

The influence of oxidized paraffin
wax on the physical properties of
LLDPE/wax and LDPE/wax blends

By

T.N. Mtshali

**“THE INFLUENCE OF OXIDIZED WAX ON THE
PHYSICAL PROPERTIES OF LLDPE/WAX AND
LDPE/WAX BLENDS”**

BY

**THATO NICHOLAS MTSHALI
[B.Sc Hons. Chemistry]**

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SUPERVISOR: PROF. A.S. Luyt

CO-SUPERVISSOR: DR. C.G.C.E. van Sittert

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“Chemistry is the science of molecules and their transformations. It is the science not so much of the one hundred elements, but of the infinite variety of molecules that may be built from them”

by Roald Hoffman

DECLARATION

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


.....
T.N. Mitshali

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SUMMARY

In this work, the characterization, thermal and mechanical properties of mechanically and extrusion mixed LLDPE/wax and LDPE/wax blends were investigated. Mechanically and extrusion mixed samples were melt pressed into sheets on which analyses were done. The samples were first characterized by using FTIR spectroscopy and GPC. From the FTIR results it was found that linking and degradation occurred. The GPC results showed that the molecular weight of the blends increased. Thermal analyses were done using DSC and TGA. From the DSC analyses, it was found that at low wax content both wax and polyethylene (in the blend) are apparently miscible in both crystalline and molten states. At higher wax content phase separation was observed. It was also found that an increase in wax content has an effect on (a) lamellar thickness of the blends, (b) the degree of crystallinity of the blends and (c) thermal stability of the blends.

The mechanical properties were determined with a tensile tester. An increase in wax content affects the yield points and the ultimate properties of the blends. It was found that elongation at yield and elongation at break decrease with an increase in wax content. Yield stress decreases for LLDPE/wax blends and increases for LDPE/wax blends. Stress at break decreases, except for the mechanically mixed LDPE/wax blends, which show an increase. Young's modulus of the blends increased with an increase in wax content.

Keywords

Oxidized wax, LLDPE/wax blends, LDPE/wax blends, characterization, thermal analysis, mechanical analysis, mechanically and extrusion mixed, linking and degradation.

LIST OF ABBREVIATIONS

DCP	Dicumyl peroxide
DSC	Differential scanning calorimetry
DMA	Dynamic mechanical analysis
FTIR	Fourier-transform infrared
ΔG	Free energy
GPC	Gel permeation chromatography
T_g	Glass transition temperature
HDPE	High-density polyethylene
iPP	Isotactic polypropylene
LLDPE	Linear low-density polyethylene
LDPE	Low-density polyethylene
MFI	Melt flow index
T_m	Melting temperature
MW	Molecular weight
MWD	Molecular weight distribution
PE	Polyethylene
PS	Polystyrene
PP	Polypropylene
PVC	Poly(vinyl chloride)
RT	Retention time
SEM	Scanning electron microscopy
ΔH	Specific enthalpy
ΔS	Specific entropy
tert-PP	Tertiary polypropylene
TGA	Thermogravimetric analysis

CHAPTER 1

INTRODUCTION

1.1 Wax

The ability of waxes to undergo plastic deformation, each within a certain temperature range, is perhaps their most important common property. In 1956 Hatt and Lamberton [1] pointed out that this ability is due to the fact that the cohesive forces are such that they are not disrupted during deformation. However, they did not offer any further explanation. Von Rosenberg [2] studied the plasticities of different waxes. Waxes are mixtures of aliphatic organic compounds that have long, chain-like molecules. Cohesion is promoted by crystallization, but waxes also contain some amorphous material. The crystalline and amorphous parts do not differ very much with respect to the structure of their molecules. They are therefore compatible and this also promotes cohesion. Waxes are mechanically much weaker than resins, plastics and rubbers. These materials, also known as polymers, are strong because they contain very long chains that are sometimes cross-linked [1,2].

For many years scientists tried to find a suitable chemical definition of waxes in general. The description from the German Society for Fat Technology best fits the requirements of industry: '*Wax*' is a collective technological term for a series of natural or synthetically produced substances that normally possess the following properties: kneadable at 20 °C, can be solid, pliable to hard, brittle at 20 °C, coarse to finely crystalline, translucent to opaque but not glassy, melt above 40 °C without decomposition, having a relatively low viscosity just above its melting point, cannot be drawn to threads, consistency and solubility strongly depend upon temperature, not tending to stringiness and can be polished under slight pressure [2,3].

Many attempts have been made to classify waxes, which are usually classified according to origin. Two main types of waxes can be defined: type I, which is highly crystalline and type II, which contains much amorphous material. Many waxes seem to fall into an intermediate class between these extremes. Paraffin waxes are from different sources and are of type I. The harder oxidized Fischer-Tropsch and microcrystalline waxes can be regarded as intermediates, while highly oxidized waxes are of type II. An important property of waxes is the average mass of its molecules, which is closely related to their average length. The softness of the waxes increases in the following order: intermediate waxes are softer than those of type I, while the type II waxes are still softer [2].

Type I waxes consist of crystallites which are thick plates. Regions in which disorder occurs, called defects, are found within these plates. These defects are caused by the ends of chains, and of branches and kinks. The extent of these regions has a large influence on all properties. Type I waxes become plastic, each above a certain temperature. Waxes are of type I if their molecules do not differ too much from each other, so that they can easily crystallize together. Type I waxes contain only carbon and hydrogen [2].

Type II and intermediate waxes contain oxygen, in addition to carbon and hydrogen. The presence of oxygen atoms can have such an effect on the distribution of electrical charges in the molecules that certain types of molecules will attract each other quite strongly. It is also said that they become "associated". This effect is called "hydrogen bonding", because it results in the linking of the hydrogen atoms to two oxygen atoms (usually of two different molecules) instead of the normal one. It was concluded that molecules in type II waxes that contain oxygen could be associated in many different ways [1]. This hampers or modifies their crystallization. The hydrocarbon waxes of type II, i.e. the microcrystalline waxes, have many branches and even rings of atoms that are attached to their molecular chains. This limits crystallization of the waxes. As proposed by Edward [4] for microcrystalline waxes, all the type II waxes are thin plates, embedded in a highly viscous, amorphous mass called a matrix [2].

The properties of type II waxes are determined by the viscosity of the matrix, the thickness (and thus flexibility) of the plates and the relative amounts of the two phases present. They can therefore also be plastic, each above a certain temperature, due to the slow viscous flow of the matrix bending of the plates. Waxes are of type II because of the differences between the molecules they contain, making it difficult for them to crystallize out together. What applies to type II waxes also applies to intermediate waxes, but to a lesser extent. It is possible that the intermediate structure is a mixture of the type I and type II structures. An intermediate wax could therefore be a good I – II mixture or it could have predominantly a type I or type II character. Most of the oxidized waxes can be regarded as intermediate waxes. Only the highly oxidized waxes which are much softer than the intermediate waxes, belong to type II [2].

The differences on a molecular level between type I and type II waxes are that, in type I waxes, differences between molecules are so small that three-dimensional crystal growth is not hampered. There is no experimental evidence of the existence of an amorphous matrix. In the type II waxes, differences between molecules severely limit crystal growth. These could be due to the presence of branches, naphthenic rings or randomly distributed functional groups. The addition of new molecular layers to crystallites is inhibited more than the growth of existing layers. The crystallites will therefore tend to be thin plates. There is also experimental evidence of the existence of a highly viscous amorphous matrix [1,2].

Although, the properties of waxes can be given in a generalized form, which distinguish them from other articles of commerce, it is convenient to subdivide them into naturally occurring waxes and synthetic waxes. The first group includes animal, vegetable and mineral waxes. The synthetic waxes encompass a very broad spectrum of chemical type from polyethylene to amide waxes. Generally, the physical and technical properties of waxes depend more on molecular structure than on molecular size and chemical constitution. Thus, paraffin waxes, consisting mainly of n-alkanes and with a closed-packed structure, differ from the more loosely packed waxes containing branched and

cyclic molecules. Waxes have a more crystalline structure than gums and resins, and may have well developed macrocrystals [3].

Hard paraffin waxes are saturated hydrocarbons synthesized from petroleum as by-product of the Fischer-Tropsch process. They normally are linear, long-chain saturated hydrocarbons with a high crystallinity. These waxes are hard, have a high melting point and low viscosity, and are white in color with exceptional opacity. Their chain lengths are in the range C28–C90 and they have melting points of about 90 °C. They have a density of approximately 0.94 g cm⁻³ at 25 °C, and they decompose thermally at 250 °C [4].

Oxidized waxes are produced by controlled, liquid phase oxidation. The products vary widely in their chemical and physical properties. The oxidates contain mixtures of organic acids, esters, oxy-acids, lactones and other oxygenated organics. By varying the selection of raw materials and the processing conditions, a wide range of molecular weights and chemical functionalities can be produced [5]. The wax oxidates are useful as chemical intermediates. They undergo reactions that are typical of most organic acids, lactones and esters. Various types of amine or metal soaps can be prepared by reaction with the oxy acids from the wax. The acids react readily with alcohols to form esters [6]. Various oxidates, with acid numbers 6-60, are mixtures of relatively high molecular weight compounds containing aldehydes, ketones, alcohols and esters. They are low cost organic acids useful in the preparation of water dispersable soaps, rust preventatives, metal working compounds and textile formulations. Oxidates are highly effective as corrosion inhibitors or as lubricants when reacted with amines, alcohols or blended with metal sulfonates. They are used as a total replacement of natural fats and oils such as tallow and oleic acid, in the formulation of cutting, drawing, rolling and penetrating alkali oils. They can also be used directly as alkali soap in textile applications [7].

Although waxes have much shorter chains, they may be regarded as polymers in the sense that they have long chains which may arrange and be cross-linked in a similar way to those of, for example, PE. Furthermore, PE in the MW range 2,000-4,000 are waxes.

Common properties are water repellency, smooth texture, low toxicity, and freedom from objectionable odor and color. They are combustible and have good dielectric properties. They are used for the preparation of candles, paper coatings, protective sealant for food products and beverages, glass-cleaning preparation, hot-melt carpet backing, biodegradable mulch, lubricants, stoppers for acid bottles, electric insulators and others [5-7].

There have been some studies on the different Fischer-Tropsch waxes. Brink and Dressler [8] cross-linked a hard Fischer-Tropsch wax using (DCP) as the cross-linking agent. The cross-linking process was initiated by stirring the two substances at 135 °C in a nitrogen atmosphere. They reported that the congealing points, GPC, FTIR and tensile properties proved that the product had been cross-linked and that the elasticity had increased when compared to the starting material. They did, however, observe unacceptable side reactions during the cross-linking process. Luyt *et al.* [9] investigated the same system thermo-analytically. They tried to establish the cross-linkability and extent of cross-linking through FTIR analyses and wax solubility. The FTIR spectra showed that an increasing DCP/wax ratio gave rise to a higher extent of cross-linking, while a decrease in solubility of the wax samples was observed with increasing DCP/wax ratio. Luyt and Ishripersadh [10] found that all three waxes cross-linked in the presence of DCP, with the extent of cross-linking increased with increasing DCP/wax ratio. From the gel content data it seemed as if the oxidized and high molar mass waxes tend to cross-link at a faster rate.

1.2 Polyethylene (PE)

Polyethylenes are produced catalytically from ethylene, and have MW that range from 2,000-4 000,000 g mol⁻¹. It is a semi-crystalline polymer. Semi-crystalline polymers range in their properties from commodity plastics (PE, PP) to high-temperature engineering resins (PEEK) used in aerospace. In general, properties of semi-crystalline polymers are less sensitive to temperature variations [11]. Semi-crystalline thermoplastics are environmentally stable, more rigid and less permeable to low molar

mass agents compared to the majority of glassy polymers. They comprise of crystalline, amorphous and partially ordered phases. Amorphous polymers do not contain any crystalline region and this phase is characterized by randomly coiled chains. Above their T_g they show less stress value (low tensile strength) accompanied by low elongation. In contrast, an amorphous polymer below its T_g shows moderate tensile strength but very low elongation [12]. Elasticity is usually observed above T_g . In crystalline polymers, an ordering of the chains into a rectangular three-dimensional state takes place [13].

Polyethylene falls into three categories: HDPE, LLDPE and LDPE. The LLDPE is synthesized through Ziegler-Natta catalysis or transition metal oxide catalyzed chain polymerization. The polymers obtained from Ziegler-Natta processes are usually characterized by a molecular heterogeneity resulting from a very different distribution of co-monomer units along the polymer chain [14]. LLDPE polymers are linear but have a significant number of branches introduced by using copolymers of ethylene and α -olefins such as 1-butene, 1-hexene and 1-octene. Their properties are strongly affected by the degree and distribution of short chain branching due to the incorporation of the α -olefins in the polymeric chain [15]. They are 8-10 % crystalline, and have densities of about $0.92\text{-}0.94\text{ g cm}^{-3}$. They melt at temperatures of about 15 % higher than the corresponding LDPE. LLDPE shows a range of properties, i.e. the low-branched fraction contribute to crystallinity, which reduces flexibility, control of melting point and clarity, while linearity provides strength. Furthermore, these materials show a rather broad MWD. Their modulus and ultimate tensile properties are significantly improved over branched LDPE [16]. LLDPE's are used for, *inter alia*, grocery bags, heavy duty shipping sacks, agricultural films, pipes, liners for consumers, land fills and waste ponds [17]. It is clear that LLDPE's themselves are not simple materials. There is some evidence that LLDPE may phase separate in the melt. If LLDPE's can undergo phase separation in the melt, it would not be surprising if the blends of LLDPE with other polymers did so, too [18]. Like conventional LDPE, the polymer contains short carbon chain side groups which reduce structural regularity and hence crystallization. Overall, the polymer has similar properties to LDPE, but has better strength properties in film, which is its major area of use [19]. LLDPE represents a relatively new class of materials that entered the

commercial market in the early 1980s. These materials were developed in order to produce a polyethylene with only short chain branches. It was first produced in the late 1970's, and was found to have good mechanical properties. Today, LLDPE's represent approximately one-third of the total world production of low-density polyethylenes [20].

Low-density polyethylene (LDPE) is made by free radical initiated chain polymerization under high pressure (15 000 to 50 000 psi), at a temperature of 180 to 250 °C, and using peroxides as initiators. It is only about 40 % crystalline, melts at about 110-125 °C, and has a density in the range 0.91-0.92 g cm⁻³. It is soluble in many solvents above 100 °C, but only a few solvent mixtures provide borderline solubility at or near room temperature. It has high impact strength, low brittleness temperature, good flexibility and film transparency, and outstanding electrical properties [21]. The physical properties of LDPE are a function of three independent structural variables: MW, short chain branching, and long chain branching. Short chain branching has an effect on the morphology and degree of crystallinity, such as stiffness, hardness, chemical resistance, and yield point, and these properties increase with increasing density or decreasing amount of short chain branching in the polymer, while long chain branching is mostly manifested in viscoelastic properties [22]. As the MW increases, so does tensile strength, softening temperature and resistance to stress cracking. LDPE is a major component of waste plastics. Wastes from different sources are frequently mixtures of LDPE with other high-volume commodity polymers such as PS, PP, HDPE, and PVC [23]. It was used during World War II to insulate radar cables. It is currently used for power and communication cable insulation, and food packaging. Several studies have been performed on the blends of PE with PS and PP, but there are few reports on LDPE/wax blends [24].

HDPE is produced either by Ziegler-Natta or by metal oxide catalysis, usually referred to as Phillips catalysis [25]. The melting points of the more linear HDPE's range between 130 and 138 °C, and they have densities of approximately 0.941-0.954 g cm⁻³. They have high crystallinity (about 90 %), in contrast with the LDPE 's 50 % crystallinity. Increasing the density increases stiffness, tensile strength, hardness, heat and chemical

resistance, heat capacity, and barrier properties, but reduces impact strength and stress-crack resistance [25].

1.3 Polymer blends

It has been generally accepted that it is not always necessary to synthesize new polymers in order to satisfy the needs for new materials. Since synthesis of new polymers is expensive, blending of virgin and used polymers is viewed as a way of solving existing problems and creating new products with better properties, and this is a promising approach to ecological and economical exploitation of waste plastics [26,27]. Presently plastics account for roughly a quarter of all solid waste. In trying to reduce this volume, there are some methods that can be applied: recycling, incineration and biodegradation [28]. However, since polymeric waste is multi-component, and separation could be done partially, a study of blending is the key in solving the problem. Presently polymer blends' consumption increases at a rate more than twice that of all plastics. As a consequence the academic and industrial interest in polymer blending is rapidly growing [29].

Over the years numerous systems have been developed and commercialized. These systems include both mechanical blends of two or more components and chemical combinations of different monomers, grafted copolymers and others [30]. Furthermore, blends between various types of polymers have been widely investigated from the viewpoint of both industry and science. Unfortunately, however, most of these studies have been carried out mainly through thermal analyses or through the observation of bulk morphology [31].

Blending of two or more polymers is a well-established strategy for achieving a specific portfolio of physical properties, and represents one of the fastest growing segments of polymer technology due to the realization that new materials with improved properties can be obtained to meet specific end-use requirements [32,33]. There are a number of good reasons for blending: developing a material with a full set of desired properties;

extending engineering resins' performance by diluting them with low-cost commodity polymers; improving a specific property. Examples of such properties are impact strength, rigidity, ductility, chemical-cum-solvent resistance, barrier properties, abrasion resistance, flammability, and gloss [34]. Blending can therefore be used to adjust material performance to fit customers' specifications at a lower cost price, and can be discussed from the perspective of material properties and economic advantages it can bring to the manufacturer from the viewpoint of commercial applications and developments [35,36].

Today, polymer blends constitute over 30 wt % of polymer consumption, and with an annual growth rate of 9 % (constant for the last 12 years) their role can only increase [37]. They are becoming very important in the polymer industry due to the strong incentives arising from their use, and a large number of scientific papers on thermosetting polymer blends are published every year. Polymer blends are being used extensively in numerous applications [38]. A blend can offer a set of properties that may give it the potential of entering an application area not possible with either of the polymers comprising the blend [39].

