

THE INFLUENCE OF TYPES AND AMOUNTS OF WAX ON THE
THERMAL AND MECHANICAL PROPERTIES OF PE/WAX BLENDS

by

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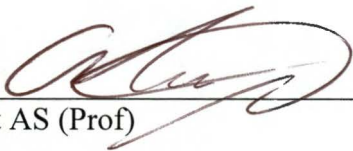
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DECLARATION

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.



Mpanza HS (Miss)



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DEDICATIONS

I would like to dedicate this book to my lovely son Syamthanda

With Love

ABSTRACT

The influence of three different waxes on the thermal and mechanical properties of low-density (LDPE) and linear low-density (LLDPE) polyethylenes was investigated. The samples were prepared through melt blending in a Brabender mixer. The thermal properties of the samples were determined using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Surface free energy analysis was used to confirm the miscibility of wax with polyethylene. The tensile and flow properties of all the samples were determined and compared. The observations are discussed in terms of possible morphological changes when wax is mixed with polyethylene. The polymer-wax miscibilities differed with the type of wax and polyethylene used, and with the amount of wax mixed into the polymer. These miscibilities, and accompanying morphologies, had a strong influence on the flow properties, thermal stabilities and tensile properties of the corresponding blends. Based on my observations, Wax 2 may be regarded as the best processing agent for LDPE. Both Wax 1 and Wax 2 have a similar influence on the tensile properties of LDPE, but Wax 2 increases the melt flow rate more than Wax 1, which was specifically designed as a polyethylene processing agent. As far as thermal stability is concerned, the blends seem to be thermally more stable in the presence of Wax 1 than in that of Wax 2. Although Wax 3 improves the melt flow rate in a similar way than Wax 2, it has a strong negative impact on the tensile properties of LDPE. In the case of LLDPE, either Wax 2 or Wax 3 can be used. Wax 3 has the strongest influence on the melt flow rates of the blends, and it has the least influence on the tensile properties of LLDPE. It does, however, strongly reduce the thermal stability of LLDPE. Wax 2, on the other hand, has only a small influence on the thermal stability of LLDPE, but like Wax 1 it strongly increases the modulus. Again Wax 1, which was specifically designed as a polyethylene processing agent, seems not to be the best wax to use for this purpose.

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CHAPTER 1

INTRODUCTION

1.1 Waxes

Paraffin waxes are a class of aliphatic hydrocarbons, characterized by straight or branched carbon chains, generic formula C_nH_{2n+2} . Paraffin waxes are white, translucent, tasteless and odourless solids consisting of a mixture of solid hydrocarbons of high molecular weight. Common properties are water repellency, smooth texture, and low toxicity. They are combustible and have good dielectric properties. They are used for the preparation of candles, paper coating, protective sealants for food products and beverages, glass cleaning preparations, hot-melt carpet backing, biodegradable mulch, lubricants, stoppers for acid bottles, and electrical insulation [1]. The major differences between paraffin waxes are their carbon number distribution and molecular mass. This is a result of the fact that all paraffin waxes come from one product. They are low melting organic mixtures of high molecular weight, solid at room temperature and generally similar in composition to fats and oils, except that they contain no glycerides. They are thermoplastics, but since they are not high polymers, they are not considered part of the family of plastics. They are soluble in most non-polar organic solvents and insoluble in water [2].

H1 wax, manufactured by Sasol Wax, is a very hard, brittle, high melting point, crystalline paraffin wax. It is pure white in colour. It has a relatively high molar mass and its viscosity is very low compared to the polyethylene waxes. It has a very low solubility in most solvents at room temperature. It is, however, soluble in most paraffinic and aromatic solvents at their boiling points. It can be used in a wide variety of applications such as polishes, printing inks, and paints. M3 wax, also manufactured by Sasol Wax, is not a good quality paraffin wax and there are a number of applications where it cannot be used. It performs well in candles, and a large quantity is sold into this market. The quality of this medium molecular weight wax can be improved considerably, but at the expense of the yield of the product produced [3]. EnHance, also manufactured by Sasol Wax, is a highly crystalline Fischer-Tropsch hydrocarbon designed to improve the processability of polyolefins during injection molding. Fischer-Tropsch hydrocarbons are highly compatible with polyolefins and at the recommended loadings are dissolved in the polymer matrix. EnHance has a melting point of

117 °C. It acts as a viscosity modifier during the processing of polyolefins, allowing faster plasticization and quicker injection. The addition of EnHance allows for the use of lower temperature profiles and hence reduces cooling times [4].

As a natural vegetable wax derived from the fronds of Brazilian palm trees (*Copernicia cerifera*), carnauba is a relatively hard, brittle wax the main attributes of which are lubricity, anti-blocking and FDA compliance [5]. Carnauba is popular in the can and coil coating as well as the film coating industries. Its melting point range is 83 to 86 °C. Michelman also manufactures several high-solids carnauba emulsions. Montan is a mineral wax which, in its crude form, is extracted from lignite formed by the decomposition of vegetable substances. Its melting point range is 79 to 89 °C. Beeswax is used extensively in the cosmetics industry as well as in a variety of other applications. In some applications synthetic waxes, that have been synthesized to specifically match certain properties of beeswax, have been successful in its substitution. A6 wax, an oxidized paraffin wax made by Sasol Wax, has properties of beeswax and can be used in certain applications as a replacement for this wax.

Microcrystalline waxes come from the distillation of crude oil. They have molecular weights of 500-675 g mol⁻¹ and melting points of 73°C to 94 °C. The waxes are highly branched and have smaller crystals [5].

1.2 Polyethylene (PE)

PE can be categorized according to the extent of its chain branching: high-density polyethylene (HDPE), low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE). HDPE has a density of about 0.96 g cm⁻³ and a melting temperature of about 133 °C; LDPE has a density of about 0.92 g cm⁻³ and a melting temperature of about 108 °C; LLDPE has a density of about 0.94 g cm⁻³ and a melting temperature of about 123 °C. The branch content of LDPE is greater than that of other PE's by an order of magnitude, and the branches are of varying length. Short-chain branching is assumed to affect morphological and solid state properties, while long-chain branching is mostly manifested in viscoelastic properties. LDPE has high impact strength, low brittleness temperature, flexibility, film transparency and outstanding electrical properties [6].

The crystalline morphology of polyethylene has been very widely studied as a model for polymer crystallinity in general, particularly as single crystals may be readily grown from dilute solutions. Crystallized from the melt, the polymer is spherulitic, having a very high nucleation rate and thus forming only small spherulites. Although it is impossible to quench a

polyethylene melt to an amorphous solid, crystallization, and hence density, may be somewhat reduced by quenching, especially if the polymer is of high molecular weight. The crystalline phase has a density of 1.00 g cm^{-3} , and the amorphous phase a density of 0.85 g cm^{-3} at 25°C [7].

The crystalline melting behaviour is dependent on density. Typically, LDPE melts over a wide range of about $80\text{-}110^\circ\text{C}$, and HDPE over a range of about $120\text{-}135^\circ\text{C}$. Polyethylene exhibits several transitions, apart from melting. These are best investigated by dynamic mechanical spectroscopy. The best characterized are the α -, β - and γ -transitions. The α -transition is associated with motions in the crystalline phase and is at about 50°C , although the value is crystallinity dependent. The β -transition is at about -20°C and is associated with motions involving branch points. The γ -transition is at about -120°C and involves motions of sequences of a few CH_2 groups. Considerable controversy exists as to whether the β - or the γ -transition should be called the glass transition.

The mechanical behaviour of polyethylene is dependent on density. LDPE is a soft and flexible material, typically with a tensile modulus of 0.2 GPa , a tensile strength of 10 MPa , an elongation at break of 800% , and an Izod impact strength of $> 15 \text{ J (12.7 mm)}$. Its major use (70%) is as a film material, especially for packaging. HDPE is a harder, stiffer material, typically having a tensile modulus of 1.0 GPa , a tensile strength of 30 MPa , an elongation at break of 500% , and an Izod impact strength of $2\text{-}8 \text{ J (12.7 mm)}$. Its main uses are as a pipe, container, film and injection molding material [8].

Although highly inert to swelling by all solvents, polyethylene may be susceptible to environmental stress cracking. It is also sensitive to thermal and photo oxidation and is frequently protected with an antioxidant [6]. Being completely non-polar, it has a very high electrical resistivity and is an exceptionally low loss material, ideal for high frequency electrical insulation. Optically, polyethylene is opaque or translucent in thin film, due to scattering of light by the spherulites.

1.3 Processing agents

Processing agents are mixed with polymers to enhance their ease of processing. Typical characteristics of processing agents are:

- toughness over and above natural waxes;
- hardness resulting in excellent abrasion resistance;

- lubricity on the surface during melt processing;
- melting point to confer temperature resistance to many formulas;
- low melt viscosity for ease of processing and handling;
- chemical resistance - a barrier to water or grease and almost completely insoluble to many chemicals and solvents at 25 °C;
- compatibility controllable with branching or polar co-monomers [9].

Wax products in the chemical industry are utilized as processing agents and raw materials in manufacturing processes, as well as components of finished products. In some applications waxes are used as inert carriers e.g. for colours, active ingredients, fragrances etc. They also impart hydrophobic characteristics and can act as sealing or release agents depending on the physical properties. Depending on the application technique, wax products also help provide consistency, form a film or act as temporary processing aids [10].

Wax and Additives was the world's first commercial manufacturer of low molecular weight polyolefin polymers, manufacturing a product that delivers functionality consistently. These include homopolymers, copolymers and polymers with grafted functionality. The following are some of their products [9]:

- Co-wax emulsion

This synthetic, carnauba-type water-based emulsion (12 % solids) can be blended with polymer emulsions, alkali-soluble resins, silicone emulsions and polyethylene emulsions to produce all types of coatings, polishes and finishes. It is used widely in aerosol polishes.

- Alcoat C-20

Specially formulated as a mold release agent for plastics, aluminum castings and fibre glass, this water-based anionic wax emulsion can be used at very high temperatures without affecting the release and slip properties.

- Epolene C-14 wax is a highly branched, medium molecular weight polyethylene that can be used in hot-melt adhesives to improve cohesive strength, for adjusting viscosity in lower-weight polymers, and for blending with paraffin wax to offer improved grease resistance and gloss.

Sadhan and Sachin [13] investigated the use of processing aids in nanofillers. Epoxy was successfully used in this study as a processing aid and dispersing agent of fumed silica particles in producing melt-mixed nanoblends of a high performance polymer. Reduction in the Brabender torque and processing temperature of polyethersulphone (PES) established the usefulness of epoxy as a processing aid. Strong interaction between the polar groups of epoxy

and the silanol groups on the surface of fumed silica particles helped dispersion of fumed silica particles into PES. TEM of stained samples confirmed coating of epoxy layers around fumed silica particles. It was also found that curing of epoxy did not affect the state of dispersion of fumed silica particles. Fumed silica particles, dispersed to nanoscale with the aid of epoxy, helped increase barrier to diffusion of solvents such as methylene chloride. The tensile strength of PES – epoxy – fumed silica composites was found to be almost as good as pure PES, while the impact strength increased due to a strong interaction between the filler and the polymer matrix.

Thermotropic liquid crystalline polymers (TLCPs) are usually wholly aromatic polymers that have very high melting temperatures. TLCPs can be used as processing aids due to their significant viscosity reduction effect in polymer blends. They can greatly improve processibility of thermoplastics without depressing their other properties, such as heat resistance and mechanical properties. As a processing aid, a TLCP should have a liquid crystalline range matching the processing window of the targeted thermoplastic. In order to match the processing windows of these thermoplastics, liquid crystalline polymers with suitable melting temperatures should be used. One way to lower the melting temperatures of the liquid crystalline polymers is to incorporate kink units or flexible chain segments into the backbones of the wholly aromatic liquid crystalline polymers. The kink units or flexible spacers would disrupt the crystal packing and thus reduce the melting temperatures of the TLCPs [11]. Such changes in the structures of the polymer backbones may also affect the liquid crystalline-isotropic transitions of the TLCPs. For a TLCP a very low liquid crystalline-isotropic transition temperature usually means a narrow liquid crystalline phase range. Such a TLCP cannot be used as an effective processing aid for thermoplastics, since the resultant processing window might be too narrow, which may lead to instability of the molding or extrusion processes. To develop a successful TLCP processing aid, contributions of various factors to the viscosity reduction effect need to be studied in depth e.g. the viscosity ratio of the matrix to the TLCP, the miscibility of the two phases and the morphology of the blend system [12].

1.4 Polymer blends

A polymer blend may be defined as an intimate mixture of two kinds of polymers, with no covalent bonds between them. Historically, the oldest and simplest methods involved

mechanical blending, where a plastic and a non cross-linked elastomer were blended either on rolls or through extruders [14]. The founder of the polymer blends industry was Alexander Parkes (an artist), who mixed two isomers of polyisoprene, amorphous *cis* natural rubber and semi-crystalline *trans* gutta percha. Owing to the difference in stiffness of the two isomers and their relative miscibility, this immediately offered a range of materials with different performance.

Blends between the various types of polymers have been widely investigated from the viewpoint of both industrial and scientific interest [15]. One main objective in the study of such blends is to find a new material combining the beneficial mechanical and processing properties of the component polymers. Practical benefits of polymer blending have been comprehensively reviewed. The introduction of LLDPE in the early 1980s offered the possibility of obtaining a new class of blends easily processable and with good overall mechanical behaviour.

There are miscible and immiscible polymer blends. Most polymer blends consist of thermodynamically immiscible components. Physical properties of a blend are determined by its morphology. The control of the morphology of an immiscible polymer melt is of vital importance in the tailoring of the final properties of the product. It is well known that the morphology of a heterogeneous polymer system is influenced by the properties of the blend components, e.g. rheological and interfacial properties, by the blend composition and by the blending conditions. The evolution of the morphology in immiscible blends is controlled by two counteracting processes: (i) particle deformation and break up, and (ii) coalescence. It is reported that well-defined copolymers can act as emulsifying agents in immiscible polymer blends. They are able to reduce the 'coalescence effect' by lowering the interfacial tension between the blend components and may lead to a well-dispersed morphology. However, the understanding of morphology changes during the blending process is limited [16].

Polyolefins are the most widely used polymers. Development of ways to compatibilize blends of polyolefins and polar polymers for the purpose of recycling is very important. Blends of polyolefins and polar polymers exhibit poor mechanical properties because of poor interfacial adhesion. The use of an appropriate interfacial agent is a way to improve the properties of the blend material [17].

1.4.1 PE/PP blends

Jun and Robert [18] investigated PE/PP blends. Samples were extruded, from a flat strip die, as sheets with a width of 30 mm and a thickness of 0.2 mm. The blend composition was 80/20 for all types of PE. PP was blended with LLDPE, LDPE, HDPE and very low density polyethylene (VLDPE). The addition of PP to the PEs improved Young's modulus and yield stress. Young's modulus was increased after thermal treatment for all the materials except pure PP. The yield strength was unchanged for most of the blends and pure polymers except for PP, VLDPE, HDPE/PP, and VLDPE/PP blends. In this work the reason for the decrease of strain at break and ultimate strength for the PP samples was that thermally treated PP samples broke before they reached a maximum value. The reason for the decreased yield stress in the VLDPE/PP and HDPE/PP blends after thermal treatment are complex because of large crystal size, more complete phase separation, and weak interfacial boundaries after annealing. Young's modulus and the strain at break were clearly seen to increase for all materials except for pure PP. Young's modulus and strain at break increased by approximately 40 % for the LLDPE/PP blend and by approximately 20 % for the VLDPE/PP blend, but by a smaller amount for the PP blends with LDPE and HDPE.

Hot-stage optical microscopy showed the different PP spherulite structures in various blends. The PP is soluble in molten LLDPE and the crystals grew from a homogeneous solution of PP and LLDPE. The growth rate of the PP spherulites in the LLDPE melt was very slow. It was also seen that the spherulites of PP in LLDPE were not as perfect as those for pure PP, because of the small portion of PP present and hindrance from molten LLDPE. In the blends with HDPE, LDPE and VLDPE, the PP crystallized as phase-separated droplets, in which almost pure PP was present. The PP droplets were smaller in VLDPE, which shows that PP is more soluble in VLDPE [19].

Li and Shanks [20] also investigated PE/PP blends. Three isotactic PP homopolymers were blended with three similar grade LLDPEs (5 % hexene copolymers). The composition of all the blends studied was 20 % of PP and 80 % of LLDPE. The results show that nuclei density, spherulite growth rate and overall crystallisation rate of PP were strongly influenced by the melt flow index (MFI) of LLDPE for a PP composition of 20 % in the PP/LLDPE blends. Particularly, the spherulite growth rate of PP was significantly decreased in the blends and was affected by the MFI of LLDPE. The lower the MFI of LLDPE, the slower was the spherulite growth rate of PP. The decrease in the spherulite growth rate of PP in the PP-LLDPE blends could be caused by a number of reasons. Firstly, the LLDPE diluted the PP concentration in the matrix and retarded the crystallisation of PP. Secondly, the viscosity of LLDPE regulated the diffusion speed of PP chain segments and hence the spherulite growth

rate of PP. Lastly, the spherulite growth rate would decrease due to the decreased supercooling degree in the miscible blends. These observations suggested that the PP was miscible with the LLDPE, which is confirmed by the open-armed diffuse PP spherulites in the PP/LLDPE blends. In addition, the decrease in both the nuclei density and the spherulite growth rate contributed to the drastic decrease in the overall crystallisation rate in the partially miscible blends. The crystallisation of PP in the PP/LLDPE blends was both nucleation and diffusion controlled.

Kukaleva and Cser [21] also investigated PP/LLDPE blends. Two different types of PP were used: the so-called hcr (high stiffness or enhanced) PP, and a conventional grade of PP. The blends were prepared by extrusion and test samples by injection molding. The ratios were 100/0, 90/10, 80/20, 70/30, 60/40, 50/50, 40/60 and 0/100. Modulated Differential Scanning Calorimetric (MDSC) tests were performed and the T_g , T_m , and T_{cr} of the blends and the pure materials were determined. There was a shift in these temperatures in blends of iPP/LLDPE, and partial miscibility of the blend components in the melt was observed. A relationship between the level of crystallinity and physical properties of the blends was expected; the drop in the level of crystallinity of PP provided an increase in toughness of its blends with other polyolefins. Mechanical tests showed that the values of Young's modulus of the hcr PP blends were higher than those of the conventional PP blends by about 20-25 %. The level of crystallinity of the hcr PP and its blends is only about 5 % higher than those of the conventional PP and its blends with LLDPE. The level of crystallinity of PP in the blends seems to be independent of composition for both the hcr PP/LLDPE and conventional PP/LLDPE systems. For both types of systems studied, the level of Young's modulus and impact strength showed no correlation with the level of crystallinity. The blends with 40-60 % of LLDPE phase and either type of PP exhibited a T_g of -52.1 ± 0.2 °C, the position of which was little affected by the presence of PP in this concentration range. This suggests that the amorphous phase of the LLDPE does not contain PP under these conditions. The blends showed an increase in MFI with increasing LLDPE content. Melt density was independent of composition across the whole concentration range. Values of melt density for hcr PP/LLDPE and conventional PP/LLDPE blends were almost equal to the melt density of the pure PP and did not depend on the type of PP. Unchanged melt density data indicate that the blends were miscible or partially miscible in the molten state, at the temperature of the MFI test.

1.4.2 LDPE/LLDPE blends

Abraham and George [22] investigated LDPE/LLDPE blends. The blend compositions were 100/0, 80/20 and 60/40 w/w LDPE/LLDPE. Rheological measurements were done for LDPE, as well as 80/20 and 60/40 w/w LDPE/LLDPE blends. The curves were nearly parallel indicating that the non-Newtonian flow behaviour remains practically the same on modification. The viscous flow curves indicated that the molten polymers, both modified and unmodified, were in the non-Newtonian flow regime. Modification increased the melt viscosity to a greater degree in the case of the pure polymer (LDPE) compared to that of the blend systems. The modified blend systems exhibited higher values of viscosity, and its variation as a function of LLDPE content was smoother and more uniform compared to that of the corresponding unmodified blend systems. This indicates enhanced compatibility of the melt in the modified blend systems resulting from bonding between the long chain molecules. The differences in viscosity between the modified and unmodified homopolymers were highest for LDPE and decreased with an increase in the concentration of LLDPE. The main conclusions were that chemical modification increased both the viscosity and elasticity of modified LDPE and the two blend systems with LLDPE. Modification enhanced compatibility of the molten polymers. LLDPE with a relatively narrow molecular weight distribution reduced the shear thinning behaviour of LDPE.

