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EFFECT OF COMPONENT INTERACTION ON THE MELTING AND CRYSTALLIZATION CHARACTERISTICS OF PE/PIB BLENDS

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Abstract: Linear low density polyethylene/polyisobutylene blends were prepared in the entire composition range. Non-isothermal and isothermal crystallization of the samples was carried out and melting behavior was studied as a function of composition and crystallization temperature. The equilibrium melting temperature of the neat PE and the blends was determined by the Hoffman-Weeks extrapolation technique. Flory-Huggins interaction parameters were calculated by the approach of Nishi and Wang. The decrease of melting temperature with increasing PIB content indicated the interaction of the polymers in the melt. Both irregular chain structure of the crystalline polymer and interaction lead to a decrease of the equilibrium melting temperature and maximum lamellar thickness. The results prove that even relatively weak dispersive forces can lead to the miscibility of two polymers.

INTRODUCTION

The number of polymer blends used in industrial practice increases continuously. Although we do not always realize, a great number of combinations of commodity polymers including those of polyolefins find application in various field. Polyethylene blends are used to produce films for packaging, car bumpers are frequently prepared from PP/EPDM blends, while PE is modified with elastomers to fabricate stretch films (Ref.1). These blends usually have

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heterogeneous structure, but they possess relatively good properties making them acceptable for a given application. The large theoretical and practical importance of these blends is shown also by the numerous papers dealing with all kinds of polyolefin blends including the combination of LDPE/HDPE (Refs. 2,3), PP/PE (Refs. 4,5), PP/EPDM (Refs. 6,7), PP/polybutene (Ref. 8) etc.

The two phase structure of polyolefin blends indicates immiscibility of the components, but the acceptable properties prove the existence of some interaction between them. The estimation of the extent of this interaction is rather difficult. The crystalline structure, the broad transitions of PE, the lack of specific interactions, all complicate the quantitative description of component interactions. The blends often seem to be homogeneous in the melt state on optical level (Ref. 9), although small angle neutron scattering experiments indicate a heterogeneous structure (Ref. 10). An estimation of the strength of interaction would be of some theoretical and practical relevance facilitating the development of commercially interesting blends.

The goal of our study was to investigate the structure and properties of polyethylene (PE)/ polyisobutylene (PIB) blends to estimate miscibility and to determine its effect on various properties. In a previous paper the changes in the T_g of PIB and the γ transition of PE were determined by DSC and DMTA as a function of composition (Ref. 11). Flory-Huggins interaction parameters were calculated which indicated limited miscibility of the compounds. The dispersed structure of the blends was studied by SEM. In this paper the effect of blending on the melting and crystallization characteristics of the PE component is reported. Interaction is estimated by established methods and conclusions are drawn about the structure of the crystalline phase.

EXPERIMENTAL

The polyethylene used in the experiments was the Stamylex 1016 LF grade LLDPE of DSM, The Netherlands, while Oppanol B50 produced by BASF, Germany was chosen as the PIB component. The most important characteristics of the polymers are compiled in Table 1.

Blends were prepared from the two polymers in the entire composition range from 0 to 1 in 0.1 volume fraction steps. The components were homogenized in a Brabender W 50 EH internal mixer at 150 °C, 50 rpm for 10 min. 1 mm thick plates were prepared at 150 °C on a Fontijne SRA 100 laboratory compression mould. Samples were taken for melting and crystallization studies from these plates.

Table 1 *Some characteristics of the polymers studied and parameters used in the calculations*

Polymer	PE	PIB
Grade	Stamylex 1016 LF	Oppanol B 50
Producer	DSM	BASF
$M_n \times 10^4$ (g/mol)	1.40	1.44
$M_w \times 10^5$ (g/mol)	1.37	3.93
Density (g/cm^3)	0.92	0.92
T_g (°C)	-119.2	-54.9
V (cm^3/mol)	36.4	84.9

Melting and crystallization characteristics of PE and the blends were studied by a Perkin Elmer DSC 7 apparatus. Non-isothermal experiments were carried out at 10 °C/min heating and cooling rate in two runs. In the isothermal crystallization study the sample was heated up to 160 °C to melt the polymer and erase thermal history. The samples were kept at 160 °C for 4 min then cooled down to the crystallization temperature (T_c) with 40 °C/min cooling rate. Subsequent heating of the samples started at T_c. Isothermal crystallization was carried out at various temperatures from 104 to 118 °C at 1 or 2 °C intervals depending on the temperature range and composition.