Many polymers can be improved by blending them with vinyl polymers. Polymer melt-blending is one of the most fascinating and fastest growing chapters in polymer science [40]. There are many reports and publications on binary PE/PE blends. Utracki and Schlund [41] looked at frequency relaxation spectra and rheological functions of LLDPE/LDPE blends and concluded that the components of their systems do not mix in the molten state. Other authors found that the addition of LDPE to LLDPE reduced the torque needed in processing (thus saving on energy) and that the extensional behavior was modified. Studies of slowly cooled blends showed that the LLDPE crystallized first, forming skeletal spherulites, within which the LDPE crystallized [42]. The mechanical properties of a set of blends of a commercial LLDPE with commercial LDPE indicated that the components were mechanically compatible over the entire composition range [43]. These authors followed the definition of mechanically compatible blends given by Utracki: "If the mechanical properties of the blend conform to a rule of mixtures, or to a

positive deviation from it, then it is said to be mechanically compatible". Kyuchool *et al.* [44] investigated miscibility and compatibility of LLDPE/*tert*-PP blends. They reported that the blend was immiscible in the amorphous as well as in the crystalline phase. Flexural modulus and yield stress were linearly increased with *tert*-PP content, while the tensile strength and elongation at break were more or less unchanged. For *i*PP/LLDPE blends, it has been found that their mechanical and thermal properties depend not only on the component proportion, but also on the crystallinity, as well as the mechanical and thermal properties of each component [45].

Krupa and Luyt investigated the thermal and mechanical properties of several uncross-linked and cross-linked polyethylene/wax blends [46-51]. Their studies on the thermal properties showed that mechanically mixed LLDPE/oxidized wax blends [46] were miscible up to 50/50 m/m ratio. Extrusion mixed LLDPE/un-oxidized wax blends containing 10 and 20 % wax were probably miscible in the crystalline phase, but for 30 % and more wax phase separation of the two components was observed [47]. In another investigation [48] they found that uncross-linked LLDPE/un-oxidized wax blends were miscible in the crystalline phase for all the samples investigated. In our previous investigation [49], and in the case of Krupa and Luyt [50], it was found that the LDPE and un-oxidized wax were miscible for the uncross-linked blend containing 10 % wax, but for 20 % and more wax both components were only partially miscible in the crystalline and the molten states. A general decrease in thermal stability of the blends with increase in wax content was observed. Their studies on the mechanical properties showed that, generally, Young's modulus increased with an increase in wax content [46-48]. Extrusion mixed LLDPE/un-oxidized wax and uncross-linked LLDPE/un-oxidized wax blends underwent a decrease in elongation at yield with an increase in wax content. A small increase in yield stress with increasing wax content was observed for the blends containing 10 and 20 % wax, but for the blends containing 30 % and more wax, no yield point, but brittle rupture was observed [47]. Uncross-linked LLDPE/un-oxidized wax blends underwent a general decrease in yield stress with an increase in wax content [48]. For mechanically mixed LLDPE/oxidized wax blends, wax content was found to have no influence on yield point (elongation at yield and yield stress), but an increase in wax

content decreases both stress and elongation at break [46]. Uncross-linked LLDPE/un-oxidized wax blends showed a stress at break that is independent of the wax content [48]. Krupa and Luyt [46,47] concluded that the route of sample preparation – mechanical mixing *versus* blending in the melt - has a marked (yet unexplained) influence on the thermal and mechanical properties of the blends. They also concluded that it did not seem as if the oxygen-containing groups in oxidized wax cause the wax to interact any differently with LLDPE than un-oxidized wax, except in the case of thermal stability, where there was a larger difference between the thermal stability of LLDPE/oxidized wax blends and the unblended oxidized wax, than was the case for LLDPE/wax blends [46,47].

It is important, when selecting polymers for blending, to decide whether they are thermodynamically miscible or mechanically compatible. Over four decades, polymer blend scientists and engineers used the terms miscibility and compatibility loosely and/or interchangeably. Many still do, and most literature is written in that way [52]. In recent years scientists and engineers began to recognize a very important distinction between these two terms. Thermodynamically miscible polymers are homogeneous at the molecular level. The mixing process must produce a decrease in free energy ΔG . This results in a single polymer blend at a specified temperature, and therefore the majority of the properties will be an average of the properties of the individual polymers [53]. Very few polymer blends belong to this category. The vast majority of polymers form heterogeneous blends on mixing. The term compatible is used to describe polymers that are not thermodynamically miscible, but have similar structures resulting in useful practical properties [54]. Many reports have been published on the miscibility and compatibility of polymers [55]. For example, PP and PE blends are compatible but only partially miscible. The polymer pairs tend to separate into two liquid phases. PP and LLDPE are compatible polymers, but they are only miscible at some compositions and at elevated temperatures. PP and LDPE or HDPE are generally considered immiscible in the liquid state [55-57].

The final properties of polymer blends are to a large extent determined by the morphology of the components, i.e. their size, shape, physical and chemical properties, their portion in the blends, interaction among components and processing route [58]. The term morphology generally refers to the “super-molecular” structural level, that is, to the presence of long-range order. Factors governing the morphology are composition, interfacial tension, processing conditions and the rheological properties of the components. In general, polymer blend morphologies can be divided into three classes: dispersed, fibrillar and co-continuous morphologies, which can be realized by melt mixing [59]. It has been reported that the morphology of the dispersed polymer affects the mechanical properties of the blends such as elasticity, yield strength, impact strength and ultimate tensile strength. For example, large particle size and weak adhesion would result in poor mechanical properties of the blend [60]. In literature many papers are dedicated to the mechanical properties of polymer blends with dispersed morphologies. Yan Lui and Truss [61] studied the dispersoid morphology of *i*PP and LLDPE blends by SEM. They found that the blends with equal component ratios were highly unstable on re-melting, while those blends with the lowest minor component ratios were the most stable ones, showing a growth in size of the dispersed particles. Another investigation [62] showed that the mechanical and thermal properties of *i*PP/LLDPE blends depend not only on the component proportion, but also on the crystallinity, the mechanical and thermal properties of each component, the morphology of the dispersoid, and the interfacial bonding between the two components. The initial work of Capaccio *et al.* [63], and later that of Irvine and Smith [64], revealed that Young’s modulus of drawn PE depends only on the draw ratio, and not on the MW and morphology of the polymer or the manner of preparation. The tensile values are affected by the portion of taut tie-molecules, as found by Penning *et al.* [65]. In this case the number of taut tie-molecules were estimated from the crystallinity of the drawn PE.

1.4 Objectives of this study

This project is motivated by the fact that LLDPE and LDPE are among the most commonly used plastics and, in recycle processing, are generally sorted into the stream of

polyolefins from the mixed waste. The properties of polyolefins can be extended by chemical modification, introducing polarity and/or functionality on the polymer backbone. For polyolefins, mechanical stress has a dominant effect over thermal effects, because polyolefins undergo thermomechanical degradation in the range of temperatures where they are practically unaffected by thermal treatment alone [66].

This study focused on the thermal and mechanical properties of LLDPE/wax and LDPE/wax blends prepared in two different ways, and the influence of wax content on these properties. Polyethylene is a semi-crystalline material, and wax is more crystalline than PE. It may therefore be assumed that wax influences the crystallinity of PE. The results of my own analyses were also compared with those of Krupa and Luyt [46,47,48, 50,51] in order to establish whether the presence of oxygen-containing groups in oxidized wax will improve the final properties of the blends.

CHAPTER 2

EXPERIMENTAL

2.1 Materials

2.1.1 Wax

An oxidized, hard Fischer–Tropsch wax was used. It was supplied by Schumann-Sasol, and has an average molar mass of 660 g mol^{-1} . It has a melting point of $99 \text{ }^{\circ}\text{C}$, boiling point of $239 \text{ }^{\circ}\text{C}$, congealing point of $86 \text{ }^{\circ}\text{C}$, density at $25 \text{ }^{\circ}\text{C}$ of 0.95 g cm^{-3} (solid) and at $110 \text{ }^{\circ}\text{C}$ of 0.82 g cm^{-3} (liquid), thermal decomposition temperature of about $250 \text{ }^{\circ}\text{C}$, C/O ratio 18.8/1, and a flash point of approximately $185 \text{ }^{\circ}\text{C}$.

2.1.2 LLDPE

Linear low-density polyethylene, with a density of 0.938 g cm^{-3} , MFI of about 3.5 g/10 min , melting point of $128\text{--}131 \text{ }^{\circ}\text{C}$, MW of $191603 \text{ g mol}^{-1}$, and particle size approximately 90 % less than $600 \text{ }\mu\text{m}$ was supplied by Sasol Polymers

2.1.3 LDPE

Low-density polyethylene, with a density of 0.925 g cm^{-3} , MFI of 20 g/10 min , melting point of $111\text{--}115 \text{ }^{\circ}\text{C}$, MW of 96057 g mol^{-1} , particle size of 90 % less than $850 \text{ }\mu\text{m}$, tensile yield of 9.5 MPa , and elongation at break of 150 %, was supplied by Sasol Polymers.

2.2 Methods

2.2.1 Preparation of blends

a) Mechanical mixed samples

Powdered samples of LLDPE and LDPE respectively were mechanically mixed (using a coffee mill) in different ratios with powdered oxidized wax (5, 10, 20, 30, 40 and 50 weight %). 20 g mixed samples were melt pressed at 160 °C for 5 minutes (LLDPE) and at 180 °C for 3 minutes (LDPE).

Table 2.1 Preparation of mechanically mixed samples for LLDPE/wax and LDPE/wax blends

LLDPE/wax or LDPE/wax	Preparation
95/5	19 g LLDPE or LDPE + 1 g wax
90/10	18 g LLDPE or LDPE + 2 g wax
80/20	16 g LLDPE or LDPE + 4 g wax
70/30	14 g LLDPE or LDPE + 6 g wax
60/40	12 g LLDPE or LDPE + 8 g wax
50/50	10 g LLDPE or LDPE + 10 g wax

b) Extrusion mixed samples

Powdered samples of LLDPE and LDPE, respectively mixed in different ratios with powdered oxidized wax (5, 10, 20, 30, 40 and 50 weight %), were blended in an industrial extruder (Brabender film blower at 1000 r.p.m) at 180 °C. The samples were hot melt pressed at 180 °C for 3 minutes (LDPE) and at 160 °C for 5 minutes (LLDPE).

Table 2.2 Preparation of extrusion mixed samples for LLDPE/wax and LDPE/wax blends

LLDPE/wax or LDPE/wax	Preparation
95/5	19 g LLDPE or LDPE + 1 g wax
90/10	18 g LLDPE or LDPE + 2 g wax
80/20	16 g LLDPE or LDPE + 4 g wax
70/30	14 g LLDPE or LDPE + 6 g wax
60/40	12 g LLDPE or LDPE + 8 g wax
50/50	10 g LLDPE or LDPE + 10 g wax

2.2.2 Differential scanning calorimetry (DSC)

DSC analyses were carried out on a Perkin Elmer DSC7 thermal analyzer under flowing nitrogen atmosphere. The instrument was calibrated using the onset of melting temperatures of indium and zinc standards, as well as the melting enthalpy of indium. The analyses were performed by heating 5-10 mg samples in aluminum pans. The samples were heated in the first scan from 25 to 160 °C at a rate of 20 °C min⁻¹, kept at 160 °C for 1 minute, and cooled at the same rate to 25 °C, in order to remove the thermal history of the material. For the second scan, the same samples were heated from 25 to 160 °C at a rate of 10 °C min⁻¹, kept for 1 minute at 160 °C, and then cooled at the same rate. Onset and peak temperatures of melting and crystallization, as well as melting and crystallization enthalpies, were determined from the second scan.

2.2.3 Thermogravimetric analysis (TGA)

TGA analyses were carried out on a Perkin Elmer TGA7 thermal analyzer. Samples of 5-10 mg were heated from 25 to 600 °C at a heating rate of 10 °C min⁻¹ under flowing air and nitrogen atmospheres respectively.

2.2.4 Tensile testing

A basic tensile tester (Hounsfield W5K) was used. The dumbbell samples were stretched at a speed of 50 mm/min. The final mechanical properties were evaluated from at least 5 different measurements. The average tensile values were calculated according to the following equations:

1. The respective values at the yield points were calculated as follows:

$$\text{Yield stress} \quad \delta_y = F_y / wt \quad [\text{MPa}] \quad (2.1)$$

where F_y is the force at yield, w is the width at the center on the dumbbell and t is the thickness of the dumbbell.

$$\text{Elongation at yield} \quad \varepsilon_y = x_y / x_o \times 100 \quad [\%] \quad (2.2)$$

where x_y is the extension at yield and x_o is the initial length of the dumbbell before deformation.

2. Ultimate properties were calculated as follows:

$$\text{Stress at break} \quad \delta_b = F_b / wt \quad [\text{MPa}] \quad (2.3)$$

where F_b is the force at break, w is the width at the center of the dumbbell and t is the thickness of the dumbbell.

$$\text{Elongation at break} \quad \varepsilon_b = x_b / x_o \times 100 \quad [\%] \quad (2.4)$$

where x_b is the extension at break, x_o is the initial length of the dumbbell before deformation.

3. Young's modulus of elasticity (tensile modulus) was calculated as follows:

$$\text{The output of the linear regression was:} \quad F = A + Bx \quad (2.5)$$

where B is the linear regression coefficient.

$$\text{Young's modulus} \quad E = B x_o / wt \quad [\text{MPa}] \quad (2.6)$$

where x_o is the initial length of the dumbbell before deformation, w is the width at the center of the dumbbell and t is the thickness of the dumbbell.

2.2.5 Fourier-transform infrared (FTIR)

FTIR was carried out on a Nicolet Impact 410 spectrometer. The melt-pressed disc was cut into a rectangular 50 × 20 mm shape (Mull cell) and analysed between 400 and

4000 cm⁻¹ at a resolution of 8 cm⁻¹ and a total number of 200 scans. The peak heights (intensities) were measured.

2.2.6 Gel permeation chromatography (GPC)

GPC was carried out on a Waters 150-C ALC/GPC instrument with a refractive index detector and two water styragel HR4E (7.8 × 300 mm) columns. Samples of about 0.1 g were dissolved into 4 ml xylene into vials, and run at a flow rate of 0.5 ml min⁻¹ and injection volume of 200.00 µl. The analyses were performed at 120 °C, and xylene was used as the mobile phase. The areas of the peaks with respect to the LLDPE/LDPE ratios in the blends were calculated as follows: first the area of each peak were calculated as a percentage of the total area of all the peaks, then the individual GPC peak areas were divided by the mass percent of LLDPE or LDPE in the blends:

$$A_{\text{tot}} = \sum A_i \quad (2.7)$$

where A_{tot} is the total area of the peaks, and A_i is the area of each individual peak,

$$P = A_i / A_{\text{tot}} \times 100 \quad (2.8)$$

where P is the percentage of the total peak area for each individual peak, A_i is the area of each individual peak and A_{tot} is the total area of all the peaks,

$$P_{\text{PE}} = P / W_{\text{PE/b}} \quad (2.9)$$

where P_{PE} is the percentage peak area with respect to the LLDPE or LDPE ratio in each respective blend, P is the percentage of the total peak area for each individual peak, and $W_{\text{PE/b}}$ is the mass % of LLDPE or LDPE in each respective blend.

CHAPTER 3

RESULTS

3.1 Characterization

The structure, as well as the thermal and mechanical properties, of LLDPE/wax and LDPE/wax blends were investigated. The samples were first characterized by FTIR and GPC in order to determine the structure and the MW, after which the influence of wax content on their thermal and mechanical properties were investigated.

3.1.1 Fourier-transform infrared spectroscopy

The FTIR spectra of pure wax, LLDPE and LDPE are shown in Figure 3.1.

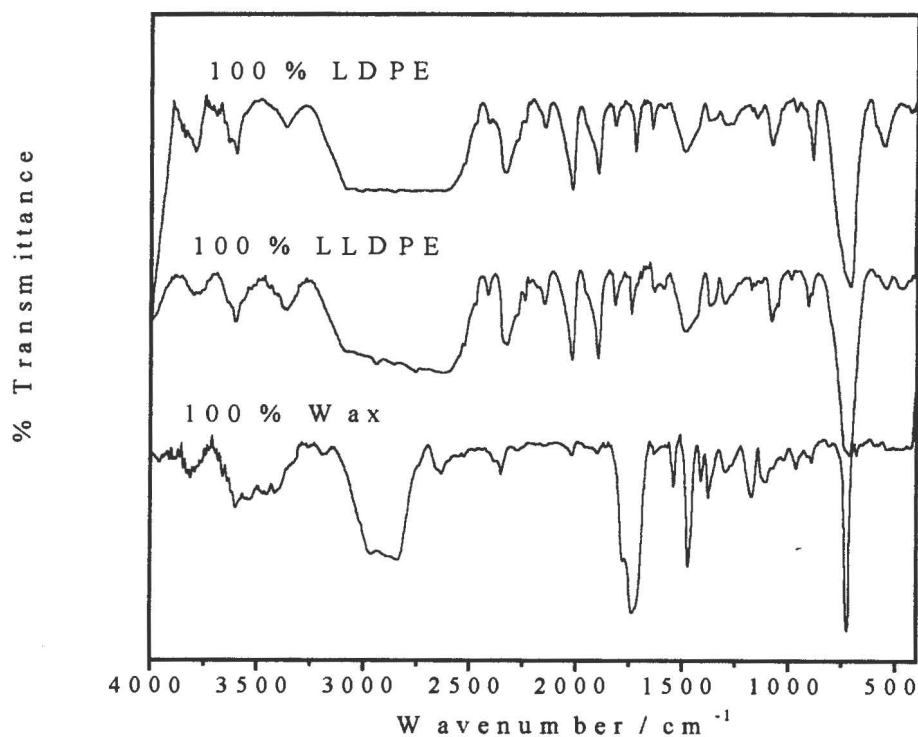


Figure 3.1 FTIR spectra of pure wax, LLDPE and LDPE

It is well known that the structure of wax as well as that of the PE's (LLDPE and LDPE) could be represented by the general formula $\text{CH}_3(\text{-CH}_2\text{-})_n\text{CH}_3$, where n indicates the degree of polymerization. The characteristic bending vibration of a long chain structure $(\text{-CH}_2\text{-})_n$ is observed in the $712\text{--}704\text{ cm}^{-1}$ region, and the $\text{-CH}_2\text{-}$ bend vibrations in the region $1474\text{--}1468\text{ cm}^{-1}$ (Figure 3.1). Since wax has shorter chains than LLDPE and LDPE, it is expected to have more end groups (-CH_3) per sample weight in its structure. In Figure 3.2, the IR-spectra show the characteristic band of the -CH_3 group in the region $1465\text{--}1375\text{ cm}^{-1}$. LDPE is more branched than LLDPE, and the wax has no C-H groups because it is not branched. It has only C-H (scissoring and bending) vibrations from the -CH_3 and $\text{-CH}_2\text{-}$ groups from the chain structure. In the IR-spectra in Figure 3.1, the C-H bending and scissoring vibrations appears in the regions $1790\text{--}780$ and $2322\text{--}2275\text{ cm}^{-1}$.

