Investigation of polyethylene-wax blends by CRYSTAF and SEC-FTIR

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Summary

Oxidized wax blends with respectively HDPE, LDPE and LLDPE were investigated using CRYSTAF and SEC-FTIR in order to determine the possibility and extent of co-crystallization of the wax with each of these polyethylenes. CRYSTAF shows very little or no co-crystallization of wax with HDPE and LDPE, while there is a strong indication of co-crystallization in the case of LLDPE. SEC-FTIR analyses show co-elution of wax with LLDPE, indicating some chemical interaction between the oxidized wax and LLDPE.

Introduction

Over the last couple of years polyolefin-wax blends have been the subject of investigation by Luyt *et al.* [1-11]. In their studies they investigated the thermal and mechanical properties of such blends as function of wax content and extent of cross-linking. They found *inter alia* that wax probably grafts onto PE chains at higher peroxide and wax contents, that both wax content and cross-linking change the thermal and mechanical properties of PE, that the route of sample preparation has a marked influence on the thermal and mechanical properties of the blends, and that oxygen containing groups in oxidized wax do not cause wax to interact differently with LLDPE than un-oxidized wax. Most of their results also indicated miscibility between wax and LLDPE up to high wax contents, but phase separation between wax and LDPE at wax contents in excess of 10 wt. % wax. In an effort to obtain more concrete evidence of possible co-crystallization, crystallization analysis fractionation (CRYSTAF) and size exclusion chromatography coupled to FTIR (SEC-FTIR) were performed on a series of LLDPE-wax and LDPE-wax blends.

CRYSTAF, which is based on the principle of crystallizability, has been introduced into polymer fractionation in the 90s and separates polymers according to their composition [12-14]. Here the sample is fractionated by the slow cooling of a solution, while the concentration of the material in the solution is monitored. CRYSTAF has been used for blend separation, and to determine the chemical composition distribution in various polyolefins like LLDPE, LDPE, PP and propylene copolymers [15-20].

The coupling of SEC and FTIR is a powerful technique for profiling the chemical

composition along the molecular weight axis. It can be achieved by a flow cell or *via* the LC-transform interface. Despite the savings in both labour and time, compared to conventional methods, there are comparatively few applications of hyphenated SEC-FTIR to the analysis of polyolefins [21-25].

Experimental

Oxidized wax blends with respectively HDPE, LDPE and LLDPE were prepared through melt extrusion. The following materials were used: LDPE Bralen RA 2-19 (MFI = 1.7 g/10 min., density = 0.916 g.cm^{-3}, particle size < 50 μm) from Slovnaft, Slovak Republic, HDPE Stamylan HD 9089 V (MFI = 8 g/10 min., density = 0.963 g.cm^{-3}) (DSM, The Netherlands), hard, brittle, oxidized straight-hydrocarbon chain paraffin wax (average molar mass 785 g.mol^{-1}, density = 0.940 g cm^{-3}, C/O ratio 18.8/1) (Sasol Waxes, South Africa), LDPE (Sasol Polymers, M_w = 96 057 g·mol^{-1}, M_w/M_n = 8.7 and density ρ = 0.925 g·cm^{-3}), and LLDPE (Sasol Polymers, MFI 3.5 g/10min, M_w = 196000 g mol^{-1}, and a density ρ = 0.938 g cm^{-3}).

The molar masses of the polymers were determined using a PL 220 chromatograph (Polymer Laboratories) at 140 °C with Waters Styragel columns (HT 2 – 6). The solvent used was 1,2,4-trichlorobenzene at a flow rate of 1 ml/min.
A CRYSTAF model 200 from Polymer Char S.A. (Valencia, Spain) was used for fractionation. 20 mg of the sample was dissolved in 30 ml 1,2,4-trichlorobenzene. The polymer was dissolved at 160 °C for 3 hours, then stabilized at 100 °C for 60 minutes and subsequently slowly cooled to 29 °C. The temperature gradient was 0.1 °C.min^{-1}.
An LC-Transform Model 300 from LabConnections coupled to a Waters 150C chromatograph was used for the SEC-FTIR analyses. The stage temperature was 160 °C, the temperature of the nozzle was 125 °C and the transfer line 150 °C. The rotating speed of the germanium disc was 10 °/min.
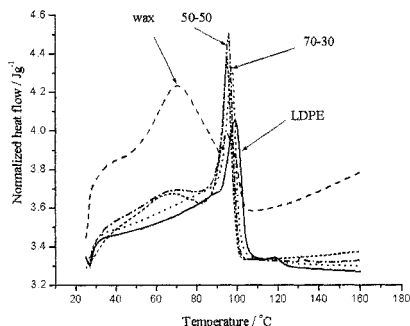
Results and discussion

