

**THERMAL FRACTIONATION AND PROPERTIES OF
DIFFERENT PE/WAX BLENDS**

by

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DECLARATION

I, the undersigned, hereby declare that the research in this thesis is my own original work, which has not partly, or fully, been submitted to any other University in order to obtain a degree.

A handwritten signature in dark ink, appearing to read 'M. Hato', written over a horizontal line.

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DEDICATIONS

I would like to dedicate this work to my daughter (Tankiso Gladys Hato) and to my late mother (Masinuku Maria Hato)

ABSTRACT

The influence of paraffin wax type and content on the properties of its blends with HDPE, LDPE and LLDPE was investigated. Differential scanning calorimetry, thermal fractionation and surface free energy results were used to clarify the morphology of the blends. Melt-mixing of HDPE with wax gave rise to completely miscible blends for both 10 and 20 % wax contents. This miscibility must be the result of co-crystallization of the wax with HDPE. This fraction, however, melts at increasingly lower temperatures with increasing amounts of wax in the blend. This is probably the result of the formation of thinner lamellae in the presence of the wax. A wax content of 30 % gave rise to a partially miscible blend. Complete miscibility was observed for all the LLDPE/Wax B blends. This indicates co-crystallization of Wax B with LLDPE, which was also evident from the thermal fractionation curves. LLDPE/Wax A blends were, however, partially miscible for all wax contents. Melt-mixing of LDPE with Wax A gave rise to a partially miscible blend for all wax contents investigated, while complete miscibility was observed for the 90/10 w/w LDPE/Wax B blend, but not for the blends containing higher Wax B contents. The main fraction of LLDPE, however, melted at increasingly lower temperatures with increasing amounts of wax in the blend. It is further clear from the thermal fractionation results that the presence of wax changed the crystallization behaviour of LDPE. All these observations were supported by the surface free energy results. Changes in the tensile properties are explained in terms of the miscibility and proposed morphologies of the different blends.

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CHAPTER 1

INTRODUCTION

1.1 Miscibility and compatibility

It has been recognized that the crystalline morphology of blends of linear and branched polyethylenes (PEs) depends on the following factors: cooling conditions, the crystallization properties of each component which are related to its molecular structure (molecular weight (MW) and branching), the composition of mixtures, and melt homogeneity. There existed an interest in establishing how these factors determine the occurrence of co-crystallization (miscibility in the solid phase, usually arising as a consequence of the quenching of a miscible melt) or molecular segregation of the components during cooling [1].

A variety of studies reported that upon evaluating blends of linear low-density polyethylene (LLDPE) and high-density polyethylene (HDPE) by differential scanning calorimetry (DSC), evidence of miscibility is when their DSC curves show single crystallization and melting peaks at temperatures between those of the pure components [2-7]. However, the dependence of the position of these peaks on composition was variable, and a trend that complied with a simple law of mixing was reported [3, 7]. There were, however, strong positive deviations from it for compositions of 70-80 % LLDPE [2, 4-7], or complex dependencies [6]. Datta and Birley [2] indicated that a single thermal transition could not, by itself, be considered as definitive evidence of co-crystallization, given that phenomena of coincidental crystallization or nucleating effects in the system may be present. Norton and Keller [8] and Barham *et al.* [9] reported partial miscibility in LLDPE or low-density polyethylene (LDPE) mixtures with HDPE. They established that the crystalline phases detected were only possible as a consequence of the existence of liquid-liquid phase separation in the melt. This had been confirmed upon analyzing the melting of PE mixtures by small angle neutron scattering (SANS).

Most pairs of polymers are thermodynamically immiscible. When a polymer blend is immiscible, it separates into two or more phases, and gives poor physical properties [10]. Partial miscibility, on the other hand, is observed when the system displays practical compatibility without any further treatment. It is probably because they form a third, mixed inter-phase, which modulates between the two separate phases [11]. For instance, the blends

of PE/modified polyamide [12] and that of poly(benzoylparaphenylene)/ polycarbonate were found to be immiscible [13]. Mechanically mixed LDPE/wax blends displayed mutual immiscibility at 20 % and more wax [35]. This behaviour was supported by the work done by Luyt and Brüll [17] when investigating the blends of oxidized wax with respectively HDPE, LDPE and LLDPE by using CRYSTAF and SEC-FTIR in order to determine the possibility and the extent of co-crystallization of the wax with each of these polyethylenes. The authors found very little or no co-crystallization of wax with HDPE and LDPE, while a strong indication of co-crystallization was observed between wax and LLDPE. SEC-FTIR showed co-elution of wax with LLDPE. This was found to indicate some chemical interaction between the oxidized wax and LLDPE. Li *et al.* [21] studied the blends of isotactic polypropylene with various types of polyethylene, LLDPE, very low-density polyethylene (VLDPE), HDPE, and LDPE with 20 % PP content in all the blends. It was concluded that PP is only miscible with LLDPE.

HDPE/LLDPE blends have limited miscibility [40]. The blends of three polyethylene (PE) samples (two HDPE grades and LLDPE) with semi-flexible crystalline polymers (LCPs) were also immiscible [36]. LLDPE/wax blends mixed in the molten state showed a lower degree of miscibility than those thoroughly mechanically mixed [14, 18].

The most important aspect of polymer blends, to be taken into consideration when selecting polymers for blending, is compatibility of the polymer components, and this depends on the materials' properties. Compatibility does not have a single definition, but rather varying definitions depending on what the user of the blend attempts to accomplish [19]. A compatible blend has recently been defined as a blend:

- with desirable physical properties upon blending [25];
- that does not exhibit large scale phase separation behaviour [25];
- that is thermodynamically miscible in the melt, but upon cooling each polymer separates and displays its own unique crystal structure [13].

Thermodynamically miscible polymers are homogeneous at the molecular level. The mixing process must produce a decrease in free energy (ΔG) [21],

$$\Delta G = \Delta H - T\Delta S \leq 0 \quad (1.1)$$

This results in a single-phase polymer blend, at a specified temperature, and therefore the majority of the properties of the blend will be an average of the properties of the individual

polymers. A vast majority of polymers form heterogeneous blends on mixing. Compatibility is used to describe polymers that are not thermodynamically miscible, but have similar structures resulting in useful properties in practice [25].

1.2 Polyolefin-polyolefin blends

It was generally accepted that it is not always necessary to synthesize new polymers to satisfy the need for new materials. Blending of existing commodity or engineering polymers is frequently more rapid and is regarded as an economic alternative to the development of new polymers [14]. Polymer blends, which are intimate mixtures of different commercially available polymers, have been extensively studied, as they proved to have broad practical significance globally. The reason is that the properties of the individual polymers can be improved by blending to meet the requirements of the customers. The main goal of blending is the modification of mechanical and thermal properties and the improvement of processability [24]. Materials with improved properties can be obtained by blending two or more polymeric materials with each other. The ultimate properties of the product generally depend on the physical and chemical properties and the morphology of the pure components, their portion in the blends and the processing routes [21-23].

Mantia *et al.* [36] investigated the blends of three PE samples (two HDPE grades and LLDPE) with experimental samples of semi-flexible liquid crystalline polymers (LCPs). The main benefits expected from the use of LCPs as blend components are a pronounced reduction in the melt viscosity, the consequent improvement of processability, and the reinforcing effect granted by the immiscible LCP particles, which can attain oriented fibrillar morphology when the blend is processed under elongational flow conditions. The thermal properties, as studied by differential scanning calorimetry (DSC), showed that the crystallization temperature (T_c) of LLDPE increased by approximately 10 °C upon addition of SBH (sebacic acid (S), 4,4'-dihydroxybiphenyl (B), and 4-hydroxybenzoic acid (H)). This behaviour indicated that the SBH acted as a nucleating agent for the crystallization of LLDPE. Since the LCP showed poor dispersion, an inadequate reinforcing effect was observed with all the HDPE samples.

Tensile properties of polymers and polymer blends are very important in many applications [20, 25, 26]. Okamoto *et al.* [26] investigated the binary blends of polypropylene (PP) with an ethylene- α -olefin copolymer using a rheo-optical technique, in which stress was measured at a constant rate of elongation. In their work, two kinds of binary blends were used

(i-PP with the 'ethylene rich' EBR and i-PP with the '1-butene rich' EBR). The former was an incompatible blend showing phase separation, and the latter was a compatible blend where the EBR chains were incorporated into the amorphous regions of i-PP. They found that the compatible blends showed deformed spherulites and plastic deformation occurred during elongation. In the case of the incompatible blends, brittle behaviour accompanied by segregation between i-PP and EBR was observed. For the i-PP homopolymer, microscopic disruption such as microvoids and crazes occurred in the initial strain region and the i-PP chains in the lamellae and crystallites were highly stressed.

In another study by Cho *et al.* [27], a PE/PP blend was studied using DSC, dynamic mechanical thermal analysis (DMTA) and scanning electron microscopy (SEM). The authors found that the melting and crystallization behaviour observed by DSC, and the α , β , and γ dynamic mechanical relaxations, indicated an immiscible blend in the amorphous and crystalline phases. They did, however, find an improvement in the physical and mechanical properties such as flexural modulus and yield strength with increasing ter-PP content.

Chen and his co-workers [28] investigated the melting behaviour of the pure copolymers and VLDPE1/LDPE1, VLDPE1/LDPE2, VLDPE1/VLDPE2 and VLDPE3/VLDPE2 blends using DSC. The components VLDPE1, VLDPE2, and VLDPE3 are LLDPEs with densities between 0.89 and 0.91 g cm⁻³, while LDPE1 and LDPE2 are LDPEs with MW equal to 474 000 and 89 000 g mol⁻¹ respectively. In the case of VLDPE1/LDPE1, they observed remarkable changes in the crystal population for the blends containing up to 30 % LDPE when comparing the calculated and experimental melting curves. An increase in peak area (crystal population) in the regions A-B [(A > 101 °C and B = (97-101 °C)] and a decrease in regions C-D [C = (62-97 °C) and D < 62 °C] were observed. These differences in peak area between the regions indicated a shift of the population to higher temperatures. These differences suggest that the two polymers had an effect on their respective crystallization in the blends. This indicated co-crystallization at all compositions, and miscibility or partial miscibility in the melt. A newly developed peak (T_{m1}) at about 101 °C was observed in the experimental curve. The appearance of this small peak suggested some molecular segments within the components. Similar melting trends were observed in the case of VLDPE1/LDPE2. In the case of VLDPE1/VLDPE2, a close agreement between the calculated and experimental curves was observed for the fractions melting below 97 °C, whereas the melting region above 97 °C, where only the VLDPE2 melted, displayed significant changes when the VLDPE2 content was below 50 %. These changes revealed that there was some co-crystallization and partial miscibility of these components. The co-

crystallization was found to decrease when the content of VLDPE2 was more than 50 %. This behaviour depended on the type of catalyst used during preparation of the pure materials and the branching content in each polymer matrix. VLDPE2 was found not to cause a significant change in the morphology of VLDPE1. This was found to be due to the relatively small number of long branches in VLDPE2 compared with the LDPEs. It was found that all the polymer blends that contained metallocene-catalysed VLDPE1 and LDPEs, showed greater co-crystallization, but the extent of co-crystallization decreased for the VLDPE1 blends containing long-chain branched VLDPE2. When using a Ziegler-Natta catalyst, it was found that the calculated and the experimental curves were similar in the blends containing 20 % VLDPE2 and below. This behaviour indicated that the two polymers could have crystallized independently. The most prominent difference was the better resolution of the 107 and 103 °C peaks in the experimental curves. The calculated and experimental curves became more similar as the VLDPE2 content was decreased. It was also found that the partial area ratios were approximately constant when the content of long-chain, branched octane VLDPE2 was reduced, indicating that co-crystallization decreased with decreasing VLDPE2. In these blends, where the branch content was dissimilar (2.4 versus 4.2 mol %), co-crystallization and/or separated crystallization was observed.

Abe and Yamaguchi [29] studied the binary blends of an LLDPE (ethylene-1-hexene copolymer) with a narrow short chain branching distribution, and an LDPE using DSC and a cone-plate rheometer. The DSC results showed only one melting peak for all the blends, independent of the blend composition. It was also noted that the melting peak temperature ($T_{p,m}$) of the LLDPE is lower than that of the LDPE. This is due to a large number of short chain branches in the LLDPE. It was also observed that the $T_{p,m}$ and the heat of fusion (ΔH_F) for the LLDPE-rich blends rapidly increased when increasing the LDPE content in the blend. This behaviour indicated that the LDPE enhanced the crystallization of the LLDPE from the molten state. The LDPE-rich crystals, which were formed before the crystallization of the bulk materials, apparently acted as nucleating agents for the crystallization of the rest of the polymers. This type of behaviour suggested that segregation of the components took place during the crystallization process.

Yu *et al.* [21] studied blends of polypropylene (PP) with various types of polyethylene, HDPE, LDPE, LLDPE, very low-density (VLDPE) and ultra low-density polyethylene (ULDPE) using DSC. All the blends contained 20 % by mass of PP. It was found that PP is only soluble in the LLDPEs. When PP crystallized from a homogeneous solution with LLDPE, broad diffuse spherulites were formed. In this case, PP was found to be the

continuous phase. Immiscibility was observed in the case of HDPE, LDPE and VLDPE. The morphology was different in each case and the rates of crystallization clearly showed whether a homogeneous or phase-separated blend was present. Crystallization of polypropylene in the phase-separated blend was found to be similar to the phase separation of bulk polypropylene.

1.3 Polyethylene-wax blends

In recent years, polyolefin-wax blends have been the subject of research by Luyt *et al.* [14, 15, 16, 17, 20, 22, 30-35, 37]. In their studies, they investigated the thermal and mechanical properties of such blends as a function of wax content and extent of crosslinking.

1.3.1 Gel content

Krupa and Luyt [14] and Mtshali *et al.* [35] investigated the effect of crosslinking of LDPE/wax and LLDPE/wax blends. It was observed that a DCP concentration of 0.5 % had a low crosslinking efficiency. By using 2 and 3 % DCP, high gel content values were obtained. The gel content relative to both LDPE and LLDPE phases gave values higher than 100 %. This behaviour indicated that the gel consisted of all the LDPE and LLDPE and some wax. They concluded that part of the wax was probably grafted onto the LDPE and LLDPE chains at higher wax concentrations.

1.3.2 Thermal properties

Krupa and Luyt [14] investigated LLDPE/wax blends prepared through mechanical mixing of powders using DSC. The authors found that the DSC curves of uncrosslinked LLDPE/wax blends showed that wax content has no influence on the melting points (T_m) and onset temperatures of melting ($T_{o,m}$) of LLDPE. Moreover, the curves of the blends showed only one endothermic peak, despite the fact that pure wax has 3 peaks (two of them significant). This may indicate miscibility in the crystalline phase, but it is not without doubt. Firstly, the main melting peak of the blends did not lie between those of LLDPE and wax as would be expected for miscible blends and, secondly, mechanical mixing followed by melt pressing may not ensure sufficient miscibility of the components. A decrease in $T_{o,m}$, T_m and enthalpy (ΔH_m) with an increase in DCP was observed. The ΔH_m values have strong

deviations from the additive rule, $\Delta H_m^{add} = \Delta H_{m,PE} W_{PE} + \Delta H_{m,w} W_w$. It is therefore clear that crosslinking reduced the polyethylene and wax crystallinity.

In another study, Krupa and Luyt [15] investigated LLDPE/ox-wax (ox-wax: oxidized paraffin wax) blends prepared through mechanical mixing of powders by using DSC. They found that the DSC analyses of LLDPE/ox-wax blends, containing up to 50 % of wax, showed only one endothermic peak, despite the fact that pure wax showed two significant peaks. This may be the result of the LLDPE and the wax being miscible in the crystalline phase, despite the method used in the preparation of the blends. An increase in wax content of the blends did not appreciably influence either the onset and peak temperatures of melting, or the specific enthalpies of melting of the blends. The same was true for the crystallization temperatures and specific enthalpies of crystallization. Only one exothermic peak was observed. This indicates that the components were miscible with each other at all LLDPE/ox-wax ratios investigated.

For LLDPE/wax blends prepared through extrusion [16], the DSC measurements indicated that the blends consisting of 10 and 20 % of wax might be miscible in the crystalline phase. Only one peak was observed in the DSC curve. For 30 % and more wax two other peaks were observed. This indicated phase separation of the components. $T_{o,m}$ and T_m decreased with an increase in wax content. For these blends it was observed that an increase in wax content slightly decreased the temperature of crystallization.

Hlangothi *et al.* [32] studied LLDPE/wax blends prepared through mechanical mixing of powders in the presence of dibenzoyl peroxide (DBP), containing up to 3 % DBP. The authors found that the melting behaviour of all the uncrosslinked blends was similar to that of pure LLDPE. This suggested possible co-crystallization of polyethylene and wax chains. A decrease in lamellar thickness with an increase in wax and DBP contents was observed.