Yamaguchi and Abe [23] investigated LLDPE/LDPE blends that were blended with a small amount of 2,6-di-tert-butyl-4-methylphenol as an oxidation inhibitor in a two-roll mill. The compositions of the LLDPE/LDPE blends were 100/0, 97.5/2.5, 95/5, 90/10, 80/20, 70/30, 50/50, 20/80, and 0/100 (w/w). The melting point of the LLDPE was lower than that of LDPE, which is the result of a large number of short chain branches in the LLDPE. Furthermore, only a single DSC melting peak was observed for each blend, irrespective of the blend composition. The melting peaks and heat of fusion of the blends were intermediate between those of the individual pure components. The compositional dependence of melting temperature and heat of fusion was prominent for the LLDPE-rich blends. Both increased rapidly with increasing LDPE content, indicating that LDPE enhances the crystallization of the LLDPE from the molten state. In an attempt to obtain further information on the crystallization mechanism, a DSC cooling run was also performed. The blending of a small amount of the LDPE enhanced the crystallization temperature. LDPE-rich crystals, which were formed before the crystallization of the bulk materials, acted as a nucleating agent for the crystallization of the rest of the polymers. This suggests that segregation of components took place during the crystallization process. There was an increase in the degree of crystallinity with increasing LDPE content in the blends. It was also found that the addition of

a small amount of LDPE enhanced the crystallinity of LLDPE. The mechanical properties were tested using tensile testing. The hardness was found to increase with increasing LDPE content in the LLDPE-rich blends. These results corresponded well with the degree of crystallinity. This fact indicates that the hardness of the blends was determined by the degree of crystallinity. Uniaxial tensile testing was performed at 22 °C K. It was found that the yield stress increased with increasing LDPE content, although the ultimate stress decreased with increasing LDPE content. The increase in yield stress was attributed to an increase in the degree of crystallinity. Furthermore, a necking band appeared and extended beyond the yield point for all the samples. This cold drawing process took place under approximate constant stress. The load increased up to the break point, which is the result of the the recrystallization of polymer chains because of a high degree of molecular orientation. The LDPE and the 20/80 w/w LLDPE/LDPE blend, however, showed little increment of the load just before the break point, which was attributed to the prevention of recrystallization because of the long chain branches. As a result, the ultimate stresses were lower than those of LLDPE and the LLDPE-rich blends.

The viscoelastic properties of LLDPE/LDPE blends show that the magnitude of E' decreased with increasing temperature, and fell off sharply at the melting temperature. The blend showed a much higher modulus than the LLDPE, although the amount of the LDPE in the blend was only 2.5 wt %. There were two relaxation peaks in the $\tan \delta$ curve for the LDPE in the temperature range: the peak located at approximately 260 K was referred to as the β relaxation, and the peak at approximately 350 K as the α relaxation. There was an ambiguous broad peak at a temperature between 240 and 320 K for the LLDPE. The peak was composed of both α and β relaxations. The shape of the $\tan \delta$ curve for the blend was different from that of pure LLDPE. In particular, the α relaxation process for the blend was located at higher temperatures than that of LLDPE. It is well known that α relaxation of crystalline polymers consists of at least two processes, referred to as α_1 and α_2 from lower temperatures. The α_1 process is pronounced in melt crystallized samples and is associated with the relaxation of grain boundaries, that is, mobility of crystalline fragments. The α_2 process is pronounced in single crystal mats and is ascribed to incoherent oscillations of the chains around their equilibrium positions in the crystalline lattice. The α relaxation in the present samples was associated with the α_1 process because of the low degree of crystallinity [24].

Graham and Predrag [25] investigated the blends of LLDPE/LDPE1 and LLDPE/LDPE2. The ratios were 100/0, 90/10, 80/20, 50/50, and 0/100. LDPE2 is a highly

long chain branched polymer while LDPE1 has a lower degree of long chain branching. The melt strength test results of LLDPE/LDPE1 and LLDPE/LDPE2, on the addition of either LDPE, showed a significant increase in the melt strength value of LLDPE. The melt strength is related to the presence of long chain branches in the LDPE, which participate in forming intermolecular interaction in the melt during elongation, thus increasing the resistance to deformation. LDPE2 was more effective in increasing the melt strength value of LLDPE than LDPE1, because of its higher level of long chain branching. The synergism in melt strength for LDPE-rich blend compositions was apparent for both sets of blends, with a maximum in the melt strength for the 60/40 w/w blends. The melt strength synergism is related to the immiscible melt morphology of these blends. DSC revealed the existence of two phases in the same range of blend compositions where the synergism in melt strength was observed, i.e. 50-100 % LDPE1 for the LLDPE/LDPE1 blends, and 20-100 % LDPE2 for LLDPE/LDPE2 blends. For LLDPE-rich non-synergistic blends, only one peak was obtained. The phase separation that was observed in the melt strength is responsible for the unexpected (synergistic) increase in the melt strength for LDPE-rich blends. The melt miscibility is related to the complex intermolecular interactions between the LLDPE and the highly long-chain branched LDPE.

Abraham and George [26] investigated LDPE and LDPE/LLDPE blends. The blends were prepared in a melt-mixing Brabender at a set temperature of 160 °C and a rotation speed of 30 rev/min. for 15 min. The blend composition was 80/20 and 60/40. The flow behaviour of LDPE and its blends with LLDPE, chemically modified with DCP, was studied as a function of blend composition and shear rate at a constant temperature using a capillary rheometer. The effect of chemical modification on the viscous and elastic properties of LDPE and two blend systems LDPE/LLDPE (80:20, 60:40) is reported. Chemical modification which is in essence a free radical process induces changes that increase melt viscosity and melt elasticity of LDPE and the two blend systems. Modification also enhances compatibility of the molten polymers. Incorporation of a small quantity of linear LDPE, having a relatively narrow molecular weight distribution, to the conventional LDPE, having a long chain branched structure and broader molecular weight distribution, reduces the shear thinning behaviour of the modified blends of the two component polymers.

Colin and Soares [27] prepared reactor blends of a (polyethylene/poly(ethylene-co-1-octene)) low molecular weight homopolymer and high molecular weight copolymer using a two-step polymerization process. The blends varied in composition from 100 % homopolymer to 100 % copolymer with mixtures ranging from 20 to 70 %. These blends were prepared by

compression molding at 150 °C and 2 MPa for 10 min, followed by quenching in air at room temperature. Using Rheometric DMTA the results showed that pure HMW copolymer exhibits greater viscosity (shear or complex) than the LMW homopolymer. It is well known that both the molecular weight and molecular weight distribution govern the melt behaviour of linear polymers, but the influence of the short chain branches on the rheological behaviour has been found to be minimal. For these blends, the viscosity of the polymer decreases with increasing fraction of LMW homopolymer. Assuming that the HMW copolymer and LMW homopolymer fractions are melt miscible, the viscosity should reflect the mixture of polymer chains. Shear thinning behaviour was observed for all the resins (decrease in viscosity with increasing frequency of the test). Shear thinning of the polymer occurs when the chains begin to disentangle and slip past each other. This slippage allows for orientation of the polymer in the flow direction, leading to a lowering of the viscosity.

1.4.3 PP/wax blends

Krupa and Luyt [28] investigated PP/wax blends that were blended in an industrial extruder. The DSC heating curves for blends containing 5 % wax showed only one endothermic peak, despite the fact that the DSC curve for wax showed three endothermic peaks, indicating miscibility at this concentration. At higher wax concentrations two significant peaks were observed, indicating that PP and wax were not completely miscible. The onset and peak temperatures of melting of polypropylene decreased with an increase in wax content. Melting enthalpies increased with an increase in wax content, since wax is more crystalline than PP. TGA results showed that the thermal stability of the blends decreased with an increase in wax content. This is a logical consequence of the lower thermal stability of the wax.

Novak *et al.* [29] also investigated surface properties of blends of PP with oxidized wax. They found that the surface free energy values of the blends increased with increasing wax content. 10 % oxidized wax increased the polar component of the surface free energy of iPP 11 times, and the polar ratio 14 times. This showed that oxidized Fischer-Tropsch wax can be effectively used as an agent for the improvement of the polarity of iPP. The strength of the adhesive joints between a cured epoxy resin and iPP increased by about 62 % when it was modified by 10 % oxidized wax. Conservation of the good mechanical properties of iPP was observed for blends containing up to 6 % oxidized wax. The wax also improved the viscosity of the blends. Only one DSC endothermic peak was seen for all the investigated blends, even though the wax has two endothermic peaks lying at different temperatures than that of pure iPP. An increase in the wax content slightly reduced the onset and peak temperatures of

melting. The specific enthalpy of melting slightly increased with an increase in the wax content. Young's modulus, elongation at break, and stress at break was found to decrease with an increase in wax content. A slight increase in the elongation at yield and a decrease in the stress at yield were observed.

1.4.4 PE/wax blends

Krupa and Luyt [30] investigated LLDPE/wax blends that were mechanically mixed and melt-pressed. In the DSC heating curves only one endothermic peak was observed, despite the fact that pure wax showed two significant peaks. An increase in the wax content of the blends did not influence the melting temperatures. The wax content also did not have a big influence on the specific melting enthalpies. This was probably due to the specific melting enthalpies of the wax and LLDPE being similar. Young's modulus of the blends slightly increased with an increase in wax content. The wax content had no influence on the yield point of the blends. For blends with 5 and 10 % of wax small strain hardening was observed. All samples containing 30-50 % of wax showed cold drawing. These samples broke close to their yield point.

Krupa and Luyt [31] also investigated LLDPE/wax blends blended in an industrial extruder. Contrary to the results discussed above, the DSC curves showed only partial miscibility at wax contents of 20 % and higher. The melting temperatures were also found to decrease with an increase in wax content. Young's modulus also increased with an increase in wax content, but an increase in wax content caused a decrease in elongation at yield. 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.

Krupa and Luyt [32] studied the physical properties of blends of LLDPE and oxidized paraffin wax. The authors found that wax slightly improved the polarity of the blends. Krump *et al.* [33] 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.

Hlangothi *et al.* [34] also investigated LLDPE/wax blends. They compared samples, cured in the presence of dibenzoyl peroxide (DBP), with blends prepared in the absence of

DCP. The gel content of the DBP treated blends decreased with an increase in wax content. The melting behaviour of all the uncross-linked blends was similar to that of pure LLDPE, which suggests possible co-crystallization of PE and wax chains. Melting temperatures and enthalpies of the uncross-linked blends decreased with increasing wax content. This trend was also observed for the cross-linked samples. However, for a specific blend composition, the melting temperature decreased with an increase in DBP concentration. It was found that an increase in wax content induced an increase in elastic modulus and yield stress of the blends. This is a consequence of the higher crystallinity of the blends in the presence of a higher amount of wax. Cross-linking improved the ultimate properties of the blends and pure polyethylene.

Mtshali *et al.* [35] investigated LDPE/wax blends, prepared through mechanical mixing and melt-pressing of the different components. The DSC curves of all the samples showed a single endothermic peak, and the presence of 5 and 10 % wax did not influence its position. LDPE and wax are therefore miscible in the crystalline phase at these concentrations. At higher wax contents a second peak was observed. Thermal stability of the blends, determined through TGA analyses, decreased with an increase in wax content. This is a logic consequence of the lower thermal stability of the wax. DCP content did not seem to have much influence on the thermal stability of LDPE or its blends.

Luyt and Krupa [36] also investigated LDPE/wax blends prepared by mechanical mixing and melt-pressing. They found that with increasing wax content the gel content after cross-linking decreased, since wax needs a much higher concentration of peroxide for cross-linking, and therefore only the PE phase was cross-linked. DSC curves for both 0.5 and 2 % DCP showed only one endothermic peak for the blends consisting of 5 and 10 % wax, while from 20 % wax a second broad peak was observed. This means that LDPE and wax were only partially miscible in this concentration region. A decrease in melting temperatures and enthalpies with an increase in DCP was observed.

Djokovic *et al.* investigated the influence of wax content on the physical properties of LDPE/oxidized wax blends [37]. The results showed that the melting temperature of the blends decrease as wax content increases. Degradation temperatures increased for small wax contents (up to 30 wt %), despite its lower thermal stability. There was a shift of the onset temperature of decomposition to higher temperatures compared to those of the pure materials. For blends with 5 and 10 % wax, the thermal stability was improved by more than 50 °C. Young's moduli of the blends were higher than that of pure LDPE. The strain at yield slightly

decreased for small amounts of wax. Lower values of stress and strain at break were obtained after blending LDPE with wax.

Mtshali *et al.* [38] investigated the influence of preparation procedure on the thermal and the mechanical properties of LLDPE/oxidized wax and LDPE/oxidized wax blends. The blends were prepared through mechanical mixing followed by melt pressing, and the same blends were also prepared through extrusion. It was found that the melting endotherms of extrusion mixed LLDPE/wax blends were similar to those of mechanically mixed samples. Melting enthalpies also did not depend on the preparation conditions. Although the melting enthalpies of the mechanically mixed LLDPE/wax samples remained unchanged, the melting enthalpies of the extruded samples decreased with increasing amount of wax in the blend. In the case of LDPE, blending with wax increased the melting enthalpies for both mechanically and extrusion mixed samples. The decomposition curves of extruded blends are slightly shifted to higher temperatures compared to PE. Mechanically mixed LLDPE/wax blends, on the other hand show the opposite behaviour. The extrusion mixed LDPE/wax blends showed better thermal stability than the mechanically mixed blends.

Novak *et al.* [39] found that oxidized wax improved the polarity of LDPE/wax and HDPE/wax blends. The increase in the polar component of the total surface free energy was exceptionally pronounced, especially for the LDPE matrix, where the polar component increased 10 times with respect to that of unmodified PE. Young's modulus of the LDPE blends slightly increased with an increase in wax content, whereas that of the HDPE blends slightly decreased. The wax content had no significant influence on the yield point for the HDPE blends. A slight decrease in the elongation at yield and an increase in the yield stress were observed for the LDPE blends. The ultimate properties were more dependent on the wax concentration. In the LDPE blends stress at break increased very slightly and for the HDPE blends a decrease in the stress at break was observed.

Mechanically mixed LDPE/wax blends displayed mutual immiscibility at 20 % and more wax [32]. This behaviour was supported by the work done by Luyt and Brüll [40] who investigated blends of oxidized wax with respectively HDPE, LDPE and LLDPE by using CRYSTAF and SEC-FTIR. The purpose was 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.

1.5 Objectives of the study

The first objective of this project is to (i) melt-blend different types of waxes in different ratios with respectively LDPE and LLDPE, (ii) determine their thermal, mechanical, flow and surface properties, and (iii) explain differences in the observed properties in terms of possible changes in the morphology and structures of the blends. The second objective is to establish and compare the usefulness of these paraffin waxes as processing agents for LDPE and LLDPE.

CHAPTER 2

EXPERIMENTAL

2.2 Materials

2.2.1 *Wax 1*

Wax 1 (supplied by Sasol Wax) is a highly crystalline Fischer-Tropsch hydrocarbon designed to improve the processability of polyolefins during injection moulding. It is claimed that it is highly compatible with polyolefins, and at the recommended loadings are dissolved in the polymer matrix. It has a melting point of 117 °C.

2.2.2 *Wax 2*

The hard, brittle, crystalline, straight hydrocarbon chain paraffin wax, used in this study, was supplied by Sasol Wax. It has a melting point of 90°C, decomposes at 250 °C, and has an average molar mass of 785 g mol⁻¹. It is white with exceptional opacity, and has a carbon distribution between C33 and C128. It has an iso-paraffin content of approximately 10 %, is chemically inert, inhibited against oxidation and free of aromatics.

2.2.3 *Wax 3*

Wax 3 is a paraffin wax consisting of approximately 99 % of straight chain hydrocarbons and very few branched chains. It was supplied by Sasol Wax. It has an average molar mass of 440 g mol⁻¹ and a carbon distribution between C15 and C78. Its density is 0.90 g cm⁻³, and its melting point is 72 °C.

2.2.4 *LDPE*

LDPE was supplied in powder form by Sasol Polymers. It has a melting point of 103 °C, a density of 0.91 g cm⁻³, an MFI of 20 g / 10 min at 160°C and an average molecular weight of approximately 96000 g mol⁻¹.

2.2.5 LLDPE

LLDPE was supplied in powder form by Sasol Polymers. It has a density 0.94 g cm^{-3} , an MFI of $3.5 \text{ g} / 10 \text{ min}$ at 180°C , a melting point of 127°C and an average molecular weight of approximately $191600 \text{ g mol}^{-1}$.

2.2 Methods

2.2.7 Preparation of blends

The blends were prepared by melt mixing in a Brabender Plastograph at a set temperature of 150°C and a rotation speed of 30 rev/min . for 10 min, after which they were compression molded into 1 mm thick slabs. Blend compositions are given in Table 2.1.

Table 2.1 Samples used in this study (the same compositions were used for Wax 1, Wax 2 and Wax 3)

w/w LDPE/Wax	w/w LLDPE/Wax
100/0	100/0
99/1	99/1
97/3	97/3
95/5	95/5
90/10	90/10

2.2.8 Thermogravimetric analysis (TGA)

TGA analyses were carried out in a Perkin Elmer TGA7 thermogravimetric analyzer in nitrogen atmosphere. Samples of 5-10 mg were heated from 25 to 600°C at $20^\circ\text{C min}^{-1}$.

2.2.9 Differential scanning calorimetry (DSC)

DSC analyses were carried out in a Perkin Elmer DSC7 thermal analyzer in nitrogen atmosphere. The samples were heated from 25 to 160°C at $10^\circ\text{C min}^{-1}$, cooled to 25°C at the same rate, and re-heated and cooled under the same conditions. Melting and crystallization

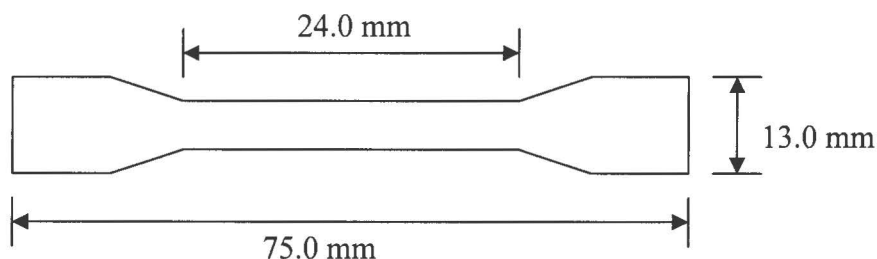
temperatures and enthalpies were determined from the second scan. Since the baselines were not straight, a sigmoidal baseline method was used to analyse the melting peaks.

2.2.10 Melt flow index (MFI)

The flow rates (MFI) of the samples were determined using a Ceast Melt Flow Junior apparatus at 150 °C and under a 1 kg mass.

2.2.5 Tensile testing

A Hounsfield H5KS tensile tester was used for determination of the mechanical properties. Test pieces were cut using a dumbbell cutter. The dimensions of the dumbbell shaped sample were as follows:



The speed of deformation was 50 mm min⁻¹. The final mechanical properties were evaluated from at least 5 different measurements.

2.2.6 Surface energy

The surface energy was determined from contact angle measurements by using a surface energy evaluation system (SEES) obtained from Bratislava, Slovak Republic. All measurements were performed at room temperature. Water, aniline, formamide, benzyl alcohol and ethylene glycol were used as test liquids. The Owens-Wendt regression method was used for surface energy calculations.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Thermal properties

3.1.1 Differential scanning calorimetry (DSC)

The DSC curves of the pure waxes are presented in Figure 3.1. The onset and peak temperatures, as well as enthalpy values are summarized in Table 3.1. Wax 1 shows melting peak temperatures at 94.1 and 108.0 °C. Wax 2 shows three endothermic peaks at 77.2 °C, at 88.1 °C (peak shoulder) and at 102.0 °C. Wax 3 shows melting peak temperatures at 56.4 and 66.2 °C (peak shoulder).