There are other vibrations that appear in the IR-spectra of both components such as overtone bands (C-H, $\text{-CH}_2\text{-}$ and -CH_3 groups) appearing in the region $2350\text{--}1704\text{ cm}^{-1}$, and these are stronger in the LLDPE and LDPE spectra than in the wax spectrum (Figure 3.1). Another broad bending vibration, which is a combination of the vibration bands for C-H, $\text{-CH}_2\text{-}$, -CH_3 and O-H groups, appears in the region $3350\text{--}2390\text{ cm}^{-1}$ in the wax, LLDPE and LDPE spectra. In Figure 3.1, the IR-spectra of wax, LLDPE and LDPE shows the characteristic band for O-H group in the region $3650\text{--}3350\text{ cm}^{-1}$. The IR-spectra of LLDPE and LDPE indicates two sharp O-H "free" bands, and the wax spectra show a broad O-H (hydrogen bonded) band.

Oxidized waxes contain oxygen atoms or oxygen containing groups such as ethers (C-O-C), alcohol (O-H) and carbonyl (C=O) groups in their structures. The characteristic bands of the C-O-C group ($1300\text{--}900\text{ cm}^{-1}$), the C=O group ($1725\text{--}1712\text{ cm}^{-1}$).

The FTIR spectra for mechanically and extrusion mixed LLDPE/wax and LDPE/wax blends are shown in Figures 3.2-3.5.

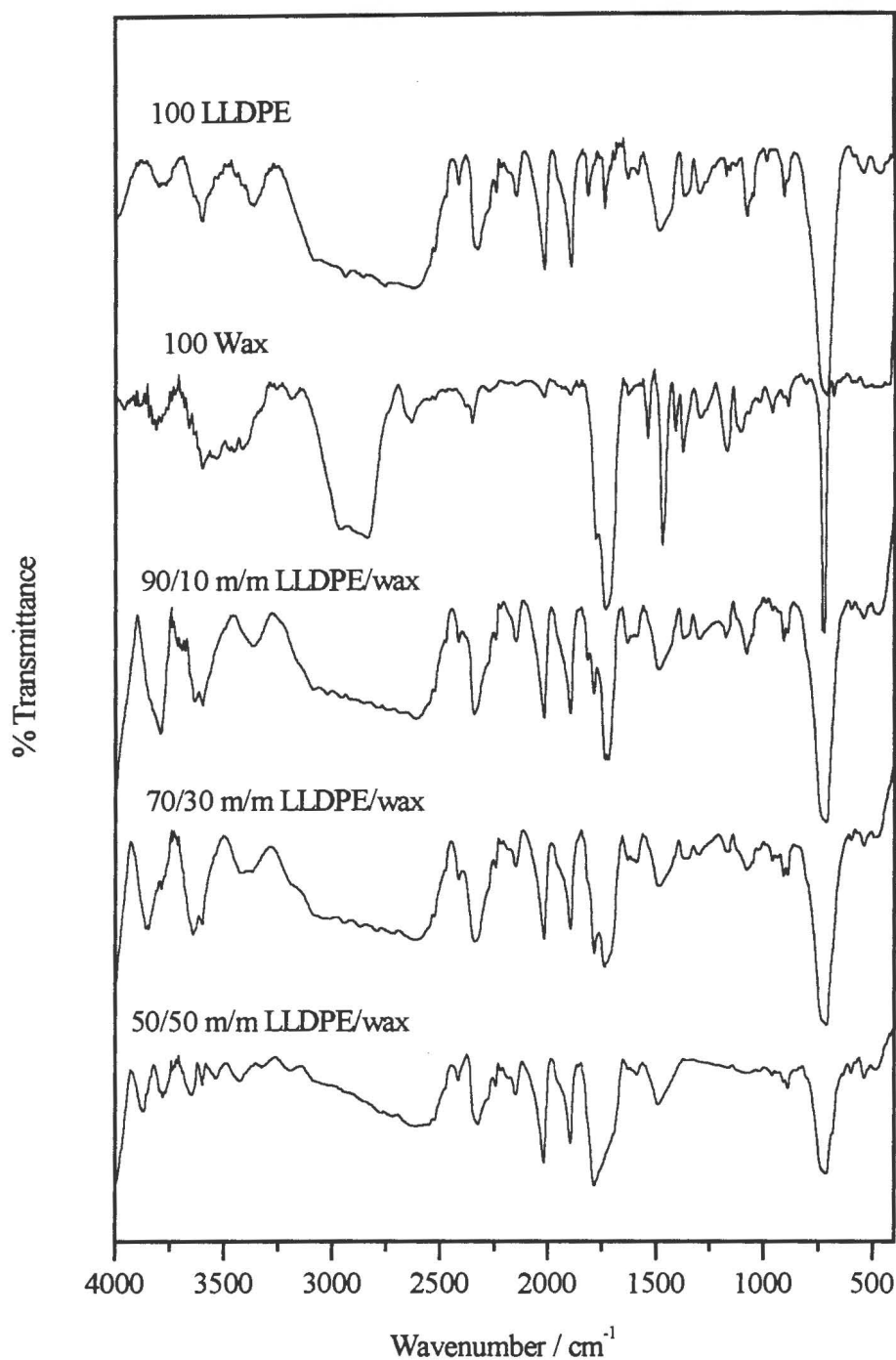


Figure 3.2 FTIR spectra for pure wax, LLDPE and mechanically mixed LLDPE/wax blends

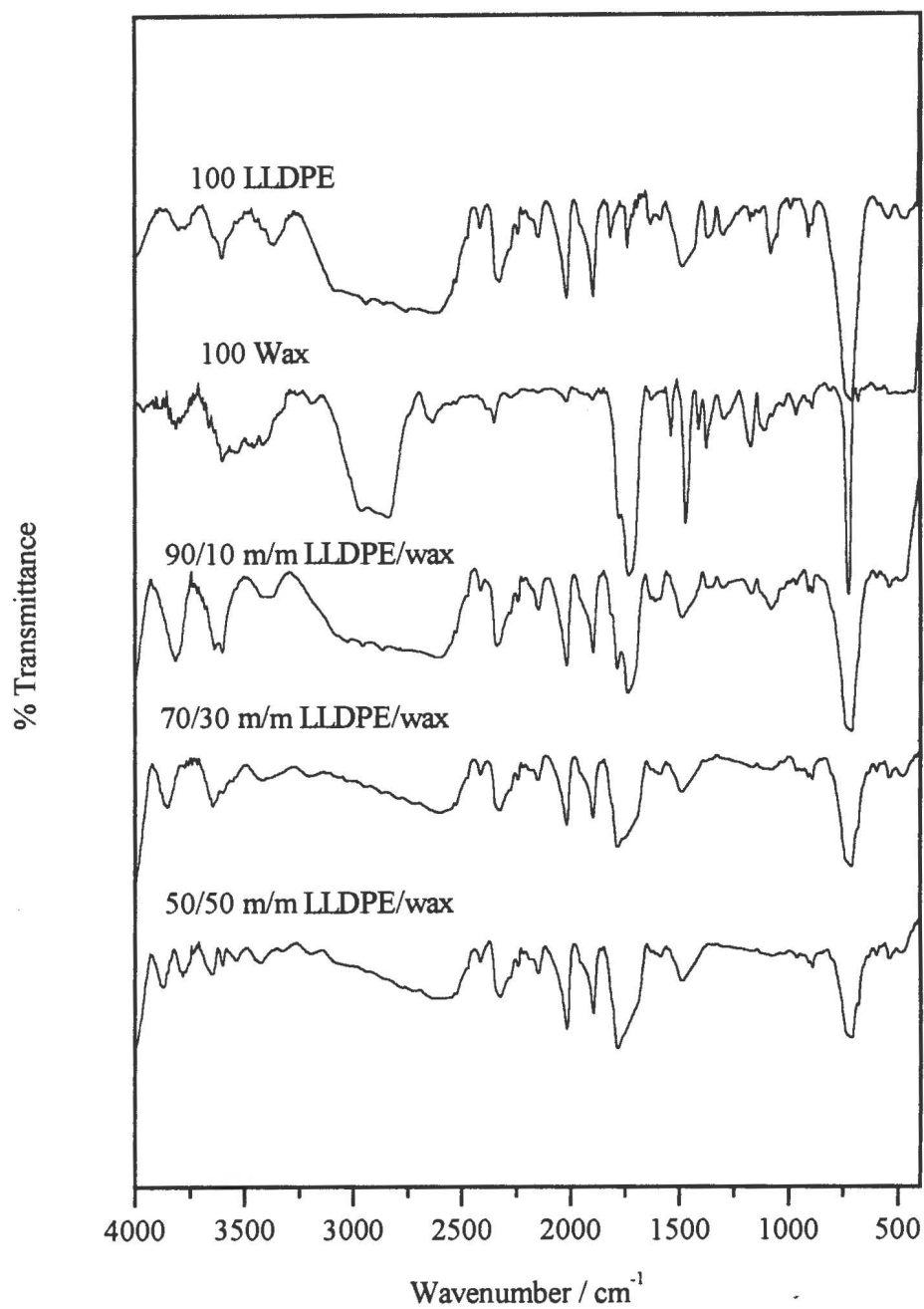


Figure 3.3 FTIR spectra for pure wax, LLDPE and extrusion mixed LLDPE/wax blends

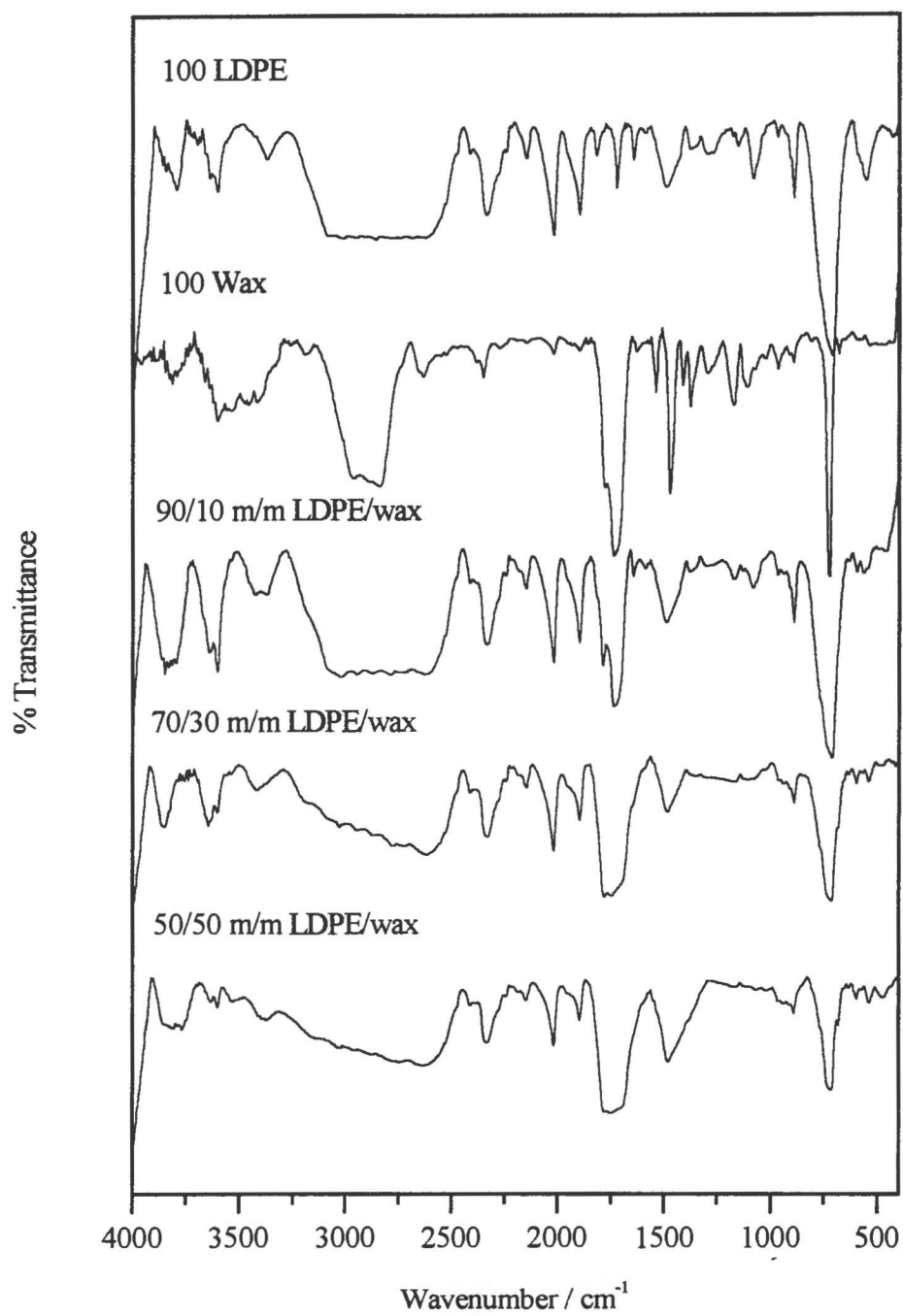


Figure 3.4 FTIR spectra for pure wax, LDPE and mechanically mixed LDPE/wax blends

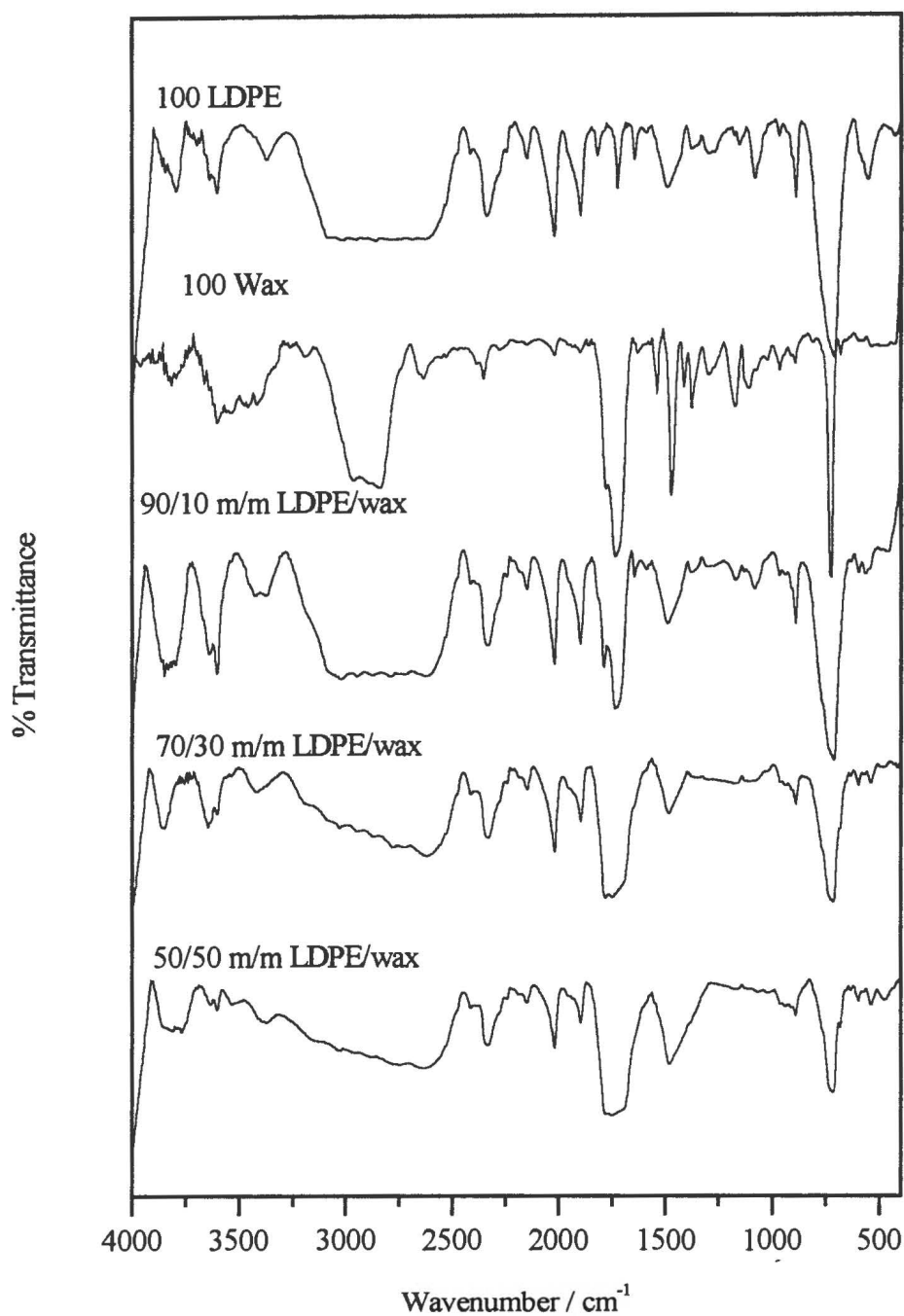


Figure 3.5 FTIR spectra for pure wax, LDPE and extrusion mixed LDPE/wax blends

The FTIR vibration intensities for pure wax, LLDPE and LDPE, and for the mechanically and extrusion mixed blends are summarized in Tables 3.1 and 3.2.