In another study by Mtshali *et al.* [35], results showed that in the absence of dicumyl peroxide (DCP), the DSC melting curves for LDPE and its blend containing 10 % wax showed one endotherm, while the blends containing higher concentrations of wax gave rise to more than one endotherm. This indicates LDPE/wax miscibility only up to 10 % wax. The same observations were made for the crosslinked blends. Specific melting enthalpies, calculated from the DSC data, were in good agreement with the additive rule for uncrosslinked blends, but deviated strongly for crosslinked blends. This indicated the reduction of LDPE crystallinity by crosslinking.

Krupa and Luyt [22] investigated the thermal properties of polypropylene/wax blends prepared through extrusion. DSC results showed that only one endothermic peak is observed

for 5 % of wax, despite the fact that the DSC curve of pure wax showed three endothermic peaks. For 10 % and more wax, clear separation between wax and PP melting peaks was observed. A decrease in $T_{o,m}$ and T_m with an increase in wax content was observed. The specific melting enthalpy increased with an increase in wax content. This indicated an increase in crystallinity of PP/wax blends.

Linear behaviour of the flow properties of uncrosslinked LLDPE/wax blends was observed [14]. This behaviour indicated that LLDPE/wax blends are mutually miscible in the observed concentration region. Krupa and Luyt [15], when investigating the flow properties of LLDPE/oxidized wax blends, found that an increase in wax content caused an increase in flow rate of the blends. A straight line was observed when the flow rate data was tested against the log-additive rule.

The thermal stability of PE/wax blends was studied using TGA [14, 15, 22, 32, 35]. Krupa and Luyt [14] found that the thermal stability of blends in synthetic air atmosphere was much lower than in nitrogen atmosphere, and it decreased with an increase in wax content. This was a logical consequence of the lower thermal stability of the wax. In another study [15] the TGA analyses of the blends showed that the thermal stability of the blends decreased with an increase in wax content, since the thermal stability of the wax was much lower than the thermal stability of LLDPE. The blends were, however, appreciably more stable than pure wax, even at wax concentrations as high as 50 %.

In another study by Krupa and Luyt [22] investigating the thermal properties of PP/wax blends prepared through extrusion, TGA results showed that the thermal stability of blends decreased with an increase in wax content.

Hlangothi *et al.* [32] found that uncrosslinked LLDPE/wax blends studied by TGA showed an increase in thermal stability of blends with an increase in wax content. It was also observed that pure polyethylene crosslinked in the presence of 1 and 2 % DBP showed higher thermal stability than uncrosslinked polyethylene.

TGA analyses of LDPE/wax blends prepared through mechanical mixing of powders [35] indicated a decrease in thermal stability with an increase in wax content. Little influence of crosslinking on the thermal stability of LDPE or its blends was observed. There was also no correlation between the thermal stability and the crosslink density characterized in terms of the gel content.

1.3.3 Mechanical properties

Krupa and Luyt [15] investigated LLDPE/ox-wax blends prepared through mechanical mixing of powders. A small increase in Young's modulus with an increase in wax content was observed. The wax content was found to have no influence on the yield point (elongation at yield and yield stress) of the blends. An increase in wax content decreased both stress and elongation at break.

In another study by Krupa and Luyt [16] LLDPE/wax blends, prepared through extrusion, were investigated. An increase in Young's modulus with an increase in wax content was observed, indicating that the modulus of the wax is higher than the modulus of LLDPE. It is probably associated with its higher degree of crystallinity. An increase in wax content caused a decrease in elongation at yield. This was to be expected, since the wax is harder than the LLDPE. A small increase in yield stress was observed for blends consisting of 10 and 20 % of wax. For blends consisting of 30 % and more wax, no yield point, but brittle rupture, was observed. The influence of wax content on stress at break depended on its concentration. Since pure LLDPE underwent significant strain hardening, its value of stress at break was the highest – even higher than the yield stress. Samples containing 10 and 20 % wax underwent strain softening after their yield points. Stress at break was therefore much smaller than yield stress. Samples, which consisted of 30 % and more wax, did not have yield points, and exhibited brittle rupture giving rise to an increase in stress at break. An increase in wax content resulted in a decrease in elongation at break in the whole concentration region. This decrease was the sharpest for 30 % and more wax in the blends. In this case, the material lost its drawability and was very brittle.

Hlangothi *et al.* [32] investigated LLDPE/wax blends in the presence of up to 3 % dibenzoyl peroxide (DBP). Higher values of the elastic modulus of uncrosslinked blends were obtained when increasing the wax content. This is due to the higher crystallinity of the blends compared to pure PE. Lower values were observed for crosslinked blends, since crosslinking reduces crystallinity. Since crosslinking did not change the functional dependence of melting enthalpies on the amount of wax, the elastic modulus generally increased with the amount of wax for one specific DBP concentration. A decrease in strain at yield with an increase in wax content for uncrosslinked blends was observed. For crosslinked blends, a decrease in yield stress with an increase in DBP concentration was observed. This decrease was higher for blends with higher wax content. A decrease in both stress and strain at break with an increase in wax content was observed.

For LLDPE/wax blends, prepared in the presence of up to 3 % DCP [34], Young's modulus slowly increased with an increase in wax content. This increase was higher for crosslinked blends than for uncrosslinked blends. A small decrease in yield stress of crosslinked LLDPE was observed when the concentrations of DCP were 0.5 and 2 %. If 3 % DCP was used, the decrease in yield stress was bigger. Crosslinking caused an increase in elongation at yield at all concentrations. An increase in wax content caused a decrease in elongation at yield. There was only a small influence of crosslinking on stress at break, both for pure LLDPE and its blends, if the concentrations of DCP were 0.5 and 2 %. In the presence of 3 % DCP the stress at break increased more. Increasing wax content caused a decrease in stress at break at all DCP concentrations. An increase in wax content resulted in a decrease in elongation at break, both for uncrosslinked and crosslinked blends. This decrease was higher for crosslinked blends, especially for DCP concentrations of 2 and 3 %. Generally, a decrease in elongation at break with an increase in DCP concentration, for crosslinked LLDPE and its blends, was observed, since crosslinking reduces PE drawability.

1.4 Polymer blend fractionation

The characterization of the branching distribution in ethylene and α -olefin copolymers was done by temperature rising elution fractionation (TREF) [38, 39]. The authors found that LLDPE and LDPE are miscible in the blends. They suggested that fractions containing similar branches were more likely to be miscible than fractions with different branch contents. This behaviour indicated co-crystallization between the similar branch segments. Due to lengthy steps and high cost involved, TREF procedures were found not to be widely used in the compositional analysis of polymers. Usually, a process of step crystallization (SC) from the melt using DSC was applied to the sample [41, 42]. This process had been inspired by the cooling procedure that took place in the TREF, although no solvent was involved. The results, obtained in a shorter time, gave preliminary qualitative information on the distribution of the α -olefins in the LLDPE copolymer [43, 44].

Müller and co-workers [45] applied a successive self-nucleation and annealing (SSA) method to study the blends of LLDPE/HDPE1, LLDPE/HDPE2 and ULDPE/HDPE2. HDPE1 is a homopolymer with unimodal molecular weight distribution (MWD) while HDPE2 is an ethylene/1-butene copolymer with bimodal molecular weight distribution. The authors found that for the melt-mixed blends of LLDPE/HDPE1, only one endotherm was observed for most compositions. The unmixed blends exhibited two very clear melting

endotherms for most of the compositions. The newly developed peaks were more pronounced for 50 % and higher content of LLDPE. In the case of LLDPE/HDPE2 blends, general behaviour similar to that of the LLDPE/HDPE1 blends was observed. The unmixed ULDPE/HDPE2 showed segregation of the blends rich in HDPE2. For the 80/20 ULDPE/HDPE2 blend, a melting point depression for the fraction annealed at 124 °C was observed. This was an indication of a dilution effect caused by the rest of the molten material.

Shanks and Amarisinghe [42] reported the use of SC methods to study the crystallization of LLDPE with single-site-polymerized branched VLDPE. The authors found that all the pure polymers and their blends exhibited a series of melting peaks. This behaviour indicated that melting crystallites are formed during the stepwise cooling. VLDPE1 showed seven peaks in the temperature range 85-120 °C, with the highest melting peak at 111 °C, which indicated that there were no unbranched sequences capable of providing higher melting temperature crystals. It was also found that most of the crystals melted in this one peak. In the case of VLDPE2, nine peaks were observed with the lowest at 76 °C and the highest at 107 °C. The lowering of the melting range of VLDPE2 indicated that VLDPE2 contained more branching that lowered the peak melting temperatures compared with VLDPE1. The addition of VLDPE1 to LLDPE diluted the larger melting peak of LLDPE. The sizes of the lower series of melting peaks increased. Blending of 20 % of LLDPE into VLDPE1 was found to separate the main melting peak into two sharper peaks. This indicated co-crystallization between the two polymers. Their work was also supported by a study of Drummond *et al.* [46] and Olabisi *et al.* [47] who studied the miscibility of hexane-rich LLDPE/LDPE blends.

1.5. Surface free energy

One of the most important characteristics of a liquid penetrant material is its ability to freely wet the surface of the object being inspected. At the liquid-solid surface interface, if the molecules of the liquid have a stronger attraction to the molecules of the solid surface than to each other (the adhesive forces are stronger than the cohesive forces), then wetting of the surface occurs. Alternatively, if the liquid molecules are more strongly attracted to each other than to the molecules of the solid surface (the cohesive forces are stronger than the adhesive forces), then the liquid beads up and does not wet the solid surface [48].

One way to quantify a liquid's surface wetting characteristics is to measure the contact angle of a drop of liquid placed on the surface of a solid object. The contact angle is the angle

formed by the solid-liquid interface and the liquid-vapour interface measured from the side of the liquid. Liquids wet surfaces when the contact angle is less than 90 degrees, and the liquid tends to spread out over the surface. If the angle θ is greater than 90° , the liquid tends to form droplets on the surface. For a penetrant material to be effective, the angle θ should be as small as possible. In fact, the contact angle for most liquid penetrants is very close to zero degrees [48 - 50].

Contact angles on polymers are not only influenced by the interfacial tension according to Young's equation [49],

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta \quad (1.2)$$

where γ_{SV} is the surface free energy or surface energy, γ_{SL} is the interfacial free energy of a plane solid surface, and γ_{LV} is the surface tension of the deposited drop. Other phenomena, such as surface roughness, chemical heterogeneity, sorption layers, molecular orientation, swelling, and partial solution of the polymer or low-molecular constituents in the polymer material, also influence surface free energy. These effects have to be considered when contact angle measurements are used to calculate the solid surface tension of materials.

Very few papers were published on the surface free energy of polyethylene-wax blends [35, 37, 51]. Krupa and Luyt [35] studied the physical properties of blends of LLDPE and oxidized paraffin wax. The authors found that wax slightly improved the polarity of the blends. In another study [51] three types of polypropylene films were examined with a number of test liquids and evaluated according to the Wu-harmonic mean method. Three different films were prepared. One film was untreated, one film was submitted to corona treatment and one to flame treatment. It was found that there were drastic differences in the contact angles between the treated films and the untreated film, although the differences were small between the treated films. Surface treatment also leads to an increase in the surface free energy. It was found that the surface treatment almost exclusively influenced the polar parts of the surface free energy, which was to be expected as a result of the creation of polar functional groups.

Krump *et al.* [37] investigated the changes in surface free energy as an indicator of HDPE/wax blend miscibility. The authors found that addition of 20 % wax in the blend resulted in a miscible blend according to DSC analysis, where only one peak was observed. The surface free energy (SFE) results showed a decrease in total SFE and an increase in its

polar part. Poor miscibility was found in the case of 60/40 and 40/60 w/w HDPE/wax blends, which was accompanied by an increase in total SFE and a decrease in its polar part.

1.5 Aims and objectives of this study

The aim of this study was to prepare different polyethylene (HDPE, LDPE, and LLDPE)/wax blends. These blends were characterized through DSC, surface energy evaluation, melt flow index (MFI), and tensile testing. The influence of different types of wax and their amounts on the physical properties of the blends were investigated. The miscibility and crystallization of the samples were studied using a DSC thermal fractionation (TF) method.

CHAPTER 2

EXPERIMENTAL

2.1 Materials

2.1.1 Wax

Hard (Wax A) and oxidized (Wax B) Fischer-Tropsch paraffin waxes were used in this study. Wax A has an average molecular weight (MW) of 785 g mol^{-1} , a drop melting point of $112 \text{ }^\circ\text{C}$, a density of 0.94 g cm^{-3} at $25 \text{ }^\circ\text{C}$, and a solidification point of $98 \text{ }^\circ\text{C}$. It decomposes at $250 \text{ }^\circ\text{C}$ and is chemically inert.

Wax B is an oxidized straight-hydrocarbon chain paraffin wax, (average molar mass of 660 g mol^{-1} , density = 0.95 g cm^{-3} (solid) and 0.82 g cm^{-3} (liquid) at $25 \text{ }^\circ\text{C}$ and $110 \text{ }^\circ\text{C}$ respectively, melting point $96 \text{ }^\circ\text{C}$). It has a thermal decomposition temperature of about $250 \text{ }^\circ\text{C}$, C/O ratio 18.8/1, and a flash point of approximately $185 \text{ }^\circ\text{C}$. Both waxes were supplied by Sasol Wax.

2.1.2 High-density polyethylene (HDPE)

HDPE was supplied in pellet form by Sasol Polymers. It has an MFI of 8 g/10 min , a molecular weight of $168\,000 \text{ g mol}^{-1}$, a melting point of $130 \text{ }^\circ\text{C}$, and a density of 0.954 g cm^{-3} .

2.1.3 Low-density polyethylene (LDPE)

LDPE was supplied in pellet form by Sasol polymers. It has an MFI of 7.0 g/10 min , a melting point of $106 \text{ }^\circ\text{C}$, a MW of $96\,000 \text{ g mol}^{-1}$, and a density of 0.918 g cm^{-3} .

2.1.4 Linear low-density polyethylene (LLDPE)

LLDPE was supplied in pellet form by Sasol Polymers. It has an MFI of 1.0 g/min , a molecular weight of $191\,600 \text{ g mol}^{-1}$, a melting point of $124 \text{ }^\circ\text{C}$, and a density of 0.924 g cm^{-3} .

2.2 Methods

2.2.1 Preparation of blends

HDPE, LDPE and LLDPE were initially melt mixed with respectively Wax A and Wax B in a Brabender Plastograph (screw speed of 30 rpm for 15 min.). Temperatures of 140, 150 and 160 °C were respectively used for LDPE, LLDPE and HDPE (and their blends). The blends were prepared in PE/wax w/w ratios of 100/0, 90/0, 80/20, 70/30 and 0/100. The blending was followed by melt-pressing at the same temperatures for 5 minutes at 90 bar in a hot-melt press.

2.2.2 Differential scanning calorimetry (DSC)

DSC analyses were performed in a Perkin-Elmer DSC 7 under flowing nitrogen. The instrument was calibrated using the onset temperatures of melting of indium and zinc standards, as well as the melting enthalpy of indium. 5-10 mg samples were sealed in aluminium pans and heated from 25 to 160 °C at a heating rate of 10 °C min⁻¹, and cooled at the same rate to 25 °C. For the second scan, the samples were heated and cooled under the same conditions. Onset and peak temperatures of melting and crystallization, as well as melting and crystallization enthalpies were determined from the second scan.

2.2.3 Thermal fractionation (TF)

Polymer samples were thermally fractionated using a Perkin-Elmer DSC 7. The thermal history of the samples was removed by heating the polymer samples to 160 °C, and keeping them there for 5 min. The temperature was then decreased in 4 °C steps to 50 °C, leaving the sample isothermal for 50 minutes after each step. A step cooling rate of 100 °C min⁻¹ was used. The fractionated sample was then heated from 25 to 160 °C at a heating rate of 10 °C min⁻¹.

2.2.4 Tensile testing

A Hounsfield H5KS tensile tester was used for the tensile analysis of the samples. The samples were stretched at a speed of 50 mm min⁻¹. Samples of length 75 mm, thickness 1.0 ±

25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100

0.1 mm, and width 4.8 mm were cut from melt-pressed sheets by a dumbbell shaped punch. The final mechanical properties were evaluated from at least 7 different measurements.

2.2.5 Surface energy evaluation (SEES)

A surface energy evaluation system (SEES, Czech Republic), which enables the calculations of surface free energy from contact angle measurements, was used. Benzyl alcohol, aniline, formamid, ethylene glycol, and water were all used as tests liquids. The Owens-Wendt Regression method [37] was used for the surface free energy calculations. The ultimate surface free energy results were calculated from at least 15 drops for each test liquid.

