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Analysis of Polyolefin Blends by CRYSTAF

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SUMMARY: Crystallization analysis fractionation (CRYSTAF) has been introduced for the analysis of the composition of polyolefin blends and the chemical composition distribution of polyolefins. Blends of syndiotactic and isotactic polypropylene (sPP and iPP) and of *s*PP/High density polyethylene (HDPE) have been fractionated by CRYSTAF and the results been compared to those from DSC. While the blends of sPP and HDPE cannot be separated by DSC a quantitative determination of both components is possible by CRYSTAF over the whole range with the detection limit being 1% on both ends. Furthermore it is demonstrated that the separation of ternary blends of sPP, iPP and HDPE is possible by CRYSTAF.

Introduction

The physical mixture of homo- and copolymers is a widespread method to combine the different properties of polymeric materials. This approach is in many cases easier than the development of new tailor-made polymers. An important advantage is that the costly development of new synthetic processes or the modification of existing ones can be avoided. Especially the combination of different polyolefins in one material is commonly used.

Since blends form an important portion of commercial polymeric materials, quality control and waste separation require fast and efficient routine methods for the identification and quantitative determination of individual components.

The analysis of blends often combines a separation step with a spectroscopic technique like FTIR or NMR. The extraction with suitable solvents or precipitation from solution are widely used [1-3]. Both methods are limited by the effects of molar mass and chemical composition. These can overlap and disturb a complete separation of the components. Size exclusion chromatography separates on the basis of the hydrodynamic volume. The method thus requires sufficiently different molar mass of the single components [4,5].

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Another approach is the analysis of the melting and crystallization behaviour. This can be done either by differential scanning calorimetry (DSC) or temperature rising elution fractionation (TREF). DSC is a powerful tool for blend analysis and has the advantage of widespread available instrumentation [6-8]. While its sensitivity is of advantage, the quantification of components is complicated by the thermal history and the fact that the crystallization depends on the molecular environment. Techniques like step crystallization or succesive self nucleation/annealing (SSA) have been developed to overcome these restrictions [9].

The problem of thermal history is completely eliminated by TREF. The method has been introduced into polymer analysis in the late 1970s and has been used for blend separation [10-16]. Blends of HDPE/LDPE and LLDPE/iPP can be separated into the individual components. This technique made it also possible to understand the effect of chemical heterogeneity, the so called short chain branching distribution (CCD) in LLDPE on the properties [17]. However the long analysis time (typically more than one day per sample) and the operational complexity prevented the widespread application of TREF as routine analytical method.

CRYSTAF has been introduced as a new technique for the analysis of semicrystalline materials recently and is, similar to TREF, based on the principle of crystallizability. Here the sample is fractionated by the slow cooling of a solution while the concentration of the material in the solution is monitored. An important advantage of this method is that compared to TREF only one full temperature cycle is necessary and five samples can be analyzed simultaneously in one run (typically 5 to 6h). This results in faster analysis time and reduced operator costs [18,19].

CRYSTAF has been used for blend separation and to determine the chemical composition distribution in various polyolefins like LLDPE, LDPE, PP and propylene copolymers [20-25]. In this paper we report the CRYSTAF analysis of binary blends of sPP/iPP and sPP/HDPE. The results from CRYSTAF will be compared to the separation by DSC and detection limits for each component be determined. Finally ternary blends of these components will be analyzed.

Experimental Part

sPP and iPP were synthesized using the catalysts *i*-Pr(Cp)(9-Flu)$ZrCl_2$ and *Bis*(2-MeBenz[e]-Ind)$_2ZrCl_2$ respectively, polyethylene (HDPE) was synthesized using the catalyst system Cp_2ZrCl_2/MAO. The detailed experimental procedures are published elsewhere [26].

The molar masses of the polymers were determined with a Waters 150C high temperature Gel

Permeation Chromatograph (GPC). The polymer (12mg) was analyzed in 1,2,4-trichlorobenzene at a flow rate of 1mL/min at 140°C with a column set of Waters HT 6+HT 5+HT 4+HT 3+HT 2. The software for data collection was from Polymer Standards Service (PSS, Mainz, Germany).