Figure 1. DSC melting curves of LDPE, wax two LDPE/wax blends
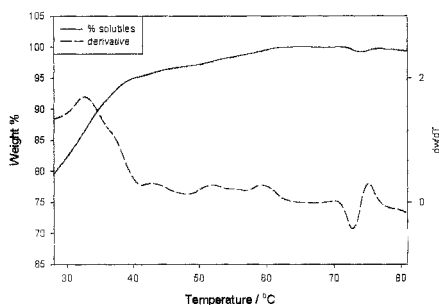
Figure 2. CRYSTAF cumulative and first-derivative curves of oxidized wax

The DSC curves as well as tensile results obtained by Luyt *et al.* [1-11] clearly indicated phase separation between LDPE and Fischer-Tropsch paraffin wax in blends containing more than 10 % wax (see Figure 1 where the DSC curves for 70/30 and 50/50 w/w LDPE/wax blends clearly show the development of a second melting peak in the wax melting temperature range). This was not observed in the case of LLDPE/wax blends. It was, however, not clear whether co-crystallization of wax with LLDPE caused this behaviour. Crystallization analysis fractionation (CRYSTAF) and SEC-FTIR were seen as a means of establishing whether there are any co-crystallization effects. Since wax also has hydrocarbon chains, SEC-FTIR will only be effective if a wax, which gave infrared absorption peaks different from those of polyethylene, could be used. In our case we used an oxidized hard paraffin wax, which interacted with polyethylene in exactly the same way than the un-oxidized wax [8], but contained carbonyl groups on the backbone chains.

Figure 2 shows the CRYSTAF curves of the oxidized wax. These curves show that the wax may have more than one different crystal fractions, and that at 29 °C, the lowest temperature of our CRYSTAF analyses, 80 % of the wax has not yet crystallized. It can therefore be expected that, if there is no co-crystallization of wax with polyethylene, at least 80 % of the wax component in the blend will still be in solution. The CRYSTAF cumulative and first-derivative curves of HDPE/wax blends, presented in Figures 3 and 4, clearly show an increasing soluble fraction with increasing amount of wax mixed into the HDPE. There is also a very good correlation between the amount of wax mixed into HDPE, and the percentage soluble fraction determined through CRYSTAF (see Table 1).
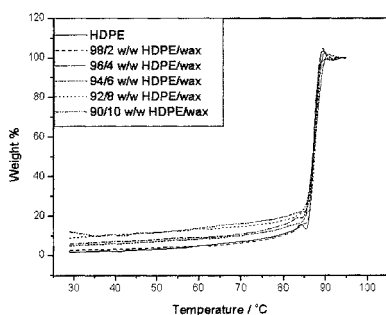

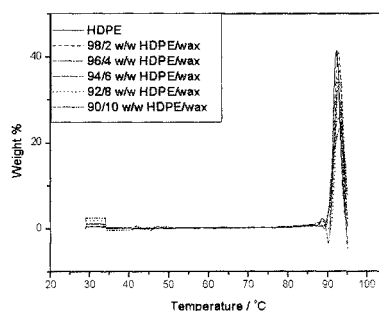**Figure 3.** CRYSTAF cumulative curves for HDPE/wax blends