2.2.6 Melt flow index (MFI)

Flow rates of PE/wax blends were determined using a Ceast Melt Flow Junior at 130, 140 and 150 °C for LDPE, LLDPE and HDPE (and their blends), respectively. All the samples were done under a 1 kg mass.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Properties of blends

3.1.1 Differential scanning calorimetry (DSC)

The DSC curves of pure polyethylenes (HDPE, LDPE and LLDPE) and waxes (Wax A and Wax B) are presented in Figure 3.1. The onset and peak temperatures, as well as enthalpy, values of the samples are summarized in Table 3.1.

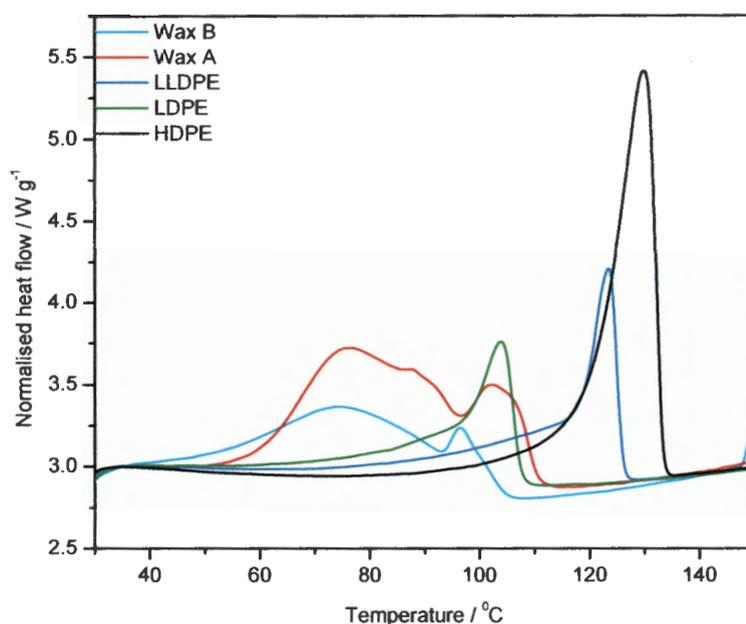


Figure 3.1 DSC heating curves of unblended materials

Figure 3.1 shows the DSC curves of all the pure polyethylenes, and they all show only one endothermic peak. The peak maxima for LDPE, LLDPE and HDPE are respectively at 104.2, 123.7 and 129.9 °C. Both Wax B, which contains carbonyl groups on the backbone chains and Wax A, which is a straight-chain hydrocarbon, melt over a broad temperature range. Wax A shows the first peak at 77 °C, the second as a shoulder at 91 °C and the third at 106 °C, while Wax B shows two melting peaks at 74 and 97 °C.

Table 3.1 DSC results of polyethylenes, waxes and their blends

Sample	$T_{o,m}$ /°C	$T_{p,m} = T_m$ /°C	ΔH_m /J g ⁻¹	$T_{o,c}$ /°C	$T_{p,c} = T_c$ /°C	ΔH_c /J g ⁻¹
Wax B	55.4	73.9	75.8	91.1	88.0	-58.9
	94.1	96.9		83.9	70.6	
Wax A	59.4	76.5	178.8	92.9	90.1	-154.6
	88.6	87.5		85.0	79.0	
	97.7	106.4		77.2	68.1	
HDPE	119.6	129.9	154.5	115.5	112.1	-127.9
LLDPE	118.0	123.7	79.7	110.8	108.1	-68.2
LDPE	95.6	104.2	62.7	91.7	88.5	-52.6
HDPE/Wax A (90/10 w/w)	118.9	131.4	150.6	117.0	113.5	-120.5
HDPE/Wax A (80/20 w/w)	119.2	129.5	166.7	114.8	112.3	-110.2
HDPE/Wax A (70/30 w/w)	119.5	128.7	170.5	115.2	112.6	-90.1
HDPE/Wax B (90/10 w/w)	121.5	131.2	119.1	115.8	112.1	-111.0
HDPE/Wax B (80/20 w/w)	120.3	129.9	119.8	115.1	112.5	-106.5
HDPE/Wax B (70/30 w/w)	120.6	129.0	122.8	111.3	108.5	-90.7
LLDPE/Wax A (90/10 w/w)	121.0	125.7	103.7	109.7	107.5	-54.4
LLDPE/Wax A (80/20 w/w)	118.1	124.5	95.3	108.5	106.3	-63.4
LLDPE/Wax A (70/30 w/w)	117.6	123.7	98.3	107.9	105.8	-45.2
LLDPE/Wax B (90/10 w/w)	119.1	123.9	71.4	107.5	109.5	-45.0
LLDPE/Wax B (80/20 w/w)	119.4	124.2	67.9	107.5	109.6	-41.1
LLDPE/Wax B (70/30 w/w)	118.9	124.2	54.8	111.8	109.3	-36.9
LDPE/Wax A (90/10 w/w)	95.4	104.0	72.1	92.1	88.1	-40.4
LDPE/Wax A (80/20 w/w)	95.8	103.7	76.9	93.1	90.1	-31.5
LDPE/Wax A (70/30 w/w)	88.8	103.4	98.1	95.6	92.1	-37.7
LDPE/Wax B (90/10 w/w)	97.5	104.7	72.5	90.4	87.0	-57.0
LDPE/Wax B (80/20 w/w)	94.0	102.0	63.5	90.1	86.8	-38.4
LDPE/Wax B (70/30 w/w)	94.4	101.0	58.6	89.6	86.6	-35.1

$T_{o,m}$, $T_{p,m}$, $T_{o,c}$, $T_{p,c}$, ΔH_m and ΔH_c are respectively the onset temperature of melting, peak temperature of melting, onset temperature of crystallization, peak temperature of crystallization, melting enthalpy and crystallization enthalpy

The DSC analysis of pure HDPE gave a relatively high crystallinity value (154.5 J.g⁻¹ or 53.7 % crystallinity), while LDPE and LLDPE respectively show values of 62.7 J.g⁻¹ or 21.8 % and 79.9 J.g⁻¹ or 27.7 %, if the enthalpy of 100 % crystalline polyethylene is taken as 288 J.g⁻¹ [52]. It is well known that HDPE has the highest crystallinity, followed by LLDPE and LDPE respectively. The values of the degree of crystallinity were calculated according to Equation 1.3.

$$X_c = \Delta H_m / \Delta H_m^+ \quad (1.3)$$

where X_c is the degree of crystallinity, ΔH_m is the specific enthalpy of melting of the sample, and ΔH_m^+ is the specific enthalpy of melting for 100 % crystalline polyethylene.

Figures 3.2 to 3.4 show the effect of wax content on the thermal properties of HDPE/wax, LDPE/wax and LLDPE/wax blends, respectively. It can be seen that most of the HDPE/wax blends show only one endothermic peak, with no indication of the wax melting peak, due to incorporation of wax into the crystal lamellae of the HDPE. This behaviour indicates that the HDPE is miscible with both waxes at almost all compositions, except for the 70/30 w/w blends that clearly show the development of a second melting peak in the wax melting temperature range. This appearance of a small, low-temperature peak in the case of higher wax contents shows phase separation of the two components. A slight decrease in melting temperatures from 131.4 to 128.4 °C for HDPE/Wax A blends and from 131.2 to 129.0 °C in the case of HDPE/Wax B blends with an increase in wax content is observed. This indicates that the presence of wax causes the HDPE to crystallize into thinner lamellae. In the case of HDPE/Wax A blends, the enthalpy increased from 150.6 to 170.5 J g⁻¹, indicating an increase in crystallinity to 57.9 % with an increase in Wax A content. Since Wax A has the same chemical structure as HDPE, one may assume that 100 % crystalline wax has the same enthalpy as 100 % crystalline polyethylene. In our case the pure Wax A has a melting enthalpy of 178.8 J.g⁻¹, which explains the increased enthalpy (crystallinity) of these blends. The melting enthalpies of the blends are lower than that of HDPE, but slightly increase from 119.1 to 122.8 J g⁻¹ with an increase in Wax B content. This is the result of the smaller enthalpy value (75.8 J g⁻¹) of Wax B when compared to that of pure HDPE (Table 3.1). The increased enthalpy (or crystallinity) with increasing wax content is probably the result of co-crystallization of the wax with HDPE. A Wax A content of 30 % gives rise to a partially miscible blend, which results in the development of a lower temperature melting

peak in the DSC curve shown in Figure 3.2, even though the peak is not very pronounced at this wax concentration. This suggests that at high wax content there is not enough space for the wax to co-crystallize with the HDPE, and therefore the wax crystallized separately. These results are in line with the work done by Krump *et al.* [37]. Wax B blended with HDPE shows the same behaviour as Wax A for both 10 and 20 % contents. This supports the conclusion drawn when Wax A was used, that the two components are miscible at lower concentrations. Addition of 30 % Wax B shows the same behaviour as the 70/30 w/w Wax A blend. It seems as if this peak corresponds to the endothermic melting peak of Wax B. This means that, if the concentration of Wax B is higher than 20 %, HDPE and the wax is only partially miscible. The explanation here is the same as for Wax A above.

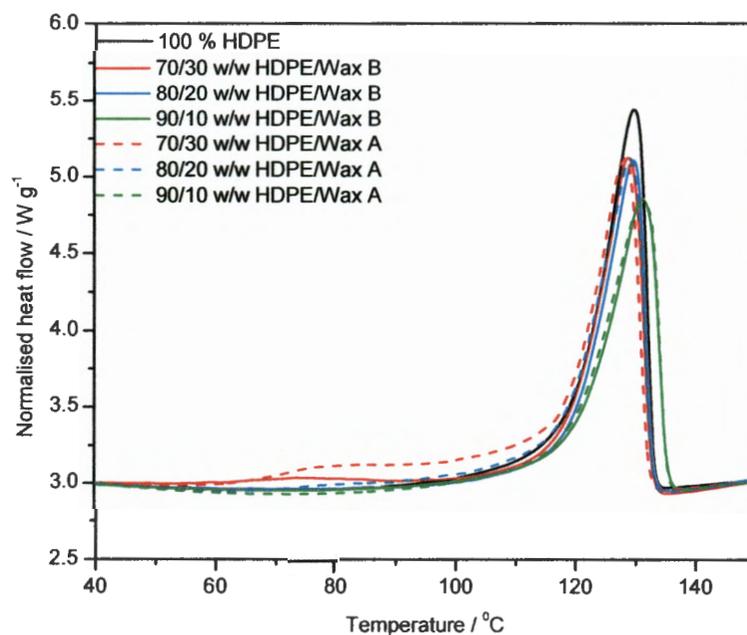


Figure 3.2 DSC heating curves of HDPE/wax blends

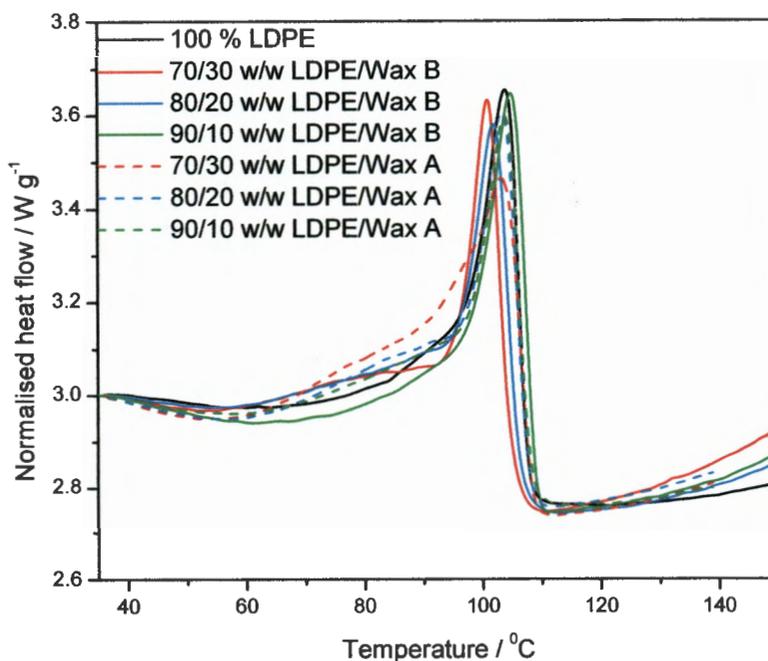


Figure 3.3 DSC heating curves of LDPE/wax blends

Figure 3.3 shows the DSC heating curves of the LDPE/wax blends. All the samples show the main endothermic peak between 100 and 104 °C, and only Wax B seems to influence its position. T_m decreased from 104.0 to 103.4 °C with an increase in the Wax A content, while a stronger decrease from 104.7 to 101.0 °C is observed with an increase in Wax B content (Table 3.1). It can be seen that Wax B has a stronger influence on LDPE crystallization than Wax A, and that Wax B causes LDPE to crystallize into thinner lamellae. For 10 % Wax B in the blends, only one endothermic peak is observed, despite the fact that pure wax shows more than two significant peaks (Figure 3.1). This shows that LDPE and Wax B are miscible in the crystalline phase in this concentration region. For 20 and 30 % of both waxes, another small broad endothermic peak is observed in the temperature range 70–85 °C, which corresponds to the main melting peak of pure wax. This probably is the melting peak of the fraction of the wax which is not miscible with LDPE. It is evident that LDPE is only partially miscible with both waxes at higher wax contents. An increase in enthalpy with increasing Wax A content is observed. Since Wax A has linear hydrocarbon chains of low molecular weight, these chains probably co-crystallize with some linear sequences of the

LDPE chains, which favours the crystallization process [33]. This can also be explained by Wax A having a melting enthalpy (178.8 J.g^{-1}) higher than that of pure LDPE (62.7 J.g^{-1}). If LDPE and Wax A co-crystallize, then the lamellar thickness may decrease when more of the shorter wax chains participate in the crystallization process, which can be seen in the slight decrease in melting temperature (Table 3.1). However, a decrease in enthalpy values is observed with increasing Wax B content. This may be the result of wax chains going into the amorphous part of the LDPE matrix, giving rise to lower crystallinity and thinner lamellae (decrease in melting temperature – Table 3.1).

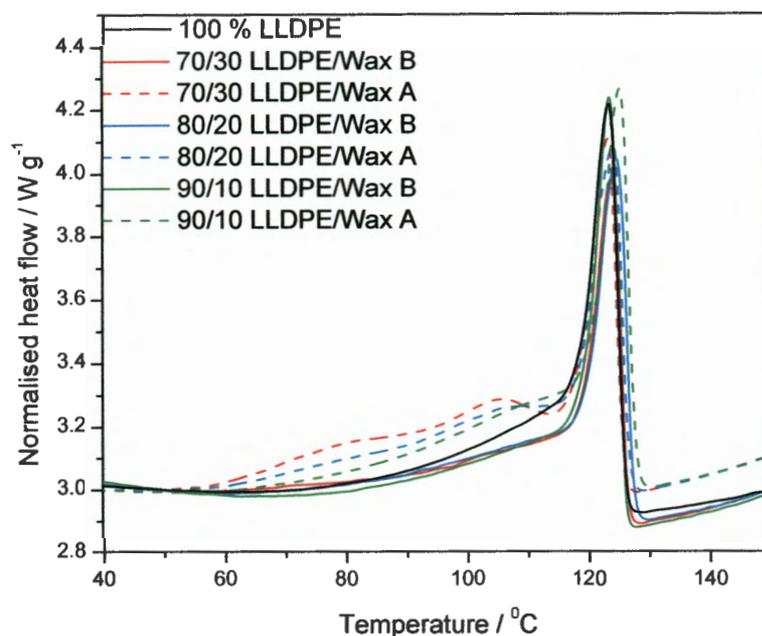


Figure 3.4 DSC heating curves of the LLDPE/wax blends

Figure 3.4 shows the DSC curves of the LLDPE/wax blends. It can be seen that LLDPE blended with Wax B shows only one endothermic peak, despite the fact that pure wax shows more than two significant peaks at lower temperatures (Figure 3.1). This behaviour indicates that LLDPE and Wax B are miscible in the crystalline phase at all compositions in the range of compositions investigated [16]. Different behaviour was observed when Wax A was used. For all wax concentrations, three peaks were observed. One of them corresponds to that of LLDPE and the other two (at about 80 and 105 °C) correspond to that of Wax A. The development of separate peaks in this concentration region indicates only partial miscibility of Wax A and LLDPE in the crystalline phase. In previous work by Krupa and Luyt [16] for

extruded mixed blends of LLDPE and Wax A, the DSC heating curves showed three significant peaks for 20 % and more Wax A at a temperature range between 80 and 109 °C. In this concentration region, LLDPE and Wax A were therefore not miscible with each other in the crystalline phase. It was also found that wax crystallization influenced the intensity of the peak observed at about 70 °C. In the case of the 90/10 w/w LLDPE/Wax A blend, only one endothermic peak was observed. In this concentration region, it was concluded that LLDPE and Wax A are miscible in the crystalline phase. For mechanically mixed blends [14, 15, 32], only one endothermic peak was observed for LLDPE/Wax A blends at all compositions investigated. This indicated that the mode of preparation influences the thermal properties of the samples. The specific melting enthalpies of LLDPE/Wax A blends are higher than that of pure LLDPE, and no trend was observed with an increase in wax content. Because Wax A clearly is only partially miscible with LLDPE (Figure 3.4), the enthalpy was calculated for the combined wax and LLDPE peaks. This explains the higher enthalpy (crystallinity), because the more crystalline wax probably crystallizes in the amorphous parts of LLDPE. These blends also show a slight decrease in melting peak temperatures (T_m) with an increase in Wax A content, which may indicate some reduction in the lamellar thickness of the crystallites. This is probably the result of the presence of wax in the amorphous parts of the polymer, which will influence the crystallization mechanism of the polymer. As a consequence the crystallinity will increase as the wax content in the blends increases, which can be seen in Table 3.1 as an increase in melting enthalpy. A decrease in enthalpy values with increasing wax content is observed when Wax B is blended with LLDPE. A probable explanation for this behaviour is the lower crystallinity of Wax B compared to pure LLDPE. In the case of Wax B blends, an increase in the wax content of the blends does not influence the melting temperatures. In previous work where Wax A was used [14], similar behaviour was observed.