DSC measurements were conducted on a Pyris 1 from Perkin Elmer. Heating and cooling rates of 10°C/min were applied. Only the DSC cooling curves and the curves of the second heating cycle were used for analysis.

A CRYSTAF apparatus, model 200, from Polymer Char S.A. (Valencia, Spain) was used to perform the fractionation. About 20 mg of sample were dissolved in 30 ml of distilled 1,2,4-trichlorobenzene. The temperature was decreased at a rate of 0.1°C/min between 90°C and 30°C. Fractions were taken automatically and the polymer concentration in solution determined by an infrared detector using 3.5 μm as the measuring wavelength.

Analysis of Blends of sPP/iPP

Blends of iPP/sPP and sPP/HDPE are analyzed in this study. The weight average molar masses as determined by SEC are 68 000 g/mol (iPP), 93 000 g/mol (sPP) and 57 000 g/mol (HDPE). Thus a separation by SEC is not possible. The endothermic and exothermic DSC curves for the iPP/sPP blends are presented in Fig. 1.

Pure iPP shows a melting point at 149.1°C, while for sPP two melting points at 145.5 and 138.8°C respectively are observed. This double peak for syndiotactic polypropylene is well documented and can be attributed to a recrystallization process [27]. The peak melting temperatures of iPP and sPP are about 4°C apart resulting in a broad melting peak for a blend of the two polymers over almost the entire range of composition. Therefore the analysis of the DSC melting curves is not an useful method to obtain even qualitative information about the blend composition. However, in the cooling cycle the exothermic peaks for iPP and sPP are much better separated. The crystallization of iPP as it is recorded by DSC occurs at 112.4°C, whereas the crystallization of pure sPP occurs at 97.3°C. It is striking that the higher crystallization process occurs always at about 112°C, whereas the position of the peak maximum of the second crystallization process depends on the blend composition. The peak is shifted to lower temperatures with increasing contents of sPP. If 5% sPP are present in a sPP/iPP blend a crystallization peak was observed at 103.5°C, whereas the exothermic peak maximum was recorded at 96.3°C for a sPP/iPP blend containing 95% sPP. The detection limit of the respective blend components using the cooling cycle of the DSC is about 5%.