Figure 4. CRYSTAF first-derivative curves for HDPE/wax blends

Figures 5 and 6 and Table 1 show similar results for LDPE/wax blends. The percentages soluble fractions are somewhat higher in this case, but it probably is the result of LDPE having a slightly higher soluble fraction at 29 °C than HDPE. This indicates a lack of co-crystallization between wax and LDPE, despite the fact that Luyt *et al.* [1-11] observed no phase separation between wax and LDPE, at wax percentages lower than 10 %, in their thermal analysis results. At wax contents higher than 10 % Luyt *et al.* observed phase separation in their DSC as well as tensile testing

results. This is confirmed by the CRYSTAF curves (Figures 7 and 8) where the percentages soluble fractions are in line (within experimental error) with the amounts of wax initially mixed into LDPE (Table 1).

Table 1. Crystallization temperatures and soluble fractions from CRYSTAF

| Sample	Crystallization temp. / °C	Soluble fraction at 29 °C / %
Wax	61 & 40	79.0
HDPE	87	1.5
98/2 w/w HDPE/wax	88	2.5
96/4 w/w HDPE/wax	88	5.7
94/6 w/w HDPE/wax	88	4.8
92/8 w/w HDPE/wax	88	8.9
90/10 w/w HDPE/wax	88	12.0
LDPE	60	3.8
98/2 w/w LDPE/wax	61	1.4
96/4 w/w LDPE/wax	61	6.6
94/6 w/w LDPE/wax	61	9.8
92/8 w/w LDPE/wax	62	10.5
90/10 w/w LDPE/wax	61	13.7
70/30 w/w LDPE/wax	57	30.1
60/40 w/w LDPE/wax	56	29.8
50/50 w/w LDPE/wax	56	45.9
LLDPE	85	3.9
90/10 w/w LLDPE/wax	83	17.0
70/30 w/w LLDPE/wax	85	16.9
60/40 w/w LLDPE/wax	85	22.6
50/50 w/w LLDPE/wax	83	21.0
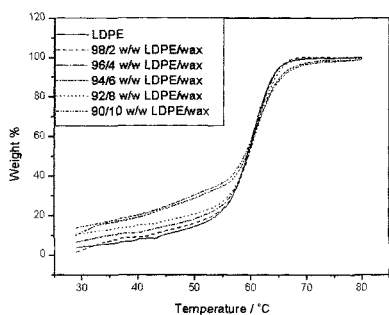
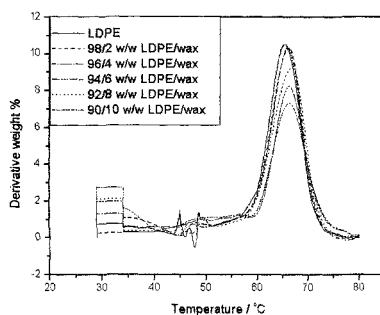**Figure 5.** CRYSTAF cumulative curves for LDPE/wax blends

Figure 6. CRYSTAF first-derivative curves for LDPE/wax blends
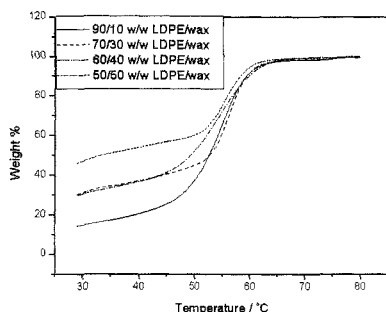
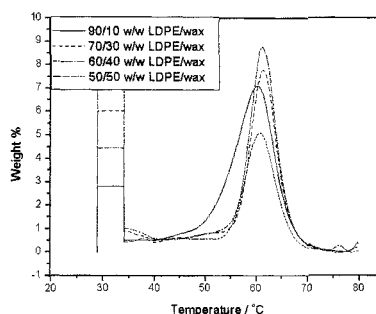**Figure 7.** CRYSTAF cumulative curves for LDPE/wax blends

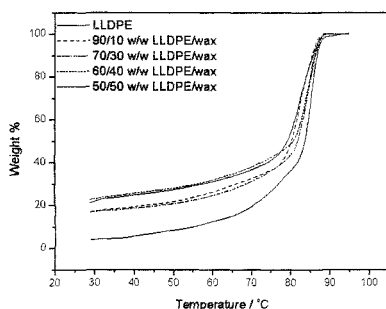**Figure 8.** CRYSTAF first-derivative curves for LDPE/wax blends