RESULTS AND DISCUSSION

As it was expressed in the introductory part, the main goal of the study was to estimate the interaction between the two polymers, i.e. between PE and PIB. This was done partly by the direct evaluation of the primary data, but a quantitative estimate was also obtained by calculation. The results obtained on PE/PIB blends are compared to literature data determined on the miscible blend of PVF$_2$/PMMA by Nishi and Wang (Ref. 12). The results are presented in four separate sections discussing non-isothermal and isothermal experiments, interaction and structure, respectively.

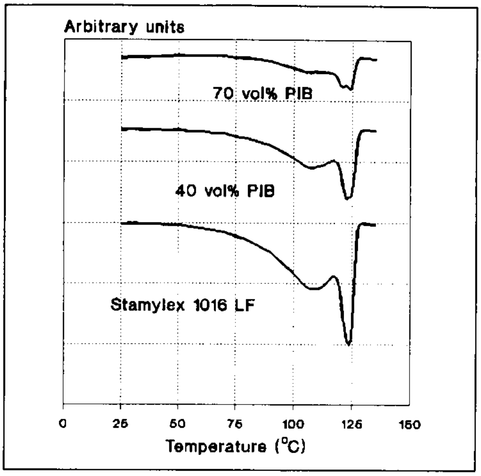

Fig. 1 *Melting endotherms of PE and two PE/PIB blends*

Non-isothermal experiments

The linear low density polyethylene used in these experiments has a complicated molecular structure, which translates into a similarly complicated crystallization and melting behavior. The melting endotherm of the neat polymer and that of the blends containing 40 and 70 vol% PIB, respectively, are presented in Fig. 1. Because of its irregular structure the melting of the selected polyethylene was complicated, a shoulder appeared on the melting endotherm before the main melting peak. The peak temperature of melting is located in the range of 120 - 124 °C and changes with composition. With increasing PIB content the second peak splits and a higher temperature peak appears. This latter becomes dominant at 80 and 90 vol% PIB content. A similar split of melting peaks was observed in PP blends earlier which was explained with changing nucleation mechanism (Refs. 13-15). However, in that case the shift occurred towards

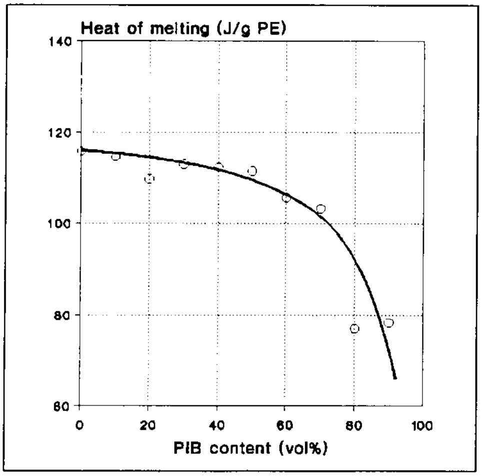

Fig. 2 *Dependence of the heat of melting of the PE phase on the PIB content of the blend*

lower temperatures, thus this explanation cannot be appropriate in the PE/PIB blends of this series. Also recrystallization may result in the appearance of additional peaks during the melting of non-isothermally crystallized samples (Ref. 16), but its effect is expected to decrease with increasing PIB content. The assumption of partial miscibility and phase separation seems to be more justified in our case. However, further study is needed in order to find a clear explanation of this phenomenon.

