*Journal of Thermal Analysis, Vol. 34 (1988) 503–508*

# THERMAL PROPERTIES OF BINARY POLYOLEFIN BLENDS

*T. Malavašič* and *V. Musil*

BORIS KIDRIČ INSTITUTE OF CHEMISTRY, LJUBLJANA,
HAJDRIHOVA 19 AND VEKŠ, DEPARTMENT OF TECHNOLOGY,
UNIVERSITY OF MARIBOR, MARIBOR, RAZLAGOVA 14, YUGOSLAVIA

The thermal properties of binary polyolefin blends (LDPE/HDPE, LDPE/PP, HDPE/PP) were examined by differential scanning calorimetry. The additon of a second polymer lowers the melting temperature although the melting temperature depression is not a defined function of the blend composition. DSC curves show two melting and two crystallization temperatures. The difference between crystallization temperatures for blends containing PP is smaller than the difference between melting temperatures. The enthalpies of fusion are nearly monotonic functions of blend composition.

Most industrial polymers have some outstanding properties. Therefore it is expected that polymer properties may be improved by blending. Two different ways of blending polymers are possible: mixing polymers in molten state, and mixing polymer solutions. These blends are in some fields increasingly replacing homopolymers. Most of the theoretical and practical investigations on the properties of polymer blends have been restricted to amorphous multicomponent systems. On the contrary, crystallizable polymer blends have received relatively little attention, although polyolefin blends are technologically very important [1–6]. This paper is a part of a more general study on the properties of polyolefin blends. In the present work differential scanning calorimetry was used for studying the thermal behaviour of binary polyolefin blends (LDPE/HDPE, LDPE/PP, HDPE/PP).

## Experimental

Low density polyethylene (LDPE) DINALEN 35, DINA Krk ($\varrho$ = 0.921 g cm$^{-3}$, MFI = 0.95 g/10 min), high density polyethylene (HDPE), HIPLEX HHM 4903, HIP Pančevo ($\varrho$ = 0.949 g cm$^{-3}$, MFI = 0.30 g/10 min), and polypropylene (PP), HIPOLEN P MA 6, HIPOL Odžaci ($\varrho$ = 0.900 g cm$^{-3}$,

*John Wiley & Sons, Limited, Chichester*
*Akadémiai Kiadó, Budapest*

MFI = 1.20 g/10 min) were used in this study. From the mentioned polyolefins three pairs of binary blends in different weight ratios were prepared by milling the mixed pellets on a two roll mill at 190° for 10 min and 30 rpm. The milled crepe was then hot pressed at 190° into compression moulded plaques of about 0.8 mm thickness. The material was quenched from this temperature by plunging the sample and moulding plates into cold water.

Thermal characteristics were measured by a Perkin–Elmer differential scanning calorimeter DSC 2. Melting and crystallization temperatures were determined from DSC curves obtained by heating resp. cooling the samples at a rate of 10 deg $min^{-1}$ and correcting the maximum melting temperatures for the melting slope of indium. The enthalpies of fusion were measured on the quenched samples. They were calculated from the areas between the DSC curves and the baseline using the melting enthalpy of indium as standard. The crystallization temperatures were measured by the following standard procedure: the sample (5–30 mg) was heated to a temperature 15–20 degrees above the highest melting temperature and kept at this temperature for 30 min. The sample was then cooled.

## Results and discussion

In Tables 1, 2 and 3 the results of the thermal studies of binary polyolefin blends are presented.

Since for all binary blend compositions two melting temperatures were detected, it could be confirmed that LDPE, HDPE and PP are incompatible. The melting temperatures of individual polyolefins were lowered with the addition of the second

**Table 1** Melting temperatures, crystallization temperatures, and overall enthalpies of fusion (LDPE + HDPE) in dependence on the LDPE/HDPE blend composition

| Composition, wt% | $T_{m_{LDPE}}$, K | $T_{m_{HDPE}}$, K | $T_{c_{LDPE}}$, K | $T_{c_{HDPE}}$, K | $\Delta H_m$, J/g |
|---|---|---|---|---|---|
| 100/0 | 385 | — | 367 | — | 114.5 |
| 90/10 | 384 | 402 | — | — | — |
| 75/25 | 383 | 403 | 367 | 385 | 135.0 |
| 60/40 | 381 | 403 | — | — | — |
| 50/50 | 381 | 406 | 369 | 388 | 148.0 |
| 40/60 | 381 | 406 | — | — | — |
| 25/75 | 381 | 406 | crystallization undetectable | 388 | 172.2 |
| 10/90 | 381 | 406 | — | — | — |
| 0/100 | — | 406 | — | 388 | 184.8 |