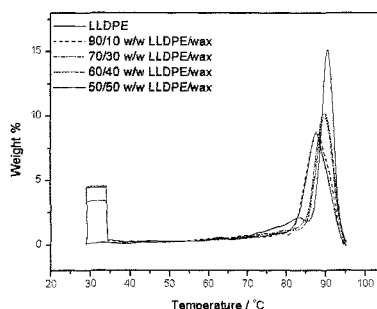**Figure 9.** CRYSTAF cumulative curves for LLDPE/wax blends

Figure 10. CRYSTAF first-derivative curves for LLDPE/wax blends

From previous work [1-11] it was clear that LLDPE interacted in a totally different way with the wax. DSC curves showed only one melting peak in the temperature range of LLDPE melting, even for blends containing up to 50 % wax. The tensile properties also showed no phase separation effects. CRYSTAF analysis explains this observation through co-crystallization at higher wax contents (Figures 9 and 10 and Table 1). With 10 % wax mixed into LLDPE, there is no indication of co-crystallization. The percentage soluble fraction is almost equal to the sum of the percentage LLDPE soluble at 29 °C and the amount of wax mixed into LLDPE. However, as the wax percentage increases, the difference between the percentage soluble fraction and the amount of wax mixed into LLDPE becomes bigger. The percentage soluble fraction in the case of 50/50 w/w LLDPE/wax is for example only 21 %, indicating a large extent of co-crystallization of wax with LLDPE. The reproducibility of the results was checked by doing five repeat analyses on the 60/40 w/w LLDPE/wax sample. These curves were almost identical, confirming co-

crystallization of wax with LLDPE for blends containing relative large amounts of wax.
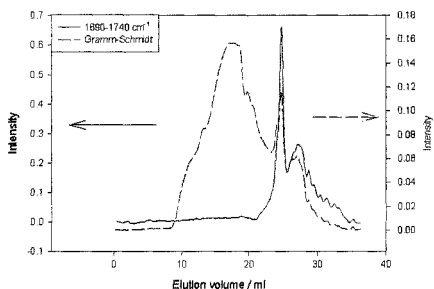

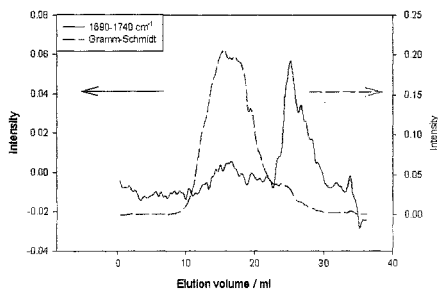**Figure 11.**SEC-FTIR plots for a 50/50 w/w LDPE/wax blends

Figure 12.SEC-FTIR plots for a 50/50 w/w LLDPE/wax blend

To investigate the possibility of chemical interaction between wax and LLDPE, which may contribute to the co-crystallization of wax with LLDPE, the samples were analysed with SEC-FTIR. Figures 11 and 12 are representative of the results obtained through these analyses. Because the wax was oxidized, it contained carbonyl groups that absorbed in the 1690-1740 cm^{-1} infrared region. It was therefore possible to see whether any wax was present in the higher molecular weight polyethylene fractions. Figure 11 shows the Gram-Schmidt plot and the 1690-1749 cm^{-1} chemigram for a 50/50 w/w LDPE/wax blend. It is clear that there are no carbonyl groups, and therefore no oxidized wax, present in the higher molecular weight fraction of the blend. On the other hand, as can be seen in Figure 12, the chemigram shows a clear presence of carbonyl groups, and therefore oxidized wax, in the higher molecular weight fraction of the blend. This is the result of wax co-eluting with LLDPE, which may be the result of wax chemically interacting with the polyethylene. This will explain why wax co-crystallizes with LLDPE, especially at high wax contents in the blend.

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