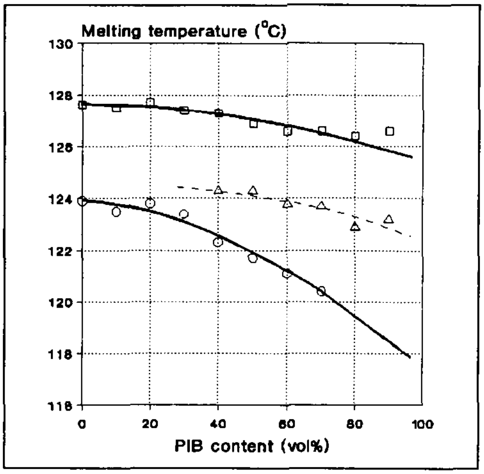

Fig. 3 *Melting temperature of PE plotted against composition; (□) final temperature, T_m; (○) peak 1, T_{mp1}; (△) peak 2, T_{mp2}*

The total area under the melting endotherm was taken as the heat of melting. This value is plotted against the composition of the blends in Fig. 2. The heat of melting continuously decreases with increasing PIB content with a significant drop at 80 vol%. The continuous decrease indicates some interaction of the components, while the drop might be related to the effect leading to the appearance of the two melting peaks discussed above. Both the peak (T_{mp}) and the final temperature (T_m) of melting were determined and they are plotted against composition in Fig. 3. The final temperature of melting was defined as the intersection of the base line and the descending leg of the melting endotherm. As it was pointed out previously, two peak temperatures can

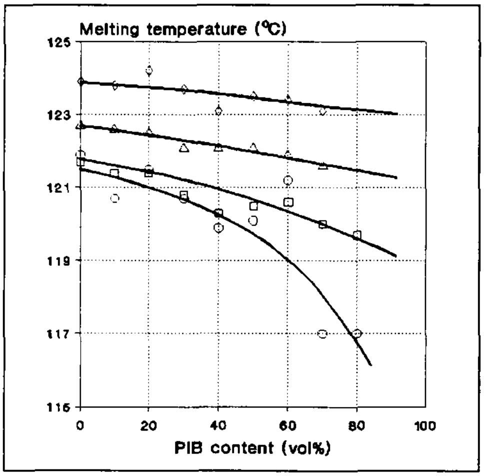

Fig. 4 *Effect of composition and temperature of crystallization on the melting peak temperature of the PE phase in PE/PIB blends; T_c: (○) 104, (□) 108, (△) 112, (◇) 115 °C*

be determined above 40 vol% PIB content. The two characteristic temperatures (T_m, T_{mp}) decrease with increasing PIB content of the blend, which indicates again some interaction of the components. Although some of the results of the non-isothermal experiments are difficult to explain, they clearly show that interaction or miscibility exists between the two components of our blend in the melt state.

Isothermal crystallization

Composition dependence of the peak temperature of melting for the isothermally crystallized samples shows a very similar behavior than the characteristic temperatures discussed above (Fig. 4). The peak temperature decreases with composition at all temperatures; the decrease of T_{mp} slows down as the crystallization temperature increases. Also the actual value of the melting temperature changes with the temperature of crystallization, as it is expected. The composition dependence of the melting temperature indicates again that the components interact with each other; the strength of the interaction depends on the temperature of crystallization.

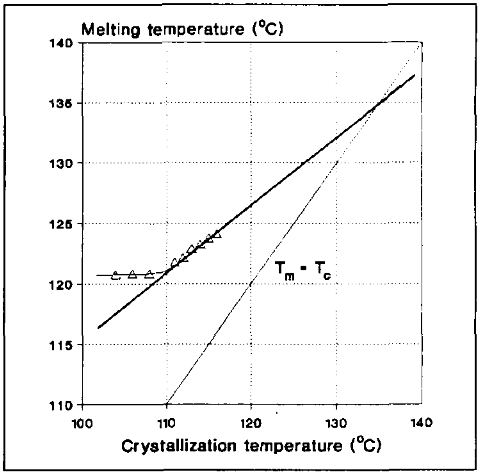

Fig. 5 *Correlation of melting and crystallization temperatures of a PE/PIB blend containing 30 vol% PIB; determination of the equilibrium melting temperature*

From isothermal crystallization experiments the equilibrium melting temperature can be determined by the extrapolation technique of Hoffman and Weeks (Ref. 17). T_m^0 was determined for the neat PE and for all the blends. An example is given in Fig. 5 for the blend containing 30 vol% PIB. The experimental values show the expected tendency, a constant value of T_m at lower crystallization temperatures and a linear correlation at higher T_c values (Ref. 16). The intersection of the $T_m = T_c$ correlation and the straight line drawn through the experimental points yields T_m^0, which is 132.6 °C for the blend with 30 vol % PIB presented in Fig. 5.