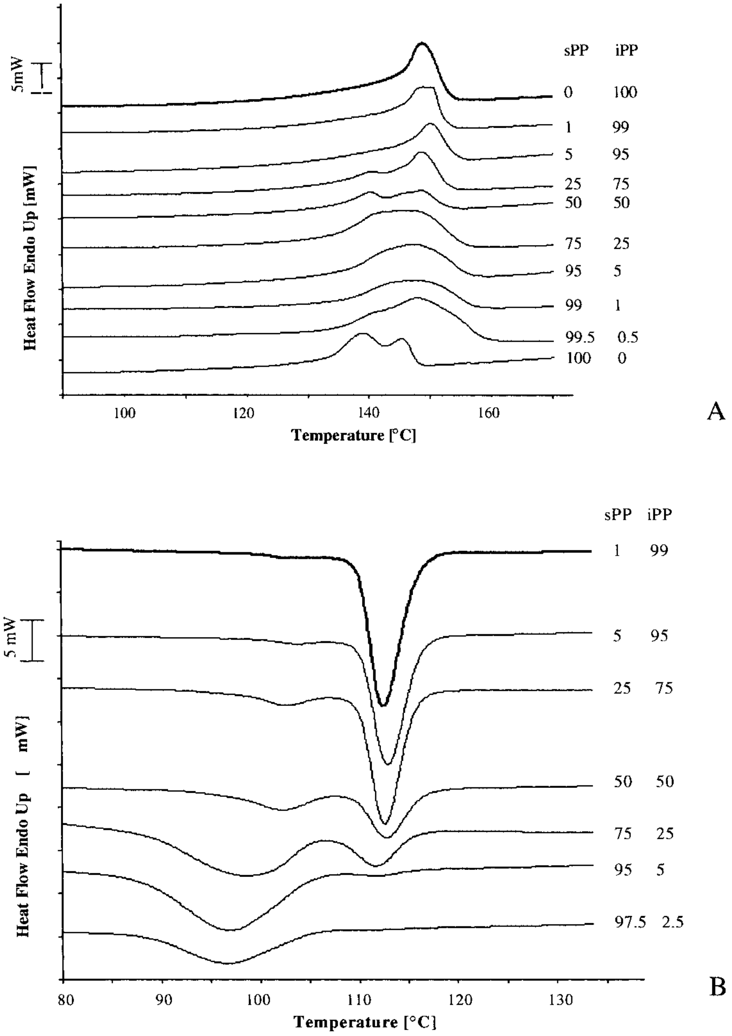

Fig. 1. DSC- melting (A) and crystallization (B) curves of blends of sPP and iPP.

The results of the CRYSTAF analysis for the sPP/iPP-blends are shown in Fig. 2 and as can be seen the individual components exhibit different crystallization temperatures.

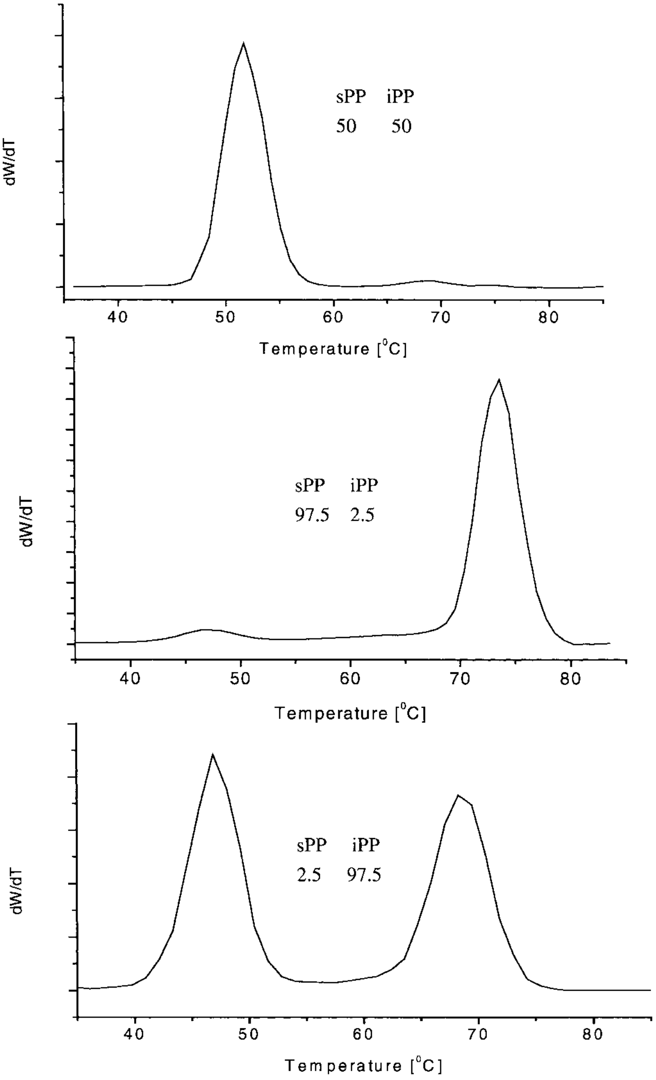

Fig. 2. CRYSTAF-curves of blends of sPP and iPP.

The isotactic polypropylene crystallizes at 72,5°C while the syndiotactic material crystallizes at 49,8°C. Both crystallization peaks are well refined and the areas do not overlap. A true concentration profile is obtained directly and from this the relative concentrations of the components can be calculated directly from the curve. As is indicated in Fig. 2 even low concentrations of each blend component can be detected. The detection limit for sPP is in the range of 1 - 2%, while iPP can be detected to a limit of 5%. Fig. 3 shows the comparison of the experimental blend composition as calculated from CRYSTAF and the nominal composition of the samples and as can be seen the correlation is good over the entire range of compositions.