Figure 3.5 shows the DSC cooling curves of the pure components, while the DSC cooling curves for the PE/wax blends are shown in Figures 3.6 to 3.8. The results are summarized in Table 3.1. It can be seen that the crystallization trends are the same than those observed for melting.

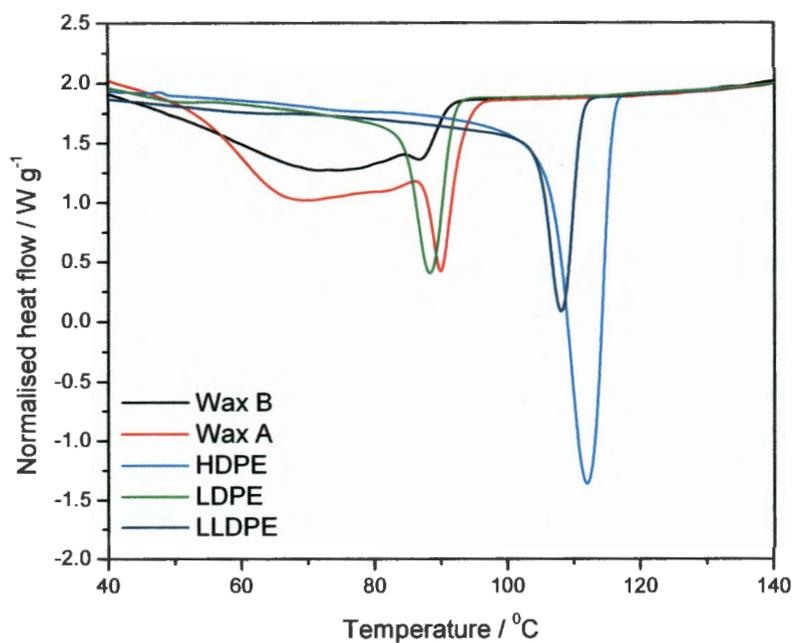


Figure 3.5 DSC cooling curves of pure polyethylenes and waxes

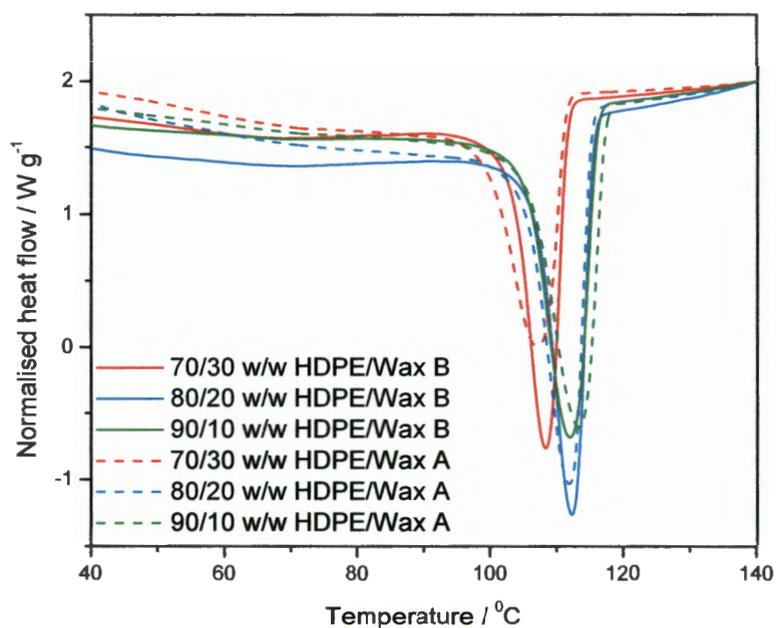


Figure 3.6 DSC cooling curves of the HDPE/wax blends

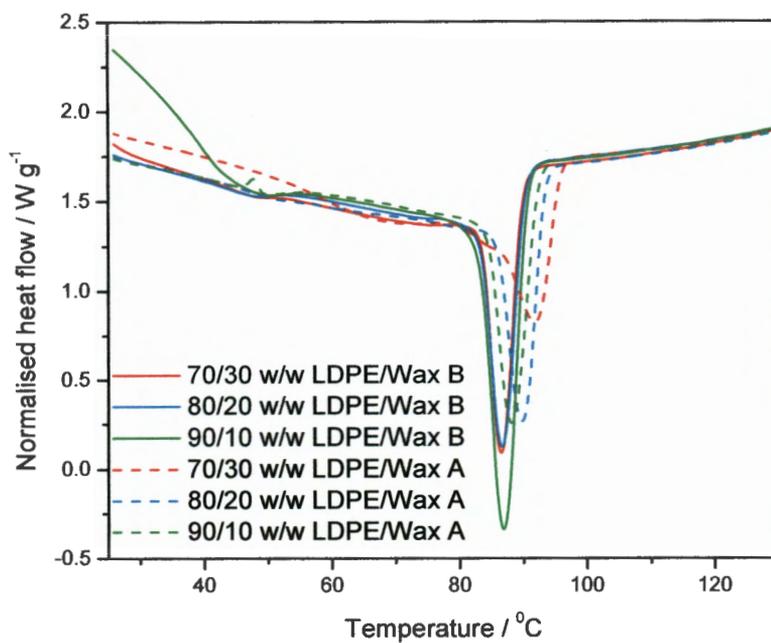


Figure 3.7 DSC cooling curves of the LDPE/wax blends

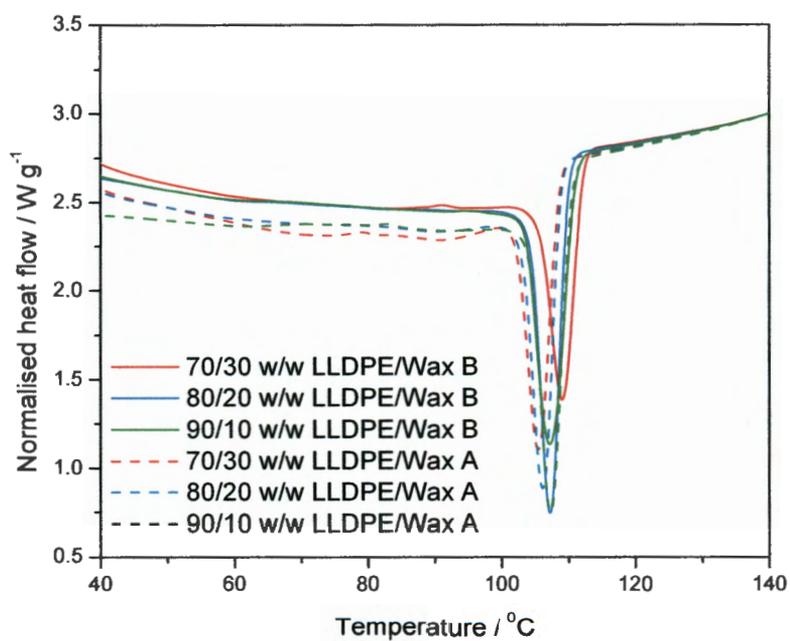


Figure 3.8 DSC cooling curves of the LLDPE/wax blends

3.1.2 Thermal fractionation (TF)

The melting curves for pure polyethylenes and waxes, obtained after thermal fractionation as described in section 2.2.3, are shown in Figure 3.9.

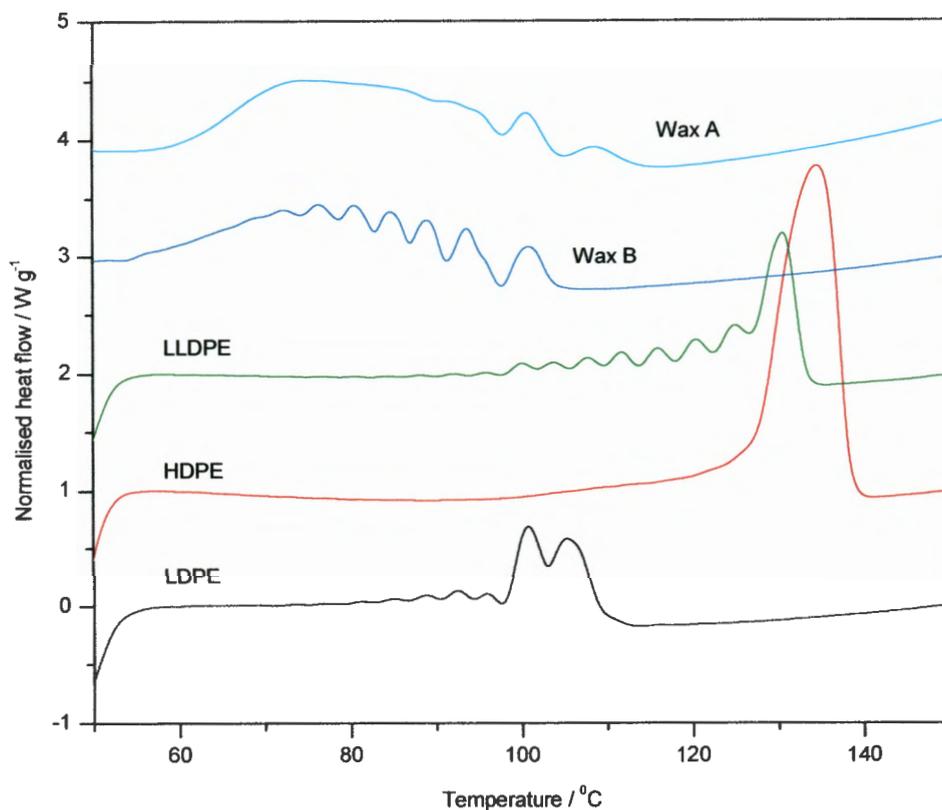


Figure 3.9 DSC heating curves of the fractionated pure polyethylenes and waxes

All the curves show a series of melting peaks that depict the melting of crystallites of specific branching density [28]. Shanks and Amarisinghe [42] reported the same behaviour of crystallization of LLDPE with single-site-polymerized branched VLDPE when using stepwise cooling (SC) methods. The authors indicated that melting crystallites are formed during the stepwise cooling. From Figure 3.9, it can be seen that HDPE shows a different behaviour in the sense that there is only one clearly defined peak. A probable explanation for this behaviour of HDPE is that all polymers with non-branched content, like polypropylene (PP) or HDPE, do not show any thermal fractionation effect [53]. It was also found that no thermal fractionation effect was observed for LLDPE prepared by metallocene catalysts (Me-LLDPE),

as these polymers are supposed to be highly homogeneous and therefore fractions with different density of branching might not be present [53]. However, Cser *et al.* [54] obtained multiple peaks after the thermal fractionation (TF) of Me-LLDPE samples by temperature modulated DSC (TMDSC). This result challenged the concept of TF or the concept of Me-LLDPE being highly homogeneous.

In this work, hexene LLDPE and LDPE behaved differently, since LLDPE and LDPE are prepared by Ziegler-Natta catalyst and free-radical polymerization, respectively. The same thermal behaviour for hexene LLDPE and LDPE, after thermal fractionation, was observed by Drummond *et al.* [46]. In our study, LDPE shows seven peaks in the temperature range 81 – 103 °C, while hexene LLDPE shows eleven peaks in the temperature range 80 – 132 °C. The highest melting peak temperatures of LDPE and LLDPE are 100.7 °C and 131.0 °C, respectively. This indicates that the specific heat curve of LDPE, after thermal fractionation, displays a narrower crystallization temperature range than that of LLDPE, suggesting a narrower size distribution of crystallites for LDPE. This is to be expected due to the narrower distribution of short and long-chain branches formed in the free-radical polymerization process of LDPE, compared to LLDPE, which is produced using a Ziegler-Natta catalyst. DSC results, obtained on thermally fractionated LLDPE, HDPE and very low density polyethylene (VLDPE), were presented in a paper by Cser *et al.* [54]. They found that branching is essential to obtain thermal fractionation of a material. Each of the peaks in these DSC curves is due to the crystallization of the molecules, or segments of molecules, of a particular length between the branches. The number of peaks in the melting curves corresponds to the number of crystallization steps used in the thermal fractionation program below the onset temperature of crystallization of the polymer [28]. In our work, the observed tailing to the peak indicates the presence of lamellae containing segments of varying branching density in both LDPE and LLDPE [46]. In the polymerization of LLDPE, the availability of multiple active sites on the Ziegler-Natta catalyst results in the heterogeneous distribution of the co-monomer, producing a broad range of crystallite sizes. LDPE is produced by a free-radical polymerization process, using a peroxide catalyst, under higher temperature and pressure. These conditions favour the formation of both long- and short-chain branching.

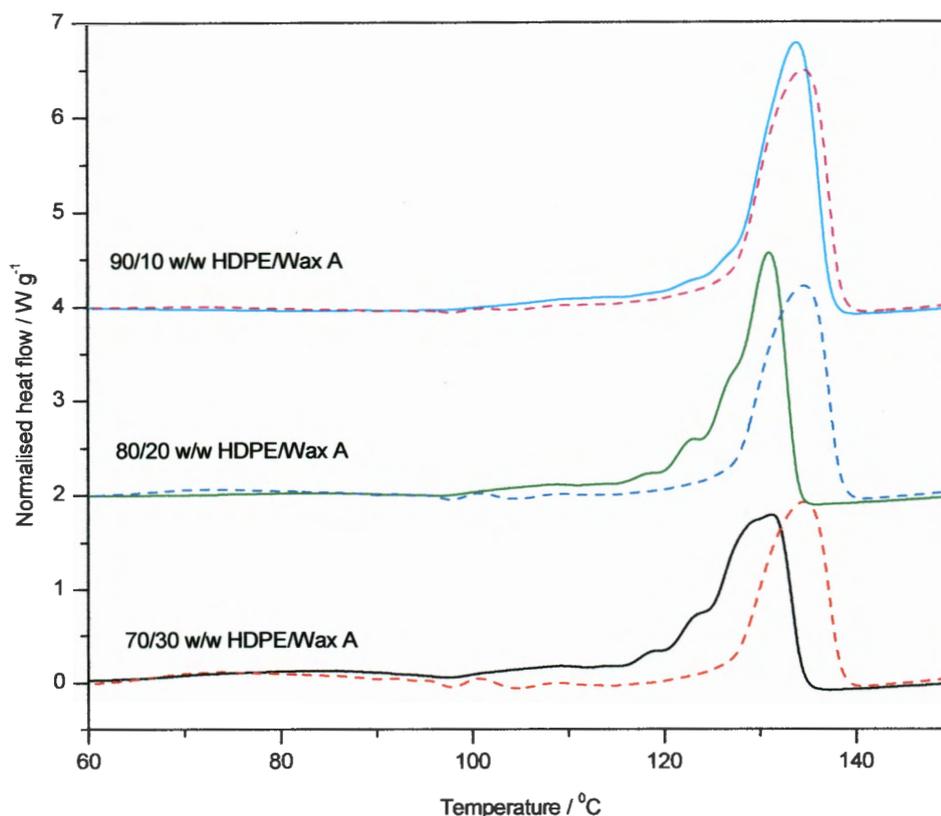


Figure 3.10 Comparison of the observed (—) and calculated (---) heat flow curves of the fractionated HDPE/Wax A blends

From Figure 3.9 it can be seen that pure Wax B shows more peaks than Wax A. A probable explanation of this behaviour is the oxygen-containing groups found on the backbone chain of Wax B, and which may influence the crystallization process in a similar way than the presence of branches would [42]. Chen *et al.* [28] reported that the extent of incorporation of branches within the crystals are mainly dependent on the crystallization conditions, and rapid or quenched crystallization allows certain branched types to be included in the crystals. Moreover, it has been shown that it is the branch content rather than branch type that is important in determining crystallization. In this study, the larger number of peaks obtained in the case of Wax B could possibly be the consequence of the oxygen-containing groups that act as branches during the fractional crystallization of Wax B. Since Wax A contains non-branched content, and Cser *et al.* [55] reported that all polymers with non-

branched content, like HDPE or PP, do not show any thermal fractionation effect, it explains the absence of fractional peaks in the case of Wax A.