**Table 2** Melting temperatures, crystallization temperatures, and overall enthalpies of fusion (LDPE + PP) in dependence on the LDPE/PP blend composition

| Composition, wt% | $T_{m_{LDPE}}$, K | $T_{m_{PP}}$, K | $T_{c_{LDPE}}$, K | $T_{c_{PP}}$, K | $\Delta H_m$, J/g |
|---|---|---|---|---|---|
| 100/0 | 385 | — | 367 | — | 114.5 |
| 90/10 | 385 | 439 | — | — | — |
| 75/25 | 387 | 440 | 368 | 398 | 100.3 |
| 60/40 | 386 | 439 | — | — | — |
| 50/50 | 386 | 439 | 368 | 395 | 94.5 |
| 40/60 | 386 | 439 | — | — | — |
| 25/75 | 386 | 439 | 368 | 393 | 85.7 |
| 10/90 | 386 | 439 | — | — | 85.3 |
| 0/100 | — | 441 | — | 392 | 81.5 |

**Table 3** Melting temperatures, crystallization temperatures, and overall enthalpies of fusion (HDPE + PP) in dependence on the HDPE/PP blend composition

| Composition, wt% | $T_{m_{HDPE}}$, K | $T_{m_{PP}}$, K | $T_{c_{HDPE}}$, K | $T_{c_{PP}}$, K | $\Delta H_m$, J/g |
|---|---|---|---|---|---|
| 100/0 | 406 | — | 388 | — | 184.8 |
| 90/10 | 406 | 437 | — | — | — |
| 75/25 | 406 | 437 | 386 | crystallization undetectable | 171.4 |
| 60/40 | 406 | 437 | — | — | 145.5 |
| 50/50 | 405 | 437.5 | 387 | 393 | 135.0 |
| 40/60 | 406 | 437.5 | — | — | 129.2 |
| 25/75 | 405 | 438 | 387 | 392 | 110.8 |
| 10/90 | 405 | 438 | — | — | — |
| 0/100 | — | 441 | — | 392 | 81.5 |

polyolefin; nevertheless, it was impossible to find a defined decrease in dependence on the composition. This type of behaviour has been detected for binary blends and has been attributed to a possible interplasticizing action caused by some molecules of one component acting as a diluent within the crystalline regions of the other component [6].

The crystallization temperatures of the individual polymers in the blends did not change appreciably with the blend composition. The crystallization temperatures in the blends were in most cases some degrees higher than the crystallization temperatures of the individual polymers. The difference between the melting and crystallization temperatures was for the studied samples of LDPE and HDPE

equal, i.e. 18 deg, for PP the difference was larger, i.e. 49 deg. For this reason the crystallization temperatures of HDPE and PP in HDPE/PP blends were very close and in blends with small quantity of PP only one crystallization peak could be detected (Figs 1 and 2).

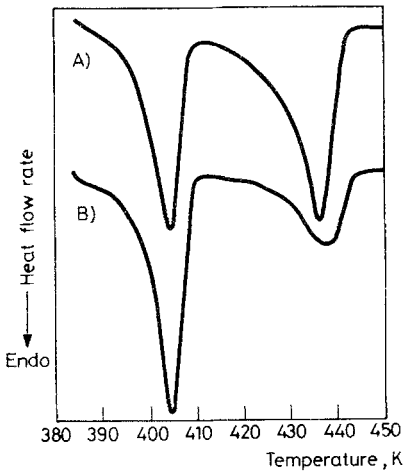


**Fig. 1** DSC melting curves of HDPE/PP blends at a heating rate of 10 deg $min^{-1}$: (A) 50 HDPE/50 PP, (B) 25 HDPE/75 PP