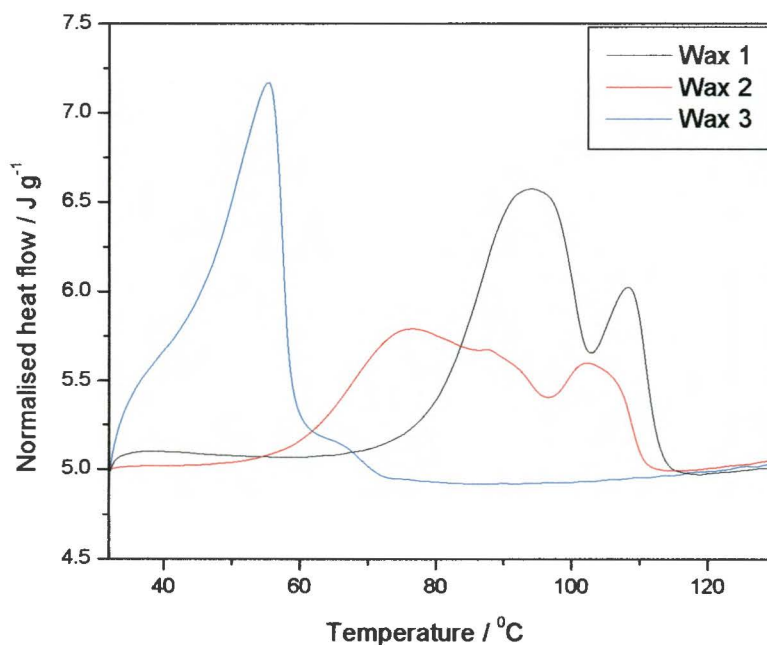


Figure 3.1 DSC heating curves of pure waxes

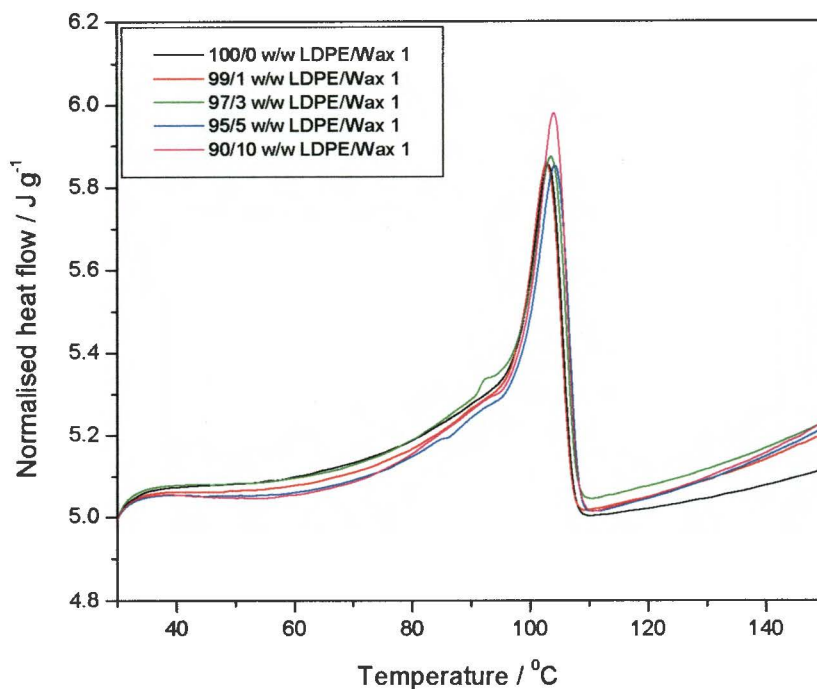


Figure 3.2 DSC heating curves for LDPE and different LDPE/Wax 1 blends

The DSC curves for the different blends are shown in Figures 3.2 – 3.13, and the values of the onset and peak temperatures, as well as the enthalpies, are summarized in Table 3.1. When there are two values for a certain property, it means that the DSC curve for that blend shows two melting peaks. Only one endothermic peak was observed for all the LDPE/Wax 1 blends. The explanation is that LDPE and Wax 1 are miscible in the crystalline phase up to 10 % wax content, and probably co-crystallize. LDPE and Wax 2 are miscible up to 3 % wax content. For 5 and 10 % wax, a second peak at 90°C can be seen, indicating that LDPE and Wax 2 are only partially miscible at these wax contents. One endothermic peak is seen for the LDPE/Wax 3 blends up to 5 % wax content. For 10 % wax, a second peak at 54 °C can be seen. This behaviour shows that LDPE and Wax 3 are partially immiscible.

Table 3.1 DSC onset and peak temperatures, as well as enthalpies, of melting and crystallization of the investigated samples

Sample	$T_{o,m} / ^\circ\text{C}$	$T_{p,m} / ^\circ\text{C}$	$\Delta H_m / \text{J g}^{-1}$	$T_{o,c} / ^\circ\text{C}$	$T_{p,c} / ^\circ\text{C}$	$\Delta H_c / \text{J g}^{-1}$
Wax 1	70.5	94.2 / 108.1	214	65.4	95.2 / 88.0	-208.0
Wax 2	54.4	102.4 / 88.3 / 77.1	205	50.1	90.1 / 65.2	-191.4
Wax 3	30.1	56.0 / 66.1	168	29.2	60.3 / 50.1	-148.5
LDPE/Wax 1						
100/0	96.1	103.2	55	89.9	86.5	-55.2
99/1	95.8	103.2	59	90.3	86.9	-55.2
97/3	95.9	103.7	62	90.4	87.0	-56.0
95/5	96.3	104.4	64	91.8	88.0	-53.7
90/10	97.1	104.0	74	92.4	89.3	-62.7
LDPE/Wax 2						
99/1	93.4	102.5	60	89.2	85.8	-55.5
97/3	94.3	103.0	59	90.4	86.9	-56.9
95/5	95.8	103.2 88.2	69 11	91.5	87.9	-56.3
90/10	96.1	90 / 103	13 / 69	91.7	88.6	-58.7
LDPE/Wax 3						
99/1	95.9	102.5	51	89.9	86.6	-52.0
97/3	95.6	101.7	49	89.3	86.6	-52.7
95/5	95.5	101.9	43	88.8	85.8	-59.6
90/10	95.0	54 / 101	10 / 42	88.5	85.5	-55.3
LLDPE/Wax 1						
100/0	119.3	127.0	81	110.8	107.2	-55.5
99/1	118.9	127.0	89	110.4	107.5	-62.8
97/3	119.9	125.2	93	110.2	108.1	-55.7
95/5	120.1	109 / 125	10 / 96	110.2	108.3	-50.1
90/10	119.9	110 / 124	14 / 105	110.1	108.3	-51.2
LLDPE/Wax 2						
99/1	119.9	128.0	82	109.5	106.8	-56.2
97/3	118.8	127.2	92	110.2	107.6	-55.8
95/5	119.9	113 / 126	10 / 85	110.1	107.6	-50.1
90/10	118.6	117 / 127	15 / 87	109.8	107.3	-45.4
LLDPE/Wax 3						
99/1	119.2	126.0	85	110.9	108.5	-55.8
97/3	119.4	125.7	81	109.9	107.6	-55.9
95/5	119.5	124.5	80	109.8	107.8	-55.6
90/10	118.7	44 / 125	11 / 70	109.2	106.8	-45.7

$T_{o,m}$, $T_{p,m}$, $T_{o,c}$, $T_{p,c}$, 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

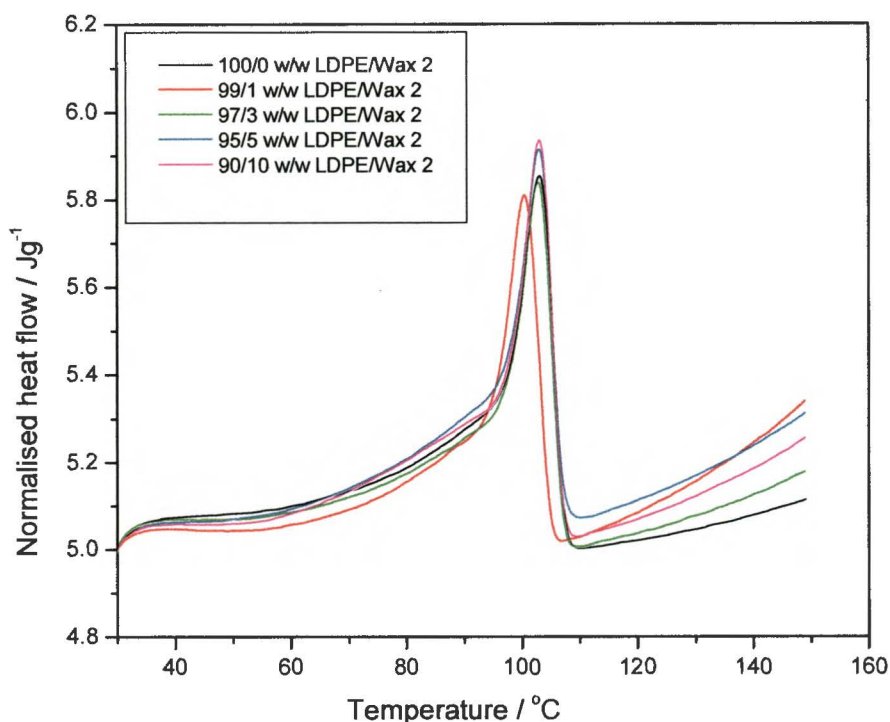


Figure 3.3 DSC heating curves for LDPE/Wax 2 blends

In the case of Wax 1 blends, the enthalpy increases with increasing wax content, and since enthalpy is proportional to crystallinity, this also indicates an increase in crystallinity of the material. Since the wax is more crystalline than LDPE ($\Delta H = 214.5 \text{ J g}^{-1}$ for Wax 1 and $\Delta H = 55 \text{ J g}^{-1}$ for LDPE, and I assume that 100 % crystalline wax and LDPE have the same melting enthalpies, since they have the same chemical structure), this observation can be expected. The peak temperature of melting slightly increases with increasing wax content, possibly indicating a small increase in lamellar thickness (Figure 3.2).

The presence of Wax 2 slightly increases the enthalpy of its blends with LDPE (Figure 3.3, Table 3.1). This also indicates an increase in crystallinity of the material. This increase in crystallinity is less than that of LDPE/Wax 1 blends. The reason is that Wax 1 has a high melting point compared to Wax 2, and it is more crystalline. Increase in wax content slightly increases the peak temperature of melting up to 5 % wax content, after which the temperature remains fairly constant. This behaviour indicates a small increase in lamellar thickness. Higher wax contents, however, do not seem to have an observable influence on lamellar thickness during crystallization. For LDPE/Wax 3 blends the onset and peak temperatures of melting very slightly decrease, and the melting enthalpy observably decreases, as the Wax 3 content increases in the blends (Figure 3.4, Table 3.1). This behaviour indicates a decrease in

the crystallinity of the material. Since Wax 3 has a higher crystallinity than LDPE, the only possible reason is that Wax 3 does not co-crystallize with LDPE and inhibits LDPE crystallization by acting as a plasticizer.

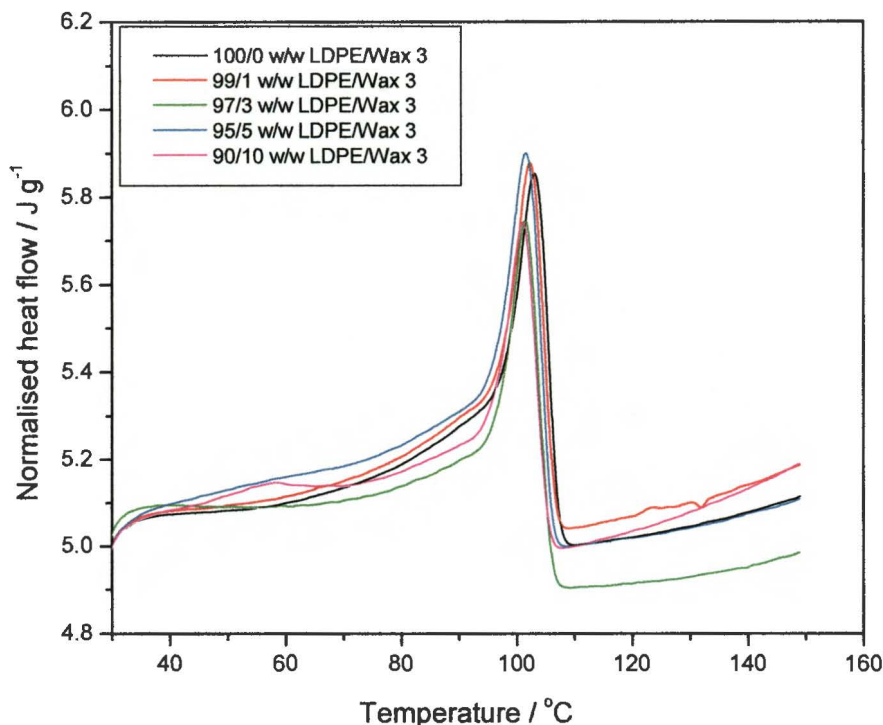


Figure 3.4 DSC heating curves for LDPE/Wax 3 blends

LLDPE/Wax 1 blends show one melting peak for the low wax content blends, but for the blends containing 5 and 10 % wax, the DSC curves show a second peak at the wax melting temperature (Figure 3.5). LLDPE and Wax 1 are therefore only partially miscible at higher wax contents. LLDPE and Wax 2 are miscible up to 3 % wax content. There is a clearly observable second peak at about 117 °C for the blends containing 5 and 10 % wax. LLDPE and Wax 2 are therefore only partially miscible at these wax contents. From the previous work by Luyt *et al* [33-38] it was clear that mechanically mixed LLDPE and Wax 2 interacted in a totally different way. DSC curves showed only one melting peak in the temperature range of LLDPE melting, even for blends containing up to 20% wax. The miscibility of LLDPE with paraffin wax is obviously affected by the mode of sample preparation. The LLDPE/Wax 3 blends show one peak, indicating miscibility of LLDPE and Wax 3, for the blends containing up to 5 % wax. For the 90/10 w/w LLDPE/Wax 3 blend, a second peak can be seen at a lower temperature of about 44 °C, indicating only partial

miscibility. Since the crystallization temperature of Wax 3 is much lower than that of LLDPE (29 °C compared to 110 °C), it is possible that at higher wax contents, some of the wax is forced out of the LLDPE crystallites during LLDPE crystallization. This wax will then crystallize in the amorphous part of LLDPE. On heating, these wax crystallites will then melt separately from the LLDPE/wax co-crystals.

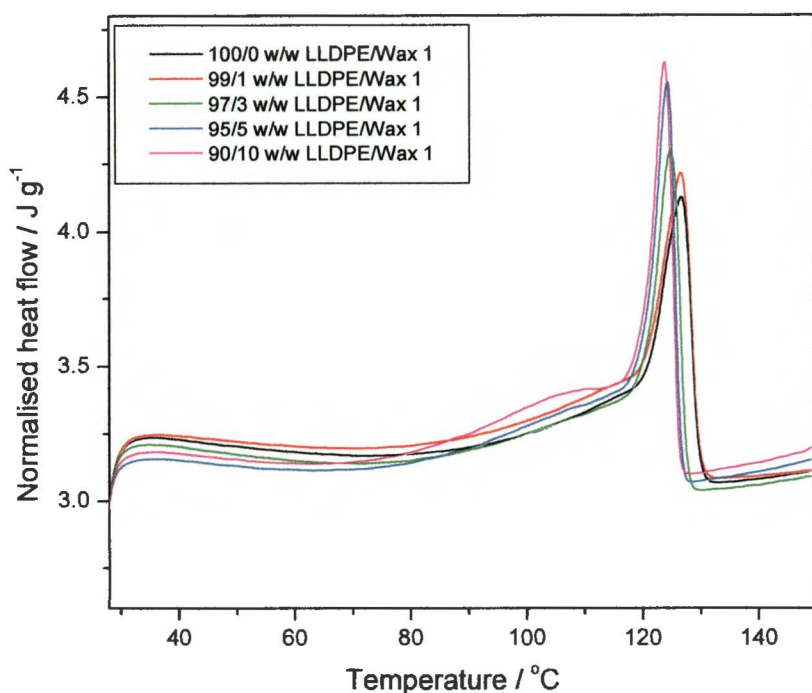


Figure 3.5 DSC heating curves for LLDPE/Wax 1 blends

The enthalpy of the LLDPE/Wax 1 blends increases with increasing wax content, indicating increasing crystallinity of the material (Table 3.1). This behaviour is expected, since Wax 1 has a higher melting enthalpy (and crystallinity, if it can be assumed that the LLDPE and wax have similar crystal structures) than LLDPE, which explains the increased enthalpy (crystallinity) of these blends. The Wax 1 chains probably co-crystallize with the linear sequences of the LLDPE chains, giving rise to improved crystallinity. The peak temperatures of melting slightly decrease as the wax content increases, suggesting a decrease in the average lamellar thickness. Decreasing of the blends' melting temperature shows that, despite increasing the crystallinity as wax content increases, the average lamellar thickness decreases. Co-crystallization of the wax with LLDPE somehow causes the blend to form thinner lamellae, although it causes a higher extent of crystallization. The Wax 2 content shows a fairly constant behaviour on the specific enthalpies of melting of LLDPE. This is

probably due to the specific enthalpy of Wax 2 and LLDPE melting being the same. There is very little change in the onset and peak temperatures of melting. The melting behaviour of the blends is similar to that of pure LLDPE. For the LLDPE/Wax 3 blends both the melting temperature and enthalpy show a decrease with increasing wax content. The decrease in the peak temperature of melting suggests a decrease in the average lamellar thickness (Figures 3.5-3.7).

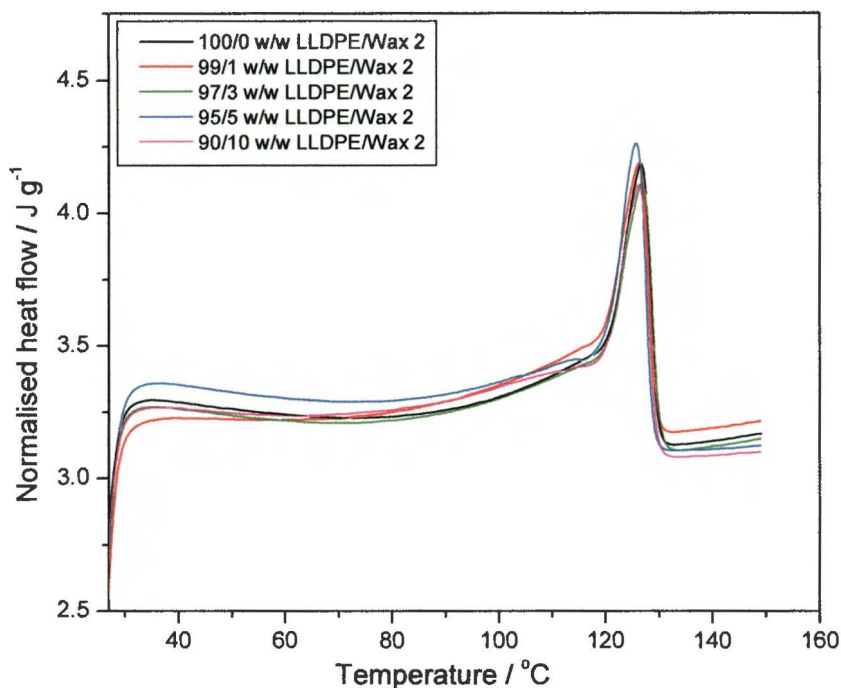


Figure 3.6 DSC heating curves for LLDPE/Wax 2 blends

The DSC cooling curves of the pure waxes are presented in Figure 3.8. Wax 1 shows cooling peak temperatures at 88.0 and 95.2 °C, Wax 2 at 65.1 °C and 90.2 °C (peak shoulder), and Wax 3 at 50.1 and 60.3 °C (peak shoulder).

The DSC cooling curves for LDPE and all its blends show a second exothermic peak at about 50 °C (Figures 3.9 – 3.11). Its intensity does not change with an increase in wax content. Its origin is probably in the LDPE structure [31].

In Figures 3.12 – 3.14 it can be seen that LLDPE with three different waxes have two exothermic peaks. Its intensity changes with an increase in wax content (in some cases it is only visible for higher wax contents), and it appears at different temperatures for the different waxes. This indicates that some of the wax, especially at higher wax contents, crystallizes separately from the LLDPE during controlled cooling of the samples.