The DSC curves of the HDPE/wax blends, after thermal fractionation, are shown in Figures 3.10 and 3.11. The influence of blending was examined by comparison of the observed curves (solid line) with the calculated curves (dashed line). The calculated curves were obtained by adding the DSC curves, obtained after fractionation, of the individual components in the same proportion in which they were present in the blend. For the 90/10 and 80/20 w/w HDPE/Wax A blends it can be seen that the experimental melting curves for the blends are different from those of the calculated curves in the temperature range 60 to 100 °C (Figure 3.10). The calculated curves show an indication of a peak in this region (not very clear), while this is absent in the experimental curve. This observation supports the conclusion drawn from the DSC results that wax co-crystallized with HDPE. However, for the 70/30 w/w HDPE/Wax A blend the calculated and experimental curves are almost identical in this region, indicating that (at least part of) the wax crystallized separately. Also, at high temperatures, small peaks developed on the lower temperature side of the main melting peak of the polymer. These peaks are more pronounced at high wax content. This also indicates that the HDPE and Wax A became partially miscible at high wax contents, which is in line with the normal DSC results (Figure 3.2). This may also mean that the presence of wax causes some of the HDPE to crystallize into thinner lamellae. The presence of wax also causes a shift in the melting temperature of the main fraction to lower temperatures, and this effect becomes more pronounced with increasing wax content. This indicates that the presence of Wax A causes the main HDPE fraction to crystallize into thinner lamellae. In the case of HDPE/Wax B blends (Figure 3.11), there are obvious differences between the experimental and calculated curves in the temperature region 80-130 °C. The experimental melting curves of all the compositions do not show any peaks related to wax melting when compared to the calculated curves. This behaviour indicates co-crystallization of Wax B and HDPE. Wax B does, however, have the same influence than Wax A on the crystallization of the main polymer fraction.

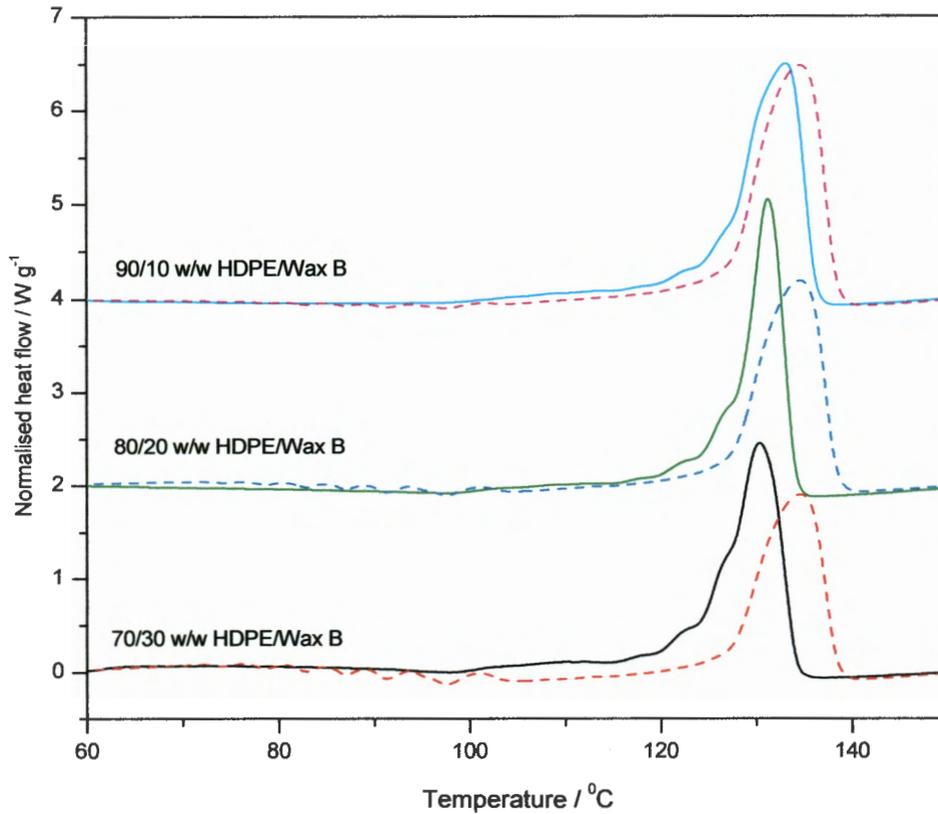


Figure 3.11 Comparison of the observed (—) and calculated (---) heat flow curves of the fractionated HDPE/Wax B blends

Figures 3.12 and 3.13 show the DSC melting curves, after thermal fractionation, of the LDPE/wax blends. All the curves show a series of melting peaks that depict the melting of crystallites of specific branching density. The number of peaks in the melting curves corresponds to the number of crystallization steps used in the thermal fractionation program below the onset temperature of crystallization of the polymer [28]. The peak temperatures of melting of all the compositions are almost the same, since they are determined by the stepwise isothermal temperatures used in the thermal fractionation. As we can see from Figure 3.12, mixing of 30 % Wax A into the LDPE matrix shows fewer crystalline fractions than both blends containing 10 and 20 % Wax A. This suggests that the addition of more short wax chains influences the crystallization behaviour of LDPE (compare Figure 3.9). These blends further show that the wax crystallizes separately at all concentrations investigated, which is in

line with the DSC observations. The reason for this is that Wax A probably crystallizes in the amorphous phase of LDPE. It is further obvious that the presence of Wax A influences the crystallization behaviour of LDPE. In the presence of 10 % wax the peak at 105 °C is much smaller than expected, while the peak at 100 °C is much larger than expected. With increasing wax content the peak at 105 °C increases in size, while the size of the peak at 100 °C remains fairly constant. It seems as if a relatively low wax content forces the polymer to crystallize into thinner lamellae, while in the presence of more wax the polymer reverts more to its normal crystallization behaviour. This is probably the result of partial co-crystallization of the wax with the polymer.

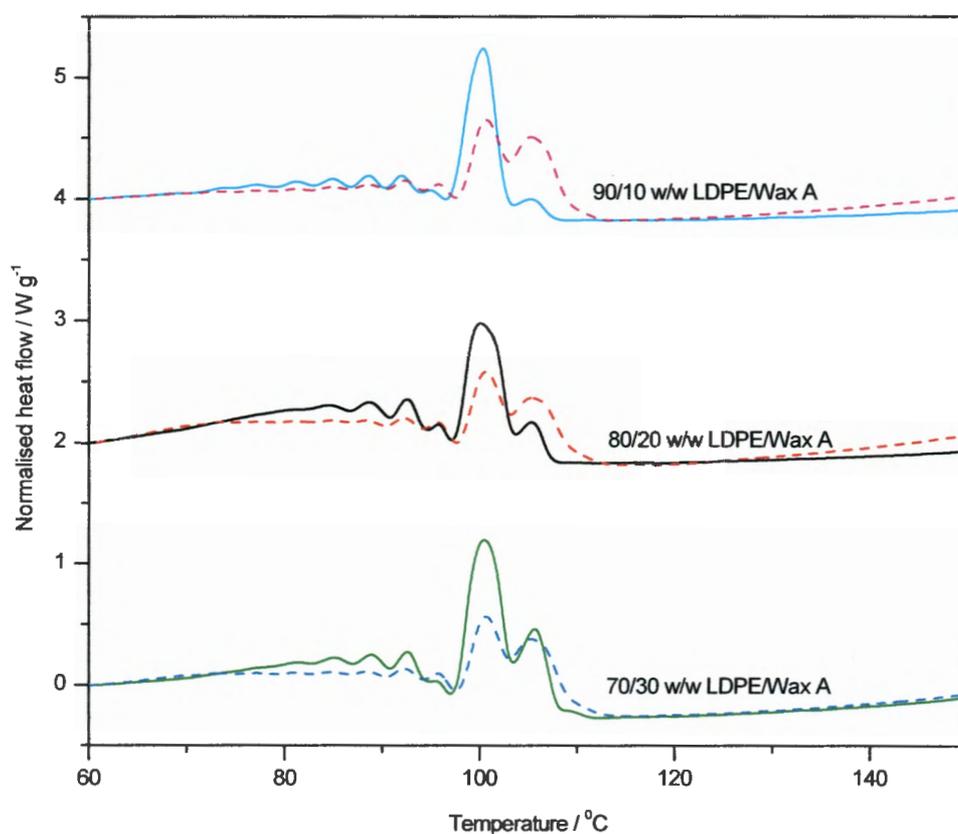


Figure 3.12 Comparison of the observed (—) and calculated (---) heat flow curves of the fractionated LDPE/Wax A blends

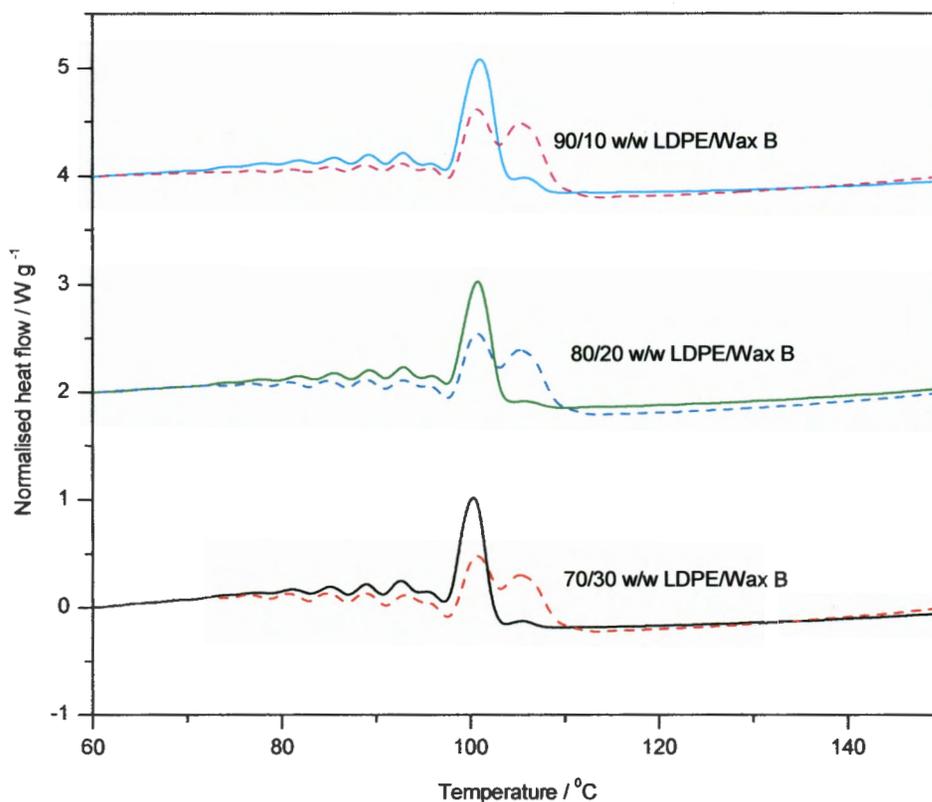


Figure 3.13 Comparison of the observed (—) and calculated (---) heat flow curves of the fractionated LDPE/Wax B blends

The behaviour is very similar for LDPE/Wax B blends (Figure 3.13), except that the peak at 105 °C remains small whatever the wax content. This is probably because of stronger interaction between the wax and LDPE which forces the LDPE to crystallize into thinner lamellae.

Figures 3.14 and 3.15 show the DSC melting curves, after thermal fractionation, of the LLDPE/wax blends. All the curves contain a well-resolved series of melting peaks between 95 and 132 °C, suggesting that independently melting crystallites are formed during stepwise cooling [42]. Addition of both Wax A and Wax B to LLDPE simply dilute the larger melting peak of the LLDPE (compare Figure 3.9), while increasing the sizes of the lower series of melting peaks with an increase in wax content. Contrary to the normal DSC results, it seems as if wax does not crystallize separately for 90/10 and 80/20 w/w LLDPE/Wax A, as well as

for all the LLDPE/Wax B blends, because the experimental curves do not show wax melting peaks when compared to the calculated curves. Wax A also seems to influence the crystallization behaviour of LLDPE (Figure 3.14), where there is a movement of the highest temperature fraction to lower temperatures.

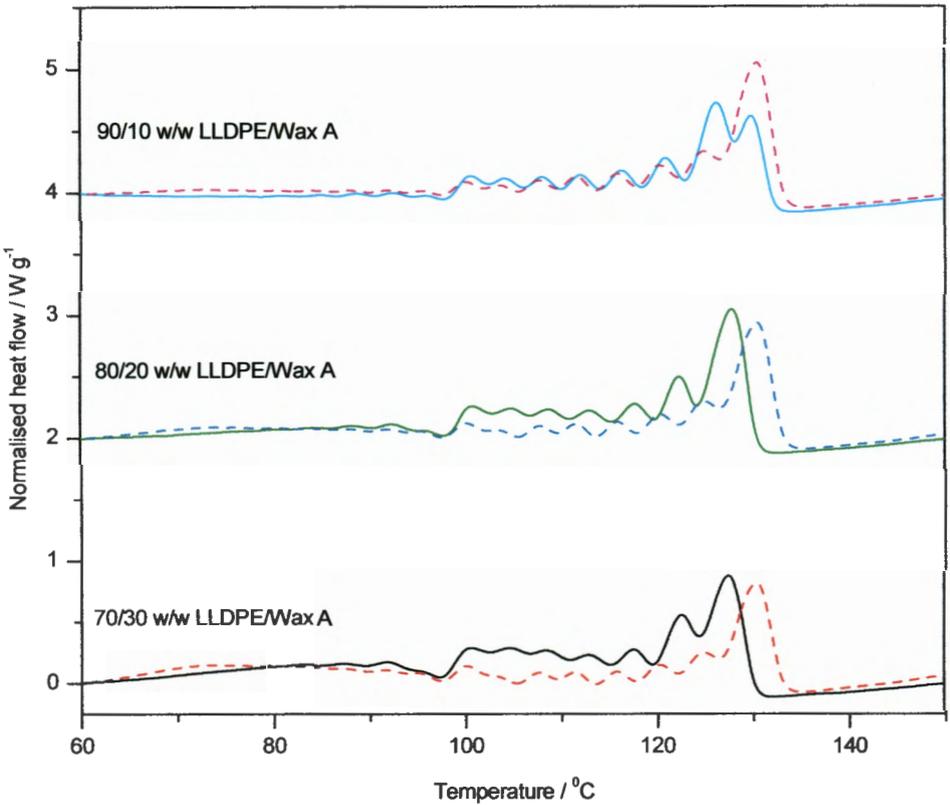


Figure 3.14 Comparison of the observed (—) and calculated (---) heat flow curves of the fractionated LLDPE/Wax A blends

From Figure 3.15 it can be seen that the LLDPE/Wax B blends show similar behaviour, except that LLDPE seems to be more miscible with Wax B at all compositions under investigation. Blending of Wax B into LLDPE decreases the peak intensity of the peak at 132 °C compared to the calculated curves, while there is an increase in the intensity of the peak at 127 °C. This becomes more pronounced with increasing wax content. This indicates that wax co-crystallization causes LLDPE to crystallize into thinner lamellae.