Table 3.1 Peak intensities of characteristic FTIR vibrations for LLDPE/wax blends

Functional groups and position (cm ⁻¹):							
LLDPE /wax	(CH ₂) _n 704	C-O-C 1300	CH ₂ 1474	C=O 1725	C-H 1785	CH ₃ 1465	O-H 3650
0/100	48.4	4.3	36.1	50.3	6.8	6.9	18.4
Mechanically mixed samples							
100/0	53.4	-	13.2	-	18.7	5.8	-
95/5	48.7	3.6	13.9	35.3	19.8	5.4	5.6
90/50	48.2	3.1	13.6	33.1	22.7	4.2	6.0
80/20	42.4	2.8	13.0	30.9	26.8	3.6	6.5
70/30	40.8	2.3	13.5	29.2	25.7	3.5	8.7
60/40	38.6	1.2	14.3	28.5	30.0	4.3	10.5
50/50	35.6	-	13.6	-	30.9	2.3	3.4
Extrusion mixed samples							
100/0	52.6	-	12.5	-	19.8	4.3	-
95/5	45.5	3.1	13.7	33.5	21.9	5.4	5.2
90/10	42.5	2.4	12.5	31.7	22.9	4.8	6.1
80/20	32.9	2.0	13.9	27.4	26.3	4.5	5.6
70/30	27.9	-	13.5	-	25.4	3.5	7.3
60/40	24.1	-	14.1	-	26.0	6.1	7.8
50/50	22.5	-	12.6	-	28.3	2.3	8.1

Table 3.2 Peak intensities of characteristic FTIR vibrations for LDPE/wax blends

LDPE/ Wax	Functional groups and positions (cm ⁻¹)						
	(CH ₂) _n 704	C-O-C 1300	CH ₂ 1474	C=O 1725	C-H 1783	CH ₃ 1465	O-H 3650
0/100	48.4	4.3	36.1	50.3	6.8	6.3	18.4
Mechanically mixed samples							
100/0	54.3	-	13.11	-	20.7	5.3	-
95/5	35.5	3.2	11.4	38.1	17.8	6.1	9.4
90/10	37.8	2.5	11.2	36.5	19.8	4.2	9.7
80/20	41.5	2.6	12.1	35.2	21.1	4.1	10.5
70/30	34.2	-	11.7	34.2	21.7	3.4	10.8
60/40	28.5	-	11.9	33.8	22.3	1.2	11.1
50/50	20.0	-	12.3	33.2	32.5	0.5	10.5
Extrusion mixed samples							
100/0	40.3	-	12.9	-	17.3	4.3	-
95/5	38.5	3.4	13.5	27.2	17.6	3.2	10.9
90/10	42.6	3.5	13.8	28.3	20.9	2.7	12.8
80/20	37.7	2.2	12.3	26.8	21.1	2.3	14.9
70/30	28.5	-	14.5	25.3	23.0	1.3	13.2
60/40	20.8	-	13.0	18.2	22.7	0.3	10.3
50/50	17.8	-	14.3	16.2	15.8	0.3	8.7

A linear decrease in intensity of the $(-\text{CH}_2)_n$ vibration ($712\text{-}704\text{ cm}^{-1}$) with an increase in wax content, as well as slight decrease in C-O-C vibration intensity ($1300\text{-}900\text{ cm}^{-1}$) with increase in wax content was observed. For mechanically mixed 50/50 m/m, extrusion mixed 70/30, 60/40, and 50/50 m/m LLDPE/wax blends, as well as both LDPE/wax blends containing 30 % and more wax, the C-O-C vibration is not pronounced. The intensity of the $-\text{CH}_2-$ bending vibration ($1474\text{-}1468\text{ cm}^{-1}$) decreases with an increase in wax content for both mechanically and extrusion mixed LLDPE/wax blends. In the case of the mechanically mixed LDPE/wax blends, an increase in wax content has no significant influence on the intensity of the $-\text{CH}_2-$ bending vibration. A slight increase in intensity of this vibration with an increase in wax content was observed for extrusion mixed blends. A linear decrease in the intensity of the C=O vibration ($1725\text{-}1712\text{ cm}^{-1}$) with an increase in wax content was observed for mechanically and extrusion mixed LLDPE/wax and LDPE/wax blends. For mechanically mixed blends containing 50 % wax, as well as extrusion mixed LLDPE/wax blends containing 30 % and more wax, this vibration is not pronounced. The C=O vibration is observed in the pure wax as well as all the blends' spectra. An increase in the intensity of the C-H aliphatic bending vibration ($1790\text{-}1784\text{ cm}^{-1}$) with an increase in wax content was observed for mechanically and extrusion mixed LLDPE/wax and LDPE/wax blends. The intensity of the $-\text{CH}_3$ bending vibration ($1465\text{-}1375\text{ cm}^{-1}$) decreases with an increase in wax content (Tables 3.1 and 3.2). An increase in the intensity of the O-H bonded vibration ($3650\text{-}3600\text{ cm}^{-1}$) with an increase in wax content for both LLDPE/wax blends and mechanically mixed LDPE/wax blends was observed. Extrusion mixed LDPE/wax blends containing 20 % and more wax show a slight decrease in the intensity of the O-H bonded vibration with an increase in wax content. This vibration is only observed for pure wax and the blends spectra.

There is another small bending vibration developing in the region of $650\text{-}640\text{ cm}^{-1}$, which is characteristic for the C-H out of plane bending vibration (oop) (Figures 3.2-3.5). This vibration is observed for mechanically mixed 50/50 m/m, extrusion mixed 70/30, 60/40, and 50/50 m/m LLDPE/wax blends, as well as for mechanically mixed 70/30, 60/40, 50/50 m/m, and extrusion mixed 80/20, 70/30, 60/40 and 50/50 m/m LDPE/wax blends.

3.1.2 Gel permeation chromatography

The GPC chromatograms of pure LLDPE and LDPE show three peaks at similar retention times. The first peak appears at about 10.9-11.8 minutes, the second peak at 23.2-23.4 minutes and the third one at 29.1-30.5 minutes. The pure wax chromatogram also shows three peaks at 15.9-16.3, 23.2-23.7 and 29.7-30.2 minutes.

The GPC results of mechanically mixed LLDPE/wax and LDPE/wax blends are summarized in Tables 3.3 and 3.4.

Table 3.3 % GPC peak areas with respect to LLDPE ratio in the blends

LLDPE/wax	<i>Peak 1</i>	<i>Peak 2</i>	<i>Peak 3</i>	<i>Peak 4</i>
100/0	33.7	52.7	11.6	-
95/5	34.6	58.4	11.2	18.3
90/10	35.6	62.5	6.9	45.9
80/20	39.1	93.5	13.0	34.5
70/30	18.6	106.7	14.8	69.1
60/40	42.1	128.5	16.0	78.4
50/50	40.1	142.2	17.7	103.6

Table 3.4 % GPC peaks areas with respect to LDPE ratio in the blends

LDPE/wax	<i>Peak 1</i>	<i>Peak 2</i>	<i>Peak 3</i>	<i>Peak 4</i>
100/0	25.2	62.9	10.2	-
95/5	30.9	59.1	15.4	8.5
90/10	31.3	78.3	14.5	12.7
80/20	21.2	92.4	11.1	24.5
70/30	32.4	99.4	10.5	45.9
60/40	17.2	131.5	18.0	42.7
50/50	21.9	173.0	15.1	87.5

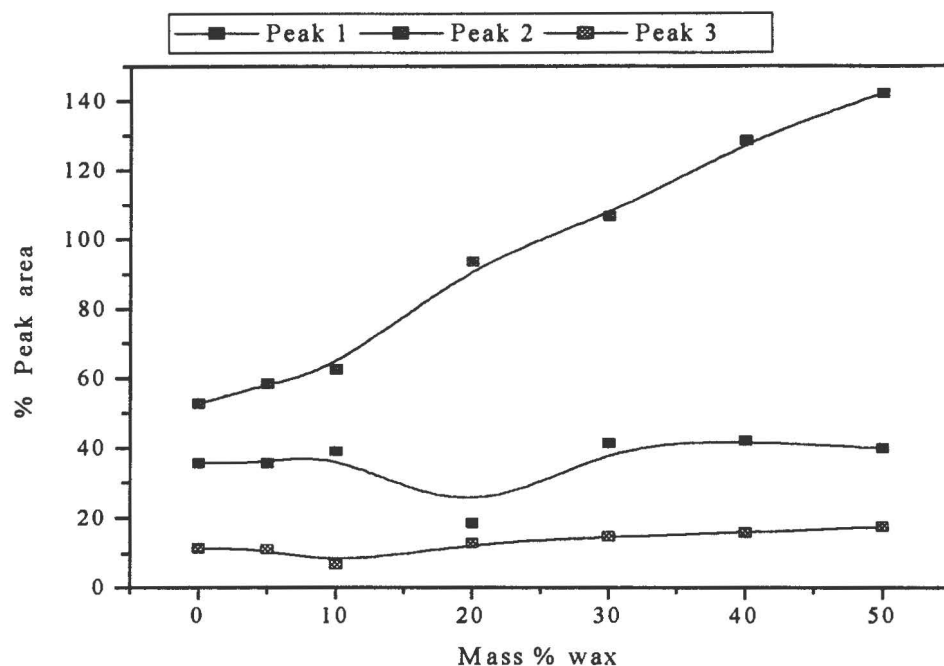


Figure 3.6 GPC peak area with respect to LLDPE ratio in the mechanically mixed LLDPE/wax blends as a function of wax content

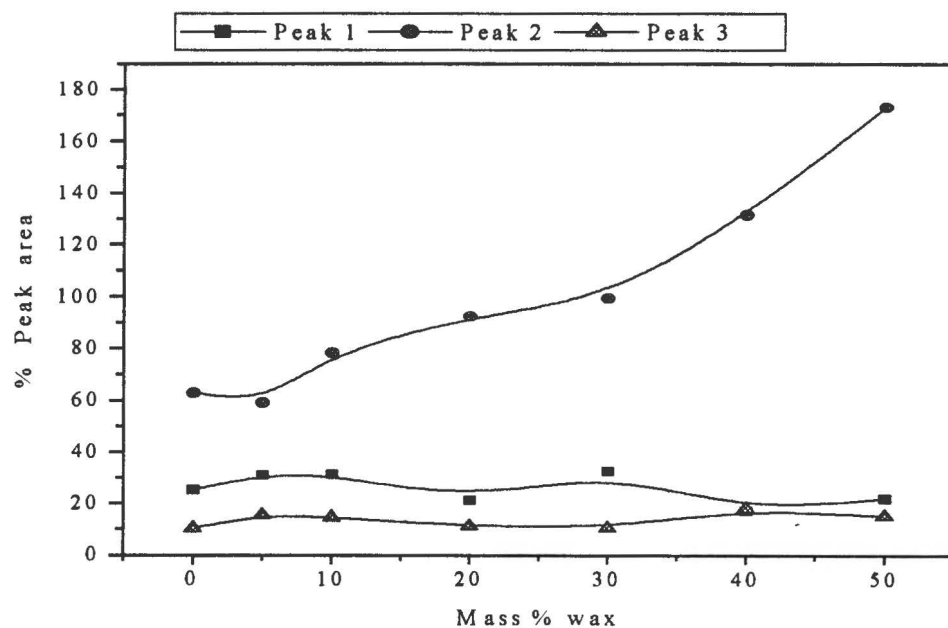


Figure 3.7 GPC peak area with respect to LDPE ratio in the mechanically mixed LDPE/wax blends as a function of wax content

Plots of peak areas with respect to LLDPE or LDPE ratio in the blends are shown as a function of wax content in Figures 3.6 and 3.7. The values were calculated according to equation (2.9). These values show that for both LLDPE and LDPE blends, the peak area of the second peak increases strongly with an increase in wax content. An increase in wax content of the blends has no apparent influence on the peak areas of the other two peaks. The chromatograms of LLDPE/wax and LDPE/wax blends also show another peak (Peak 4 in Tables 3.3 and 3.4). This peak appears in the chromatogram of pure wax, but not in those of the pure PEs (LLDPE and LDPE), and it increases with an increase in wax content in the blends. An increase in wax content causes a slight shift of the first and second peaks for both systems to lower RT values.

Thermal properties

3.2 Differential scanning calorimetry

The DSC heating curves for pure wax, LLDPE and LDPE are shown in Figure 3.8.

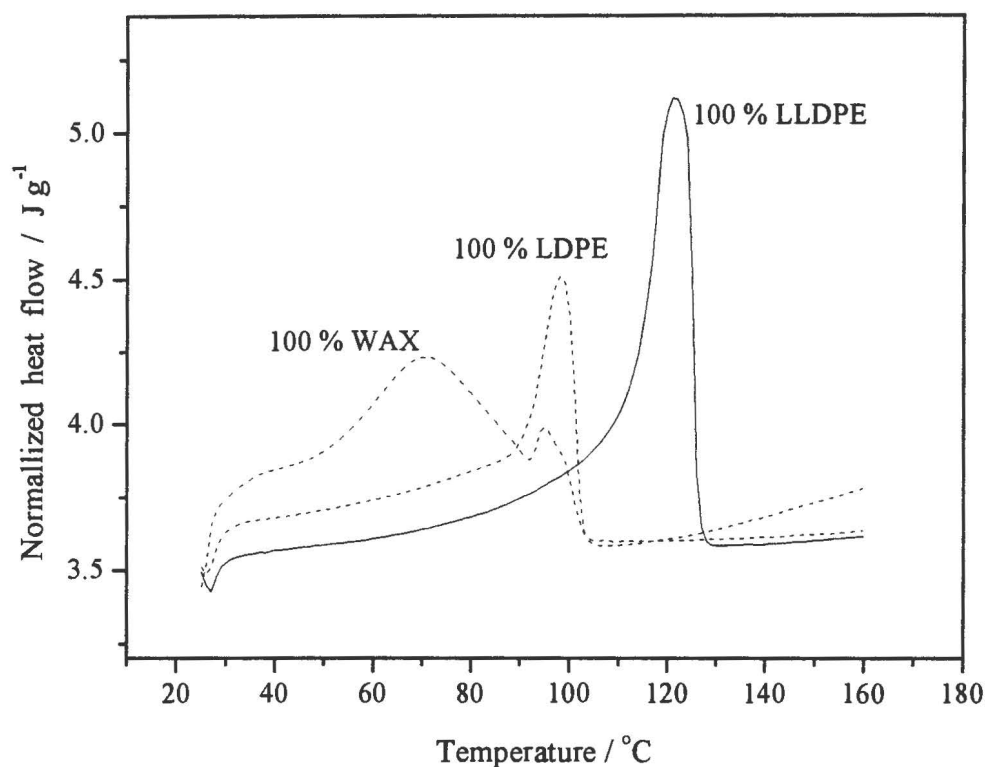


Figure 3.8 DSC heating curves for pure wax, LLDPE and LDPE

Pure wax shows two significant endothermic peaks, a broad main peak at 70.4 °C and a second small peak at 93.7 °C. Pure LLDPE and LDPE show only one endothermic peak each at 121.4 °C and 98.5 °C respectively. The melting peak of LLDPE is much more intense than that of LDPE.

The DSC heating curves for mechanically and extrusion mixed LLDPE/wax blends are shown in Figures 3.9 and 3.10.

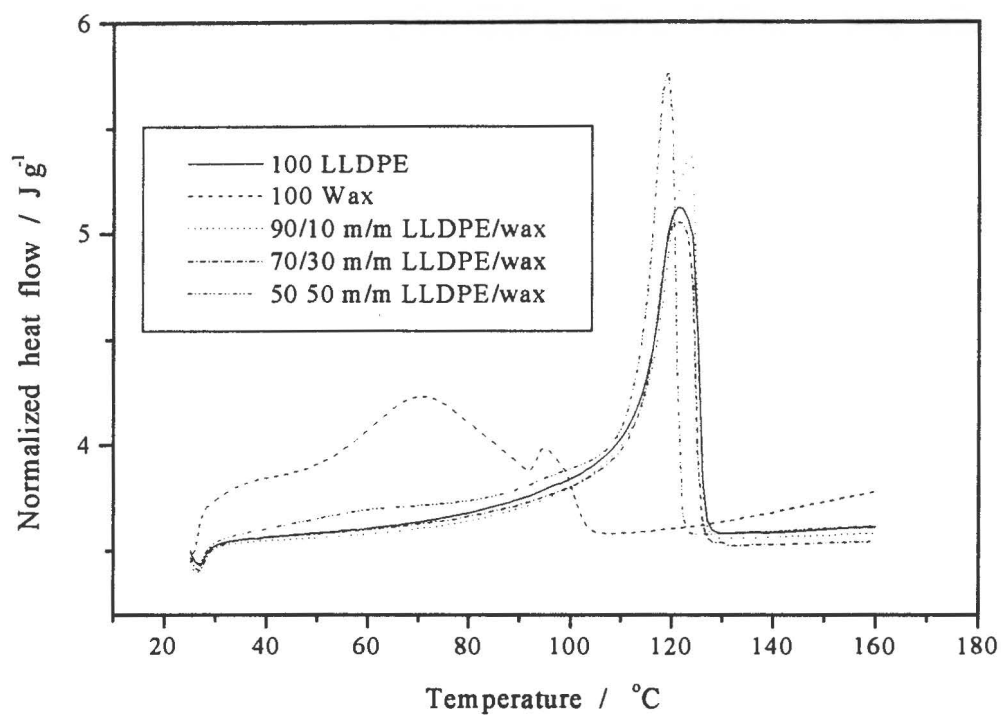


Figure 3.9 DSC heating curves for mechanically mixed LLDPE/wax blends

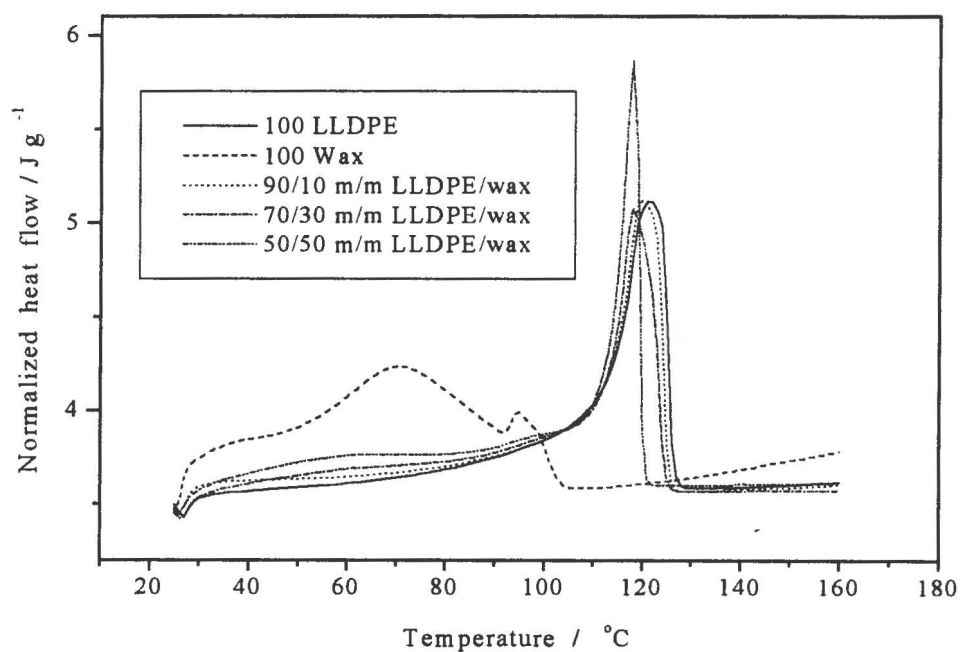


Figure 3.10 DSC heating curves for extrusion mixed LLDPE/wax blends

For mechanically mixed LLDPE blends containing 5, 10, 20, 30 and 40 % wax, as well as extrusion mixed blends containing 5, 10, and 20 % wax, only one endothermic peak is observed, despite the fact that wax shows two significant endothermic peaks, and this peak is in the same temperature region than that of pure LLDPE. However, the mechanically mixed 50/50 m/m as well as the extrusion mixed 70/30, 60/40 and 50/50 m/m LLDPE/wax blends show also a low intensity, broad peak at about 60-80 °C. The temperature of this peak corresponds to that of the wax main peak (Figures 3.9 and 3.10)

The DSC heating curves for mechanically and extrusion mixed LDPE/wax blends are shown in Figures 3.11 and 3.12.

