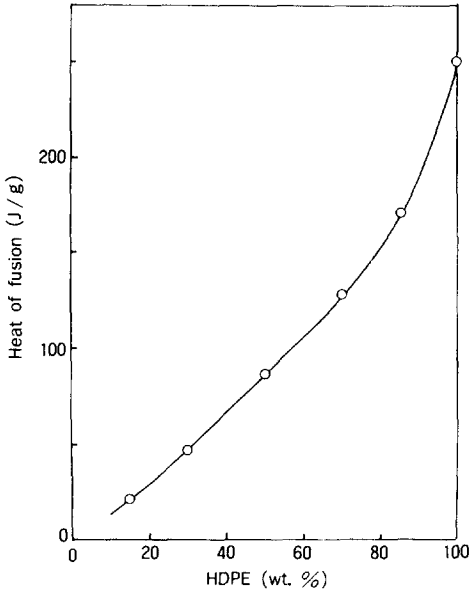


Fig. 4. Variation in heat of fusion of PS / HDPE blends.

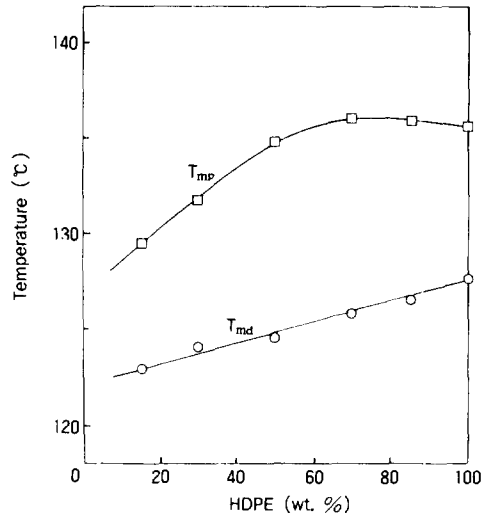


Fig. 5. Transition temperatures of PS / HDPE blends.  $T_{mp}$  is peak temperature and  $T_{md}$  is deflection temperature after onset.

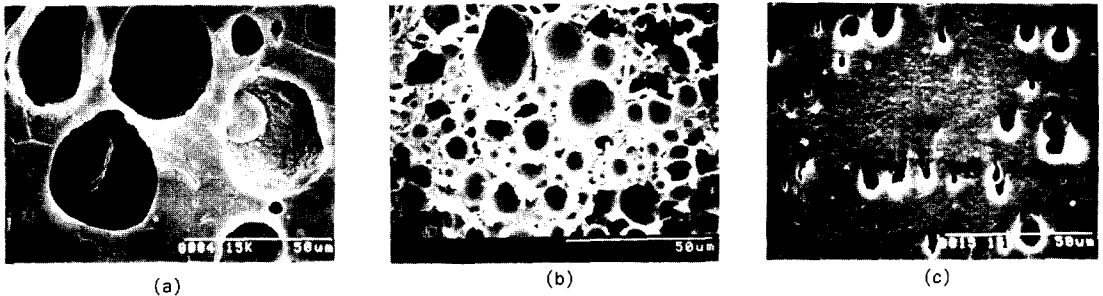


Fig. 6. Scanning electron micrographs of PS / HDPE blends ( $\times 1,000$ ): (a) PS / HDPE = 50 / 50, (b) 30 / 70, (c) 15 / 85.

particle size of three PS / HDPE blends, showing the higher HDPE content gives the smaller particle size in these HDPE-rich blends. This different morphology of different PS / HDPE blending ratios would give different thermal behavior. HDPE as the continuous medium has  $35.0 \text{ J/}^\circ\text{K}$ -mole heat capacity at the melting temperature around  $415^\circ\text{K}$  ( $148^\circ\text{C}$ ).<sup>10,11</sup> On the other hand, PS as the dispersed phase has about  $210 \text{ J/}^\circ\text{K}$ -mole heat capacity at  $420^\circ\text{K}$ ,<sup>12,13</sup> a value of about 6 times of HDPE. Thus, a mild maximum of  $T_{\text{mp}}$  at PS / HDPE=30 / 70 could be a result of low heat transfer to PS particles through low heat capacity medium HDPE with the given heating rate of  $10^\circ\text{C} / \text{min}$ . In other words, the PS particle is too large to melt instantaneously, yet the distance between particles is too far to give effective heat flow through HDPE medium.

Another possible explanation, with a great thank to one of the referees, is that  $T_{\text{mp}}$  may vary up to certain level of HDPE then level off. That is, in PS / HDPE blends with more than 70% HDPE,  $T_{\text{mp}}$  may remain constant to be about  $136^\circ\text{C}$  (neglecting the small variation) which is  $T_{\text{mp}}$  of HDPE. In other words, PS as dispersed phase would not give any noticeable change to  $T_{\text{mp}}$  of these HDPE-rich blends. However,  $T_{\text{md}}$  may be affected by the PS phase even at low levels since it is related to the broadness of melting speak(or area).

## CONCLUSION

Crystallinity of PS / HDPE blends is increased as HDPE content increases. Heat of fusion exhibits similar behavior.

Transition temperatures of the blend in terms of the deflection point  $T_{\text{md}}$  and peak temperature  $T_{\text{mp}}$  vary with the blending ratio.  $T_{\text{md}}$  varies linearly with the HDPE content while  $T_{\text{mp}}$  shows a mild maximum at PS / HDPE=30 / 70. The

maximum of  $T_{\text{mp}}$  may be attributable to the morphology of PS / HDPE blends balanced with the specific heating rate of  $10^\circ\text{C} / \text{min}$ . Another way to explain the behavior of transition temperatures is:  $T_{\text{mp}}$  of blends with more than 70% HDPE may be constant, and  $T_{\text{md}}$  is varied linearly with PS content since it is related to the peak broadness.

Peak overlapping of PS( $T_g$ ) and HDPE( $T_m$ ) prevents to use the onset temperature as a characteristic transition temperature of the PS / HDPE blend.

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