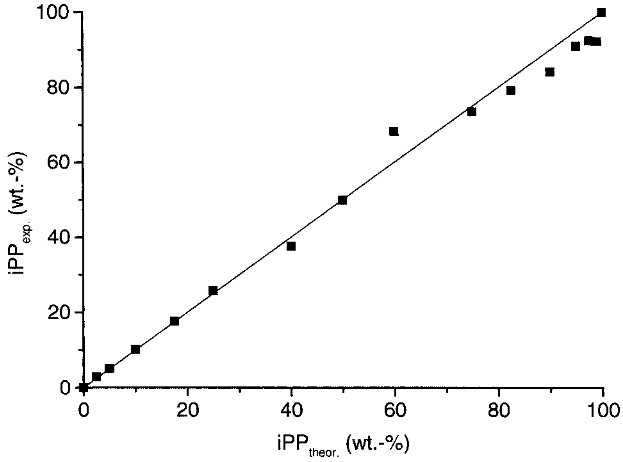

Fig. 3. Comparison of experimental vs. nominal content of sPP in sPP/iPP-blends.

Analysis of Blends of sPP and HDPE

The separation of sPP and metallocene catalyzed polyethylene by DSC is very difficult due to the fact that the melting peaks are not well refined and overlap in the heating and cooling cycle (Fig. 4). Analysis of the cooling cycle allows the identification of the polyethylene part over the entire range while the crystallization peak for sPP is not observable when the blend contains more than 60% polyethylene. Analysis of the blends by CRYSTAF (Fig. 5) shows that the crystallization peaks are well separated. The polyethylene part crystallizes at 85.5°C while the sPP fraction precipitates at 50.8°C. Even very low amounts can be detected and the limit is 1% for each of the components.

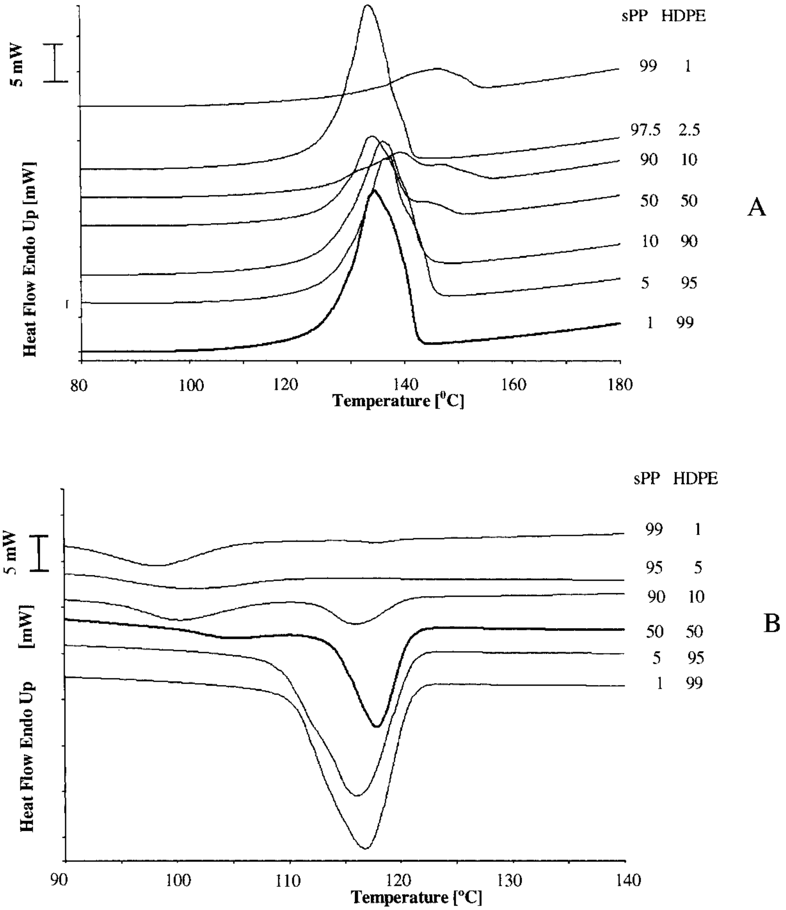

Fig. 4. DSC-melting (A) and crystallization (B) curves of sPP/HDPE-blends.