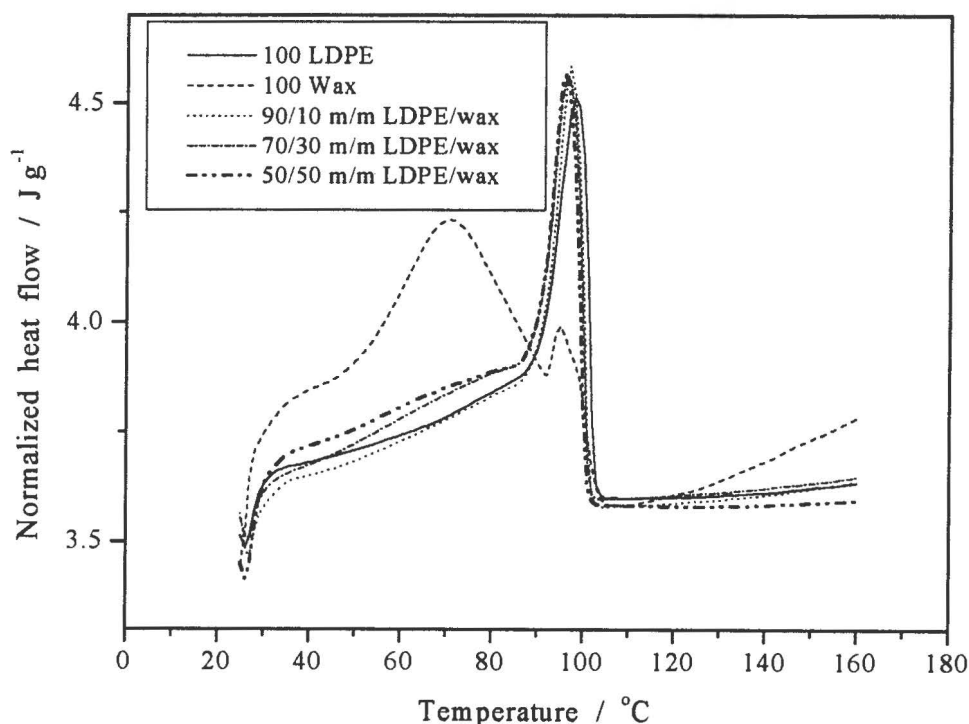


Figure 3.11 DSC heating curves for mechanically mixed LDPE/wax blends

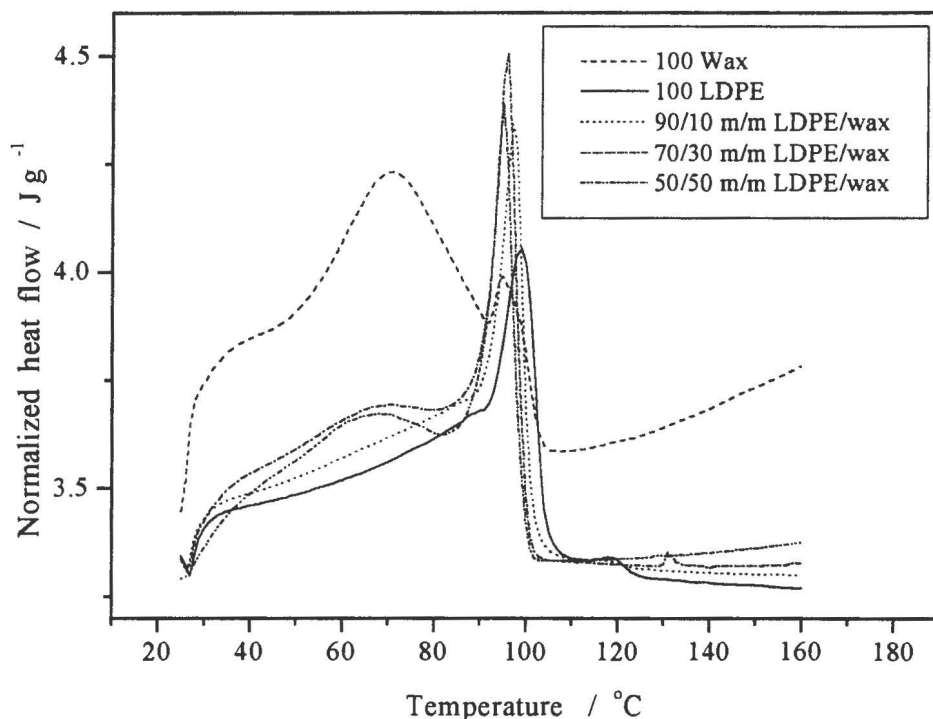


Figure 3.12 DSC heating curves for extrusion mixed LDPE/wax blends

Only one endothermic peak was observed for mechanically mixed blends containing 5, 10 and 20 % wax, as well as extrusion mixed blends containing 5 and 10 % wax, in the same temperature region than that of pure LDPE, which is the same than that of the second peak maximum in the wax melting peak (Figure 3.8 and 3.12). A low-intensity, broad peak at about 60-80 °C developed in the case of the mechanically mixed 70/30, 60/40 and 50/50 m/m, as well as the extrusion mixed 80/20, 70/30, 60/40 and 50/50 m/m LDPE/wax blends. This peak is in the same temperature region than the first peak maximum in the wax melting peak.

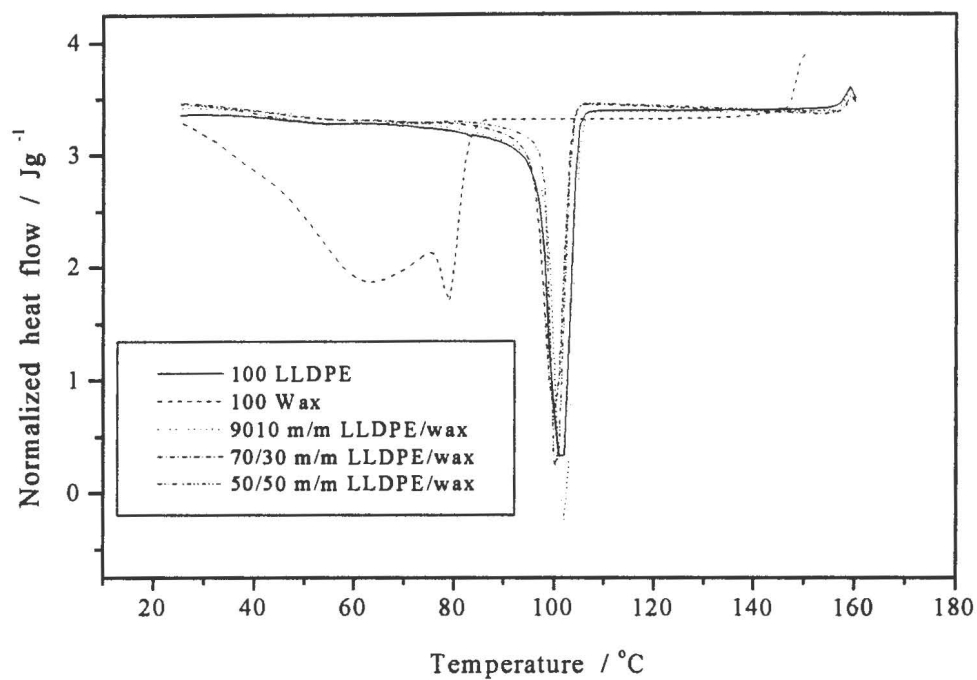


Figure 3.14 DSC cooling curves for mechanically mixed LLDPE/wax blends

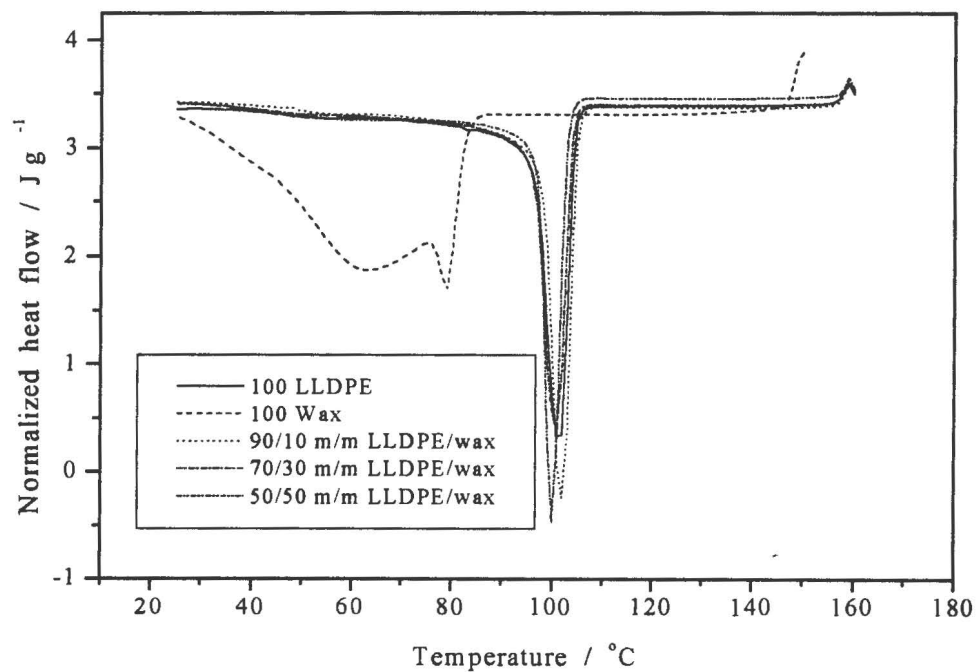


Figure 3.15 DSC cooling curves for extrusion mixed LLDPE/wax blends

Only one exothermic peak is observed for mechanically mixed 95/5, 90/10, 80/20, 70/30 and 60/40 m/m, as well as extrusion mixed 95/5, 90/10 and 80/20 m/m LLDPE/wax blends, despite the fact that wax shows two significant exothermic peaks, and the temperature of this peak corresponds to that of the crystallization peak for pure LLDPE. The mechanically mixed blend containing 50 % wax as well as the extrusion mixed blends containing 30 % and more wax, show another low intensity peak at 60 °C and its temperature corresponds to that of the wax main peak.

The DSC cooling curves for mechanically and extrusion mixed LDPE/wax blends are shown in Figures 3.16 and 3.17.

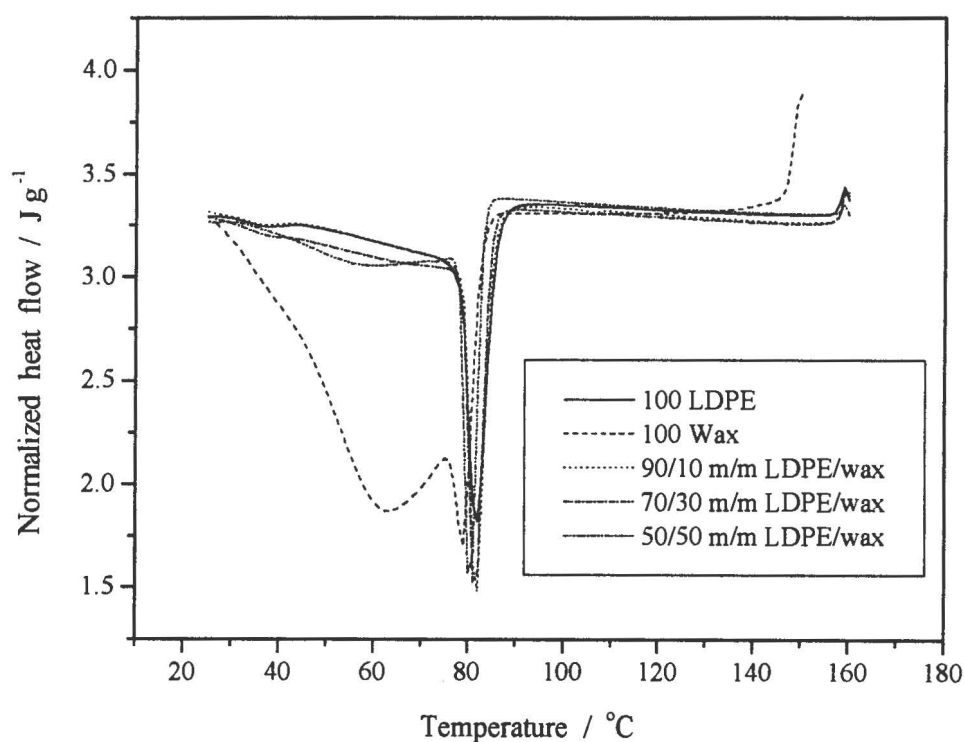


Figure 3.16 DSC cooling curves for mechanically mixed LDPE/wax blends

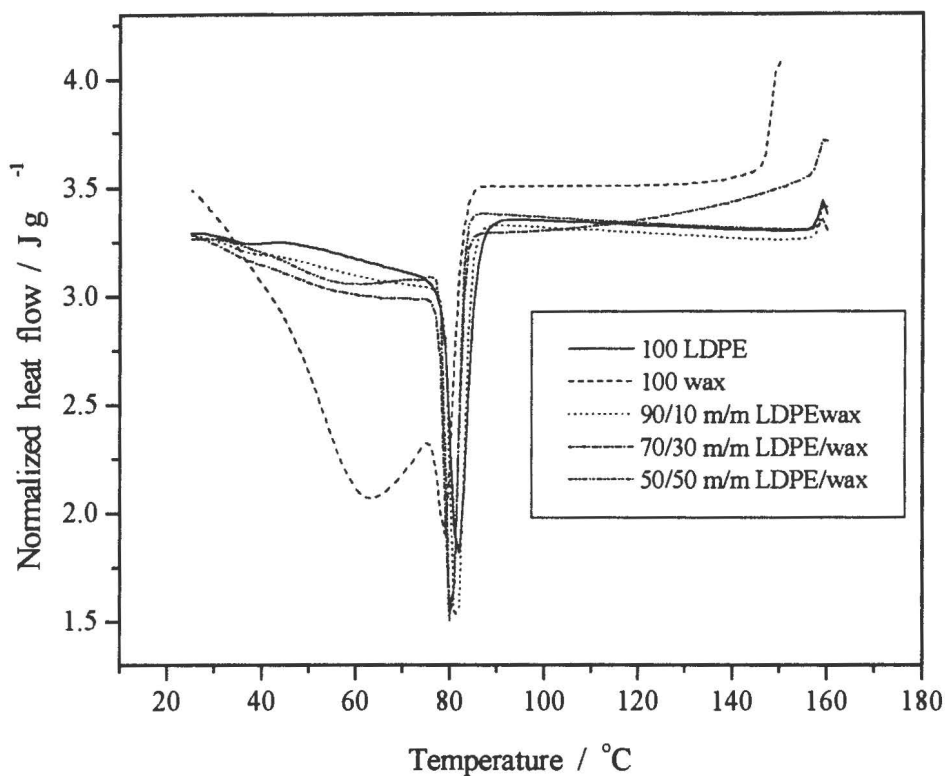


Figure 3.17 DSC cooling curves for extrusion mixed LDPE/wax blends

Mechanically mixed samples containing 5, 10, 20 and 30 % wax, and extrusion mixed samples containing 5, 10 and 20 % wax show only one exothermic peak in the same temperature region than that of pure LDPE. A low-intensity peak is, however, observed for mechanically mixed blends containing 40 % and more wax, as well as for extrusion mixed blends containing 30 % and more wax.

The DSC results are summarized in Tables 3.5 and 3.6.

Table 3.5 DSC results for LLDPE/wax blends

LLDPE/ wax	T _{o,m} [°C]	T _{p,m} =T _m [°C]	ΔH _m [J g ⁻¹]	T _{p,c} =T _c [°C]	T _{o,c} [°C]	ΔH _c [J g ⁻¹]	ΔH _m ^{add} [J g ⁻¹]
0/100	25.7	70.4 ^a	204.8	65.5 ^b	79.2	-148.9	204.8
Mechanically mixed							
100/0	112.8	121.4	150.9	104.3	101.6	-123.8	150.8
95/5	113.7	123.7	151.7	104.5	101.6	-124.6	154.1
90/10	113.2	123.5	152.7	104.8	101.9	-126.5	157.9
80/20	113.7	122.5	148.6	104.6	100.8	-125.3	159.8
70/30	113.1	121.5	146.0	103.8	100.9	-124.6	163.7
60/40	113.3	120.5	145.4	103.7	100.9	-126.3	169.2
50/50	113.7	120.5	146.0	103.7	100.9	-124.2	175.4
Extrusion mixed							
100/0	113.1	121.8	153.6	104.0	100.4	-110.5	153.6
95/5	113.0	122.2	158.6	105.4	102.4	-110.4	160.9
90/10	113.0	120.0	142.2	104.3	102.5	-111.7	148.5
80/20	112.0	119.5	140.5	103.2	101.3	-110.6	153.4
70/30	112.0	118.0	138.6	103.8	100.3	-111.6	155.0
60/40	113.2	118.2	132.2	103.2	101.0	-110.0	161.2
50/50	112.5	118.3	132.5	103.2	100.3	-110.2	168.2

T - temperature, ΔH - melting enthalpy, m - melting, c - cooling, o - onset, p - peak, ΔH_m^{add} - additive rule given by $\Delta H_m^{add} = \Delta H_{m,PE} W_{PE} + \Delta H_{m,w} W_w$ where ΔH_{m,PE} and ΔH_{m,w} are the melting enthalpies of PE and wax respectively, W_{PE} and W_w are the weight percent of PE and wax in the blends.

^a The main endothermic peak (since wax has two endothermic peaks). The second peak is at 93.7 °C

^b The main exothermic peak (since wax has two exothermic peaks). The second peak is at 82.6 °C

Table 3.6 DSC results for LDPE/wax blends

LDPE /wax	T _{o,m} [°C]	T _{p,m} =T _m [°C]	ΔH _m [J g ⁻¹]	T _{p,c} =T _c [°C]	T _{o,c} [°C]	ΔH _c [J g ⁻¹]	ΔH _m ^{add} [J g ⁻¹]
0/100	25.7	70.4 ^a	204.8	65.5 ^b	79.2	-148.9	204.8
Mechanically mixed							
100/0	89.9	98.5	83.5	82.3	78.6	-71.9	56.8
95/5	89.3	98.4	86.3	82.2	78.5	-73.4	75.1
90/10	89.9	97.0	87.1	82.1	78.3	-73.7	89.9
80/20	89.7	96.0	84.9	82.0	78.8	-74.8	100.9
70/30	89.2	95.9	87.3	82.2	78.8	-75.7	115.5
60/40	88.9	95.5	92.9	82.3	76.5	-77.2	131.7
50/50	88.2	95.5	95.8	82.9	80.5	-76.8	145.3
Extrusion mixed							
100/0	91.4	99.6	84.6	83.7	82.4	-55.4	65.3
95/5	91.9	98.2	88.7	85.6	81.8	-54.1	78.4
90/10	91.8	99.2	90.4	87.1	82.7	-58.6	89.3
80/20	91.5	97.5	97.9	84.9	81.7	-54.7	103.1
70/30	91.4	96.5	98.2	84.4	81.5	-51.3	143.7
60/40	91.2	95.7	102.3	83.0	80.3	-46.8	138.1
50/50	90.9	95.2	104.2	82.9	80.5	-43.7	149.5

T - temperature, ΔH - melting enthalpy, m - melting, c - cooling, o - onset, p - peak, ΔH_m^{add} - additive rule given by $\Delta H_m^{\text{add}} = \Delta H_{m,\text{PE}} W_{\text{PE}} + \Delta H_{m,\text{w}} W_{\text{w}}$ where ΔH_{m,PE} and ΔH_{m,w} are the melting enthalpies of PE and wax respectively, W_{PE} and W_w are the weight percent of PE and wax in the blends.