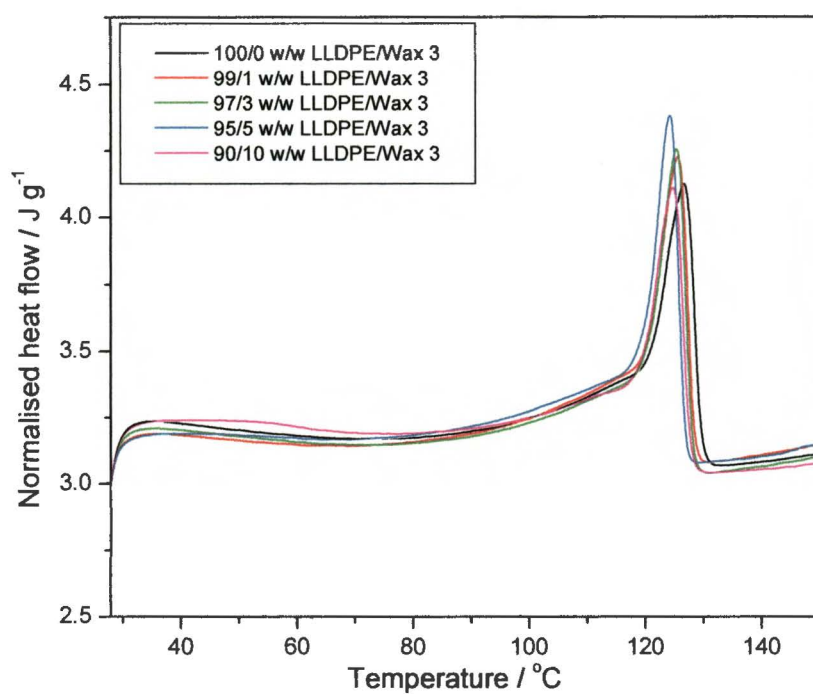


Figure 3.7 DSC heating curves for LLDPE/Wax 3 blends

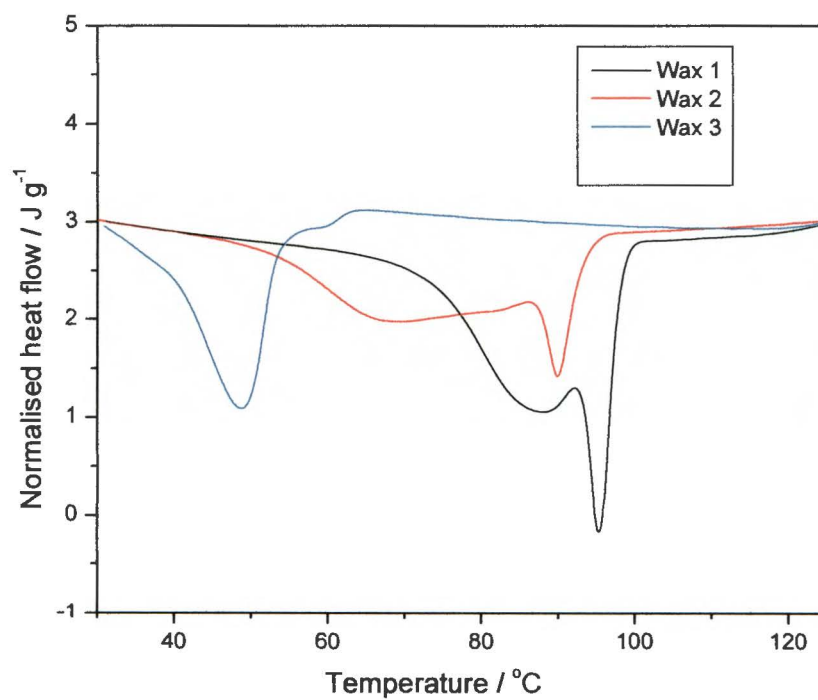


Figure 3.8 DSC cooling curves for waxes

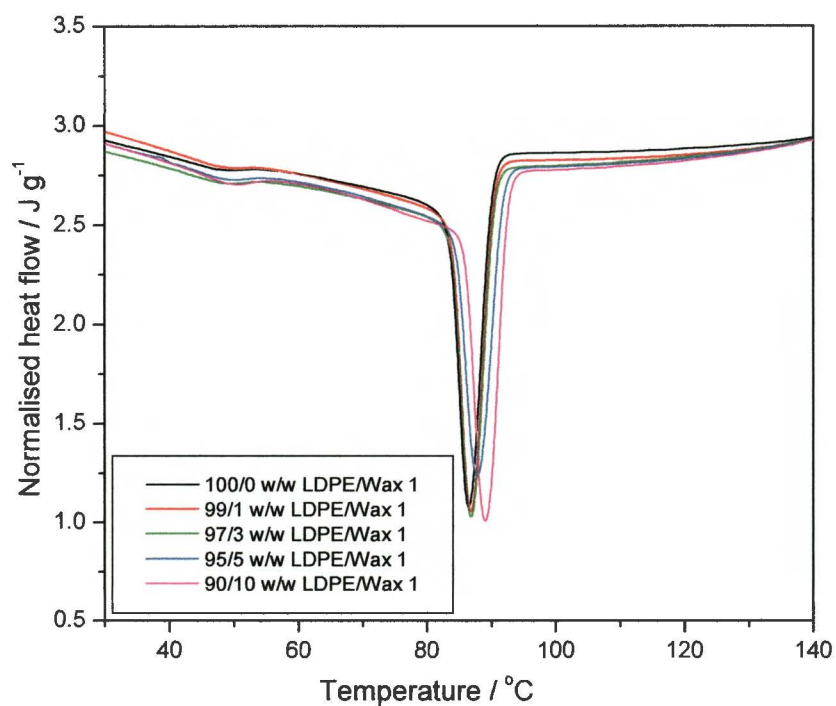


Figure 3.9 DSC cooling curves for LDPE/Wax 1 blends

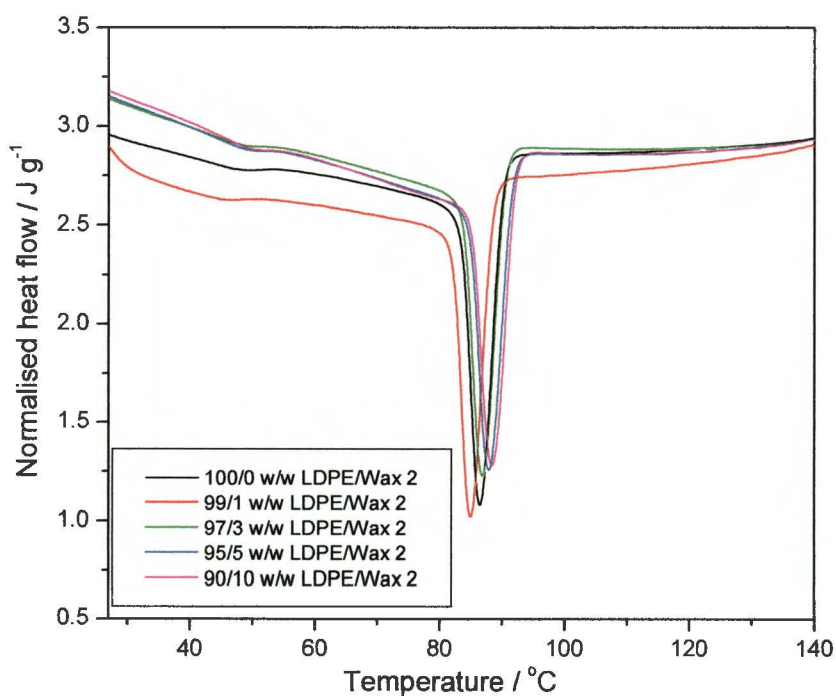


Figure 3.10 DSC cooling curves for LDPE/Wax 2 blends

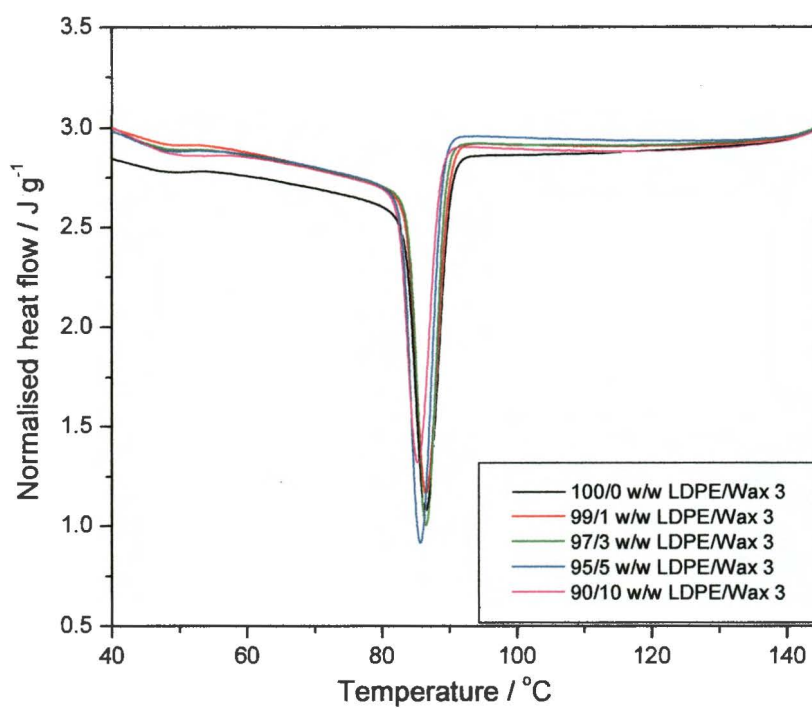


Figure 3.11 DSC cooling curves for LDPE/Wax 3 blends

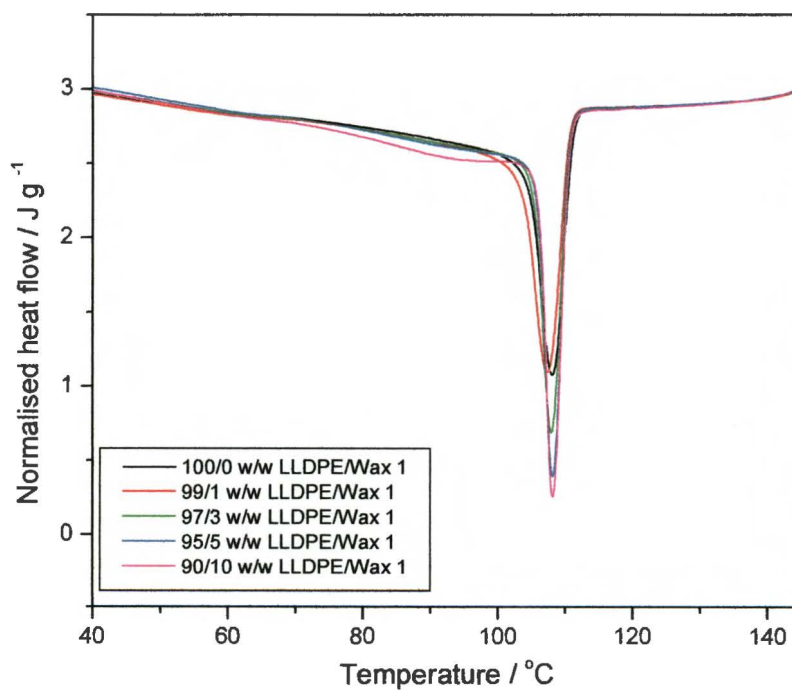


Figure 3.12 DSC cooling curves for LLDPE/Wax 1 blends

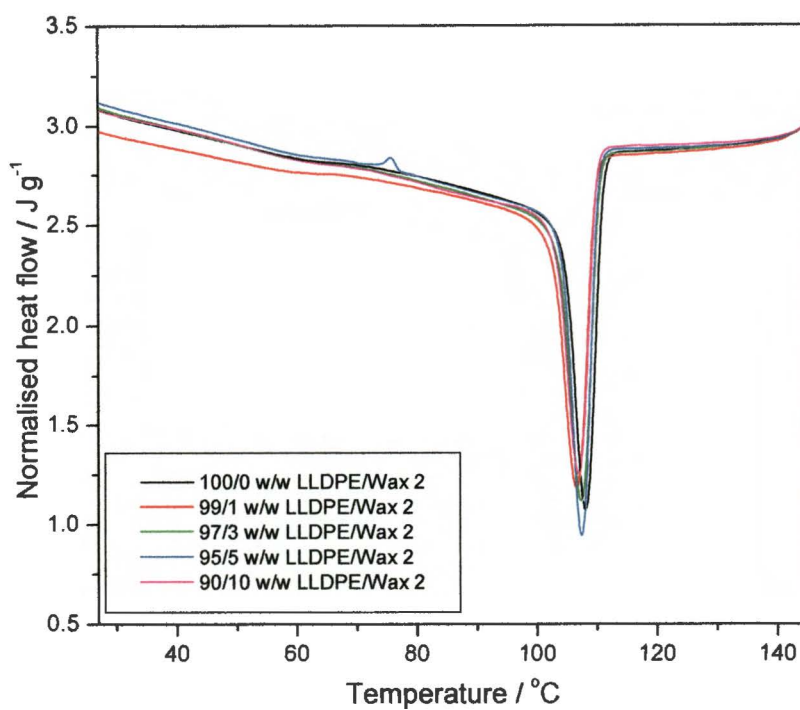


Figure 3.13 DSC cooling curves for LLDPE/Wax 2 blends

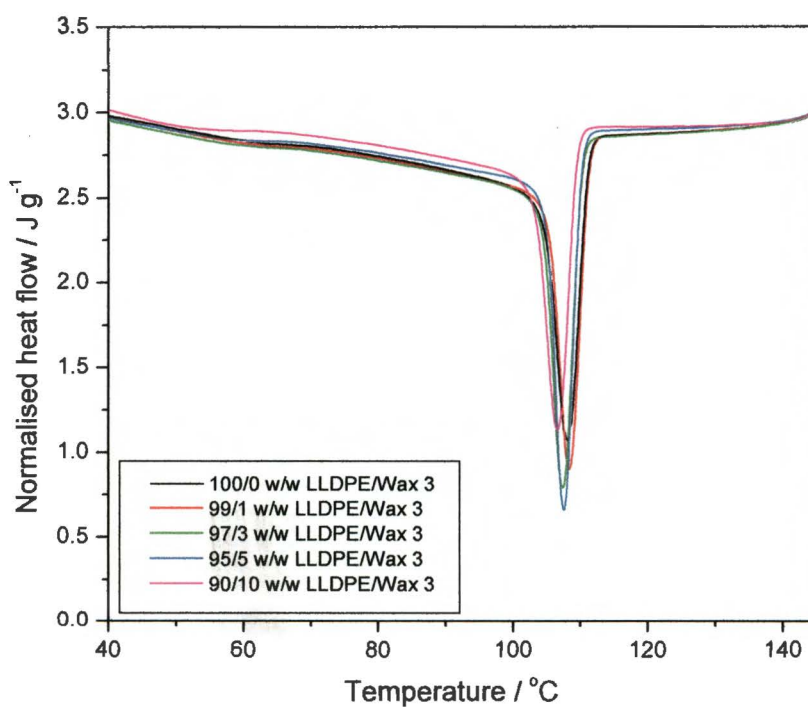


Figure 3.14 DSC cooling curves for LLDPE/Wax 3 blends

3.1.2 Thermogravimetric analysis (TGA)

Figure 3.15 shows the TGA and Figure 3.16 the DTGA curves of pure LDPE, pure Wax 1 and their blends, and the onset of decomposition temperatures are summarized in Table 3.2. It is clear that the wax starts decomposing at a much lower temperature than LDPE. It is, however, interesting that the presence of small amounts of wax improves the thermal stability of LDPE. The sample containing 1 % wax is the most stable, and the stability decreases with increasing wax content. Up to 10 % wax the stability, however, does not fall below that of pure LDPE. The more crystalline a polymer sample, the higher is its thermal stability. From Table 3.1 it is clear that the crystallinities of the samples substantially increase with increasing wax content. However, since wax itself is thermally less stable than LDPE, the two effects will balance out, and therefore the thermal stability does not generally increase with increasing wax content.

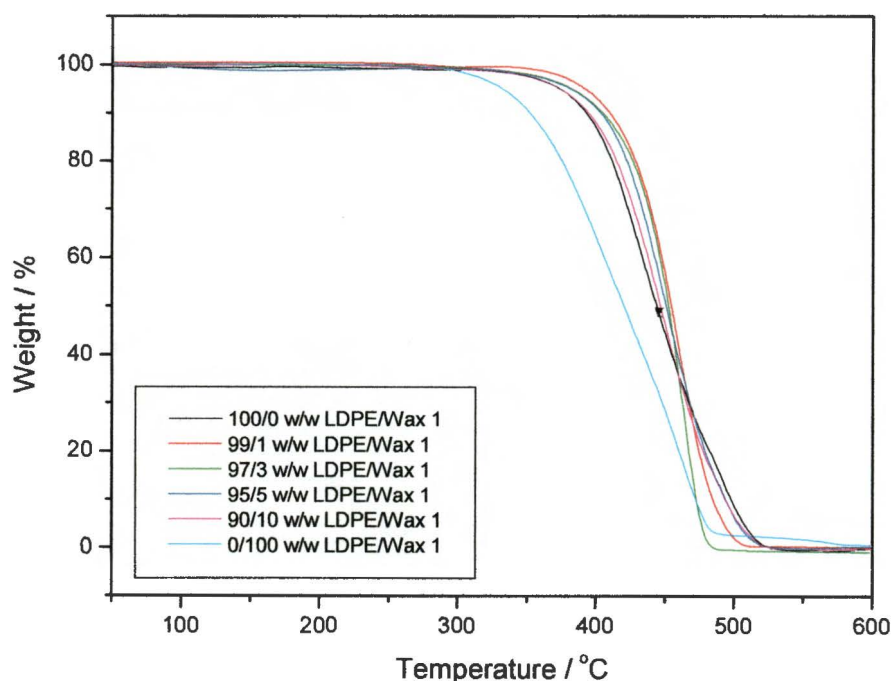


Figure 3.15 TGA curves for LDPE, Wax 1 and different LDPE/Wax 1 blends

Figure 3.17 shows the TGA and Figure 3.18 the DTGA curves of pure LDPE, pure Wax 2 and their blends. Wax 2 is clearly less thermally stable than LDPE, with almost a 90 °C difference between their respective onset temperatures of decomposition. The blends show a shift of the onset of decomposition to higher temperatures compared to the pure materials.

Since thermal degradation starts at weak bonds or chain ends, it is possible that the less thermally stable wax chains are somehow protected in the thicker PE lamellae. At the same time the wax chains improve the stability of the blend by increasing its crystallinity. The 99/1 w/w LDPE/Wax 2 sample, however, has a lower onset of decomposition temperature than pure LDPE. The reason for this behaviour is not clear.

Table 3.2 Onset temperatures of degradation of LDPE/wax and LLDPE/wax blends

Sample	T / °C	Sample	T / °C
LDPE/Wax 1		LLDPE/Wax 1	
100/0	391	100/0	482
99/1	423	99/1	474
97/3	423	97/3	481
95/5	409	95/5	397
90/10	403	90/10	355
0/100	347	0/100	347
LDPE/Wax 2		LLDPE/Wax 2	
99/1	348	99/1	417
97/3	398	97/3	429
95/5	419	95/5	431
90/10	421	90/10	420
0/100	300	0/100	300
LDPE/Wax 3		LLDPE/Wax 3	
99/1	425	99/1	371
97/3	423	97/3	398
95/5	418	95/5	422
90/10	364	90/10	400
0/100	299	0/100	299

Wax 3 is clearly much less thermally stable than LDPE, with almost a 91 °C difference between their respective onset temperatures of decomposition (Figures 3.19 and 3.20; Table 3.2). The blends have higher onset of decomposition temperatures compared to the pure materials, except for the 90/10 w/w blend. The temperatures of degradation increase for low Wax 3 content, despite lower thermal stability of the wax. In case of 1 wt % Wax 3, the thermal stability improved by more than 30 °C. This sample is the most stable, and the stability decreases with increasing wax content. For 10 % wax, however, the stability falls below that of pure LDPE. This is probably because Wax 3 has much shorter chains and is thermally less stable than LDPE.