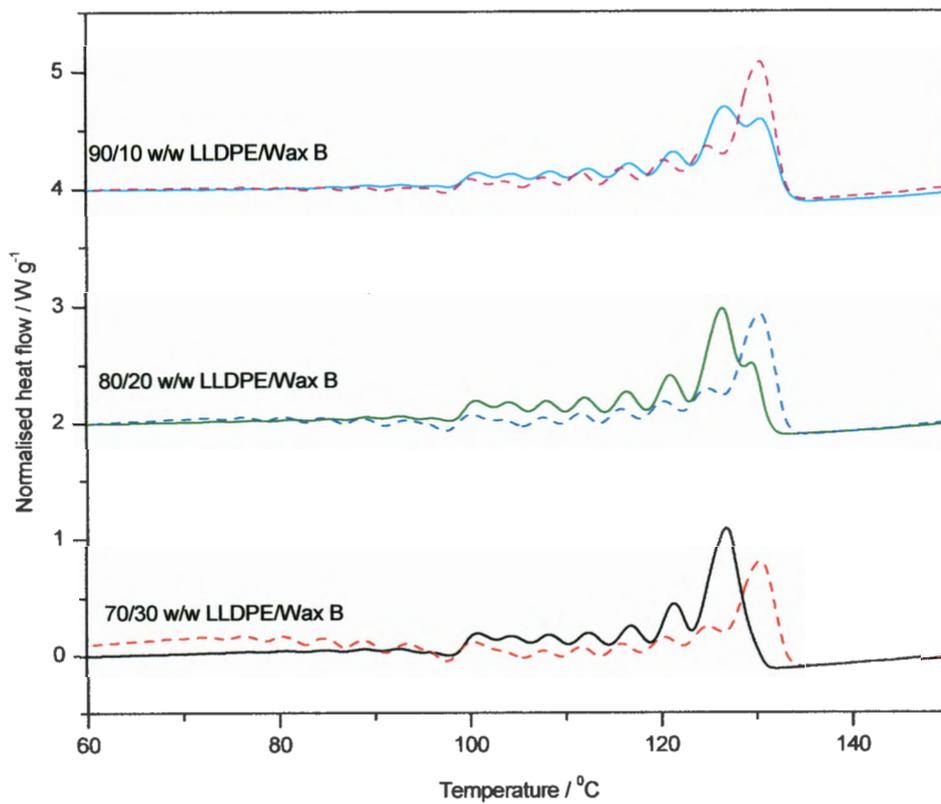


Figure 3.15 Comparison of the observed (—) and calculated (---) heat flow curves of the fractionated LLDPE/Wax B blends

3.1.3 Mechanical properties

The elongation at yield, yield stress, elongation at break, stress at break, and Young's modulus of all the samples are summarized in Table 3.2. The influence of wax content on Young's modulus of the blends is shown in Figure 3.16. For all the samples an increase in Young's modulus with an increase in wax content is observed. This is associated with the higher degree of crystallinity of the material when wax is present. There is an interaction between the crystalline and amorphous regions due to the elongation energy to be transmitted from the amorphous to the crystalline phase. The interaction between the wax and polyethylene chains may affect the transfer of energy to the crystalline phase, and may be responsible for the increase in stiffness of the polyethylene/wax blends. On the other hand, the change in material isotropy can explain the observed increase in Young's modulus with increasing wax content. Another reason for the increase in modulus may be the higher lamellar perfection obtained by melt mixing. Even before the macroscopic yield point, in the so-called linear domain, fracture of lamellae under tension takes place, usually at the crystal defect points. Incorporation of short, linear wax chains improves lamellar perfection, which will enhance their resistance to crack formation [32]. This may increase the stress necessary to stretch the material, i.e. the material's modulus. The Wax A blends generally show higher modulus values than the Wax B blends, indicating that the modulus of Wax A is higher than that of Wax B. This is probably associated with the higher degree of crystallinity of Wax A (62.1 %) compared to that of Wax B (26.3 %). When Wax B is blended with both LDPE and LLDPE, an increase in Young's modulus is observed, despite a decrease in crystallinity according to the DSC results (Table 3.1). The only explanation of this behaviour is the stronger interaction between LLDPE or LDPE and the oxygen-containing groups in the wax.

Yield stress of the different polyethylene/wax blends as a function of wax content is shown in Figure 3.17. A slight increase in yield stress for all the LDPE/wax and LLDPE/wax blends with increasing wax content is observed. An explanation for this behaviour is associated with an increase in the degree of crystallinity of these particular blends, since yield stress is a function of crystallinity. It can be seen that the increase is more pronounced in the case of Wax A. A slight decrease in yield stress in the case of HDPE/wax blends is observed. This is contrary to the increase in crystallinity observed in the DSC results, and cannot be explained at this point in time.

Table 3.2 The mechanical properties of polyethylenes, waxes and their blends

Sample PE/wax	$\epsilon_y \pm s\epsilon_y / \%$	$\sigma_y \pm s\sigma_y / \text{MPa}$	$\epsilon_b \pm s\epsilon_b / \%$	$\sigma_b \pm s\sigma_b / \text{MPa}$	$E \pm sE / \text{MPa}$
HDPE	17.5 ± 0.3	27.1 ± 0.4	886.0 ± 16.4	25.4 ± 2.6	332.7.0 ± 12.3
LDPE	49.7 ± 1.3	9.1 ± 0.1	539.5 ± 6.5	9.4 ± 0.4	94.8 ± 2.1
LLDPE	22.2 ± 0.9	12.3 ± 0.1	1216.0 ± 55.2	27.1 ± 0.7	111.8 ± 4.7
HDPE/Wax A (90/10 w/w)	17.3 ± 0.3	27.2 ± 0.5	712.0 ± 33.6	13.1 ± 1.4	334.1 ± 15.5
HDPE/Wax A (80/20 w/w)	17.5 ± 0.4	26.6 ± 0.4	158.2 ± 18.1	12.9 ± 2.3	340.1 ± 14.6
HDPE/Wax A (70/30 w/w)	20.4 ± 0.7	24.7 ± 0.3	28.9 ± 1.5	10.3 ± 1.4	354.0 ± 3.5
HDPE/Wax B (90/10 w/w)	19.3 ± 0.3	23.8 ± 0.7	566.7 ± 55.6	10.1 ± 1.7	354.0 ± 15.5
HDPE/Wax B (80/20 w/w)	17.7 ± 0.8	23.0 ± 0.5	29.8 ± 3.6	7.9 ± 1.2	334.1 ± 14.6
HDPE/Wax B (70/30 w/w)	19.1 ± 0.1	21.4 ± 0.3	7.4 ± 0.9	5.3 ± 1.1	340.4 ± 3.5
LDPE/Wax A (90/10 w/w)	25.0 ± 0.7	10.4 ± 0.2	81.2 ± 1.7	2.5 ± 0.2	134.2 ± 3.2
LDPE/Wax A (80/20 w/w)	21.3 ± 0.3	12.2 ± 0.5	54.2 ± 3.1	4.7 ± 0.8	141.7 ± 7.2
LDPE/Wax A (70/30 w/w)	18.6 ± 0.2	12.9 ± 0.2	31.7 ± 2.2	1.2 ± 0.3	154.3 ± 2.5
LDPE/Wax B (90/10 w/w)	28.7 ± 0.5	8.7 ± 0.1	88.9 ± 9.4	1.9 ± 0.6	100.2 ± 1.9
LDPE/Wax B (80/20 w/w)	25.6 ± 0.2	8.9 ± 0.1	72.9 ± 5.0	2.2 ± 0.6	107.8 ± 1.0
LDPE/Wax B (70/30 w/w)	22.8 ± 0.5	9.5 ± 0.1	43.8 ± 1.3	1.5 ± 0.6	129.2 ± 2.3
LLDPE/Wax A (90/10 w/w)	21.4 ± 0.9	14.8 ± 0.4	990.0 ± 11.9	22.2 ± 0.6	187.8 ± 5.4
LLDPE/Wax A (80/20 w/w)	20.7 ± 1.5	15.4 ± 0.3	999.2 ± 36.1	19.9 ± 2.0	192.4 ± 13.9
LLDPE/Wax A (70/30 w/w)	17.3 ± 0.4	16.1 ± 0.5	960.6 ± 49.0	17.3 ± 1.2	201.7 ± 15.3
LLDPE/Wax B (90/10 w/w)	21.9 ± 0.5	13.0 ± 0.1	1024.4 ± 40.7	22.5 ± 0.4	148.2 ± 8.7
LLDPE/Wax B (80/20 w/w)	21.8 ± 0.3	13.1 ± 0.1	1006.0 ± 21.4	20.8 ± 0.3	158.0 ± 10.3
LLDPE/Wax B (70/30 w/w)	19.9 ± 0.3	14.6 ± 0.1	1004.2 ± 13.9	18.5 ± 0.3	161.8 ± 10.7

ϵ_y , σ_y , ϵ_b , σ_b , E are elongation at yield, yield stress, elongation at break, stress at break, and Young's modulus of elasticity; $s\epsilon_y$, $s\sigma_y$, $s\epsilon_b$, $s\sigma_b$, sE are their standard deviations

Very little influence of wax type and content on the elongation at yield of HDPE and LLDPE is observed. There is, however, a pronounced influence in the case of LDPE, where the strain at yield decreases with increasing wax content (Figure 3.18). Since movement of chains mainly occurs in the amorphous part of the polymer, LDPE is expected to have a much higher elongation at yield than the other two polymers. Wax crystals in the amorphous phase will, however, restrict chain mobility. Both the DSC and thermal fractionation results strongly indicate wax crystallization in the amorphous phase of LDPE, which explains the pronounced decrease in elongation at yield with increasing wax content. The decrease is also more pronounced in the case of Wax A. The reason for this is not clear, because one would expect stronger interaction between the oxygen-containing groups in Wax B and the LDPE chains, which would further reduce the LDPE chain mobility. This observation can, however, be explained through the lower crystallinity of Wax B, giving rise to fewer wax crystals in the LDPE amorphous phase.

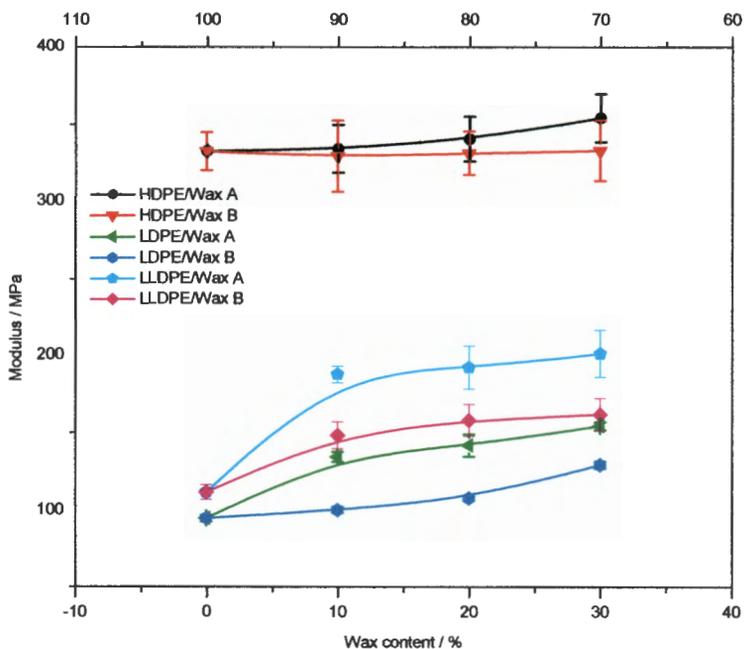


Figure 3.16 Young's modulus as function of wax content in the blends

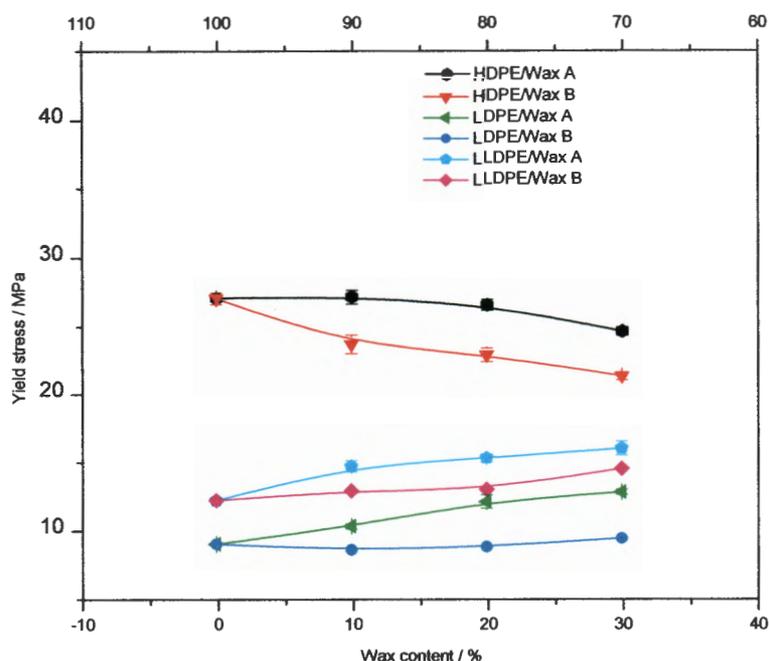


Figure 3.17 Yield stress as function of wax content

Stress at break as a function of wax content is depicted in Figure 3.19. It can be seen that both Wax A and Wax B reduce stress at break of the blends. The tensile strength at break generally depends on the polymer or material structure in a complicated way. Shorter chains in the materials imply that low elongation is needed to stretch the molecules and the chains are easier to draw from the lamellae. For the material to break, the tie-molecules should be tightly stretched, and the tightly stretched tie-molecules should be drawn out of the lamellae. It is well known that the strength of semi-crystalline polymers depends on the number of tie chains. Because of shorter wax chains co-crystallizing with the polymers, the average tie chain concentration decreases with increasing amount of wax. The maximum length of the extended wax chain ($\sim C_{120}$) is about 18 nm, which is much shorter than $2L_c + L_a$, where L_c is the average lamellar thickness and L_a is the thickness of the amorphous layer [32]. Only molecules that are longer than $2L_c + L_a$ can form tie chains. This means that the average tie chain concentration will decrease with increasing amount of wax in the blend. In the case of HDPE, Wax B seems to reduce the stress at break more than Wax A. The only possible explanation for this behaviour is the substantially lower crystallinity of Wax B, which reduces the total crystallinity and the ultimate strength of the blend. It is further obvious that wax

content does not have such a large influence on the stress at break of LLDPE. The only explanation for this is that the wax co-crystallizes with LLDPE in such a way that it has a much smaller influence on the tie chain concentration between LLDPE lamellae.

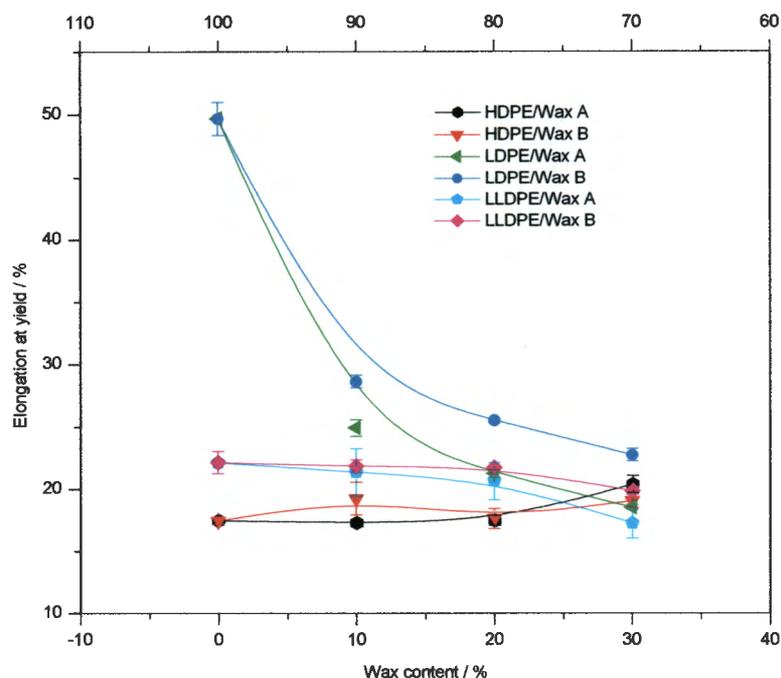


Figure 3.18 Elongation at yield as function of wax content

Figure 3.20 depicts the elongation at break of different polyethylene/wax blends as function of wax content. An increase in wax content results in a decrease in elongation at break of all the blends. Since wax molecules are too short to form tie chains, the number of chain ends, i.e. the number of dislocations, will increase with an increase in wax content. This will induce a decrease in the strain at break. Elongation at break may also be influenced by the miscibility of the components. When there is phase separation in the blends, as in the case of LDPE/Wax A, LDPE/Wax B and 30 % Wax A with HDPE, the material loses drawability and elongation at break strongly decreases. Possible crack initiation can start at the domains of segregation of low molecular weight material [32]. It can be seen that wax has much less influence on LLDPE than on the other two polymers. As discussed in the previous paragraph, the co-crystallized wax for some reason has little influence on the tie chain concentration between LLDPE lamellae.