^a The main endothermic peak (since wax has two endothermic peaks). The second peak is at 93.7 °C

^b The main exothermic peak (since wax has two exothermic peaks). The second peak is at 82.6 °C

The onset temperature of melting ($T_{o,m}$) as a function of wax content for mechanically and extrusion mixed LLDPE/wax and LDPE/wax blends are shown in Figure 3.18.

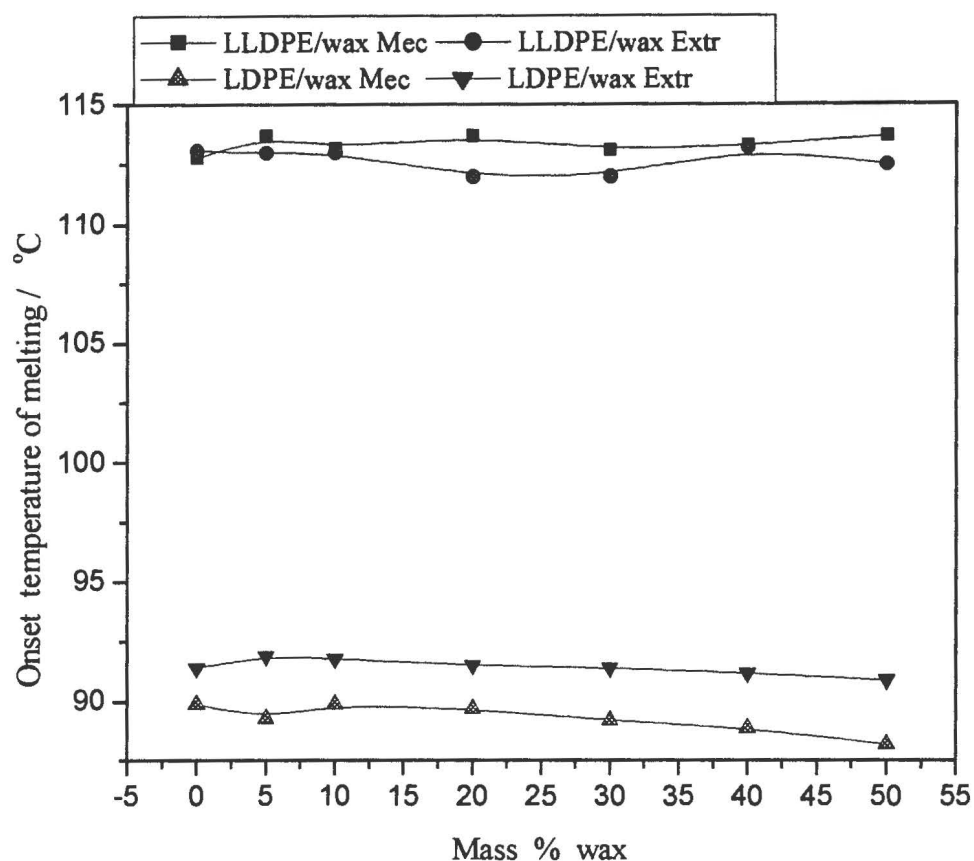


Figure 3.18 Onset temperature of melting vs mass % wax for mechanically and extrusion mixed LLDPE/wax and LDPE/wax blends as a function of wax content

An increase in wax content does not have a significant influence on the $T_{o,m}$ of LLDPE/wax blends, while a slight decrease in $T_{o,c}$ with an increase in wax content was observed for LDPE/wax blends. The $T_{o,m}$ of LLDPE/wax blends are higher than that of LDPE/wax blends. It is interesting that the $T_{o,m}$ for the extrusion mixed blends are generally higher than those for the mechanically mixed blends.

The peak temperature of melting (T_m) for mechanically and extrusion mixed LLDPE/wax and LDPE/wax blends is shown as a function of wax content in Figure 3.19.

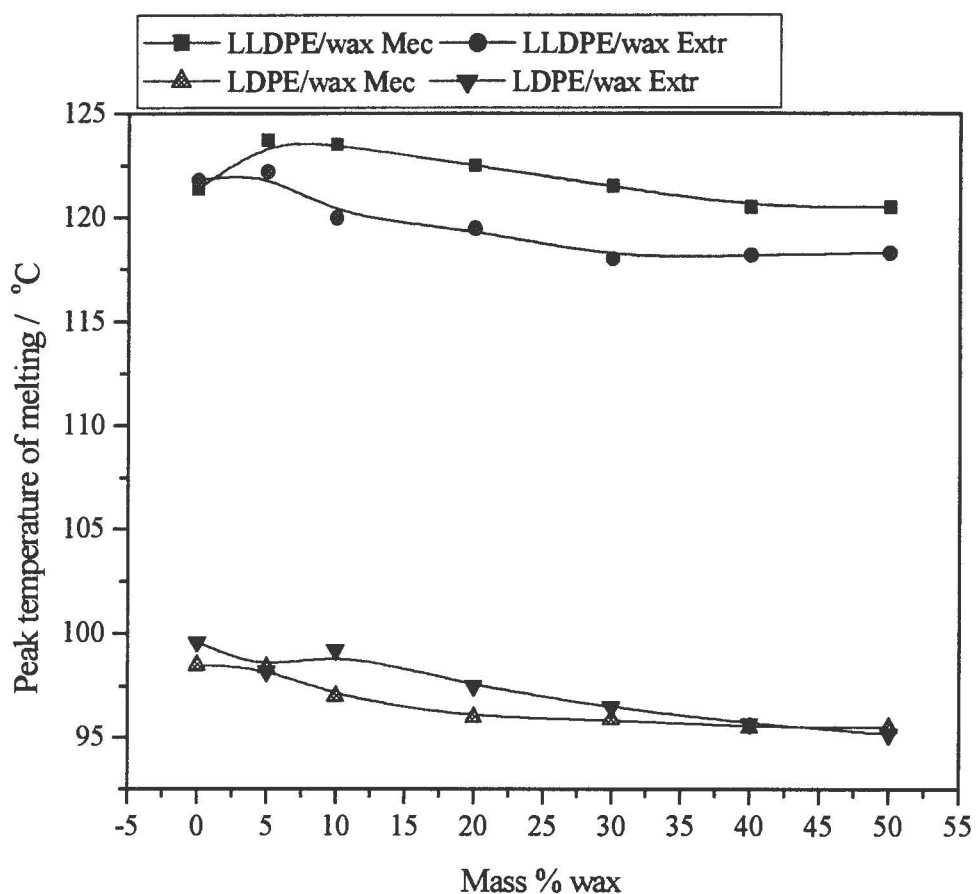


Figure 3.19 Peak temperature of melting vs mass % wax for mechanically and extrusion mixed LLDPE/wax and LDPE/wax blends as a function of wax content

The T_m decreases slightly for LLDPE/wax and LDPE/wax blends with an increase in wax content. Mechanically mixed LLDPE/wax blends also show a higher T_m than extrusion mixed blends. For most of the LDPE blends the extrusion mixed samples have higher T_m than the mechanically mixed samples.

The specific melting enthalpy (ΔH_m) of mechanically and extrusion mixed LLDPE/wax and LDPE/wax blends are shown as a function of wax content in Figure 3.20.

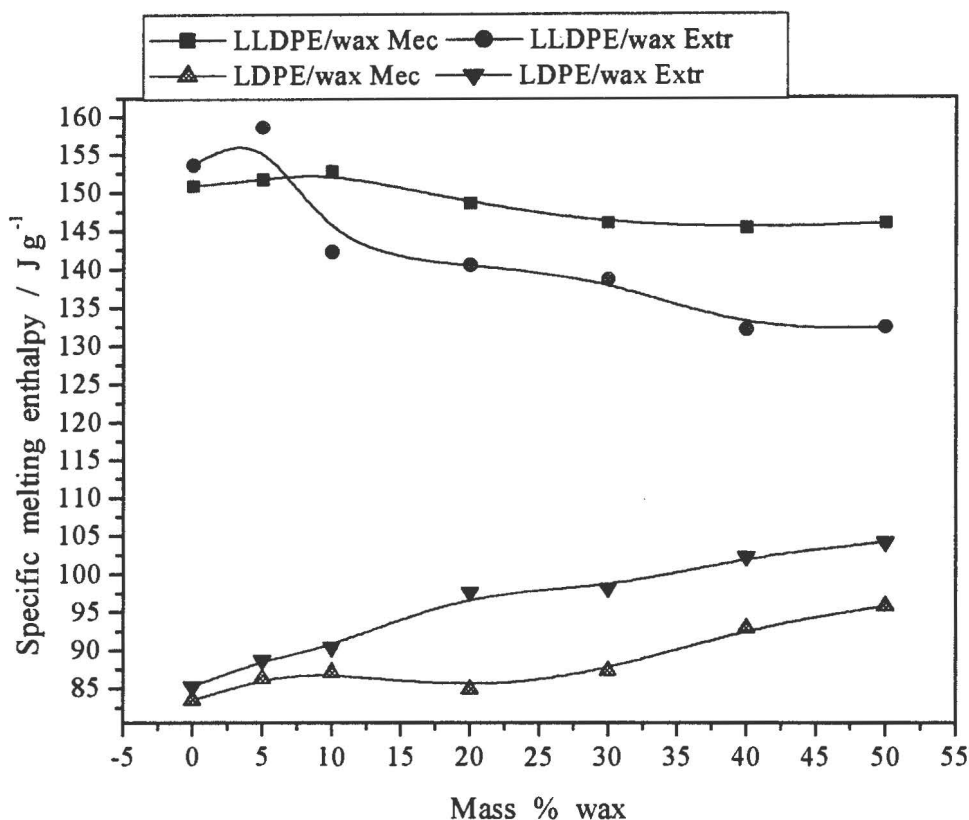


Figure 3.20 Specific melting enthalpies vs mass % wax for mechanically and extrusion mixed LLDPE/wax and LDPE/wax blends as a function of wax content

ΔH_m LLDPE/wax blends slightly decrease with increase in wax content. For LDPE/wax blends an increase in ΔH_m values with increase in wax content was observed. The mechanically mixed LLDPE/wax blends have higher ΔH_m values than the extrusion mixed blends. In the case of LDPE/wax blends, the extrusion mixed blends have higher ΔH_m than the mechanically mixed blends. In both cases it seems as if the ΔH_m difference increases with increasing wax content.

The onset temperature of crystallization ($T_{o,c}$) of mechanically and extrusion mixed LLDPE/wax and LDPE/wax blends are shown as a function of wax content in Figure 3.21.

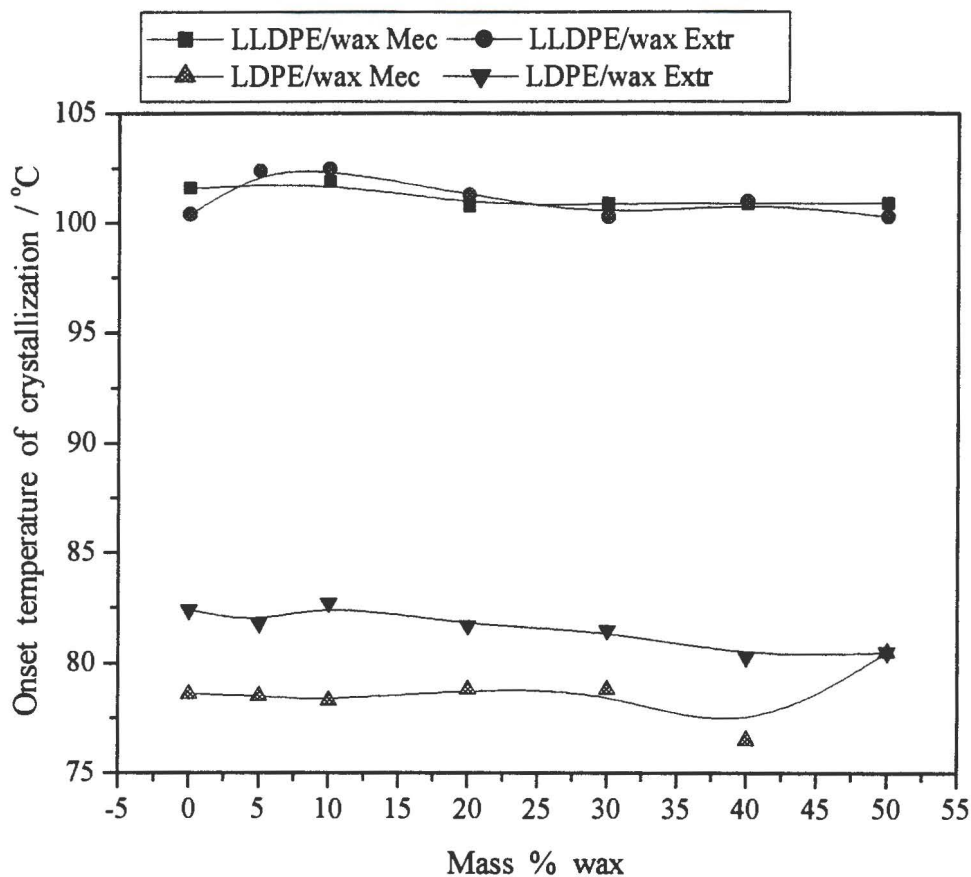


Figure 3.21 Onset temperature of crystallization vs mass % wax for mechanically and extrusion mixed LLDPE/wax and LDPE/wax blends

The onset temperature of crystallization ($T_{o,c}$) of mechanically and extrusion mixed LDPE/wax and LDPE/wax blends remains virtually constant with an increase in wax content.

The peak temperature of crystallization (T_c) for mechanically and extrusion mixed LLDPE/wax and LDPE/wax blends are shown as a function of wax content in Figure 3.22.

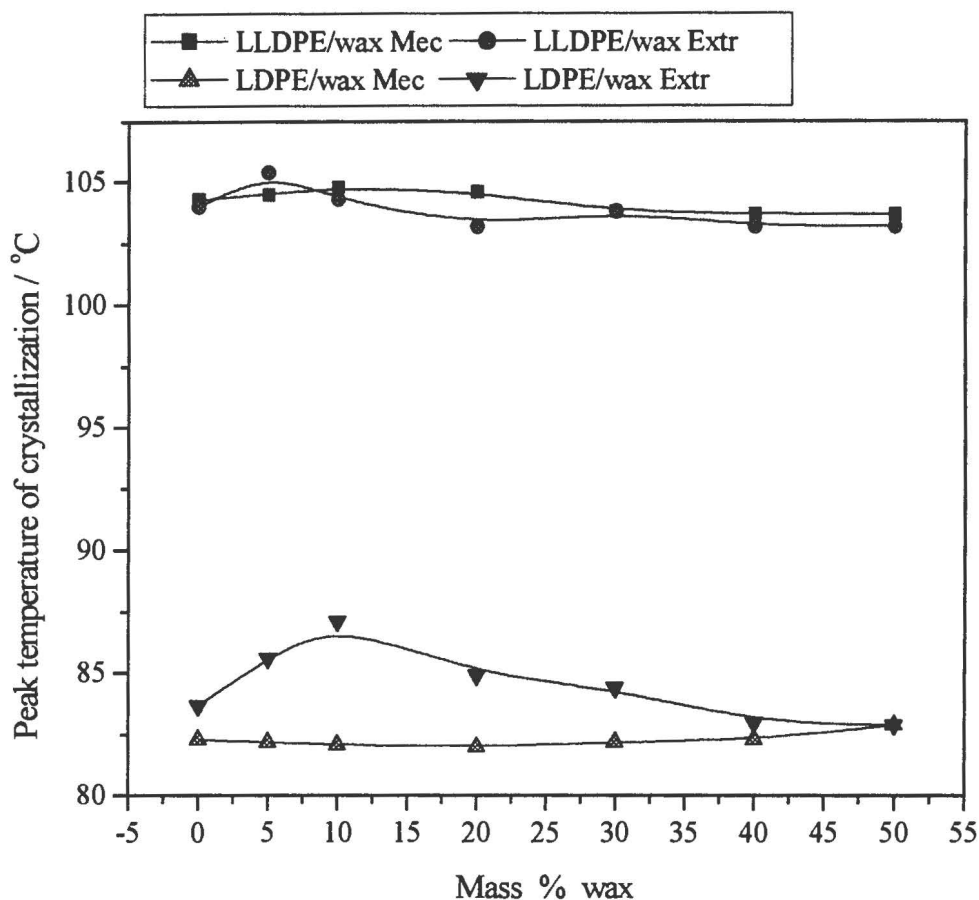


Figure 3.22 Peak temperature of crystallization vs mass % wax for mechanically and extrusion mixed LLDPE/wax and LDPE/wax blends

Mechanically and extrusion mixed LLDPE/wax blends show a slight decrease in T_c with an increase in wax content. An increase in wax content seems to have no significant influence on T_c for mechanically mixed LDPE/wax blends, but extrusion mixed LDPE/wax blends show an initial increase followed by a decrease in T_c with increasing wax content.

The specific enthalpies of crystallization (ΔH_c) of mechanically and extrusion mixed LLDPE/wax and LDPE/wax blends are shown as a function of wax content in Figure 3.23.