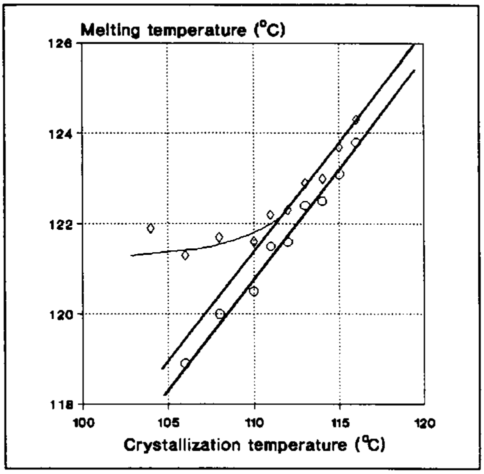

Fig. 6 *T_m vs T_c correlation for the neat PE (◇) and the blend containing 70 vol% PIB (○)*

Fig. 6 shows the correlation of the melting and crystallization temperature for the neat polymer and for the blend containing 70 vol% PIB. A few differences can be observed between the T_m - T_c functions which are characteristic throughout the experiments. In the case of the neat polyethylene and for the blends with low PIB content the first part of the correlation was independent of T_c as usual. At high PIB content this first horizontal part is absent in the temperature range studied, the measured T_m values fall on a straight line. Another interesting fact is that the standard deviation of the measurement is much larger at low, than at high PIB content. The correlation for the virgin PE is the average of 5 series of measurements, while that for the blend of 70 vol% PIB was measured in a single series. A clear explanation cannot be given for these observations, but they definitely merit further attention.

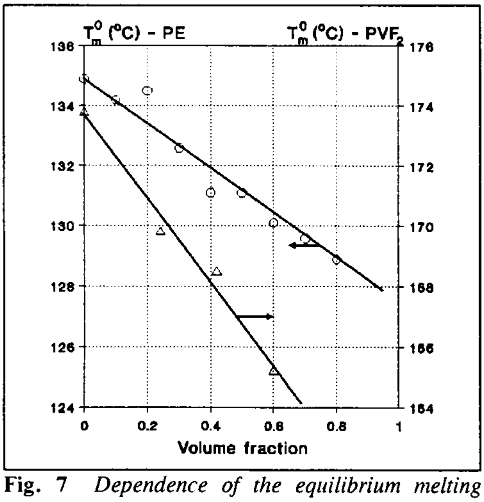

Fig. 7 *Dependence of the equilibrium melting temperature on the amount of the amorphous component in the PE/PIB (○) and the PVF$_2$/PMMA (△) blends, respectively*

The two straight lines presented in Fig. 6 run more or less parallel to each other; with increasing PIB content the correlation shifts towards lower T_m values. This shifting of the T_m vs T_c correlation could be observed at all PIB contents, and it results in a decrease of T_m^0 with composition. A similar phenomenon was observed by Nishi and Wang (Ref. 12) in PVF$_2$/

PMMA blends. The T_m^0 values determined by the Hoffman-Weeks (Ref. 17) extrapolation technique are plotted against composition in Fig. 7. As a comparison also the results of Nishi and Wang (Ref. 12) are presented in the same figure. In both cases the volume fraction of the amorphous polymer in the blend is the independent variable of the correlation, it is plotted on the horizontal axis of the plots. A strong similarity can be observed between the two correlations. Both are linear as a function of composition, T_m^0 decreases with increasing amount of amorphous polymer in the blend. The PVF_2/PMMA blend is miscible, the Flory-Huggins interaction parameter determined at 160 °C is -0.30. The decrease of T_m^0 with the PIB content of the PE/PIB blends indicates strong interaction of the components in the melt phase and similarity with the miscible PVF_2/PMMA blends strongly supports this observation. If we assume that the strength of the interaction is related to the magnitude of the decrease in T_m, interaction is weaker in the PE/PIB than in the PVF_2/PMMA blends. From 0 to 60 vol% amorphous polymer content the decrease of T_m^0 is 8.6 °C in the latter case, while it is only 4.7 °C in the PE/PIB blend. This difference must be definitely related to the type and magnitude of the forces creating the interaction of the components.