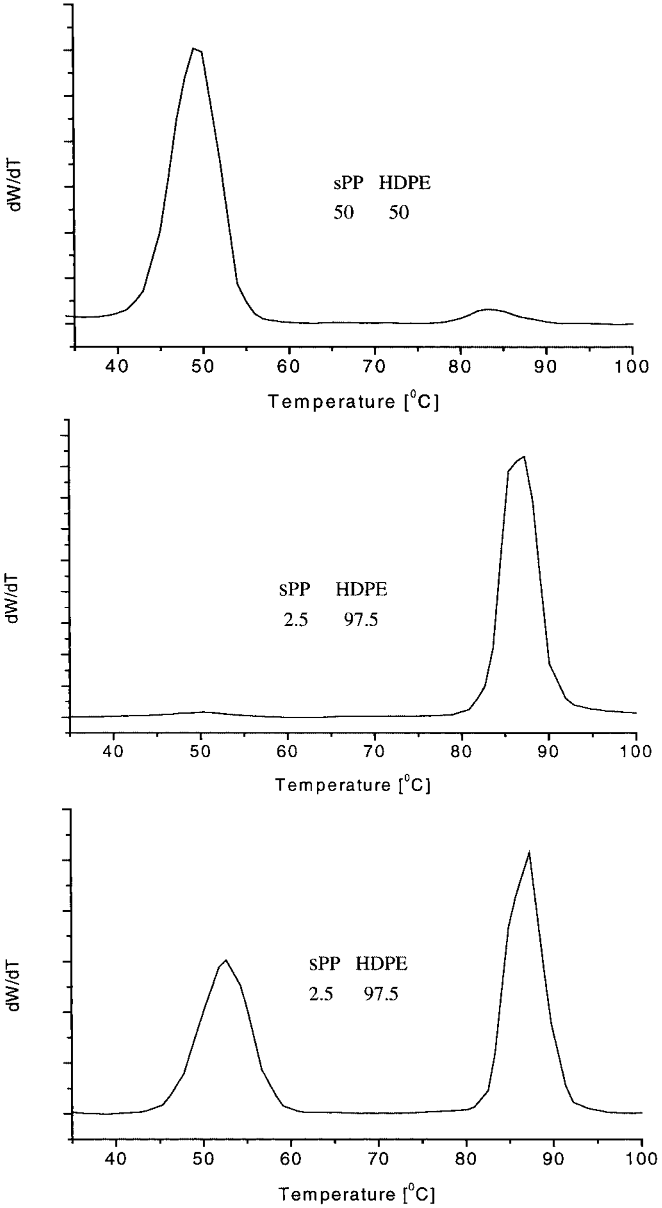

Fig. 5. CRYSTAF of sPP/HDPE-blends.

Fig. 6 shows the comparison of the experimental blend composition from CRYSTAF and the nominal blend composition. As can be seen the correlation is good over the entire range of composition.

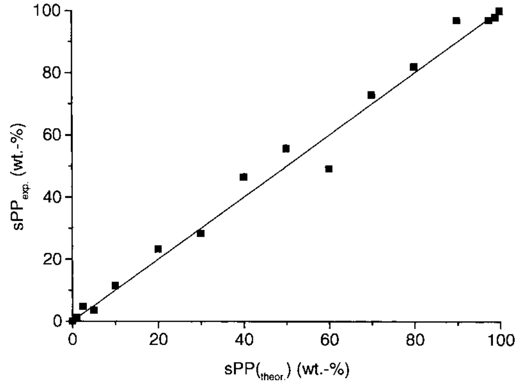

Fig. 6. Comparison of experimental vs. nominal content of sPP in sPP/HDPE-blends.

Analysis of Ternary Blends Consisting of iPP, sPP and HDPE

The difference between DSC and CRYSTAF is impressively demonstrated by the separation of ternary blends consisting of iPP, sPP and HDPE. The heating and cooling curves for the individual components and blends are shown in Fig. 7 and 8. Not even qualitative information can be obtained from the DSC.