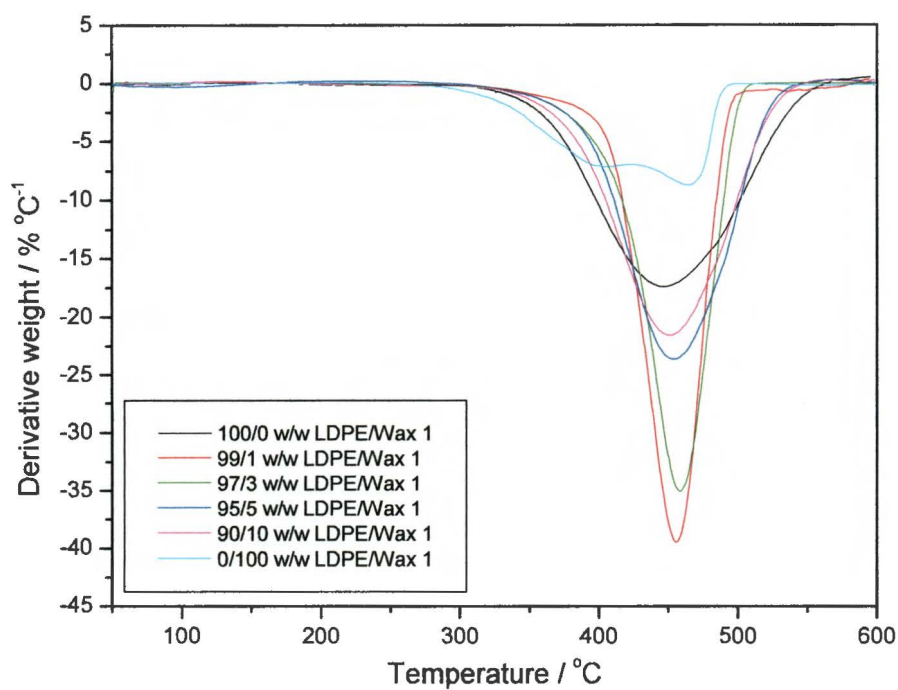


Figure 3.16 DTGA curves for LDPE, Wax 1 and different LDPE/Wax 1 blends

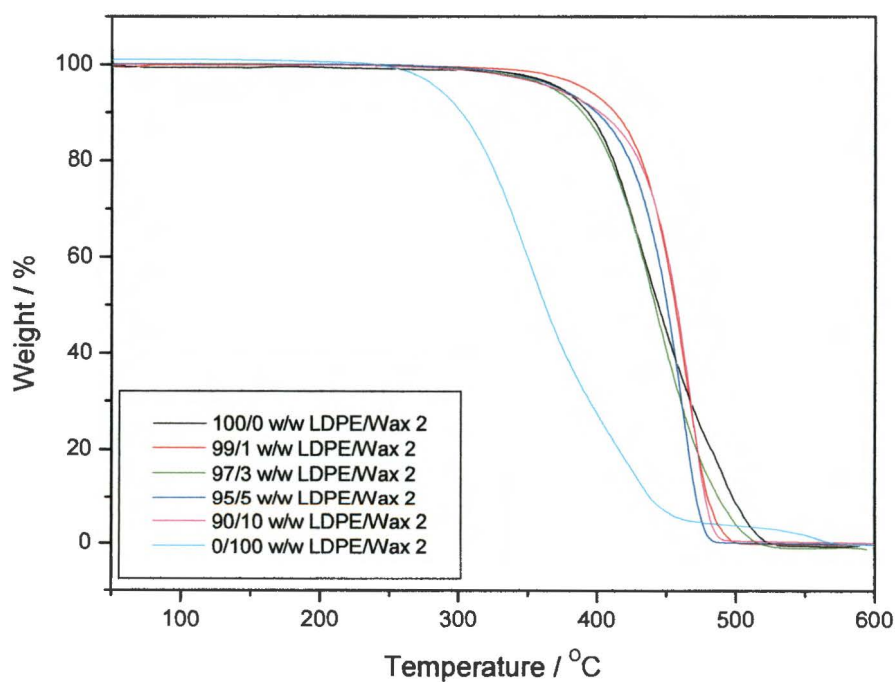


Figure 3.17 TGA curves for LDPE, Wax 2 and different LDPE/Wax 2 blends

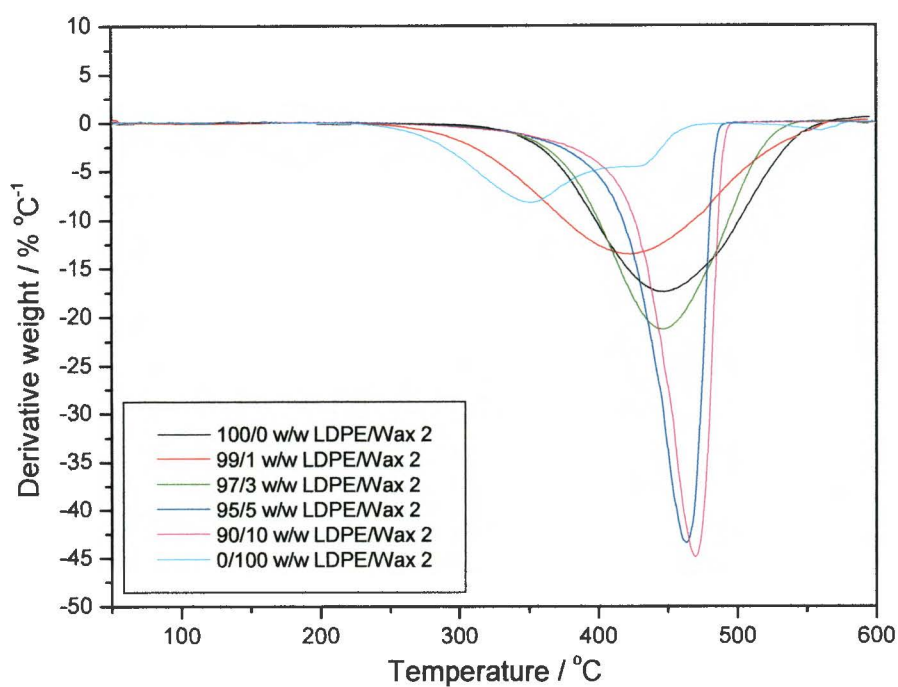


Figure 3.18 DTGA curves for LDPE, Wax 2 and different LDPE/Wax 2 blends

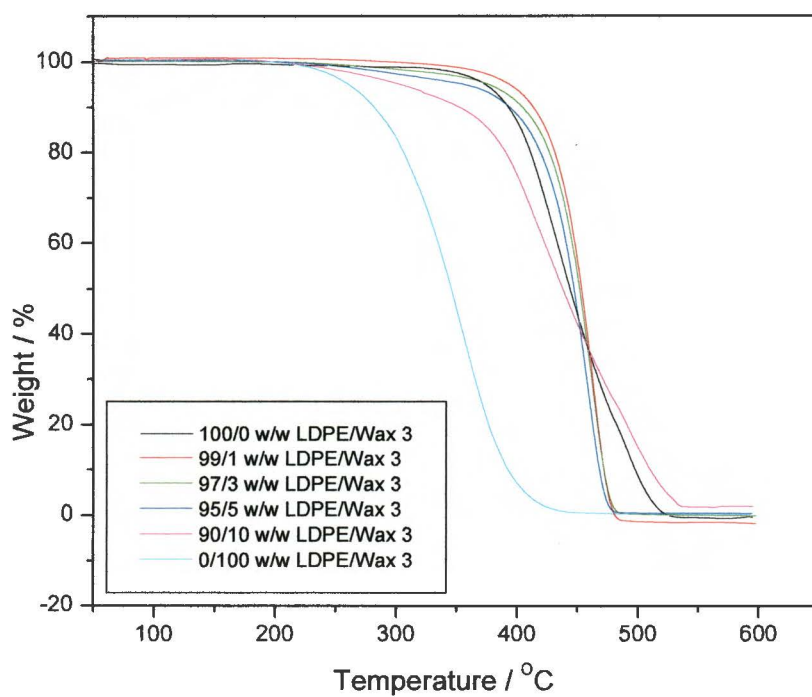


Figure 3.19 TGA curves for LDPE, Wax 3 and different LDPE/Wax 3 blends

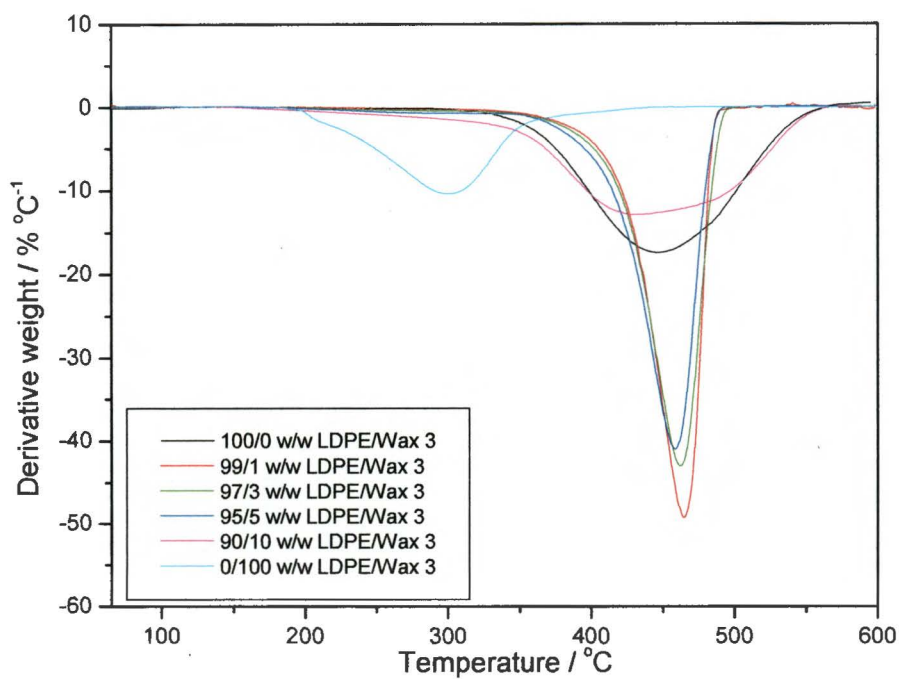


Figure 3.20 DTGA curves for LDPE, Wax 3 and different LDPE/Wax 3 blends

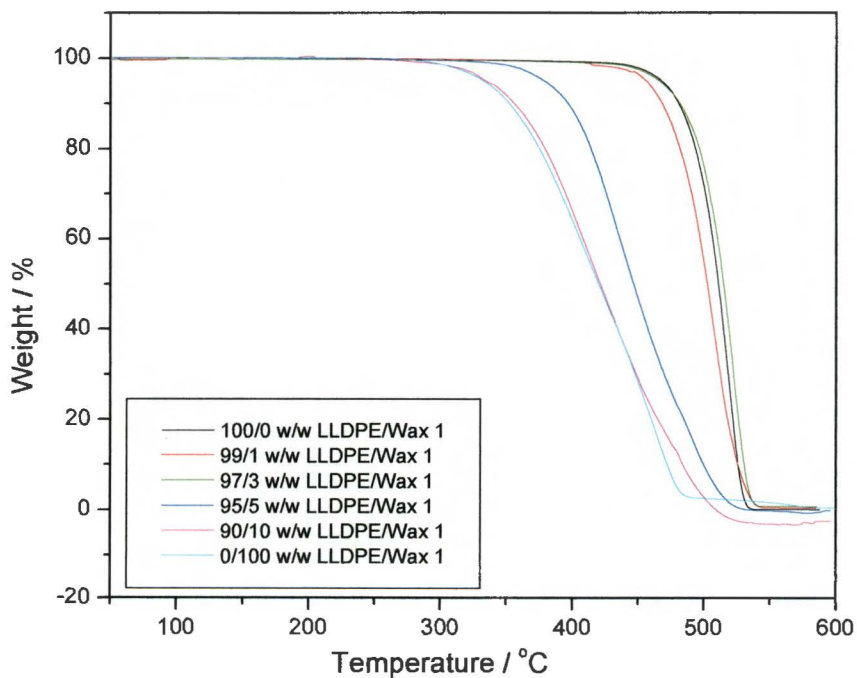


Figure 3.21 TGA curves of LLDPE, Wax 1 and different LLDPE/Wax 1 blends

The TGA curves of LLDPE/Wax 1 blends show a decrease in onset temperatures of decomposition with increasing wax content (Figure 3.21 and 3.22; Table 3.2). The values are somewhere between those of pure wax and pure LLDPE. Short chain fractions of the wax, as well as fragments formed by chain scission, will have sufficient energy to escape from the matrix at lower temperatures. Thus, introducing more of the low molecular weight material induces a gradual decrease in temperature at which decomposition starts. This is a logic consequence of lower stability of the wax (Figure 3.21).

Figures 3.23 and 3.24 show that the thermal stabilities of LLDPE/Wax 2 blends are between those of LLDPE and Wax 2, with no specific trend for the blends themselves. Wax 2 is clearly less thermally stable than LLDPE, with almost a 180 °C difference between their respective onset temperatures of decomposition. The possible presence of free wax chains in the amorphous phase induces deterioration of the thermal stability of the blends.

The TGA curves of LLDPE/Wax 3 blends show that their thermal stabilities fall between those of pure wax and pure LLDPE (Figures 3.25 and 3.26). Wax 3 is clearly less thermally stable than LLDPE, with an almost 182 °C difference between their respective onset temperatures of decomposition. A possible reason for the poor resistance of LLDPE/wax blends to thermal degradation is the low molecular weight of the wax.

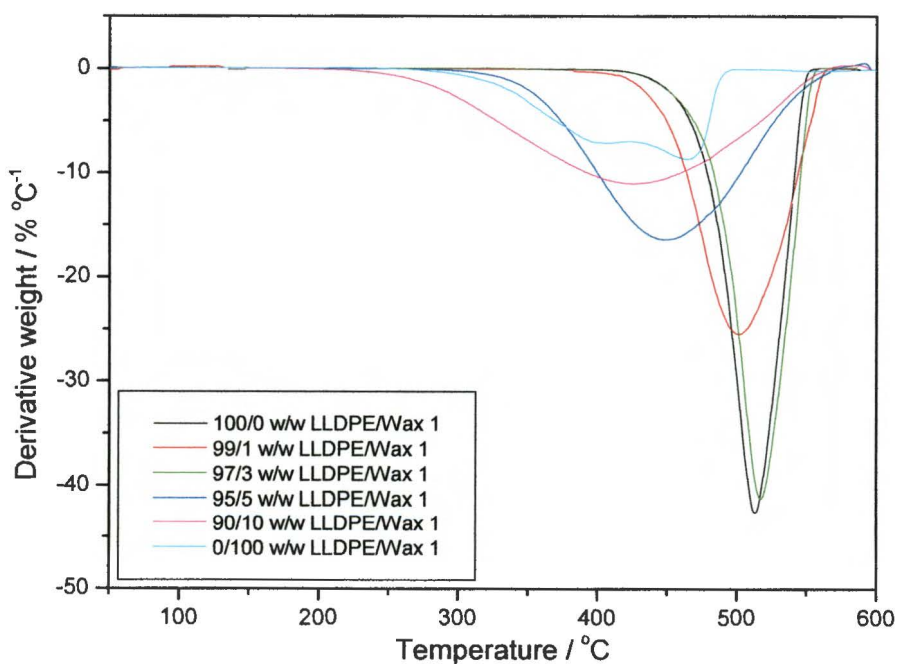


Figure 3.22 DTGA curves of LLDPE, Wax 1 and different LLDPE/Wax 1 blends

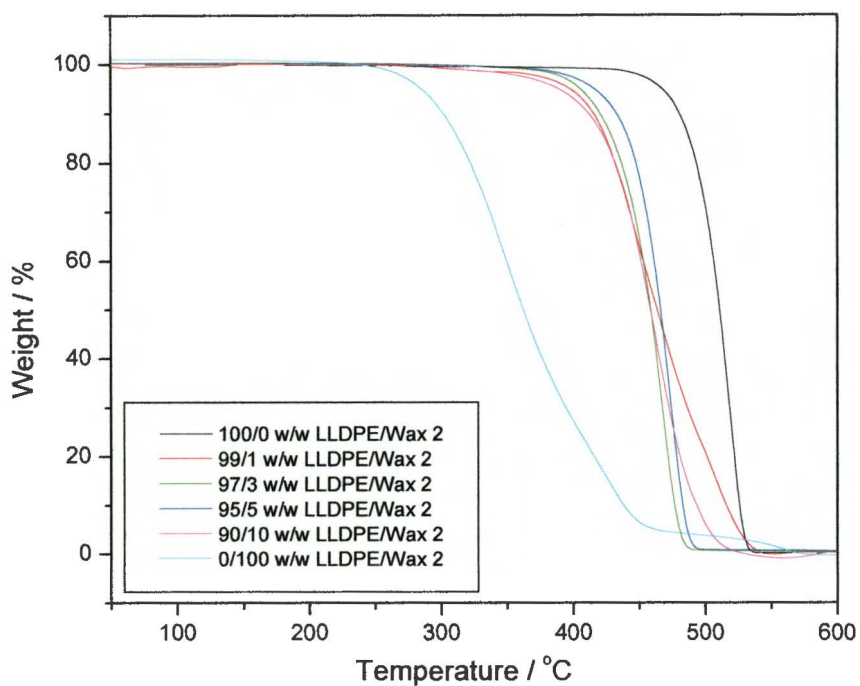


Figure 3.23 TGA curves of LLDPE, Wax 2 and different LLDPE/Wax 2 blends

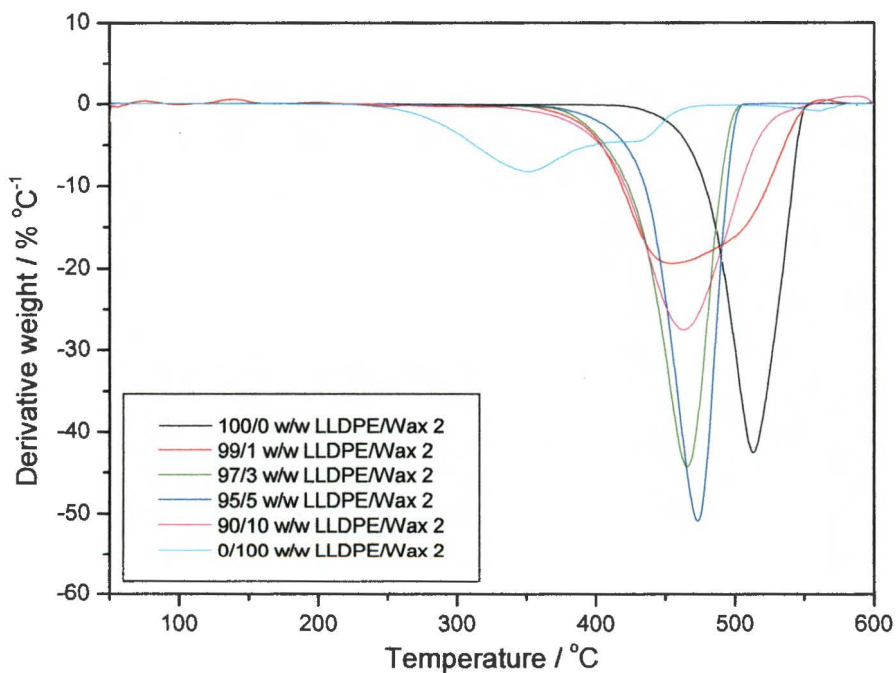


Figure 3.24 DTGA curves of LLDPE, Wax 2 and different LLDPE/Wax 2 blends

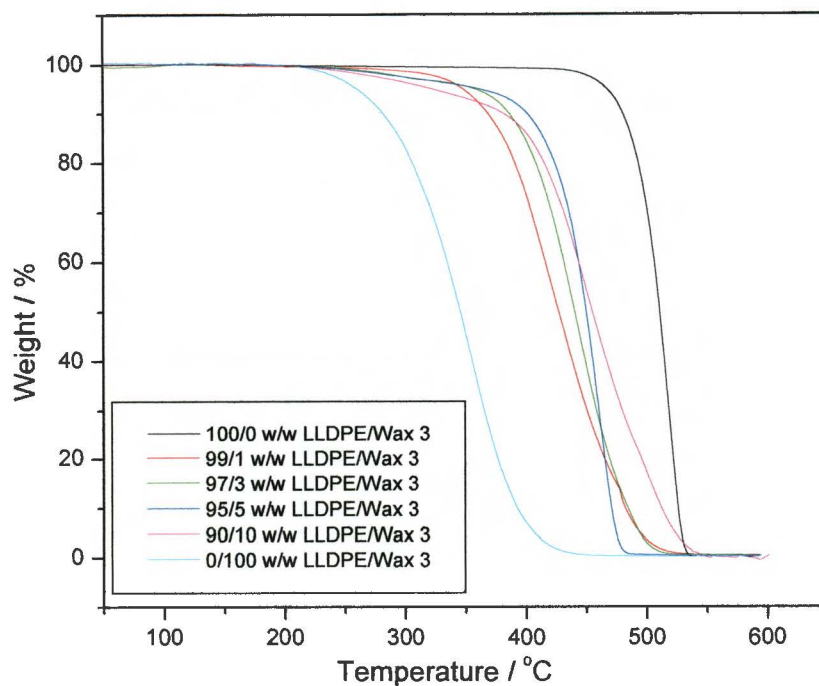


Figure 3.25 TGA curves of LLDPE, Wax 3 and different LLDPE/Wax 3 blends

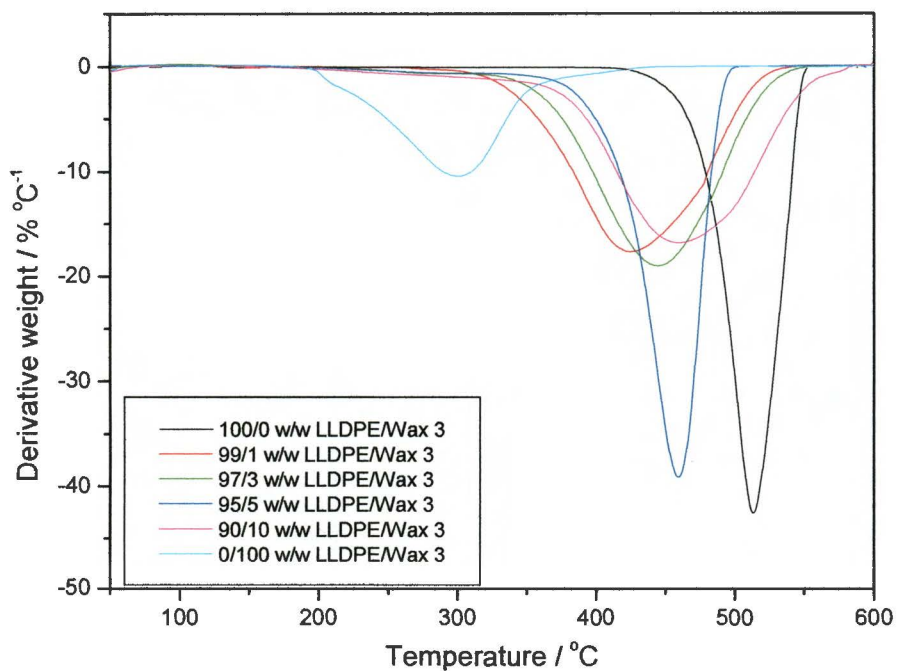


Figure 3.26 DTGA curves of LLDPE, Wax 3 and different LLDPE/Wax 3 blends

In all the LLDPE/wax blends there is a substantial difference in onset temperature of decomposition between that of pure LLDPE and that of the 99/1 w/w LLDPE/wax blend. This temperature increases with increasing wax content in the blend up to 95/5 w/w LLDPE/wax. For all three waxes the 90/10 w/w LLDPE/wax blend, however, shows a lower onset temperature of decomposition than the 95/5 w/w LLDPE/wax sample.

3.1.3 Melt flow index (MFI)

Table 3.3 shows the MFI values for the different polyethylene/wax blends, and these values are plotted in Figures 3.27 - 3.28 as function of wax content. For all the blends the flow rate increases with an increase in wax content. Since the MFI is an inverse measure of a material's viscosity, these results indicate that the presence of wax reduces the viscosity of the polyethylenes. Lower viscosity (higher flow rate) will improve the processability of polyethylene.