The evaluation of both the non-isothermal and isothermal crystallization experiments indicate, that the PE and PIB used in this study are miscible in the melt state. The decrease of both T_m and T_m^0 with composition, as well as the composition dependence of the heat of fusion strongly corroborates this statement.

Calculation of the interaction parameter

Nishi and Wang (Ref. 12) adapted the Flory-Huggins theory (Ref. 18) to estimate interaction in their PVF_2/PMMA blends. The basic correlation used for the evaluation is

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{R V_2}{\Delta H_2 V_1} \chi_{12} (1 - \varphi_2)^2 \qquad (1)$$

where T_m is the melting temperature determined on a non-isothermally crystallized sample, T_m^0 the equilibrium melting temperature, R the universal gas constant, V_1 and V_2 are the molar volumes of the repeat units of the two components, ΔH_2 is the enthalpy of fusion of PE, χ_{12} the Flory-Huggins interaction parameter and φ_2 is the volume fraction of PE in the blend. The molar volumes used in the calculations are given in Table 1, while for ΔH_2 a value of 4.1 kJ/mol was applied. Eq. 1 can be rearranged into the following form

$$\frac{1}{\varphi_1}\left[\frac{1}{T_m} - \frac{1}{T_m^0}\right] = -\frac{B V_2}{\Delta H_2}\,\frac{\varphi_1}{T_m} \tag{2}$$

where φ_1 is the volume fraction of PIB in the blend and B the interaction energy density characteristics of the polymer pair. B is related to χ_{12} in the following way

$$\chi_{12} = \frac{B V_1}{R T} \tag{3}$$

Plotting the experimental results according to Eq. 2 should result in a straight line, from the slope of which B and consequently χ_{12} can be calculated. An example is given in Fig. 8 where the melting temperature (T_m) of the non-isothermally crystallized samples are presented; at 120 °C a value of -0.022 was obtained for χ_{12} in this way. Although the scatter of the points is significant, the correlation is unambiguous, a reasonable χ_{12} value can be determined.

The determination of χ_{12} can be carried out the same way also for the isothermally crystallized samples. The peak temperature of melting (T_{mp}) was used in these calculations. The results are plotted as a function of temperature in Fig. 9. With increasing temperature the interaction parameter decreases indicating the existence of a lower critical solution temperature. The extrapolation of the correlation gives a χ_{12} = 0 value around 120 - 122 °C, a positive χ_{12} above this temperature means immiscibility of the components.

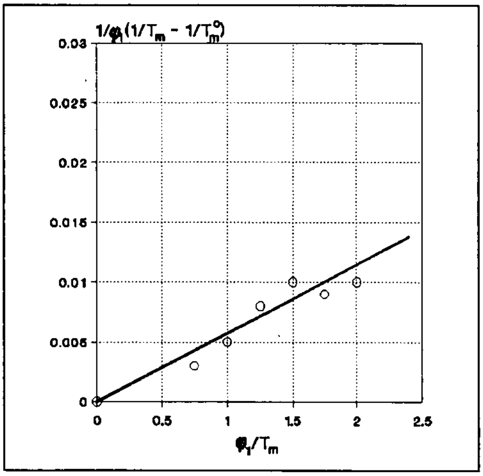

Fig. 8 *Determination of χ_{12} from the final melting temperature of the blends according to Eq. 2; χ_{12} = -0.022 at 120 °C*

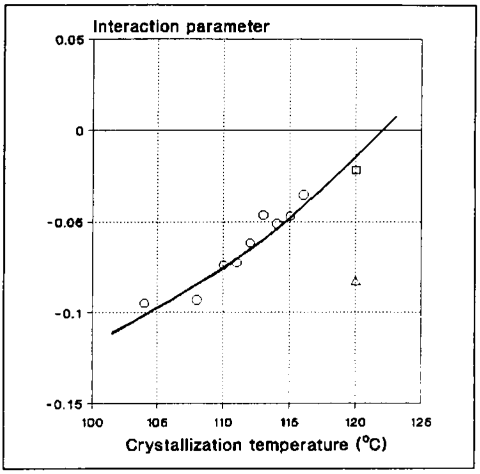

Fig. 9 *Temperature dependence of χ_{12} in PE/PIB blends; (○) isothermally crystallized samples, non-isothermal crystallization: (□) final temperature, (Δ) peak temperature*