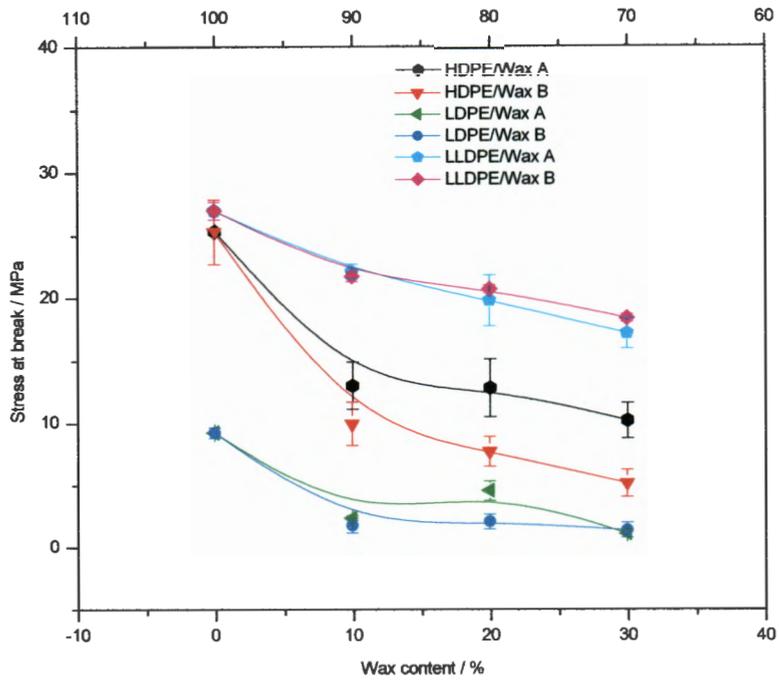


Figure 3.19 Stress at break as function of wax content

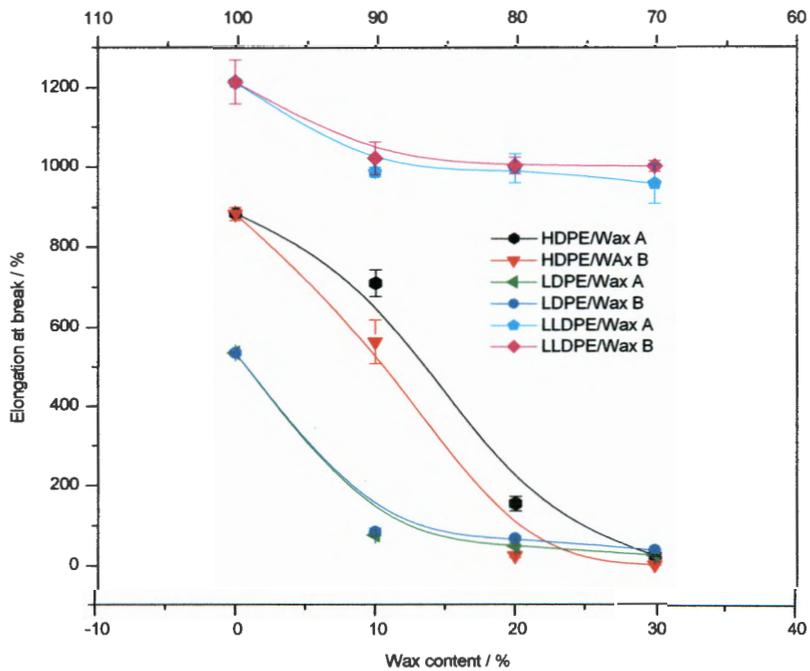


Figure 3.20 Elongation at break as function of wax content

3.1.4 Surface free energy

Table 3.3 summarizes the values of the surface free energy of the pure polyethylenes and waxes. It can be seen that both HDPE and LDPE have a strong non-polar nature, which is evident from the values of the disperse component of the surface energy. Wax A is similarly non-polar, which is evident from the very low value of the polar component. Wax B has a higher polar component of the surface free energy than Wax A. The reason is that Wax B contains oxygen groups attached on its backbone, which increases the polarity of the wax.

Table 3.3 Total surface free energy, as well as its disperse and polar parts, of the pure polyethylenes and waxes

Sample	Surface free energy / mJ.m^{-2}		
	g_{Total}	g_{LW}	g_{AB}
HDPE	39.4 ± 2.3	39.3 ± 2.3	0.1 ± 0.2
LDPE	36.6 ± 2.1	35.9 ± 1.7	0.7 ± 0.3
LLDPE	19.8 ± 0.7	19.4 ± 0.5	0.4 ± 0.2
Wax A	29.4 ± 3.1	29.0 ± 3.1	0.4 ± 0.4
Wax B	29.2 ± 5.2	27.7 ± 5.0	1.5 ± 1.3

g_{Total} = total surface energy, g_{LW} = disperse part, and g_{AB} = polar part

Table 3.4 summarizes the surface free energy data of HDPE/wax blends, and the curves for these blends are shown in Figures 3.21 and 3.22. In the case of HDPE/Wax A the total surface free energy initially decreases and then increases, while the polar part slightly increases and then decreases with increasing wax content. This observation is in line with the miscibility trends observed with DSC. Krump and co-workers [37] showed this relationship between blend miscibility and surface free energy. The surface free energy of the HDPE/Wax B blends show similar trends, that can be explained in a similar way. In this case, however, the surface free energy values are somewhat higher, which is the result of the more polar character of Wax B.

Table 3.4 Total surface free energy, as well as its disperse and polar parts, of the HDPE/wax blends

Sample	Surface free energy / $\text{mJ}\cdot\text{m}^{-2}$		
	g_{Total}	g_{LW}	g_{AB}
HDPE/Wax B (90/10 w/w)	34.0 ± 3.9	31.7 ± 3.7	3.3 ± 1.1
HDPE/ Wax B (80/20 w/w)	32.2 ± 4.0	28.5 ± 3.7	3.8 ± 1.5
HDPE/ Wax B (70/30 w/w)	35.6 ± 3.5	34.4 ± 3.4	1.2 ± 0.7
HDPE/Wax A (90/10 w/w)	29.8 ± 4.7	27.6 ± 4.5	2.2 ± 1.4
HDPE/ Wax A (80/20 w/w)	28.9 ± 3.2	25.1 ± 2.8	3.8 ± 1.3
HDPE/ Wax A (70/30 w/w)	30.3 ± 3.1	29.4 ± 1.3	0.9 ± 0.2

g_{Total} = total surface energy, g_{LW} = disperse part, and g_{AB} = polar part

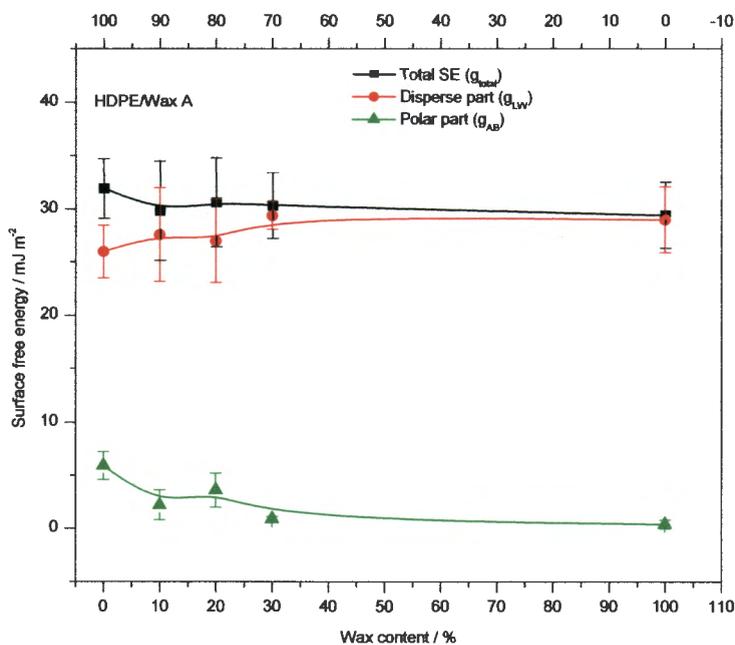


Figure 3.21 The surface free energy, as well as its disperse and polar parts, of the HDPE/Wax A blends as function of wax content

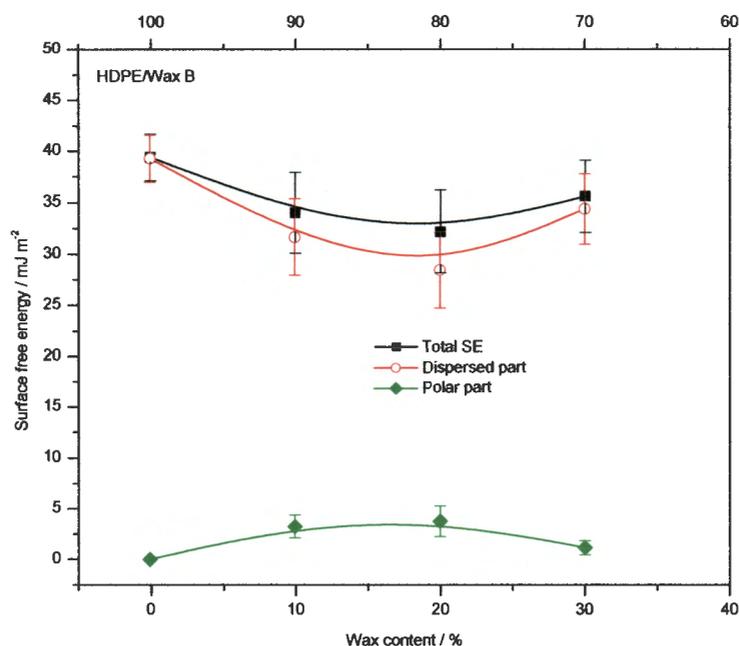


Figure 3.22 The surface free energy, as well as its disperse and polar parts, of the HDPE/Wax B blends as function of wax content

Table 3.5 Total surface free energy, as well as its disperse and polar parts, of the LDPE/wax blends

Sample	Surface free energy / mJ.m ⁻²		
	g_{Total}	g_{LW}	g_{AB}
LDPE/Wax B (90/10 w/w)	38.1 ± 2.1	32.7 ± 2.0	5.4 ± 0.9
LDPE/ Wax B (80/20 w/w)	36.6 ± 2.5	32.4 ± 2.4	4.2 ± 0.9
LDPE/ Wax B (70/30 w/w)	40.5 ± 4.3	38.2 ± 2.4	2.3 ± 1.1
LDPE/Wax A (90/10 w/w)	26.6 ± 3.4	23.2 ± 3.1	3.4 ± 1.3
LDPE/ Wax A (80/20 w/w)	27.6 ± 4.3	25.4 ± 4.1	2.2 ± 1.3
LDPE/ Wax A (70/30 w/w)	29.4 ± 2.5	27.5 ± 2.0	1.9 ± 1.0

g_{Total} = total surface energy, g_{LW} = disperse part, and g_{AB} = polar part

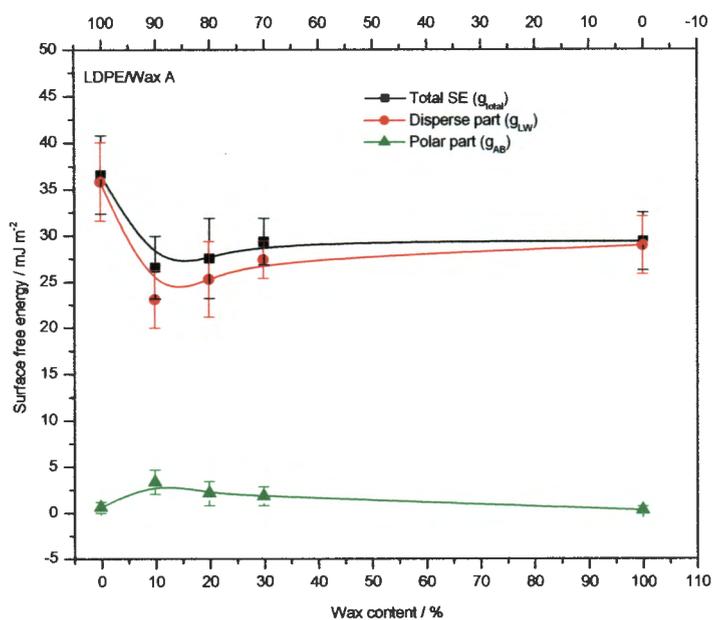


Figure 3.23 The surface free energy, as well as its disperse and polar parts, of the LDPE/Wax A blends as function of wax content

Table 3.5 summarizes the surface free energy data for the LDPE/wax blends and the wax content dependence of these blends are shown in Figures 3.23 and 3.24. The trends are similar than those observed for HDPE/wax blends, and can also be explained through the LDPE/wax miscibility (as observed in the DSC analyses) and the higher polarity of Wax B.

Figure 3.25 and 3.26 depict the surface free energy of the LLDPE/wax blends as function of wax content, and the results are summarized in Table 3.6. LLDPE/Wax B blends are miscible for all the investigated samples. This is clear from the continuously decreasing total surface free energy, and increasing polar part, with increasing wax content. The polar part also increases as a result of the polar nature of Wax B. The miscibility observation is in line with the DSC results discussed earlier. In the case of the LLDPE/Wax A blends there is, however, a continuous increase in total surface free energy and a continuous decrease in the polar part. This is in line with the partial miscibility of these blends observed in the DSC results.

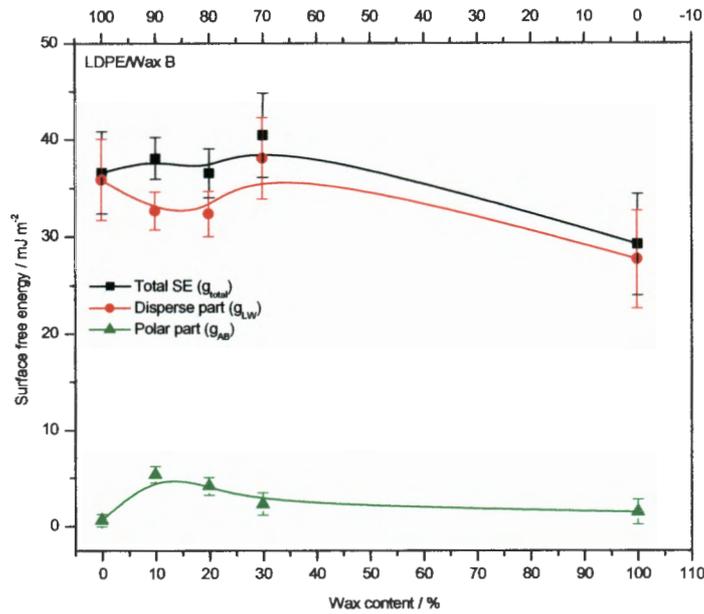


Figure 3.24 The surface free energy, as well as its disperse and polar parts, of the LDPE/Wax B blends as function of wax content

Table 3.6 Total surface free energy, as well as its disperse and polar parts, of the LLDPE/wax blends

Sample	Surface free energy / mJ.m ⁻²		
	g _{Total}	g _{LW}	g _{AB}
LLDPE/Wax B (90/10 w/w)	35.1 ± 1.8	32.7 ± 1.6	2.4 ± 0.8
LLDPE/ Wax B (80/20 w/w)	34.3 ± 5.0	31.2 ± 4.5	3.1 ± 2.0
LLDPE/ Wax B (70/30 w/w)	33.4 ± 3.7	29.7 ± 3.6	3.7 ± 1.0
LLDPE/Wax A (90/10 w/w)	30.0 ± 4.2	27.7 ± 4.0	2.3 ± 1.3
LLDPE/ Wax A (80/20 w/w)	32.4 ± 2.9	30.9 ± 2.8	1.5 ± 0.7
LLDPE/ Wax A (70/30 w/w)	32.6 ± 4.5	31.5 ± 4.0	1.1 ± 0.9

g_{Total} = total surface energy, g_{LW} = disperse part, and g_{AB} = polar part



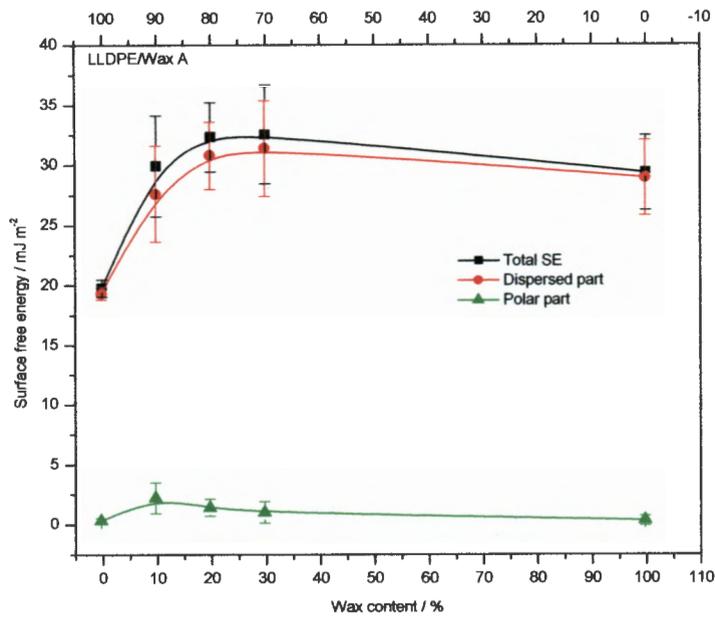


Figure 3.25 The surface free energy, as well as its disperse and polar parts, of the LLDPE/Wax A blends as function of wax content