Table 3.3 MFI values of LDPE/wax and LLDPE/wax blends

Sample	FR(g min ⁻¹)	FR/FR _{PE}	Sample	FR(g min ⁻¹)	FR/FR _{PE}
LDPE/Wax 1			LLDPE/Wax 1		
100/0	5.19	1.00	100/0	0.20	1.00
99/1	5.74	1.10	99/1	0.21	1.08
97/3	5.81	1.12	97/3	0.22	1.16
95/5	8.13	1.57	95/5	0.24	1.22
90/10	10.87	2.09	90/10	0.29	1.49
LDPE/Wax 2			LLDPE/Wax 2		
99/1	6.42	1.24	99/1	0.21	1.07
97/3	7.07	1.36	97/3	0.22	1.14
95/5	8.86	1.71	95/5	0.24	1.25
90/10	13.45	2.59	90/10	0.30	1.55
LDPE/Wax 3			LLDPE/Wax 3		
99/1	6.69	1.29	99/1	0.21	1.08
97/3	8.01	1.54	97/3	0.23	1.16
95/5	8.94	1.72	95/5	0.25	1.28
90/10	12.43	2.39	90/10	0.32	1.62

All three waxes improve the flow rate of LDPE (Figures 3.27). Wax 3 has the largest influence on the MFI of LDPE at lower contents, while Wax 2 has a larger influence at higher wax contents. Wax 1 is inferior to both Wax 2 and Wax 3 in improving the melt flow properties. Low melt-flow rates are associated with higher molecular weights, while higher melt-flow rates indicate a lower average molecular weight. Wax 1 is inferior because of its higher molecular weight, followed by Wax 2. Wax 3 has the lowest molecular weight, which is why it has the strongest influence on the flow properties of LDPE. It was not possible to determine the MFI of the waxes with the available equipment, because their MFI is too high at the analysis temperature.

LLDPE/wax blends have higher MFI values than pure LLDPE (Figures 3.28). All waxes have a similar influence on the MFI of LLDPE at lower contents, while Wax 3 has the largest influence at higher wax contents, followed by Wax 2 and then Wax 1. LLDPE has a higher molecular weight than LDPE. This will lead to a lower flow rate. Wax 1, which was developed to improve processability, is inferior to both Wax 2 and Wax 3 in improving the melt flow properties.

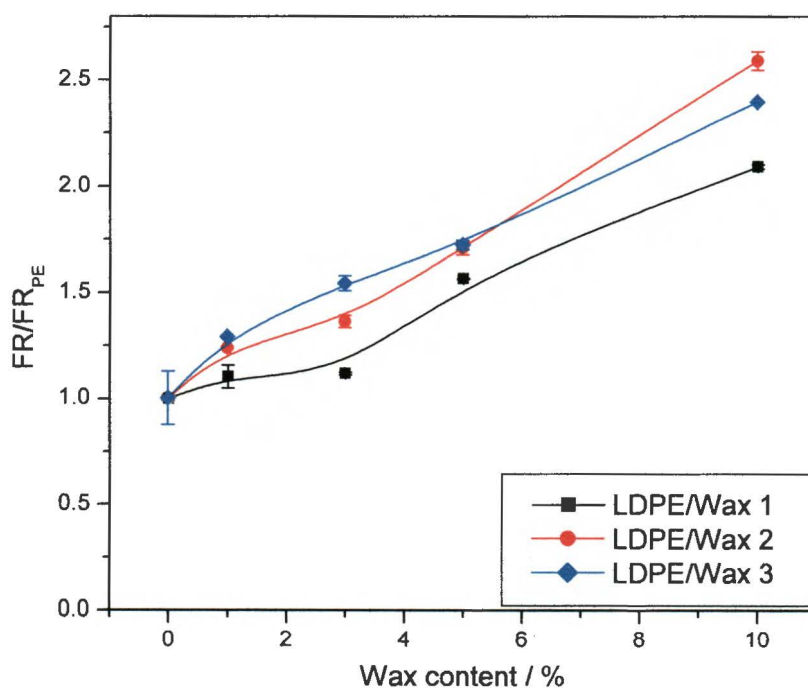


Figure 3.27 Melt flow rates, calculated as a ratio to that of pure LDPE, of LDPE blended with three different types of wax

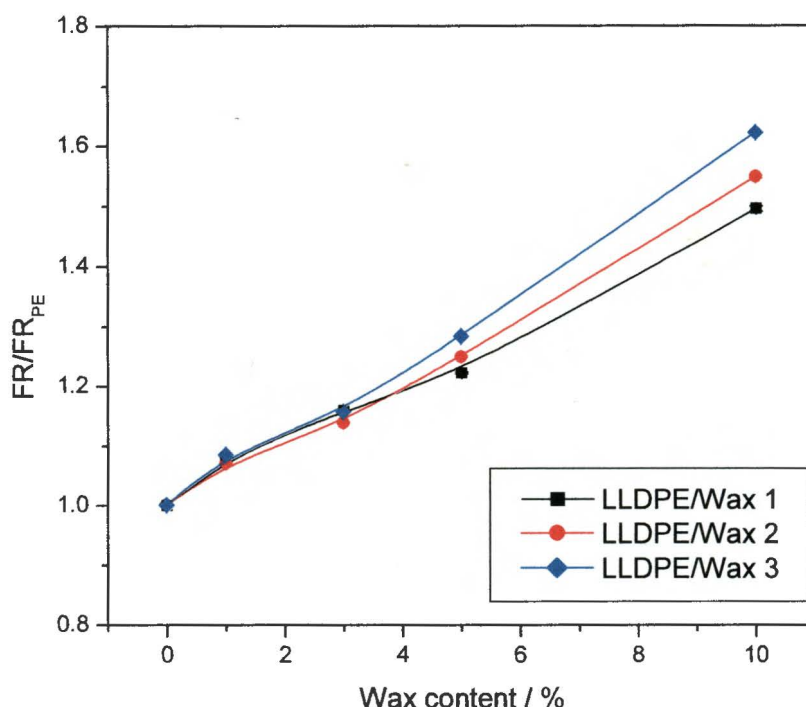


Figure 3.28 Melt flow rates, calculated as a ratio to that of pure LLDPE, of LLDPE blended with three different types of wax

3.2 Tensile properties

The tensile properties of the different PE/wax blends are summarized in Table 3.4, and changes in these properties are illustrated in Figures 3.29 – 3.38. For both LDPE and LLDPE the yield stress slightly increases with increasing wax content in the blends (Figures 3.28 and 3.30). This behaviour is expected, since wax increases the crystallinity of the blend (see DSC results), and yield stress depends on crystallinity. This is in line with results obtained by Mtshali *et al* [38]. Changes in the yield stress with increasing wax content are within experimental uncertainty, and in agreement with small changes in melting enthalpies as shown in Table 3.1. Wax 1 has a higher enthalpy (crystallinity) than Wax 2, and so do its blends, and this is reflected in the differences in yield stress between LDPE/Wax 1 and LDPE/Wax 2 blends. The increase in yield stress in the case of LDPE/Wax 3 blends is, however, not in line with the decrease in enthalpy (crystallinity) of these blends with increasing wax content. A possible reason for this is the probable crystallization of Wax 3 in the amorphous part of LDPE, and the influence of such crystallites on the chain mobility.

The three waxes had a similar influence on the yield stress of LLDPE as was the case with LDPE. In the case of Wax 1 and Wax 2, the improvement in yield stress can also be linked to changes in blend crystallinity. Again there is no correlation between decreasing crystallinity (melting enthalpy) and increasing yield stress in the case of LLDPE/Wax 3 blends. In this case a possible reason is also the formation of wax crystals in the amorphous phase which may influence the chain mobility.

An increase in wax content causes a decrease in elongation at yield for all the LDPE/wax and LLDPE/wax blends (Figures 3.31 and 3.32). The decrease is more pronounced in the case of Wax 3 blends. Elongation at yield is the onset of strain value at which plastic deformation takes place i.e. the material starts to flow. This decrease is the result of a decrease in amorphous content with increasing wax content. This will lead to the decrease of the strain at which the plastic deformation starts. The reason that the wax content gives low elongation at yield values is related to (i) an increase in crystallinity or (ii) wax crystallization in the amorphous phase, both of which reduces chain mobility. In the case of LLDPE, Wax 1 and Wax 2 have the same influence on the elongation at yield, while Wax 3 much more reduces this property as function of wax content.

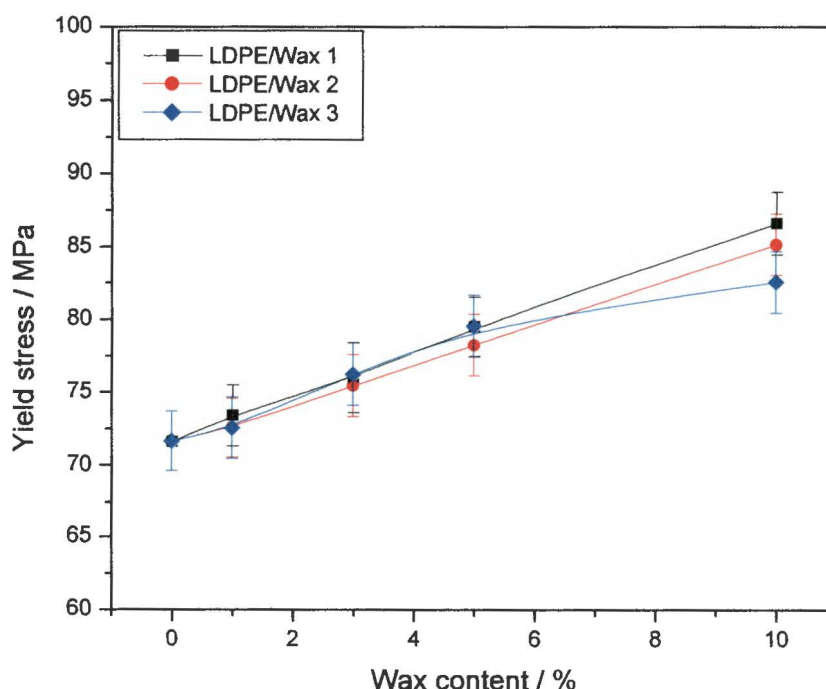


Figure 3.29 Yield stress as function of wax content for LDPE/wax blends

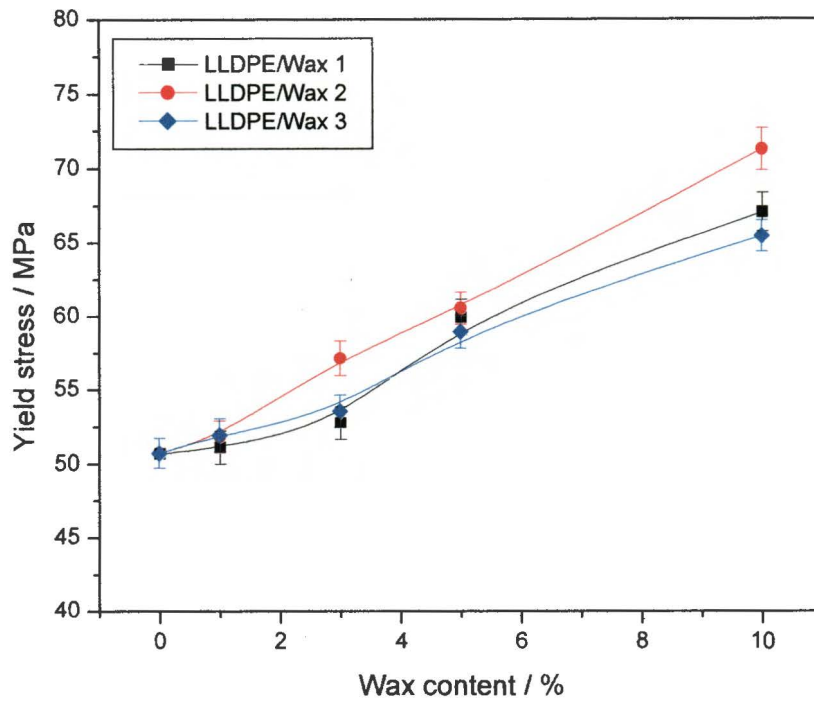


Figure 3.30 Yield stress as function of wax content for LLDPE/wax blends

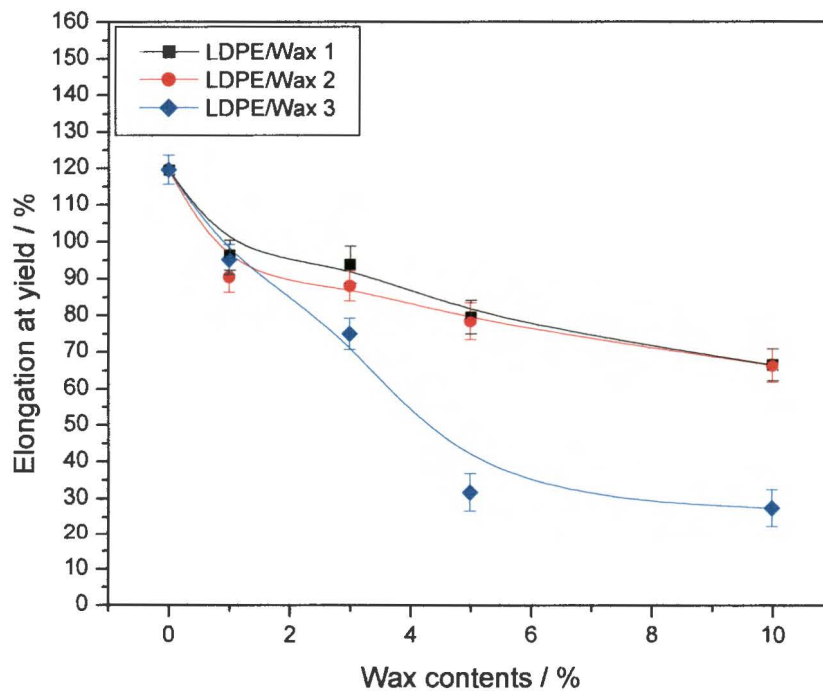


Figure 3.31 Elongation at yield as function of wax content for LDPE/wax blends

Table 3.4 Mechanical properties of LDPE/wax and LLDPE/wax blends

Sample	$\sigma_y \pm S\sigma_y /$ MPa	$\varepsilon_y \pm S\varepsilon_y /$ %	$\varepsilon_b \pm S\varepsilon_b /$ %	$\sigma_b \pm S\sigma_b /$ MPa	$E \pm S_E /$ MPa
LDPE/Wax 1					
100/0	71.6 \pm 2.1	119.4 \pm 4.0	272.8 \pm 14.5	78.8 \pm 1.6	748.6 \pm 19.4
99/1	73.4 \pm 2.1	96.3 \pm 4.1	225.0 \pm 14.2	74.4 \pm 1.2	746.4 \pm 18.2
97/3	76.0 \pm 2.4	93.8 \pm 5.0	165.0 \pm 14.4	72.3 \pm 1.5	732 \pm 17.9
95/5	79.5 \pm 2.1	79.5 \pm 4.6	156.3 \pm 14.2	70.3 \pm 1.6	816 \pm 17.6
90/10	86.6 \pm 2.2	66.5 \pm 4.3	145.0 \pm 14.3	66.8 \pm 1.5	898.8 \pm 17.9
LDPE/Wax 2					
99/1	72.5 \pm 2.1	90.2 \pm 4.2	223.8 \pm 14.2	65.4 \pm 1.6	616.2 \pm 16.0
97/3	75.4 \pm 2.1	87.8 \pm 4.1	191.3 \pm 14.0	64.8 \pm 1.9	702.0 \pm 18.6
95/5	78.2 \pm 2.1	78.2 \pm 5.1	119.2 \pm 14.0	63.7 \pm 1.5	735.0 \pm 18.8
90/10	85.1 \pm 2.1	66.2 \pm 4.6	107.2 \pm 14.1	60.2 \pm 1.7	933.8 \pm 18.0
LDPE/Wax 3					
99/1	72.5 \pm 2.1	95.0 \pm 4.1	220.0 \pm 13.8	73.9 \pm 1.4	678.2 \pm 19.8
97/3	76.2 \pm 2.2	74.8 \pm 4.3	162.8 \pm 14.5	70.8 \pm 1.6	808.8 \pm 17.0
95/5	79.5 \pm 2.1	31.5 \pm 5.0	116.7 \pm 15.0	67.8 \pm 1.5	833.4 \pm 18.1
90/10	82.5 \pm 2.2	27.3 \pm 5.0	86.3 \pm 15.0	64.8 \pm 1.6	866.8 \pm 16.1
LLDPE/Wax 1					
100/0	50.7 \pm 1.0	25.0 \pm 0.6	1029 \pm 25.0	141.7 \pm 6.3	454.2 \pm 38.4
99/1	51.1 \pm 1.1	24.2 \pm 0.5	904 \pm 24.5	110.5 \pm 5.9	617.0 \pm 30.6
97/3	52.8 \pm 1.1	24.0 \pm 0.5	863 \pm 24.8	86.7 \pm 6.0	620.0 \pm 35.0
95/5	59.9 \pm 1.2	21.9 \pm 0.5	829 \pm 24.6	83.9 \pm 6.1	695.0 \pm 29.8
90/10	67.1 \pm 1.3	19.8 \pm 0.6	810 \pm 25.4	82.0 \pm 5.8	808.8 \pm 28.5
LLDPE/Wax 2					
99/1	51.8 \pm 1.1	25.0 \pm 0.5	1017 \pm 25.3	122.3 \pm 5.4	460.0 \pm 24.6
97/3	57.1 \pm 1.2	24.0 \pm 0.6	954 \pm 25.4	120.6 \pm 6.2	556.8 \pm 25.0
95/5	60.5 \pm 1.1	23.0 \pm 0.5	933 \pm 25.1	115.6 \pm 6.0	696.8 \pm 24.5
90/10	71.2 \pm 1.4	21.0 \pm 0.4	896 \pm 24.9	106.7 \pm 6.1	757.8 \pm 24.1
LLDPE/Wax 3					
99/1	51.9 \pm 1.1	23.3 \pm 0.4	1021 \pm 24.8	127.4 \pm 5.9	562.4 \pm 35.0
97/3	53.5 \pm 1.1	23.0 \pm 0.4	996 \pm 24.6	122.1 \pm 6.0	569.2 \pm 36.6
95/5	58.9 \pm 1.1	21.0 \pm 0.5	950 \pm 25.0	114.7 \pm 5.8	549.6 \pm 35.0
90/10	65.4 \pm 1.1	18.0 \pm 0.4	917 \pm 25.3	99.2 \pm 6.1	603.6 \pm 35.0

σ_y , ε_y , ε_b , σ_b , E are yield stress, elongation at yield, elongation at break, stress at break and Young's modulus – $S\sigma_y$, $S\varepsilon_y$, $S\varepsilon_b$, $S\sigma_b$ and S_E are their standard deviations

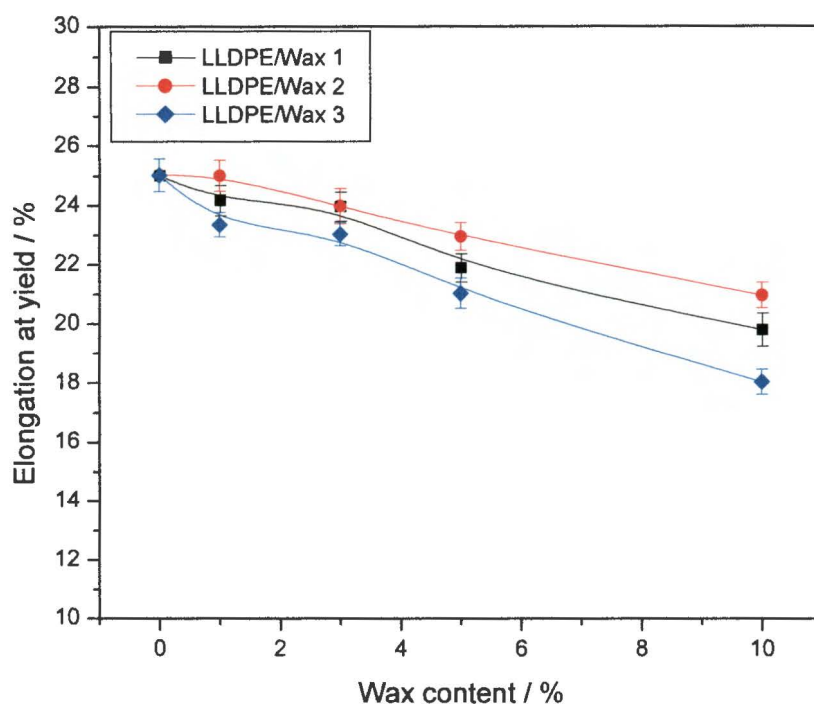


Figure 3.32 Elongation at yield as function of wax content for LLDPE/wax blends

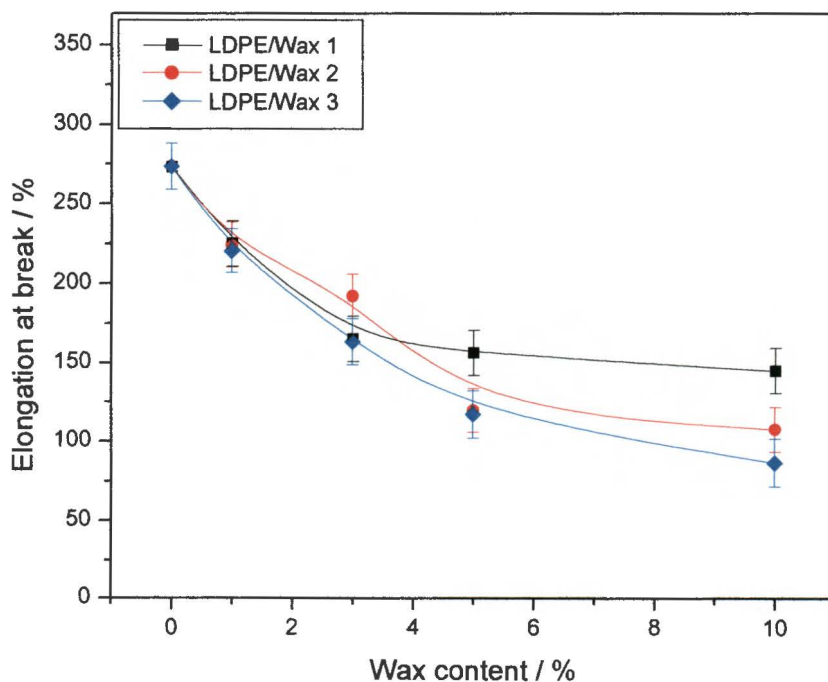


Figure 3.33 Elongation at break as function of wax content for LDPE/wax blends

Elongation at break of LDPE decreases with increasing wax content (Figure 3.33). Up to 3 wt % wax, all three waxes have a similar influence on the elongation at break. At higher wax contents, Wax 3 reduces the elongation at break more than Wax 2, and Wax 2 more than Wax 1. Pure LDPE has enough space and time to orientate when force is applied to the polymer chains. When chains are oriented, they start to form orientation crystallinity, which increases the sample strength. 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. All three waxes reduce the elongation at break of LLDPE, but to a much smaller extent than in the case of LDPE. Wax 1 has a much larger influence than the other two waxes. A probable reason is the co-crystallization of Wax 1 with LLDPE [39], reducing the number and length of tie chains between LLDPE lamellae [36].