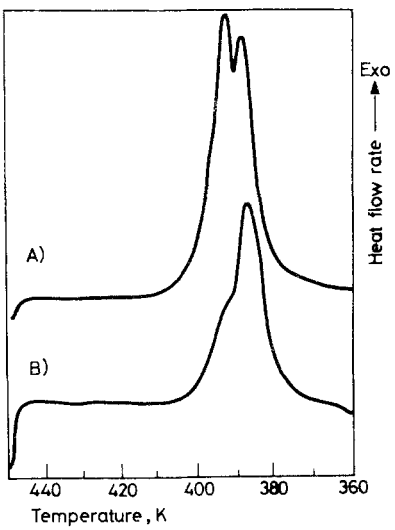


**Fig. 2** DSC crystallization curves of HDPE/PP blends at a cooling rate of 10 deg $min^{-1}$: (A) 50 HDPE/50 PP, (B) 25 HDPE/75 PP

The enthalpies of fusion were nearly monotonic functions of the binary blend composition, as established also by Donatelli [6]. In the blends of LDPE/HDPE the enthalpies of fusion increased with increasing amount of HDPE while in the blends LDPE/PP and HDPE/PP they decreased with incresing PP content. In the blends with small quantity of one of the components it was sometimes difficult to define the portions of the enthalpy of individual components because the melting peaks were not clearly separated. Hence, the enthalpies given in the tables are the overall values.

## Conclusions

The LDPE/HDPE, LDPE/PP and HDPE/PP blends have two melting temperatures since the blends are, as known, incompatible. The addition of the second polymer lowers the melting temperature although the melting temperature depression is not a function of the blend composition.

DSC curves obtained by the programmed cooling of the blends show two crystallization temperatures as well. The difference between the two crystallization temperatures for the blends containing PP is smaller than the difference between melting temperatures. Therefore compositions with small proportion of PP show only one crystallization peak.

The enthalpies of fusion are nearly monotonic functions of the blend composition. In the blends with small quantity of a second component the proportion of the individual components cannot be clearly defined.

It should be finally pointed out that the DSC method is appropriate for the evaluation of the blend composition.

## References

1 Z. Bartczak, A. Galeski and M. Pracella, Polymer, 27 (1986) 537.
2 A. Galeski, Z. Bartczak and M. Pracella, Polymer, 25 (1984) 1323.
3 J. W. Teh, J. Appl. Polym. Sci., 28 (1983) 605.
4 A. K. Gupta, V. B. Gupta, R. H. Peters, W. G. Harland, and J. P. Berry, J. Appl. Polym. Sci., 27 (1982) 4669.
5 E. Martuscelli, M. Pracella, A. Avella, R. Greco and G. Ragosta, Makromol. Chem., 181 (1980) 957.
6 A. A. Donatelli, J. Appl. Polym. Sci., 23 (1979) 3071.

**Zusammenfassung** — Die thermischen Eigenschaften binärer Polyolefinmischungen (LDPE/HDPE, LDPE/PP, HDPE/PP) wurden mittels DSC untersucht. Durch Zugabe eines zweiten Polymers wird die Schmelztemperatur erniedrigt, obwohl die Erniedrigung der Schmelztemperatur keine Funktion der Mischungszusammensetzung ist. Die DSC-Kurven zeigen zwei Schmelz- und zwei Kristallisationspeaks. Bei PP enthaltenden Mischungen ist der Unterschied zwischen den Kristallisationstemperaturen geringer als zwischen den Schmelztemperaturen. Die Schmelzenthalpie ist eine nahezu monotone Funktion der Mischungszusammensetzung.

**Резюме** — Методом ДСК изучены термические свойства полимерных смесей полиэтилен низкой плотности — полиэтилен высокой плотности, полиэтилен низкой плотности — полипропилен, полиэтилен высокой плотности — полипропилен. Добавка второго полимера понижает температуру плавления смесей, хотя такое понижение и не является функцией их состава. Кривыя ДСК показали наличие двух температур плавления и кристаллизации. Различие между температурами кристаллизации смесей с полипропиленом меньше, чем между их температурами плавления. Установлена монотонная зависимость энтальпии плавления смесей от их состава.