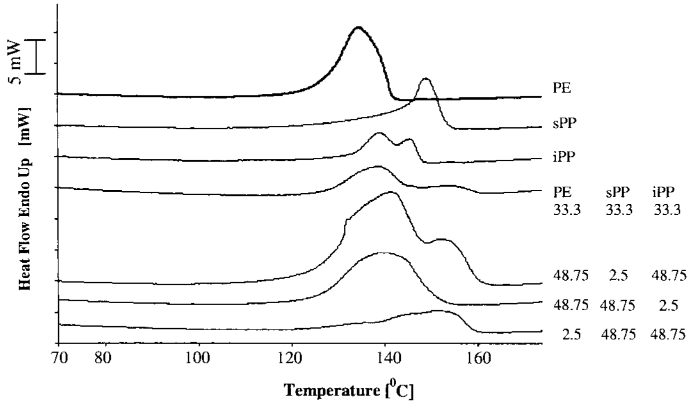

Fig. 7. DSC-melting curves for ternary blends of HDPE, sPP and iPP.

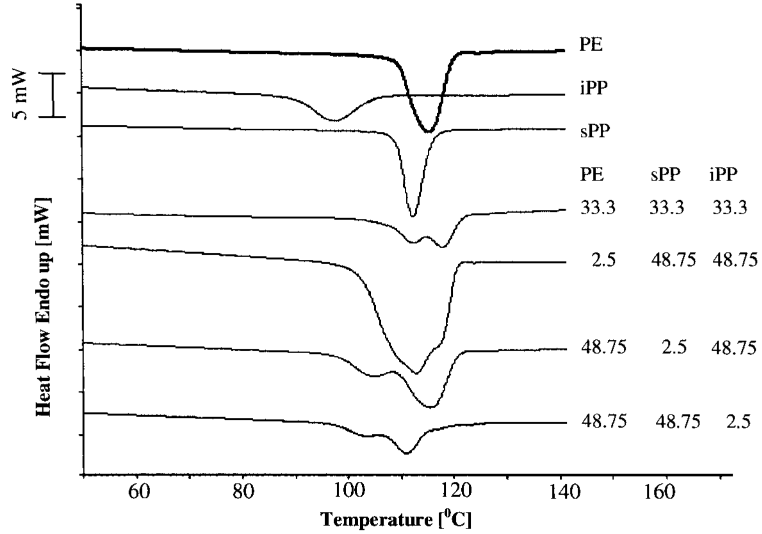

Fig. 8. Crystallization curves for ternary blends of HDPE, sPP and iPP.

CRYSTAF by contrast allows the identification as the individual crystallization peaks are well separated. The comparison of the experimental blend composition from CRYSTAF and the nominal composition is given in Tab. 1 and even amounts as low as 2.5% for one component can be quantified.

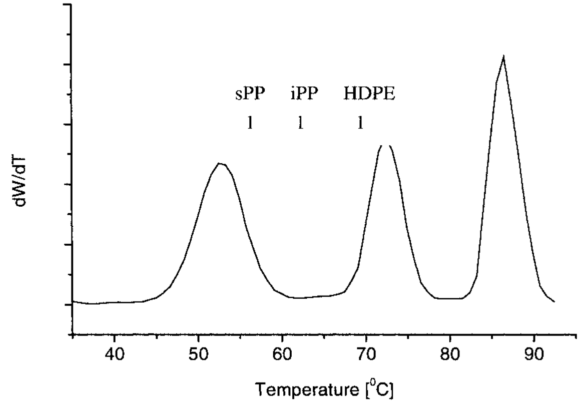

Fig. 9. CRYSTAF of a ternary blend of HDPE, iPP and sPP.

Table 1. Comparison of experimental and nominal contents of ternary blends of iPP, sPP and HDPE dertermined by CRYSTAF.

$iPP_{theor.}$	$iPP_{exp.}$	$sPP_{theor.}$	$sPP_{exp.}$	$HDPE_{theor.}$	$HDPE_{exp.}$
33.3	30	33.3	36	33	35
48.75	65	2.5	2	48.75	35
48.75	50	48.75	47	2.5	2
2.5	4	48.75	50	48.75	46

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