Two facts must be emphasized here. The χ_{12} value calculated from the peak temperature of melting (T_{mp}) for the non-isothermally crystallized samples is significantly smaller (-0.083) than the one obtained from the final temperature of melting (T_{m} = -0.022) at the same temperature. The difference is not easy to explain, it must be related to the irregular molecular structure of the polyethylene used, crystallites formed at various temperatures with different perfection and thickness are influenced by the presence of PIB in a different way. Even more important is the magnitude of χ_{12} obtained for the PE/PIB blend. The application of the approach presented above yields always a negative value for χ_{12}, but its magnitude has some importance as well. Compared to the χ_{12} value of the PVF$_2$/PMMA blend determined by Nishi and Wang (Ref. 12), the interaction parameter calculated for the PE/PIB blend is much smaller, its average value is around - 0.05. This large difference and the relative small absolute value is in complete agreement with earlier experiments indicating a two phase structure and limited miscibility of the components in the solid state. The larger χ_{12} is in accordance also with the smaller change in T_m^0 with increasing amount of the amorphous polymer, as it was explained above.

Structure

The melting temperature of the polymer is determined by the thickness of the lamellae (Ref. 19). At the equilibrium melting temperature crystals with infinite size should be obtained. The correlation of the melting temperature and lamella thickness can be expressed as (Ref. 20)

$$T_m = T_m^0\left(1 - \frac{2\,\sigma_e}{l\,\Delta H_f}\right) \tag{4}$$

where σ_e is the surface free energy of the lamella, ΔH_f is the heat of fusion per unit volume and *l* is the lamellar thickness. The equilibrium melting temperature of polyethylene was the subject of numerous studies, it was determined by various methods including extrapolation of the melting temperatures of n-paraffin homologs (Refs. 21,22) or the use of diluents (Ref. 23). Most of the values obtained can be found in the range of 413 - 418 K corresponding to 140 - 145 °C (Refs. 21-25).

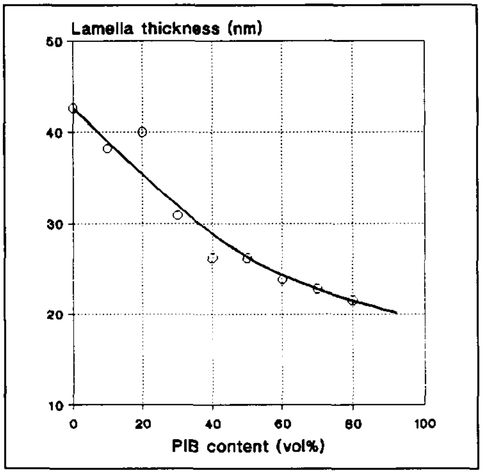

Fig. 10 *Changes in maximum lamella thickness of PE as a function of PIB content of the blend*

The equilibrium melting temperature determined for the polyethylene used in these experiments is 134.9 °C, much lower that the values reported in the literature. The discrepancy cannot be caused by erroneous measurement since the determination was repeated several times. Moreover, as it is indicated in Fig. 7 blending with PIB results in a further decrease of T_m^0. A similar phenomenon was observed by Nishi and Wang (Ref. 12) who compared this behavior to the polymer/diluent systems and explained it with the miscibility of the polymers.

Critical evaluation of all data available indicates that copolymerization of our PE polymer leads to an irregular chain structure which hinders the formation of perfect crystals. Thus the extrapolated equilibrium melting temperature seems to depend on the molecular structure of the polymer. Blending further decreases T_m^0. The miscibility of the components in the amorphous phase further hinders the formation of thick crystals, a continuous decrease of lamella thickness is observed at the equilibrium melting temperature. This is clearly supported by Fig. 10 presenting the change in lamellar thickness as a function of blend composition. Lamellar thicknesses were calculated by Eq. 4 using 414.2 K of the T_m^0 of linear PE, 4.11 kJ/mol for ΔH_f and 9.18 x 10^{-2} J/m^2 for σ_e (Ref. 20). The T_m^0 values determined for the virgin Stamylex 1016 LF PE and for the PE/PIB blends were introduced as T_m values to obtain *l* at different compositions. As a consequence, changing T_m^0 is a clear indication of the strong interaction or miscibility of the components.