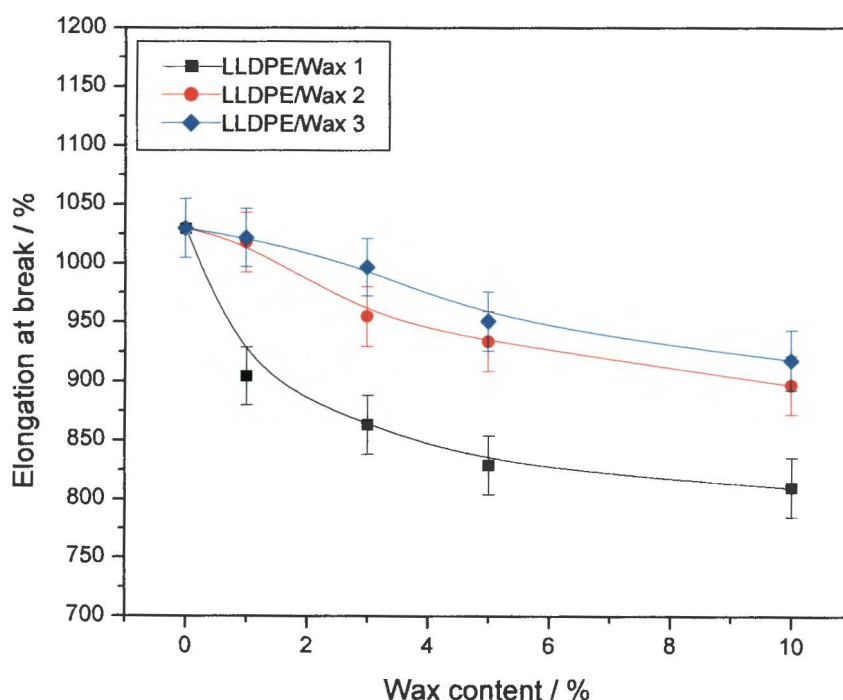


Figure 3.34 Elongation at break as function of wax content for LLDPE/wax blends

Stress at break decreases with increasing wax content for both LDPE/wax and LLDPE/wax blends (Figures 3.35 and 3.36). The influence is much more pronounced in the case of LLDPE. The reason for this is probably that the wax preferably co-crystallizes with LLDPE, having a substantial influence on its tie chain concentration, while the wax preferably crystallizes in the amorphous part of LDPE, having much less influence on its tie chain concentration. In the case of LDPE, Wax 2 has the largest influence, followed by Wax 3 and then Wax 1. In the case of LLDPE, Wax 2 and Wax 3 have a similar influence, while Wax 1 much more strongly reduces the stress at break. For the material to break, many of the tie-molecules should be tightly stretched, and the tightly stretched tie-molecules should be drawn out of the lamellae. During stretching of the blends less force is needed to draw out the stretched tie-molecules from the lamellae. If wax co-crystallizes with the polymer, the number of tie chains is reduced, because wax chains are too short to form tie chains [36]. A reduction in the number of tie chains reduces the ultimate strength of the polymer.

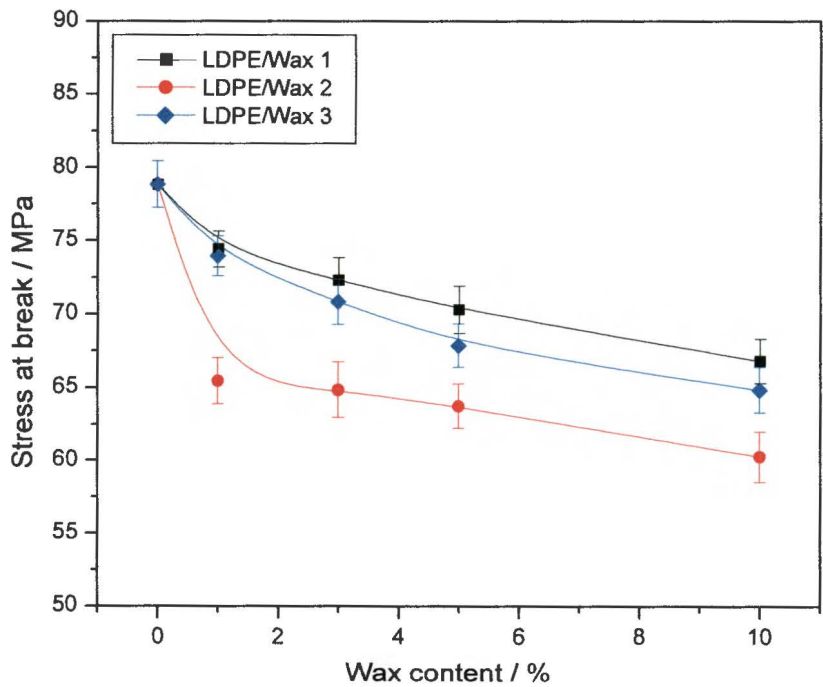


Figure 3.35 Stress at break as function of wax content for LDPE/wax blends

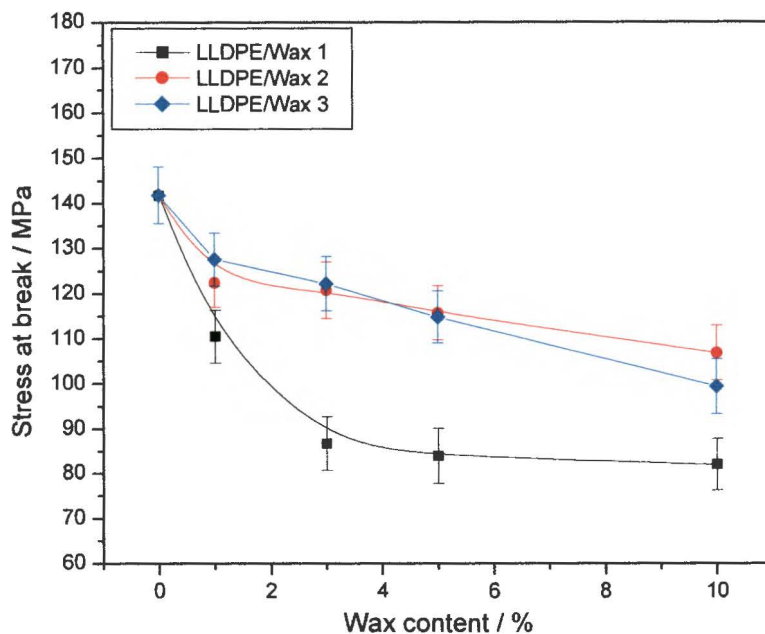


Figure 3.36 Stress at break as function of wax content for LLDPE/wax blends

For both LDPE and LLDPE, Young's modulus increases as the wax content increases (Figures 3.37 and 3.38). This behaviour is expected, since Young's modulus depends on crystallinity, which increases with increasing wax content. Young's modulus depends on the 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 (crystallized in the amorphous phase of the polymer) and polyethylene chains affects the transfer of energy to the crystalline phase, and is responsible for the increase in stiffness of the blends. The three waxes have a similar influence on Young's modulus in the case of LDPE (although the values tend to become constant at higher Wax 3 contents), while Wax 1 and Wax 2 have a much greater influence than Wax 3 in the case of LLDPE, especially at higher wax contents. The influence of Wax 3 is also restricted to very low wax contents – Young's modulus remained fairly constant at wax contents higher than 1 %. The increase in modulus is the result of increasing crystallinity (see DSC results). Since the crystallinity does not increase with increasing wax content for LDPE/Wax 3 and LLDPE/Wax 3 blends, the smaller influence of Wax 3 on Young's modulus can be understood.

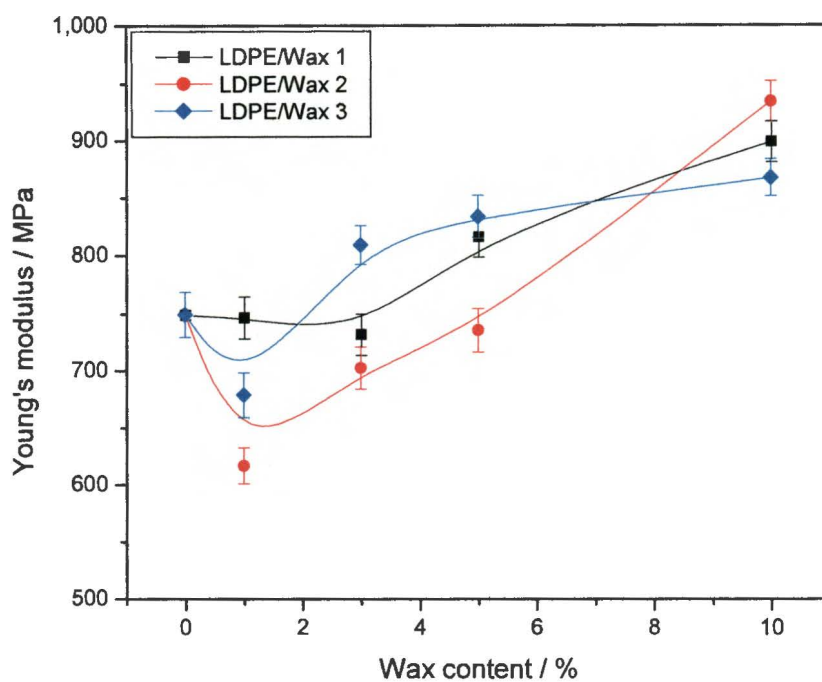


Figure 3.37 Young's modulus as function of wax content for LDPE/wax blends

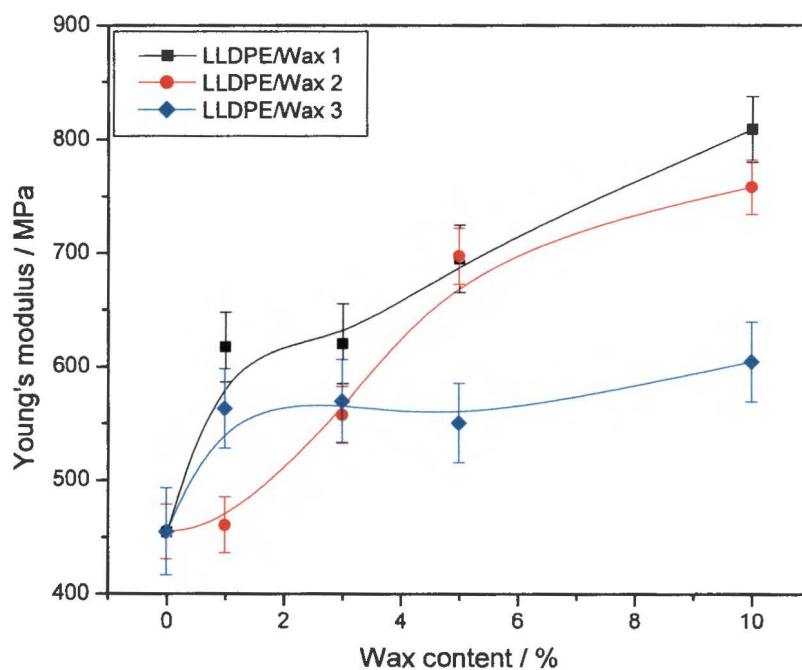


Figure 3.38 Young's modulus as function of wax content for LLDPE/wax blends

3.3 Surface free energy

The surface free energy results for LDPE/wax and LLDPE/wax blends are summarized in Table 3.5. The LDPE/Wax 1 blends show a decrease in the polar component of the surface free energy, while both the total surface free energy and its disperse part increase with increasing wax content (Figures 3.39 – 3.41). The DSC results showed that LDPE/Wax 1 blends are miscible for all wax contents, and therefore an increase in the polar part of the surface free energy should be expected. The polar component remains constant with increasing wax content in LDPE/Wax 2 blends. The total surface free energy decreases and the dispersed part increases with increasing Wax 2 content in the blend. The DSC results showed that the LDPE/Wax 2 blends are not fully miscible at higher wax contents, and this may be the reason for the polar part of the surface free energy remaining fairly constant. The LDPE/Wax 3 blends show a decrease in the polar part, an increase in the disperse part, and a fairly constant total surface free energy with increasing wax content. As in the case of Wax 2, the blends are only partially miscible at higher wax contents, and this observation is in line with the findings of Krump *et al* [32].

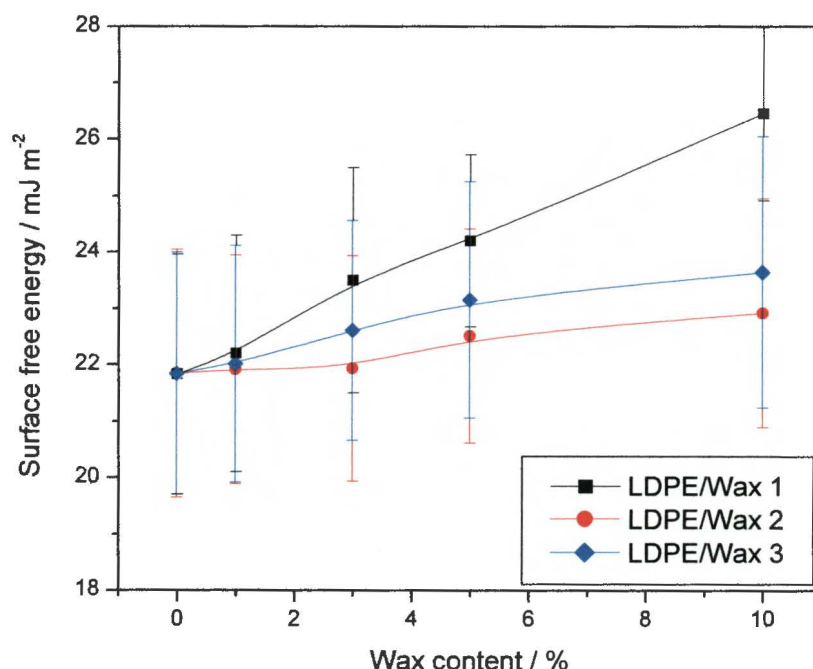


Figure 3.39 Comparison of the disperse parts of the surface free energy of LDPE blended with three different types of wax

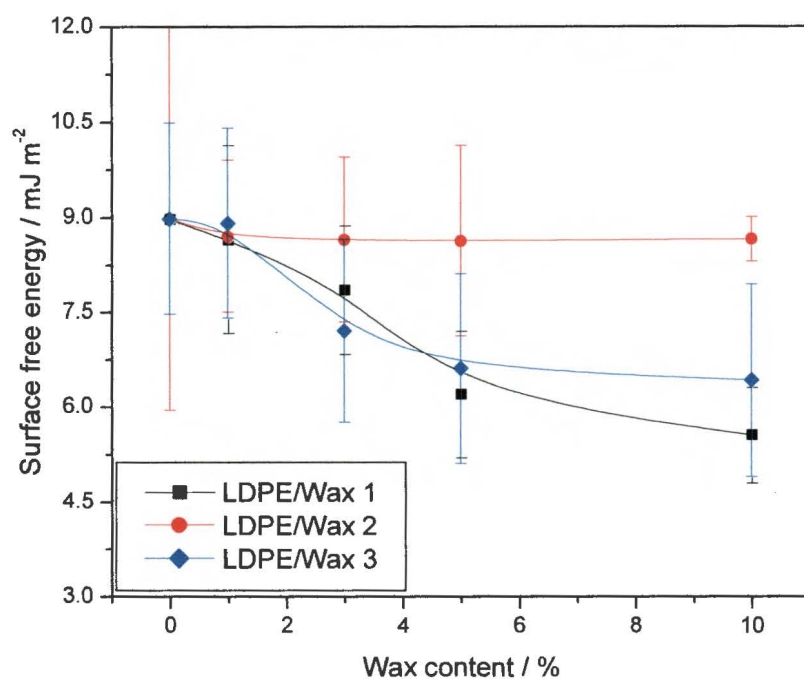


Figure 3.40 Comparison of the polar parts of the surface free energy of LDPE blended with three different types of wax

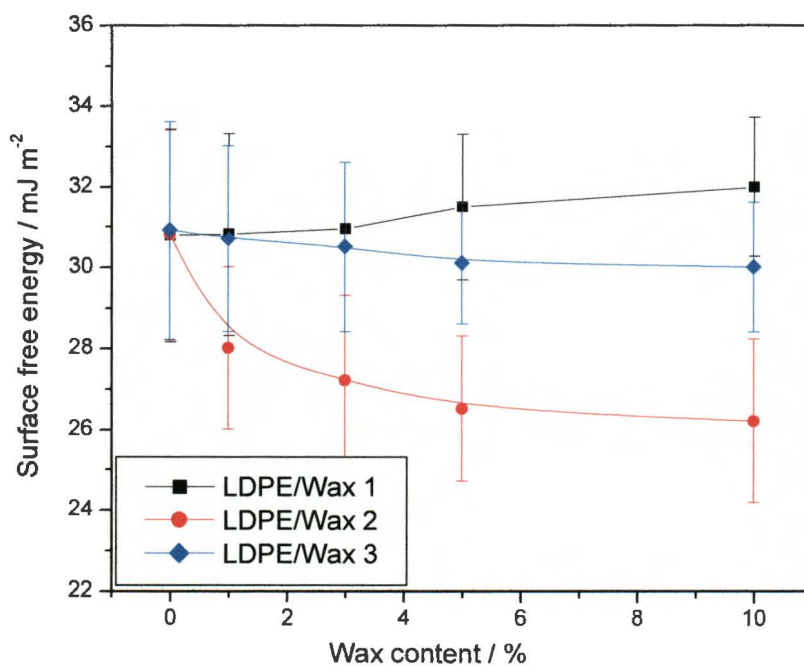


Figure 3.41 Comparison of the total surface free energy of LDPE blended with three different types of wax

The LLDPE/Wax 1 blends show a constant value for the polar component, while both the total surface free energy and dispersed part show a slight increase. The DSC results showed that LLDPE/Wax 1 are miscible up to 3 % Wax 1. This may be the reason for the polar part of the surface free energy to remain fairly constant. The LLDPE/Wax 2 blends show an increase in the polar part, a decrease in the disperse part, and a fairly constant total surface free energy with increasing wax content. The DSC results showed that LLDPE/Wax 2 blends were miscible up to 3 % wax. In this case it is not clear why there was an increase in the polar part of the surface free energy. The total surface free energy, as well as its polar and disperse parts, remains constant with increasing wax content in the LLDPE/Wax 3 blends. The DSC results showed that the LLDPE/Wax 3 blends were not fully miscible at higher wax contents, and this may be the reason for the polar part of the surface free energy remaining fairly constant.