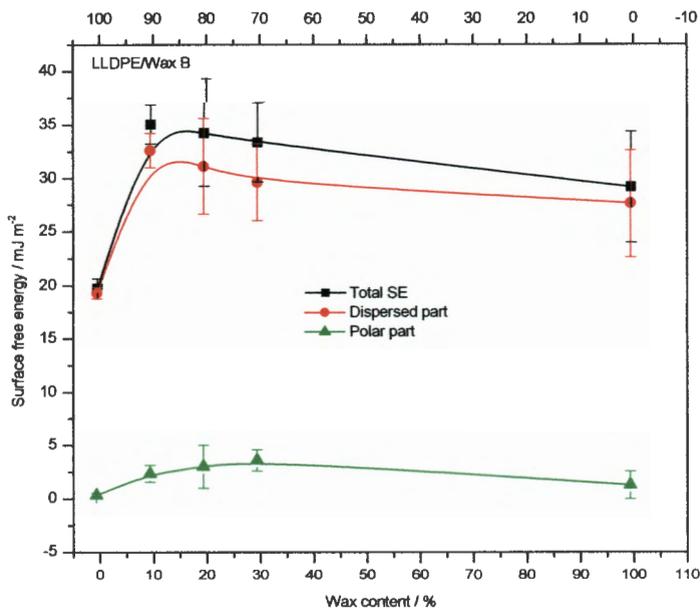


Figure 3.26 The surface free energy, as well as its disperse and polar parts, of the LLDPE/Wax B blends as function of wax content

3.1.5 Melt flow index (MFI)

Table 3.4 shows the MFI values for the different polyethylene/wax blends, and these values are plotted in Figures 3.27 as function of wax content. It can be seen that pure LDPE gives a higher flow rate (lower viscosity) compared to that of HDPE and LLDPE. This is the result of the higher branching content of the LDPE, as well as its lower molecular weight ($96\ 000\ \text{g mol}^{-1}$) compared to those of LLDPE ($191\ 000\ \text{g mol}^{-1}$) and HDPE ($168\ 000\ \text{g mol}^{-1}$). Billmeyer [53] reported that the flow of the material depends primarily on its molecular weight. The flow rate of 100 % wax samples could not be measured, because they flowed too rapidly. This is the consequence of their similar and very small molecular weights.

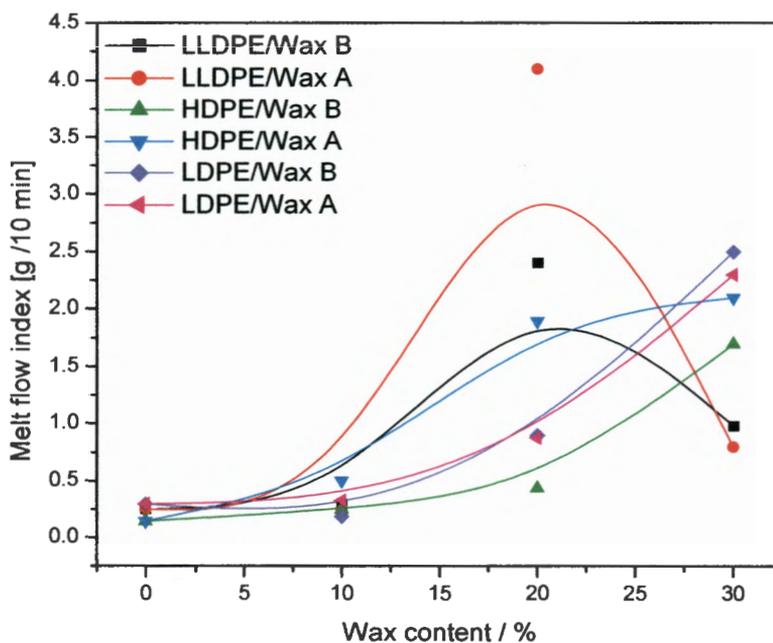


Figure 3.27 Melt flow index of different polyethylene/wax blends as function of wax content

Table 3.4 Melt flow index data

Sample	FR [g / 10 min]	FR/FR_{PE}
HDPE	0.15	1.00
LDPE	0.30	1.00
LLDPE	0.25	1.00
HDPE/Wax B (90/10 w/w)	0.25	1.67
HDPE/Wax B (80/20 w/w)	0.44	2.93
HDPE/Wax B (70/30 w/w)	1.66	11.07
HDPE/Wax A (90/10 w/w)	0.51	3.40
HDPE/Wax A (80/20 w/w)	1.90	12.70
HDPE/Wax A (70/30 w/w)	2.10	19.30
LDPE/Wax B (90/10 w/w)	0.19	0.60
LDPE/Wax B (80/20 w/w)	0.90	3.00
LDPE/Wax B (70/30 w/w)	2.50	8.30
LDPE/Wax A (90/10 w/w)	0.33	1.10
LDPE/Wax A (80/20 w/w)	0.88	2.93
LDPE/Wax A (70/30 w/w)	2.30	7.67
LLDPE/Wax B (90/10 w/w)	0.30	1.20
LLDPE/Wax B (80/20 w/w)	2.40	9.60
LLDPE/Wax B (70/30 w/w)	0.98	3.92
LLDPE/Wax A (90/10 w/w)	0.25	1.00
LLDPE/Wax A (80/20 w/w)	4.10	16.4
LLDPE/Wax A (70/30 w/w)	0.80	3.20

FR = flow rate, FR/FR_{PE} = flow rate of blend divided by the flow rate of unblended polyethylene

The plot of the flow rate of the blends (FR/FR_{PE}) as a function of wax content (Figure 3.28) shows an exponential increase in the case of HDPE/wax and LDPE/wax blends with increasing wax content for both Wax A and Wax B. This indicates the appreciable influence of wax on the flow properties of the polymer material. Different behaviour is observed in the case of LLDPE/wax blends. Addition of 30 % Wax A and Wax B causes a reduction in the flow rate of the blends. In previous work [15] a linear relationship was observed when plotting the flow rate of the LLDPE/Wax B blends as function of wax content. However, these authors observed complete miscibility at all wax contents, while my DSC results showed partial miscibility at higher wax contents. There must therefore be a relationship between melt flow behaviour and polymer-wax miscibility.

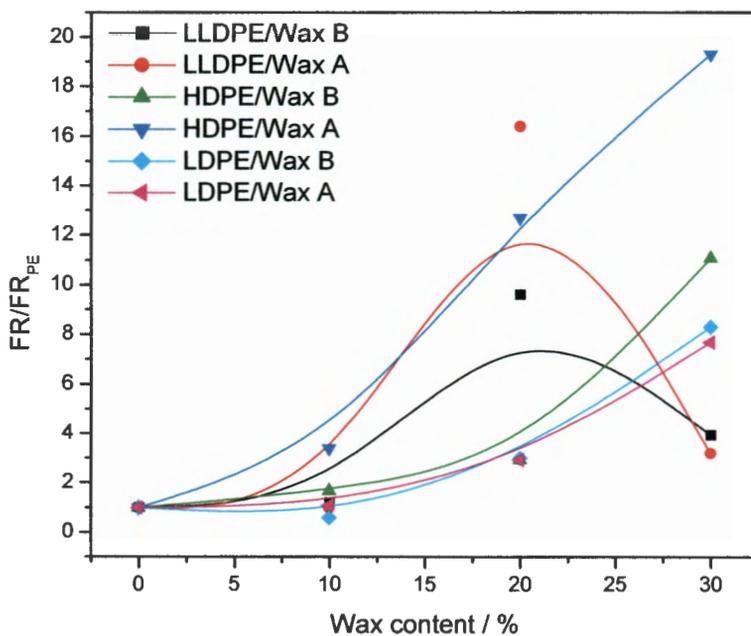


Figure 3.28 FR/FR_{PE} of different polyethylene/wax blends as function of wax content

CHAPTER 4

SUMMARY AND CONCLUSIONS

The high demand for polymers is due to their high strength-to-weight ratio, ease of fabrication, low cost, etc. As man is in search of newer and more valuable materials, the quest for such materials is increasing day by day. Though polymers are serving the society, they simultaneously pose some environmental problems due to their non-judicious usage. The main problem with most of the polymers is their non-degradable nature. It is the primary duty of all scientists in general, and polymer scientists in particular, to see that the polymers do not pollute the environment.

Melt-mixing of HDPE with Wax A gives rise to a completely miscible blend for both 10 and 20 % wax contents. This is clear from the DSC curves that show only one melting peak at the HDPE melting temperature. This miscibility must be the result of co-crystallization of Wax A with HDPE, which is clear from the thermal fractionation curves that show only one melting peak after fractionation. This fraction, however, melts at increasingly lower temperatures with increasing amounts of wax in the blend. This is probably the result of the formation of thinner lamellae in the presence of Wax A. A Wax A content of 30 % gives rise to a partially miscible blend. This is clear from the development of a lower temperature melting peak in the DSC curve, and from the thermal fractionation curves that show a similarity between the calculated and experimental curves in the temperature range 60 to 100 °C. These observations were further supported by the surface free energy results, where the polar part showed an increase for the miscible blends, but a decrease in the case of 70/30 w/w HDPE/Wax A. The presence of Wax A had very little influence on the modulus and yield point of HDPE, probably because the two components have similar crystallinity and co-crystallize to a large extent. However, the presence of Wax A caused a substantial decrease in both stress and strain at break of the blends. The reason for this is that co-crystallization of HDPE and Wax A, combined with the fact that the wax has very short chains compared to HDPE, cause a reduction in the tie-chain concentration of the crystallites. The melt flow of the blend increased exponentially with increasing wax content. Since the wax co-crystallizes with HDPE, and since it starts melting at a lower temperature than HDPE, it has a plasticizing effect at higher temperatures and enhances the mobility of the HDPE chains, giving rise to higher melt flow rates.

In the case of the HDPE/Wax B blends the miscibility is similar to that of HDPE/Wax A blends for both 10 and 20 % wax contents. This is clear from the DSC curves that show only one melting peak at the HDPE melting temperature, and from the thermal fractionation curves that show only one melting peak after fractionation. This indicates co-crystallization of Wax B with HDPE. This fraction, nevertheless, melts at increasingly lower temperatures as in the case of HDPE/Wax A blends, when the amount of wax in the blend was increased. This is probably because of the formation of thinner lamellae in the presence of Wax B. A wax content of 30 % gives rise to a partially miscible blend. This is evident from the DSC curve which shows the development of a lower melting peak in the wax melting temperature range. These differences in miscibilities are clearly reflected in the surface free energy results that show an increase in the polar part for both the 90/10 and 80/20 w/w HDPE/Wax B blends, while the blend containing 30 % wax content showed a decrease in the polar part. The presence of Wax B had the same influence on the mechanical properties of the blends, despite the fact that Wax B has a lower crystallinity than Wax A. It also had the same influence on the melt flow of the blends, although the HDPE/Wax B blends had much lower MFI values than the HDPE/Wax A blends. This is the result of the higher molecular weight of Wax A.

Complete miscibility was observed for all the LLDPE/Wax B blends, which is clear from the DSC curves that showed only one melting peak at the LLDPE melting temperature. This indicates co-crystallization of Wax B with LLDPE, which is evident from the thermal fractionation curves that show the dilution of the fractional peak at 131 °C into the peak at 125 °C with increasing wax content. In addition, the thermal fractionation curves show dissimilarities between the experimental and calculated curves in the temperature range 96 to 130 °C, which also indicates co-crystallization of the two components. These conclusions were further supported by the surface free energy results, where the polar part increased with increasing wax content. This may indicate complete miscibility of LLDPE and Wax B in the blends, although the polar nature of Wax B will also influence this property. The main fractional peak of LLDPE, however, melts at increasingly lower temperatures with increasing amounts of wax in the blend. This is the result of the formation of thinner lamellae in the presence of Wax B. The complete miscibility had an influence on the mechanical properties, where there was an increase in both stiffness and yield stress with increasing amounts of wax. This is probably due to lamellar perfection obtained by melt mixing of the two components, and an increase in crystallinity with increasing wax contents. The presence of Wax B had very little influence on the elongation at yield. This is probably because of the wax co-crystallizing with LLDPE, so that there were almost no wax crystals in the amorphous phase

that could restrict chain mobility. Wax B caused a decrease in both stress and elongation at break with increasing wax contents. As already explained above, the reason for this is the reduced tie chain concentration because of the shorter wax chains. The melt flow index of the blends increased up to 20 % wax content, after which it decreased. The initial increase can be expected because of the much higher melt flow index of the wax, as well as the co-crystallization of LLDPE and Wax B. It is not clear why there was a decrease at 30 % wax content.

LLDPE/Wax A blends were partially miscible for all wax contents. This is clear from the DSC curves that show two or more peaks for all the samples. This partial miscibility is also evident from the thermal fractionation peaks that show a similarity between the calculated and experimental fractionation peaks in the temperature range 60 to 100 °C. The main fractions of the LLDPE/Wax A blends showed similar behaviour than those of the Wax B blends, which is probably because of the formation of thinner lamellae with increasing amounts of wax. These observations were further supported by the decrease in the polar part of the surface free energy results, indicating decreasing polymer-wax miscibility with increasing wax content. The presence of Wax A caused an increase in both modulus and stress at yield with increasing wax contents, probably because of an increase in the degree of crystallinity of these blends. Addition of Wax A caused a slight decrease in the elongation at yield with increasing wax content. This is probably because of wax crystals in the amorphous fraction of LLDPE hindering chain mobility. Stress and elongation at break showed an almost identical decrease than was observed for the LLDPE/Wax B blends. The melt flow of the blends showed the same behaviour as the Wax B blends.

Melt-mixing of LDPE with Wax A gives rise to a partially miscible blend for all wax contents investigated. This is evident from the DSC curves that show more than one endothermic peak for all wax contents. The presence of Wax A also does not have much influence on the crystallization behaviour of LDPE. This is clear from the DSC curves that show a very slight shift in the melting peak temperature of the LDPE with increasing amounts of wax in the blend. This is probably because wax crystallized separately in the amorphous part of LDPE. This partial miscibility is clear from the thermal fractionation curves that showed melting peaks in the wax melting temperature range 60 to 100 °C. These observations were further supported by the surface free energy results, where the polar part showed a decrease with increasing wax content. The presence of Wax A in LDPE caused an increase in both modulus and stress at yield with increasing wax content. This is probably because of a higher melting enthalpy of Wax A compared to LDPE. Stress at break,

elongation at yield and elongation at break decreased with an increase in wax content. The reduction of the stress and elongation at break is probably the result of phase separation in the blends, causing the material to lose drawability and strength. If there was co-crystallization, another contribution to the decrease may have been the reduction in tie chain concentration. The melt flow rate increased with increasing wax content, which is probably the result of the plasticizing effect of the molten wax.

In the case of Wax B blended with LDPE, melt-mixing gives rise to complete miscibility for only the 90/10 w/w LDPE/Wax B blend. This is clearly indicated by the DSC curves that show only one endothermic peak at the LDPE melting temperature. This is probably the result of co-crystallization between the two components, which is clearly reflected by the thermal fractionation curves that depict the dissimilarity between the calculated and experimental fractionation curves at the LDPE melting temperature. Wax contents of 20 and 30 % give rise to a partially miscible blend. This is evident from the development of a lower temperature melting peak in the DSC curve, and from the thermal fraction curves that show a similarity between the experimental and calculated curves in the temperature range 60 to 80 °C. These observations were further supported by the surface free energy results, where the polar part showed an increase for the miscible blend, but a decrease in the case of 80/20 and 70/30 w/w LDPE/Wax B. The presence of Wax B showed a slight increase in the modulus with increasing wax content, and no change in the yield stress, despite decreasing crystallinity with increasing wax content. This is probably because of the stronger interaction between LDPE and oxygen-containing groups in the wax. As with the other blends, stress and strain at break decreased with increasing wax content. In this case, however, there is not a substantial decrease after addition of more than 10 % wax. This is probably because the wax mainly crystallizes in the LDPE amorphous fraction at higher wax contents. Because of this the tie chain concentration does not change significantly when going to higher wax contents. The melt flow of these blends showed a wax content dependence similar to the HDPE blends, and there is almost no difference between the behaviour of LDPE/Wax A and LDPE/Wax B blends. This further supports the probable crystallization of the wax in the LDPE amorphous phase.

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