CONCLUSIONS

A DSC study of isothermally and non-isothermally crystallized samples of PE/PIB blends of various compositions has shown that the two polymers strongly interact in the melt phase. The strength of the interaction is weaker than in the miscible PVF_2/PMMA blends shown by the different absolute value of the interaction parameters. A χ_{12} value of -0.30 was calculated in the PVF_2/PMMA blend, while an average value of -0.05 was obtained in the case of the polyolefin system. The difference is clearly related to the lack of specific interaction in the latter system. Nevertheless, the results clearly prove that even non-specific, dispersive forces can lead to the miscibility of polymers. Component interaction influences the melting and crystallization characteristics of the PE phase. Both the molecular structure of the crystalline polymer and interaction influence the size of the crystallites. The maximum lamellar thickness developing at the equilibrium melting temperature determined by the Hoffman-Weeks extrapolation technique was significantly lower for the LLDPE sample studied than for a linear PE and it further decreased on blending.

REFERENCES

(1) L.A. Utracki "*Polymer Blends and Alloys*", Hanser, Munich, 1990
(2) D.R. Norton, A. Keller, *J. Mater. Sci.* **19**, 447 (1984)
(3) S. Marinow, M. May, K. Hoffmann, *Plaste Kautsch.* **30**, 620 (1983)
(4) G. Meszlényi, A. Janek, G. Körtvélyessy, *Muanyag Gumi* **27**, 169 (1990)
(5) J.J. Gunderson, S.M. Chilcote, *Polym. Mater. Sci. Eng.* **64**, 393 (1991)
(6) N. Inaba, T. Yamada, S. Suzuki, T. Hashimoto, *Macromolecules* **21**, 407 (1988)
(7) J. Karger-Kocsis, A. Kalló, V.N. Kuleznev, *Polymer* **25**, 279 (1984)
(8) T.H. Lee, H. Marand, *Polym. Prepr.* **32**, 316 (1991)
(9) J. Varga, *Angew. Makromol. Chem.* **180**, 15 (1990)
(10) D.J. Lohse, *Polym. Eng. Sci.* **26**, 1500 (1986)
(11) P. Szabó, B. Pukánszky, *Miscibility of Crystalline and Amorphous Polymers: Polyethylene/Polyisobutylene Blends*, accepted in Macromol. Symp.
(12) T. Nishi, T.T. Wang, *Macromolecules* **8**, 909 (1975)
(13) B. Pukánszky, F. Tüdős, A. Kalló, G. Bodor, *Polymer* **30**, 1399 (1989)
(14) B. Pukánszky, F. Tüdős, A. Kalló, G. Bodor, *Polymer* **30**, 1407 (1989)

(15) A. Ghijsels, N. Groesbeek, C.W. Yip, *Polymer* **23**, 1913 (1982)

(16) J. Varga, Á. Solti, J. Menczel, *Period. Polytechn.* **23**, 261 (1978)

(17) J.D. Hoffman, J.J. Weeks, *J. Res. Natl. Bur. Stand.* **66A**, 13 (1962)

(18) P.J. Flory "*Principles of Polymer Chemistry*", Cornell University Press, Ithaca, 1953

(19) D.C. Bassett "*Principles of Polymer Morphology*", Cambridge University Press, Cambridge (1981)

(20) B. Wunderlich, G. Czornyj, *Macromolecules* **10**, 906 (1977)

(21) P.J. Flory, A. Vrij, *J. Am. Chem. Soc.* **85**, 3548 (1963)

(22) M.G. Broadhurst, *J. Res. Natl. Bur. Stand.* **66A**, 241 (1962)

(23) F.A. Quinn, L. Mandelkern, *J. Am. Chem. Soc.* **80**, 3178 (1958)

(24) J.D. Hoffman, *Polymer* **24**, 3 (1983)

(25) M.G. Broadhurst, *J. Res. Natl. Bur. Stand.* **70A**, 481 (1966)