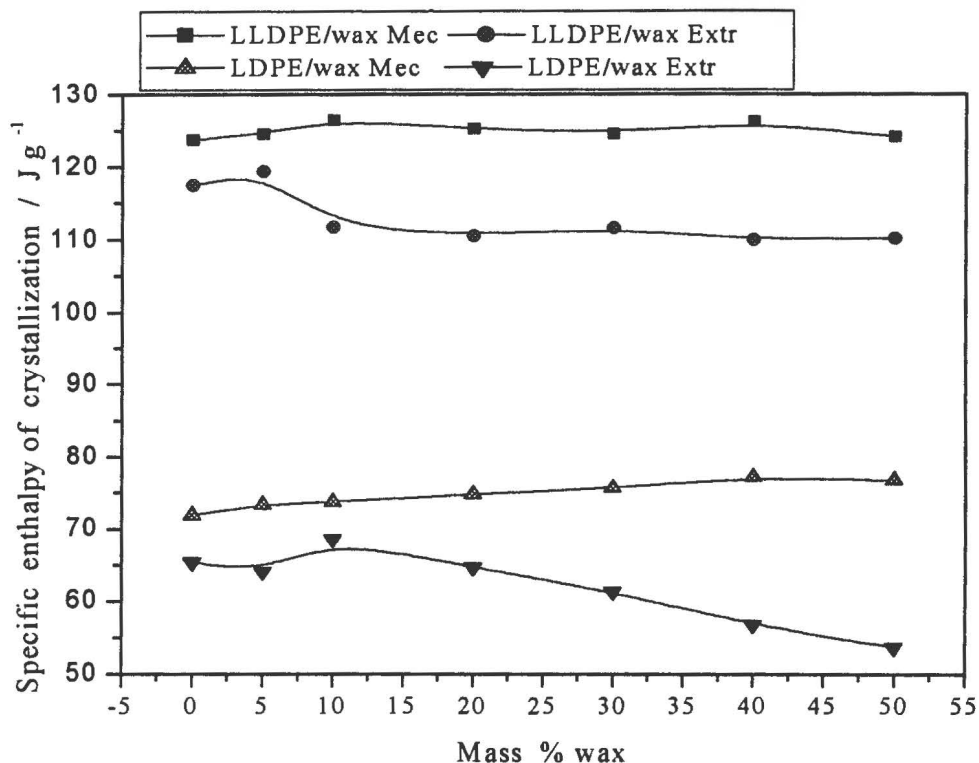


Figure 3.23 Specific enthalpy of crystallization vs mass % wax for mechanically and extrusion mixed LLDPE/wax and LDPE/wax blends

An increase in wax content has little influence on the ΔH_c for mechanically mixed LLDPE/wax blends. A slight increase in ΔH_c with an increase in wax content for mechanically mixed LDPE/wax blends was observed. The extrusion mixed LLDPE/wax and LDPE/wax blends both show a decrease in ΔH_c with increase in wax content.

3.2.2 Thermogravimetric analysis

The TGA curves for pure wax, LLDPE and LDPE are shown in Figure 3.24.

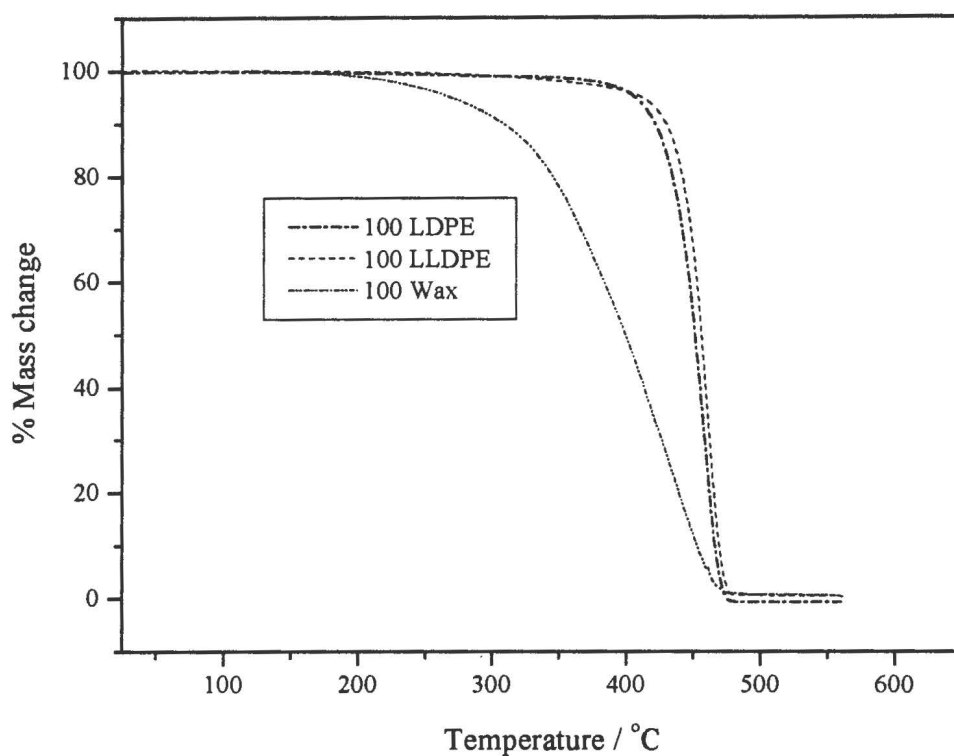


Figure 3.24 TGA curves for pure wax, LLDPE and LDPE

These curves show that pure wax, LLDPE and LDPE each undergo decomposition in a single step. The onset temperatures of decomposition are at 309.1 °C for pure wax, at 487 °C for LLDPE, and at 465.1 °C for LDPE. Pure wax has a lower thermal stability than LLDPE and LDPE, and LLDPE has a higher thermal stability than LDPE.

The TGA curves for mechanically and extrusion mixed LLDPE is shown in Figures 3.25 and 3.26.

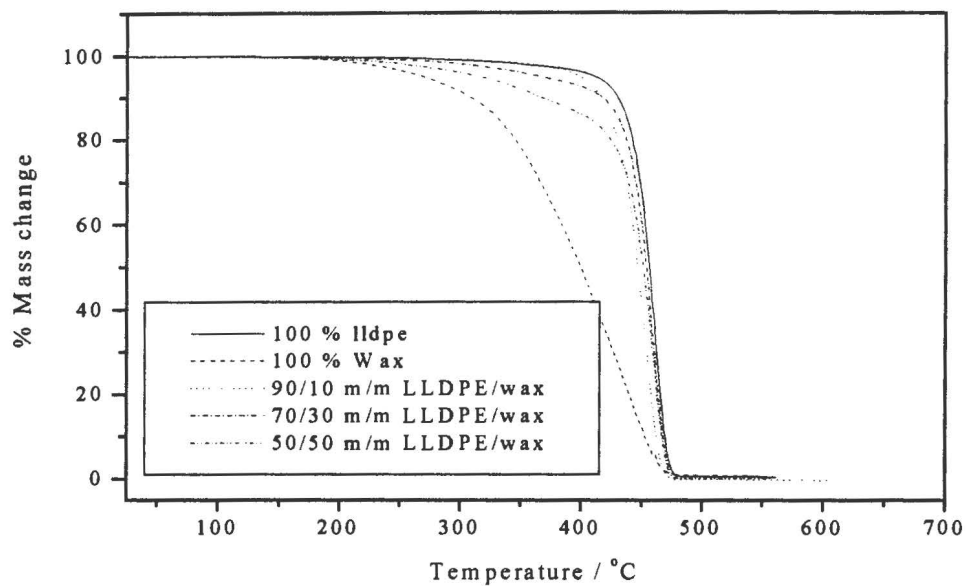


Figure 3.25 TGA curves for pure wax, LLDPE and mechanically mixed LLDPE/wax blends

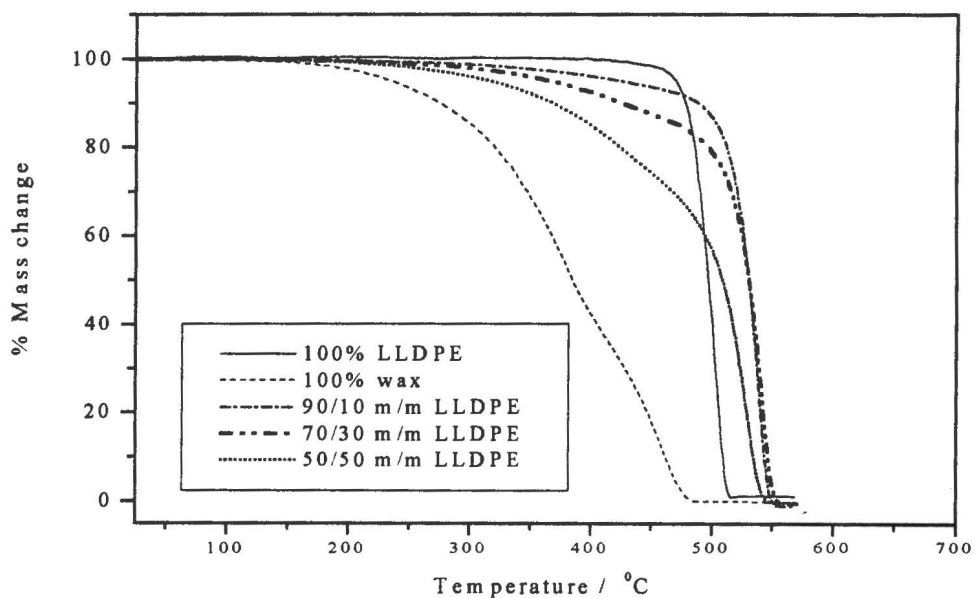


Figure 3.26 TGA curves for pure wax, LLDPE and extrusion mixed LLDPE/wax blends

These curves show that the mechanically mixed blends undergo decomposition in a single step, except the 50/50 m/m blends where there is a hint of a two-step process. The extrusion mixed blends show a two-step mass loss with the second step generally at higher temperatures than that of the decomposition of pure LLDPE. The mechanically mixed blends show onset temperatures of decomposition at 476.7 °C for the 90/10 m/m blend, at 425.1 °C for the 70/30 m/m blend, and at 408.2 °C for the 50/50 m/m blend. The onset temperature of decomposition for extrusion mixed blends are at 496.7 °C for the 90/10 m/m blend, at 484.7 °C for the 70/30 m/m blend, and at 487.1 °C for the 50/50 m/m blend. Char yield is observed at a temperatures higher than 500 °C for all blends.

The TGA curves for mechanically and extrusion mixed LDPE/wax blends are shown in Figures 3.27 and 3.28.

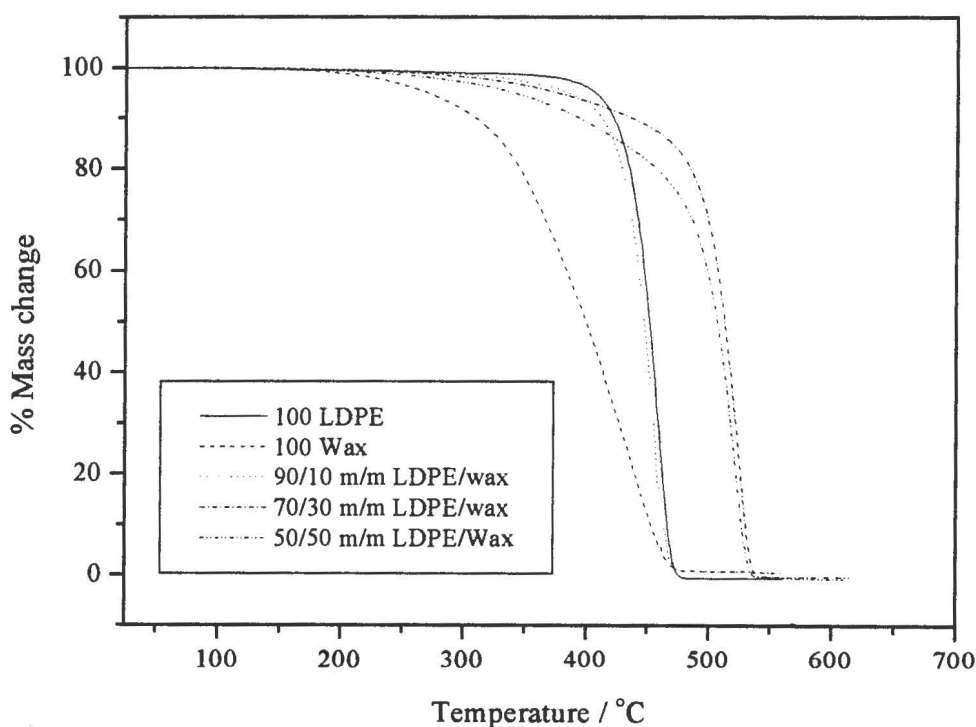


Figure 3.27 TGA curves for pure wax, LDPE and mechanically mixed LDPE/wax blends

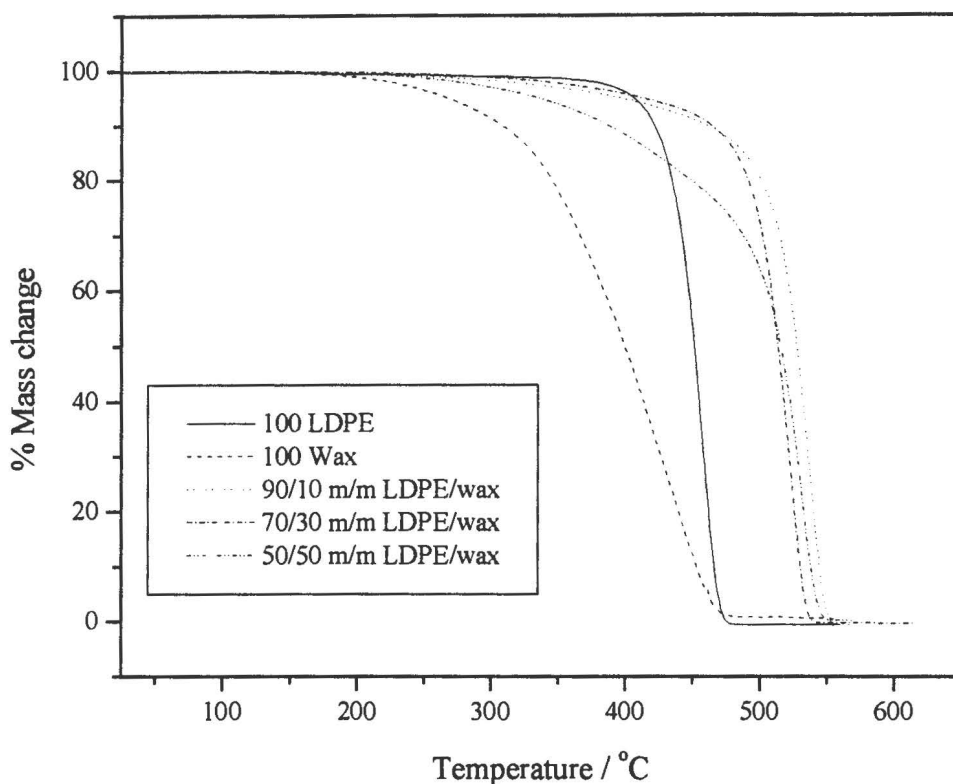


Figure 3.28 TGA curves for pure wax, LDPE and extrusion mixed LDPE/wax blends

Mechanically mixed blends containing 40 % and more wax as well as the extrusion mixed blend containing 50 % wax shows a two-step mass loss with the second step at a higher temperature than that of pure LDPE. The mechanically mixed blends shows onset temperature of decomposition at 402.7 °C for the 90/10 m/m blend, at 472.7 °C for the 70/30 m/m blend, and at 453.6 °C for the 50/50 m/m blend. The onset temperatures of decomposition for extrusion mixed blends are at 498 °C for the 90/10 m/m blend, at 485.0 °C for the 70/30 m/m blend, and at 477.6 °C for the 50/50 m/m blend. Char yield was observed at a temperatures higher than 500 °C for all the blends.

The thermal stability of the blends was characterized in terms of 10 and 20 % degradation under nitrogen atmosphere. The results are summarized in Tables 3.7 and 3.8.

Table 3.7 TGA results for LLDPE/wax blends

Mechanically mixed			Extrusion mixed		
LLDPE/wax	T _{10 %} [°C]	T _{20 %} [°C]	X/Y	T _{10 %} [°C]	T _{20 %} [°C]
100/0	467.1	489.1	100/0	498.3	501.2
0/100	275.0	320.2	0/100	275.0	320.2
95/5	460.5	468.5	95/5	512.2	515.1
90/10	465.5	464.5	90/10	506.3	512.5
80/20	426.8	462.3	80/20	500.2	510.3
70/30	369.5	457.8	70/30	489.7	503.4
60/40	360.2	452.1	60/40	450.3	465.6
50/50	320.3	445.3	50/50	376.4	450.9

Table 3.8 TGA results for LDPE/wax blends

Mechanically mixed			Extrusion mixed		
LDPE/wax	T _{10 %} [C]	T _{20 %} [C]	X/Y	T _{10 %} [C]	T _{20 %} [C]
100/0	448.7	452.9	100/0	458.2	460.6
0/100	275.0	320.2	0/100	275.0	320.2
95/5	462.1	462.8	95/5	502.3	514.3
90/10	468.9	441.1	90/10	492.7	512.3
80/20	472.5	461.4	80/20	462.8	498.3
70/30	468.6	473.7	70/30	489.2	508.3
60/40	439.2	445.6	60/40	418.3	462.5
50/50	420.2	430.4	50/50	409.8	451.9

The temperatures of 10 and 20 % degradation for both mechanically and extrusion mixed LLDPE/wax and LDPE/wax blends are shown as a function of wax content in Figures 3.29 -3.32.