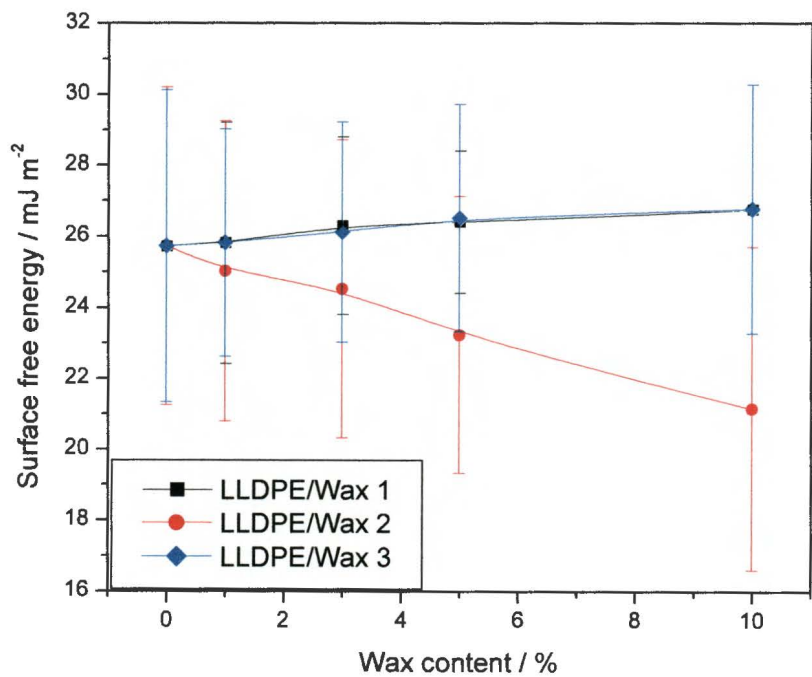


Figure 3.42 Comparison of the disperse parts of the surface free energy of LLDPE blended with three different types of wax

Table 3.5 Surface free energy results for LDPE/wax and LLDPE/wax blends

Sample	$\gamma_{\text{Total}} \pm S_{\gamma_{\text{Total}}}$	$\gamma_{\text{LW}} \pm S_{\gamma_{\text{LW}}}$	$\gamma_{\text{AB}} \pm S_{\gamma_{\text{AB}}}$
100/0 w/w LDPE/Wax 1	30.7 \pm 2.6	21.8 \pm 2.1	8.9 \pm 1.5
99/1 w/w LDPE/Wax 1	30.8 \pm 2.5	22.2 \pm 2.1	8.7 \pm 1.5
97/3 w/w LDPE/Wax 1	30.9 \pm 1.7	23.5 \pm 2.0	7.9 \pm 1.0
95/5 w/w LDPE/Wax 1	31.5 \pm 1.8	24.2 \pm 1.5	6.2 \pm 1.1
90/10 w/w LDPE/Wax 1	32.0 \pm 1.7	26.5 \pm 1.5	5.6 \pm 0.9
99/1 w/w LDPE/Wax 2	28.0 \pm 2.0	21.9 \pm 2.0	8.7 \pm 1.2
97/3 w/w LDPE/Wax 2	27.2 \pm 2.1	21.9 \pm 2.0	8.6 \pm 1.3
95/5 w/w LDPE/Wax 2	26.5 \pm 1.8	22.5 \pm 1.9	8.6 \pm 1.5
90/10 w/w LDPE/Wax 2	26.2 \pm 2.0	22.9 \pm 2.1	8.7 \pm 0.4
99/1 w/w LDPE/Wax 3	30.7 \pm 2.3	22.0 \pm 2.1	8.9 \pm 1.5
97/3 w/w LDPE/Wax 3	30.5 \pm 2.1	22.6 \pm 2.0	7.2 \pm 1.4
95/5 w/w LDPE/Wax 3	30.1 \pm 1.5	23.1 \pm 2.1	6.6 \pm 1.5
90/10 w/w LDPE/Wax 3	30.0 \pm 1.6	23.6 \pm 2.4	6.4 \pm 1.4
100/0 w/w LLDPE/Wax 1	28.0 \pm 4.7	25.7 \pm 4.5	2.4 \pm 1.5
99/1 w/w LLDPE/Wax 1	28.1 \pm 3.5	25.8 \pm 3.4	2.4 \pm 1.3
97/3 w/w LLDPE/Wax 1	28.5 \pm 3.2	26.3 \pm 2.5	2.5 \pm 1.1
95/5 w/w LLDPE/Wax 1	29.2 \pm 3.4	26.4 \pm 2.0	2.6 \pm 1.0
90/10 w/w LLDPE/Wax 1	29.5 \pm 3.6	26.8 \pm 3.5	2.8 \pm 1.3
99/1 w/w LLDPE/Wax 2	28.0 \pm 2.0	25.0 \pm 4.3	3.2 \pm 1.6
97/3 w/w LLDPE/Wax 2	27.6 \pm 2.2	24.5 \pm 4.2	3.6 \pm 2.1
95/5 w/w LLDPE/Wax 2	27.4 \pm 2.0	23.2 \pm 3.9	5.2 \pm 2.5
90/10 w/w LLDPE/Wax 2	27.3 \pm 2.0	21.1 \pm 4.6	6.4 \pm 3.0
99/1 w/w LLDPE/Wax 3	28.1 \pm 4.3	25.8 \pm 3.2	2.4 \pm 1.4
97/3 w/w LLDPE/Wax 3	28.2 \pm 4.0	26.1 \pm 3.1	2.5 \pm 1.3
95/5 w/w LLDPE/Wax 3	28.3 \pm 4.2	26.5 \pm 3.2	2.6 \pm 1.4
90/10 w/w LLDPE/Wax 3	28.3 \pm 4.4	26.8 \pm 3.5	2.8 \pm 1.6

γ_{Total} – total surface free energy; γ_{LW} – disperse part of surface free energy; γ_{AB} – polar part of surface free energy

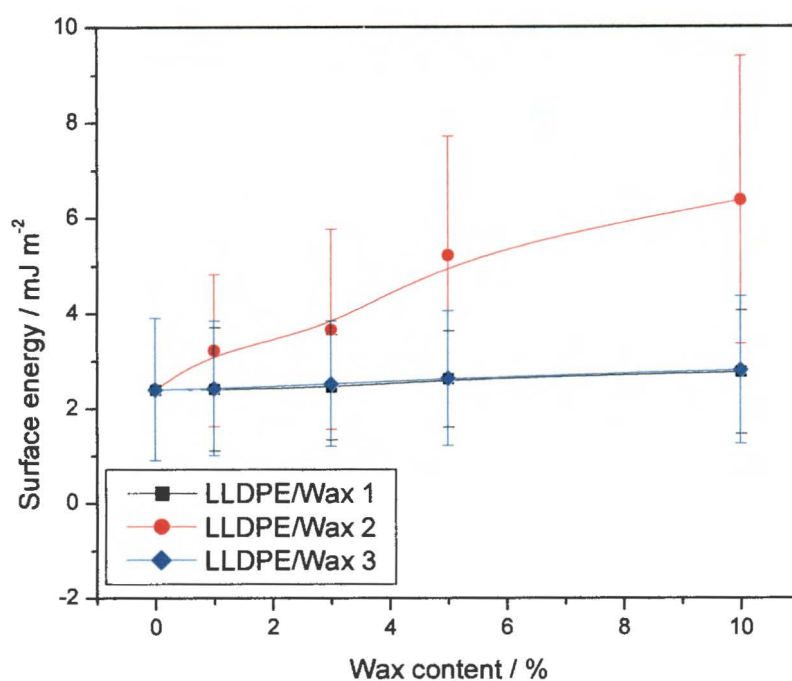


Figure 3.43 Comparison of the polar parts of the surface free energy of LLDPE blended with three different types of wax

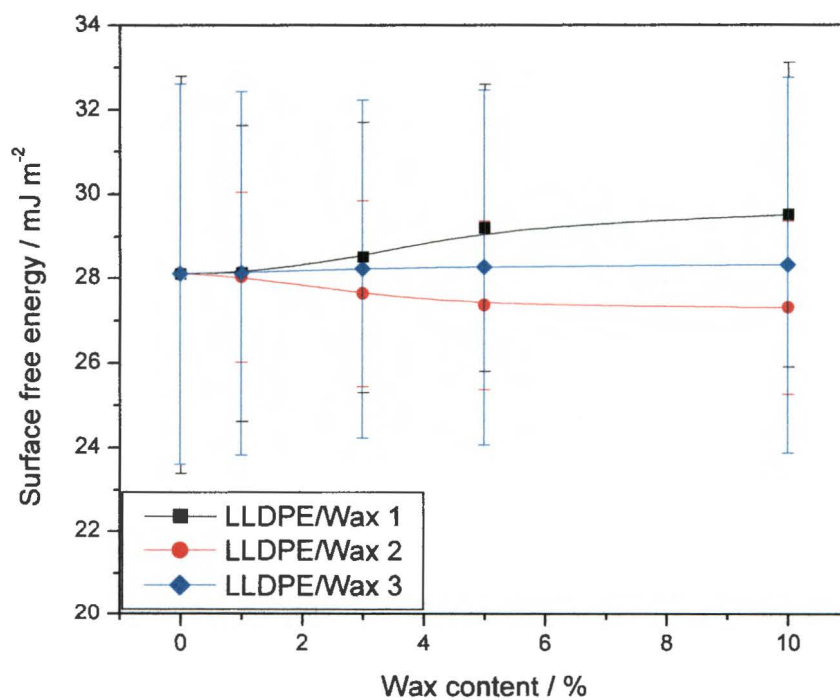


Figure 3.44 Comparison of the total surface free energy of LLDPE blended with three different types of wax LLDPE

CHAPTER 4

CONCLUSIONS

4.1 Summary of observations

The DSC curves for LDPE with Wax 1 showed one endothermic peak for all the blends, indicating that LDPE and Wax 1 were miscible in the crystalline phase up to 10 % wax content, and probably co-crystallized. The enthalpy was found to increase with increasing wax content, indicating an increase in crystallinity of the material. The peak temperature of melting slightly increased, possibly indicating a small increase in lamellar thickness. The surface free energy results showed a decrease in the polar component of the surface free energy, which could not be readily explained. The TGA results showed that the sample containing 1 % wax was the most stable, and that the stability decreased with increasing wax content. Up to 10 % wax the stability did, however, not fall below that of pure LDPE. At all concentrations Wax 1, which was developed to improve processability, had a small influence on the melt flow properties. The presence of Wax 1 gave rise to an increase in yield stress and Young's modulus. This behaviour was expected, since wax increased the crystallinity of the blend. Elongation at yield decreased in the presence of Wax 1, because of a decrease in amorphous content with increasing wax content. However, the presence of Wax 1 caused a decrease in the stress and elongation at break as a result of decreasing tie chain concentration when the wax co-crystallized with LDPE.

The DSC curves for LDPE and Wax 2 showed that they were miscible up to 3 % wax content. For 5 and 10 % wax, a second peak could be seen, indicating that LDPE and Wax 2 were only partially miscible at these wax contents. The presence of Wax 2 slightly increased the enthalpy of its blends with LDPE, indicating an increase in crystallinity of the material. The peak temperature of melting slightly increased up to 5 % wax content, after which the temperature remained fairly constant, indicating a small increase in lamellar thickness. Higher wax contents, however, did not seem to have an observable influence on the lamellar thickness during crystallization. These observations were further supported by the surface free energy results, where the polar part of the surface free energy remained fairly constant. The TGA results showed that Wax 2 is clearly less thermally stable than LDPE, but that the blends were more stable, except for the sample containing 1 % wax. Wax 2 generally improved the

flow rate of LDPE. The presence of Wax 2 gave rise to an increase in yield stress and Young's modulus. This behaviour is expected, since wax increased the crystallinity of the blend, and yield stress and Young's modulus depends on crystallinity. Elongation at yield decreased in the presence of Wax 2. However, the presence of Wax 2 caused a decrease in the stress and elongation at break.

LDPE/Wax 3 blends showed one DSC melting peak up to 5 % wax content. For 10 % wax, a second peak was seen. This behaviour shows that LDPE and Wax 3 are partially miscible. The peak temperatures of melting very slightly decrease, and the melting enthalpies observably decrease, as the Wax 3 content increases. This behaviour indicates a decrease in the crystallinity of the material. These observations were supported by the surface free energy results, where the polar part showed a decrease with increasing wax content. The TGA results showed an increase in onset temperature of degradation for low Wax 3 contents, despite the lower thermal stability of the wax, but the stability decreased with increasing wax content. For 10 % wax, however, the stability fell below that of pure LDPE. Wax 3 has the lowest molecular weight, which is why it had the strongest influence on the flow properties of LDPE. The increase in yield stress and Young's modulus (the values tend to be constant at higher Wax 3 contents) was, however, not in line with the decrease in enthalpy (crystallinity) of these blends with increasing wax content. A possible reason for this is the probable crystallization of Wax 3 in the amorphous part of LDPE, and the influence of such crystallites on the chain mobility. Wax 3 had a more pronounced influence on elongation at yield. Stress and elongation at break decreased with increasing wax content.

The DSC results for LLDPE/Wax 1 blends showed one melting peak for the low wax content blends, but for the blends containing 5 and 10 % wax a second peak was seen. LLDPE and Wax 1 were therefore only partially miscible at higher wax contents. The melting enthalpy increased with increasing wax content. The Wax 1 chains probably co-crystallized with the linear sequences of the LLDPE chains, giving rise to improved crystallinity. The peak temperatures of melting slightly decreased as the wax content increased, suggesting a decrease in the average lamellar thickness. The polar part of the surface free energy remained fairly constant with increasing wax content. The TGA curves of LLDPE/Wax 1 blends showed a decrease in onset temperatures of decomposition with increasing wax content. The values were somewhere between those of pure wax and pure LLDPE. The melt flow index increased with increasing amounts of Wax 1 in the blends. There was an increase in yield stress and Young's modulus with increasing wax content, since wax increased the crystallinity of the blend. Elongation at yield decreased because of reduced chain mobility.

Stress and elongation at break decreased with increasing wax content, probably as a result of the reduction in tie chain concentration.

LLDPE and Wax 2 were miscible up to 3 % wax content. There was a clearly observable second peak for the blends containing 5 and 10 % wax. The presence of Wax 2 did not change the melting enthalpies of the blends, probably due to the crystallinity of Wax 2 and LLDPE being similar. There was very little change in the peak temperatures of melting with increasing wax content. The surface free energy results showed an increase in the polar part of the surface free energy, contrary to what was expected. The presence of wax substantially reduced the thermal stabilities of the LLDPE/Wax 2 blends, with the onset temperatures of decomposition of the blends about 50 °C lower than that of pure LLDPE. Wax 2 improved the melt flow of LLDPE, with the melt flow index increasing with increasing wax content. Yield stress and Young's modulus increased with increasing wax content. Elongation at yield decreased because of the reduced chain mobility. Both stress and elongation at break decreased with increasing wax content.

The LLDPE/Wax 3 blends showed one DSC melting peak, indicating miscibility of LLDPE and Wax 3, for the blends containing up to 5 % wax. For the 90/10 w/w LLDPE/Wax 3 blend, a second peak could be seen at a lower temperature. It is possible that at higher wax contents, some of the wax was forced out of the LLDPE crystallites during LLDPE crystallization. Both the melting temperature and enthalpy showed a decrease with increasing wax content. The decrease in the peak temperature of melting suggested a decrease in the average lamellar thickness. These observations were further supported by the surface free energy results, where the polar part of the surface free energy remained fairly constant with increasing wax content. The TGA curves showed that the thermal stabilities of the LLDPE/Wax 3 blends fell between those of pure wax and pure LLDPE. A possible reason for the poor resistance of LLDPE/Wax 3 blends to thermal degradation is the low molecular weight of the wax. Wax 3 had a slightly larger influence on the melt flow properties of the blends than the other two waxes, with the melt flow index increasing with increasing wax content. There was no correlation between the decreasing crystallinity (melting enthalpy) and increasing yield stress and Young's modulus of the blends, with increasing wax content. In this case a possible reason was the formation of wax crystals in the amorphous phase, which may have influenced the chain mobility. Elongation at yield decreased with increasing wax content. Stress and elongation at break also decreased with increasing wax content.

4.2 Which wax is the best processing agent?

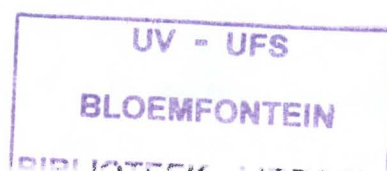
Based on the observations summarized in section 4.1, Wax 2 may be regarded as the best processing agent for LDPE. Both Wax 1 and Wax 2 have a similar influence on the tensile properties of LDPE, but Wax 2 increases the melt flow rate more than Wax 1, which was specifically designed as a polyethylene processing agent. As far as thermal stability is concerned, the blends seem to be thermally more stable in the presence of Wax 1 than in that of Wax 2. Although Wax 3 improves the melt flow rate in a similar way than Wax 2, it has a strong negative impact on the tensile properties of LDPE.

In the case of LLDPE, either Wax 2 or Wax 3 can be used. Wax 3 has the strongest influence on the melt flow rates of the blends, and it has the least influence on the tensile properties of LLDPE. It does, however, strongly reduce the thermal stability of LLDPE. Wax 2, on the other hand, has only a small influence on the thermal stability of LLDPE, but like Wax 1 it strongly increases the modulus. Again Wax 1, which was specifically designed as a polyethylene processing agent, seems not to be the best wax to use for this purpose.

REFERENCES

1. http://www.sasolwax.com/polymer_Additives.html
2. Research and Development, *Sasol tech. LTD.*, 1-12 (1983)
3. Rigde A, Training Lecture, *Sasol tech. PTY.*, 1-10 (1983)
4. <http://www.sasolwax.com/EnHance.html>
5. www.performanceadditives.com/waxtypes.htm
6. Manson JA and Sperling LH, *Polymer Blends and Composites*, Plenum Press (1976)
7. Lu X and Brown N, *Polymer*, **38**, 5749-5753 (1997)
8. <http://www.efunda.com/materials/polymers/properties.htm>
9. www.polymerdoctor.com/fine/plsql/dictionary_main.htm
10. www.leuna-polymer.de/polymer_englisch/produkte/le_wachse/chapter_11.htm
11. <http://patft.uspto.gov/netacgi.htm>
12. <http://www.devicelink.com/mpb/archive/97/11/003.html>
13. Sadhan JC and Sachin J, *Polymer*, **42**, 6897-6905 (2001)
14. Young RJ, *Introduction to Polymers*, Chapman and Hall, London (1981)
15. Steinmann S, Gronski W and Friedrich C, *Polymer*, **42**, 6619-6629 (2001)
16. Puing CC, *Polymer*, **42**, 6579-6585 (2001)
17. Fahmy T and Ahmed MT, *Polym. Test.*, **20**, 477-484 (2001)
18. Li J, Shanks RA and Long Y, *J. Appl. Polym. Sci.*, **76**, 1151-1164 (2000)
19. Lopez JMR and Brana MTC, *Polymer*, **29**, 1045-1051 (1988)
20. Li J and Shanks RA, *Polymer*, **42**, 1941-1951 (2001)
21. Kukaleva N and Cser F, *J. Appl. Polym. Sci.*, **77**, 1591- 1599 (2000)
22. Daniel A, George KE and Francis DJ, *Polymer*, **39**, 117-121 (1998)
23. M Yamagushi, S Abe, *J. Appl. Polym. Sci.*, **74**, 3153-3159 (1999)
24. M Yamagushi, S Abe, *J. Appl. Polym. Sci.*, **74**, 3160-3164 (1999)
25. Graham JF, Predrag M, *Polym. Int.*, **48**, 461-466 (1999)
26. Pospíšil J and Kuroda S, *Polym. Degr. Stabil.*, **65**, 405-414 (1999)
27. Colin LPS, Soares JBP and Penlidis A, *Polymer*, **44**, 177-185 (2003)
28. Krupa I, Luyt AS, *Thermochim. Acta.*, **372**, 137-141 (2001)
29. Novak I, Krupa I, Luyt AS, *J. Appl. Polym. Sci.*, **94**, 529-533 (2004)
30. Krupa I, Luyt AS, *Polymer*, **42**, 7285-7289 (2001)
31. Krupa I, Luyt AS, *Polym. Degr. Stabil.*, **70**, 111-117 (2000)

32. Krupa I, Luyt AS, *Polym. Degr. Stabil.*, **73**, 157-161 (2001)
33. Krump H, Luyt AS and Molefi JA, *Mater. Lett.*, **69**, 517-519 (2005)
34. Hlangothi SP, Krupa I and Luyt AS, *Polym. Degr. Stabil.*, **79**, 53-59 (2003)
35. Mthali TN, Krupa I and Luyt AS, *Thermochim. Acta.*, **380**, 47-54 (2001)
36. Luyt AS and Krupa I, *Macromol. Symp.*, **178**, 109-116 (2002)
37. Djokovic V, Mtshali TN and Luyt AS, *Polym. Int.*, **52**, 999-1004 (2003)
38. Mtshali TN, Van Sittert CGCE, Djokovic V and Luyt AS, *J. Appl. Polym. Sci.*, **89**, 2446-2456 (2003)
49. Novak I, Krupa I and Luyt AS, *J. Appl. Polym. Sci.*, **95**, 1164-1168 (2004)
40. Luyt AS and Brüll R, *Polym. Bull.*, **52**, 177-183 (2004)



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