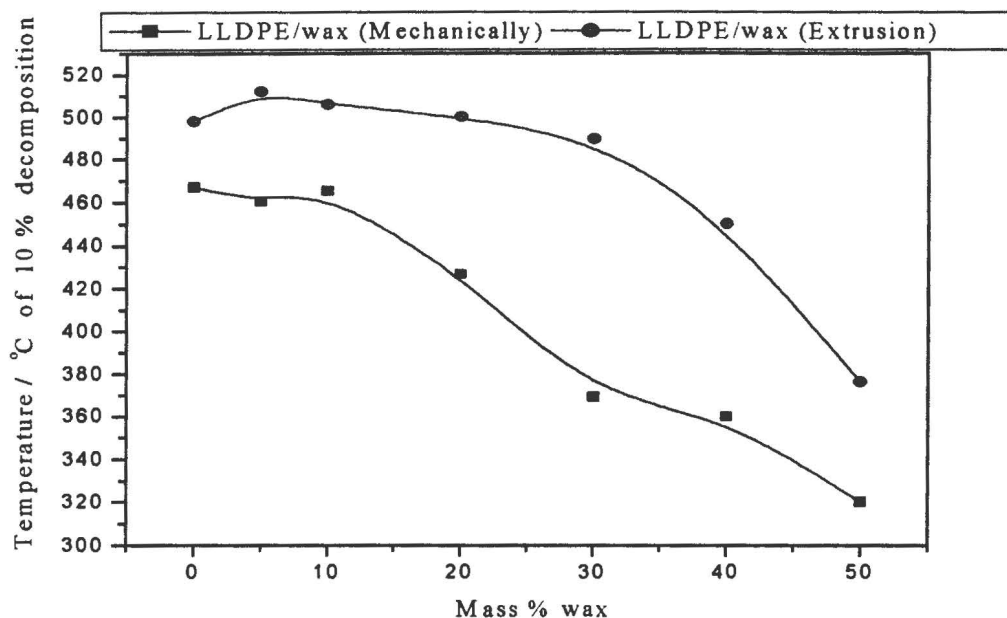


Figure 3.29 Temperatures of 10 % decomposition vs mass % wax for mechanically and extrusion mixed LLDPE/wax blends

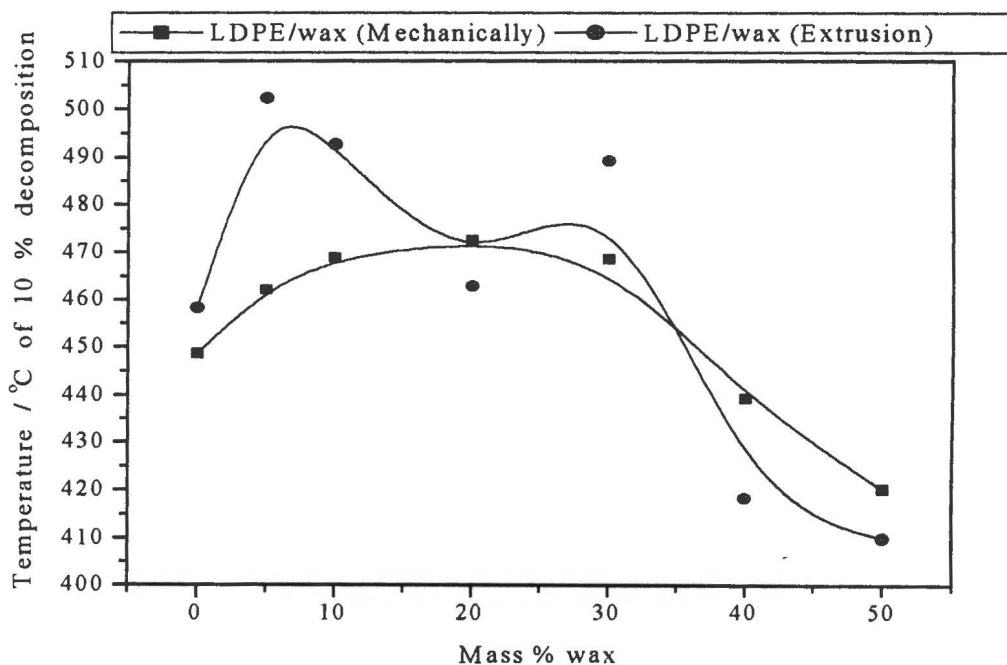


Figure 3.30 Temperatures of 10 % decomposition vs mass % wax for mechanically and extrusion mixed LDPE/wax blends

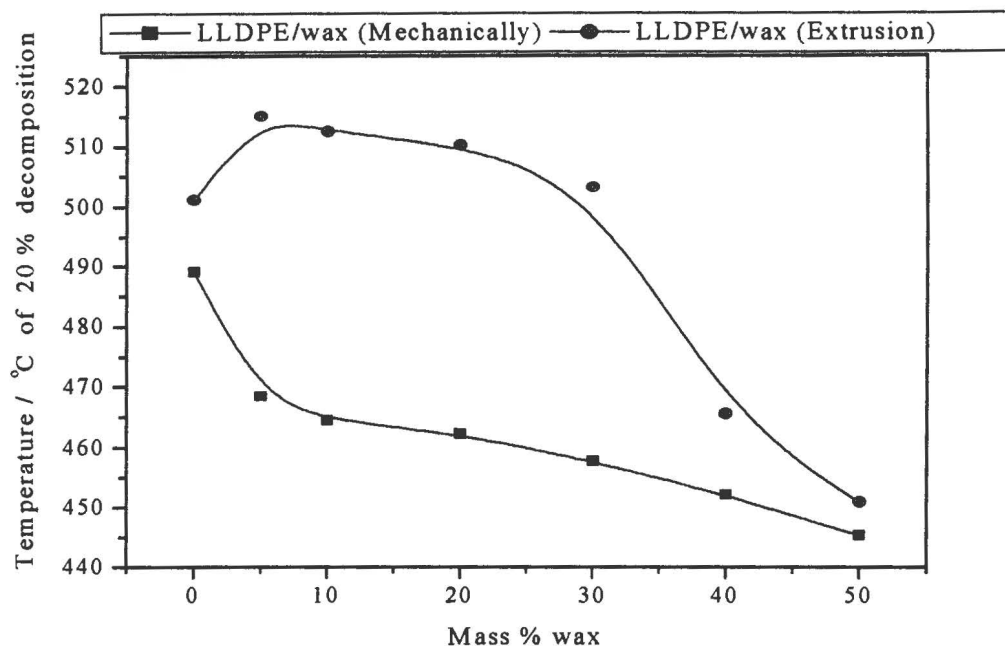


Figure 3.31 Temperatures of 20 % decomposition vs mass % wax for mechanically and extrusion mixed LLDPE/wax blends

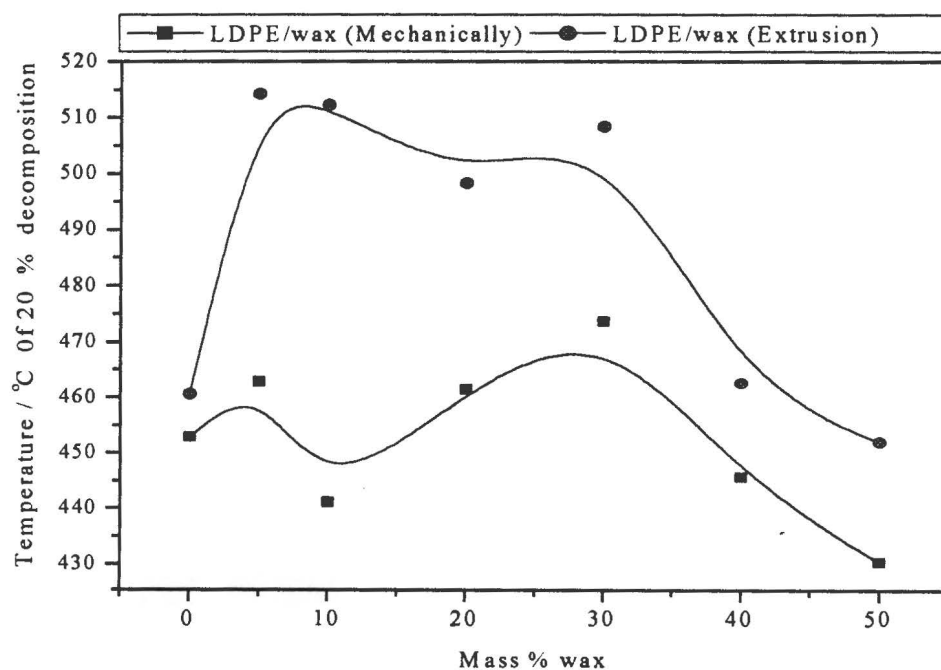


Figure 3.32 Temperatures of 20 % decomposition vs mass % wax for mechanically and extrusion mixed LDPE/wax blends

A decrease in thermal stability of the blends with an increase in wax content was observed.

3.3 Mechanical properties

3.3.1 Tensile testing

The values for the tensile properties of mechanically and extrusion mixed LLDPE/wax and LDPE/wax blends are summarized in Tables 3.9 and 3.10.

Table 3.9 Mechanical properties of LLDPE/wax blends

LLDPE /wax	$\epsilon_y \pm s\epsilon_y$ [%]	$\delta_y \pm s\delta_y$ [MPa]	$\epsilon_b \pm s\epsilon_b$ [%]	$\delta_b \pm s\delta_y$ [MPa]	$E \pm s_E$ [%]
Mechanically mixed					
100/0	21.8±2.5	9.5±1.3	1017.3±92.5	13.7±1.2	67.5±12.1
95/5	20.7±2.6	9.8±0.5	989.3±67.4	11.2±2.7	70.9±13.8
90/10	18.3±1.3	9.7±0.9	616.1±62.3	7.8±0.1	82.8±10.7
80/20	18.8±1.2	9.2±0.4	289.2±53.6	6.0±1.5	107.4±9.5
70/30	16.7±1.7	8.2±1.9	444.0±35.4	7.3±1.4	86.5±4.9
60/40	14.2±1.5	4.4±0.2	274.5±10.3	4.2±0.1	91.5±3.5
50/50	16.1±0.3	4.2±0.4	184.5±16.4	3.6±0.5	115.3±5.2
Extrusion mixed					
100/0	21.2±1.5	7.6±0.5	978.9±111.2	10.2±0.4	134.8±3.4
95/5	20.9±0.6	9.1±0.8	950.5±85.8	9.9±0.2	146.6±3.7
90/10	19.0±0.6	8.2±1.2	493.3±46.7	6.8±0.1	154.3±1.2
80/20	18.5±0.7	6.4±0.4	388.9±34.2	5.7±0.3	139.7±2.2
70/30	18.3±0.3	9.3±1.6	332.0±23.9	6.4±1.5	149.9±1.9
60/40	17.7±0.1	9.4±0.3	358.0±10.2	5.9±1.2	156.5±3.2
50/50	16.6±2.8	4.3±0.4	224.7±9.4	4.2±0.1	172.1±1.5

Young's modulus (E), elongation at yield (ϵ_y), stress at yield (δ_y), elongation at break (ϵ_b), stress at break (δ_b)

s - is the standard deviation of each parameter

Table 3.10 Mechanical properties of LDPE/wax blends

LDPE/wax	$\epsilon_y \pm s\epsilon_y$ [%]	$\delta_y \pm s\delta_y$ [MPa]	$\epsilon_b \pm s\epsilon_b$ [%]	$\delta_b \pm s\delta_b$ [MPa]	$E \pm s_E$ [%]
Mechanically mixed					
100\0	27.1±1.5	7.5±1.3	1148.8±22.3	3.1±0.9	42.1±14.2
95/5	25.7±1.2	7.9±1.5	1134.1±21.4	3.3±0.6	44.3±10.2
90/10	23.4±2.4	7.8±0.9	765.6±18.7	8.3±1.2	48.5±11.0
80/20	22.3±3.8	9.6±3.8	560.6±16.2	3.0±1.5	34.1±13.5
70/30	20.1±1.9	10.4±2.7	436.8±21.3	4.3±0.9	55.5±17.2
60/40	-	-	15.2±1.2	6.3±1.6	66.1±9.8
50/50	-	-	18.8±2.5	6.9±1.4	69.6±5.7
Extrusion mixed					
100\0	23.8±2.4	10.2±1.3	1181.5±21.5	15.1±2.5	76.8±11.5
95/5	22.1±1.2	9.4±1.5	1194.5±20.4	13.4±1.4	80.5±21.2
90/10	21.5±2.3	10.3±0.9	1087.6±22.8	12.1±1.9	88.1±15.6
80/20	18.5±2.5	10.9±3.8	968.3±31.2	9.8±3.7	86.8±16.1
70/30	18.1±1.6	11.3±2.7	736.8±18.9	8.3±1.5	89.8±13.5
60/40	17.3±3.1	13.7±1.4	528.5±17.5	7.4±6.1	102.8±10.2
50/50	18.7±1.8	12.7±1.9	322.9±25.6	6.3±2.4	109.9±12.4

Young's modulus (E), elongation at yield (ϵ_y), stress at yield (δ_y), elongation at break (ϵ_b), stress at break (δ_b)

s - is the standard deviation of each parameter

Young's modulus for mechanically and extrusion mixed LLDPE/wax and LDPE/wax blends are shown as a function of wax content in Figures 3.33 and 3.34.

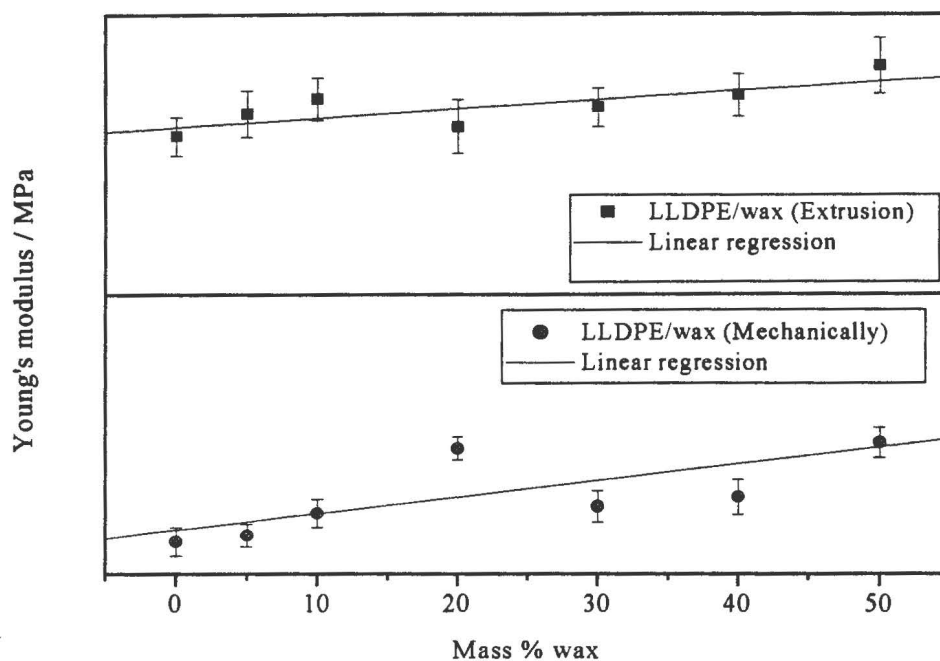


Figure 3.33 Young's modulus vs mass % wax for LLDPE/wax blends

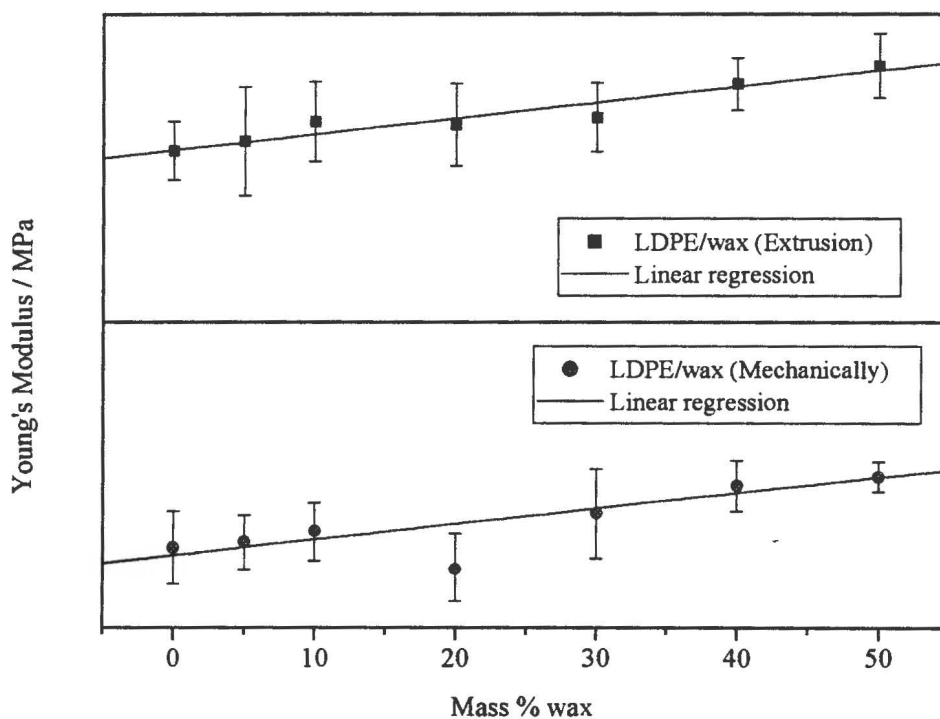


Figure 3.34 Young's modulus vs mass % wax for LDPE/wax blends

An almost equal increase in Young's modulus of the blends with an increase in wax content was observed. In both cases Young's modulus of extrusion mixed blends is higher than that of the mechanically mixed blends.

The elongation at yield for mechanically and extrusion mixed LLDPE/wax and LDPE/wax blends are shown as a function of wax content in Figures 3.35 and 3.36.

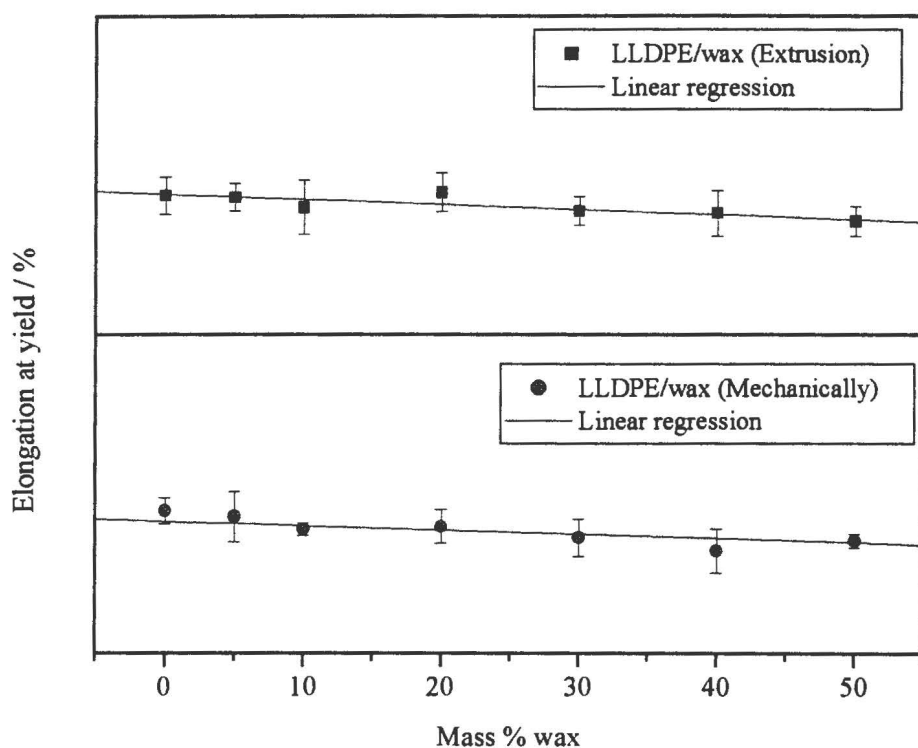


Figure 3.35 Elongation at yield vs mass % wax for LLDPE/wax blends

There is an almost equal decrease in elongation at yield as a function of wax content for both types of blends. The mechanically mixed LDPE/wax blends show a linear decrease with increase in wax content, but for the 60/40 and 50/50 m/m samples no yield point, but brittle rupture, was observed (Figure 3.36).

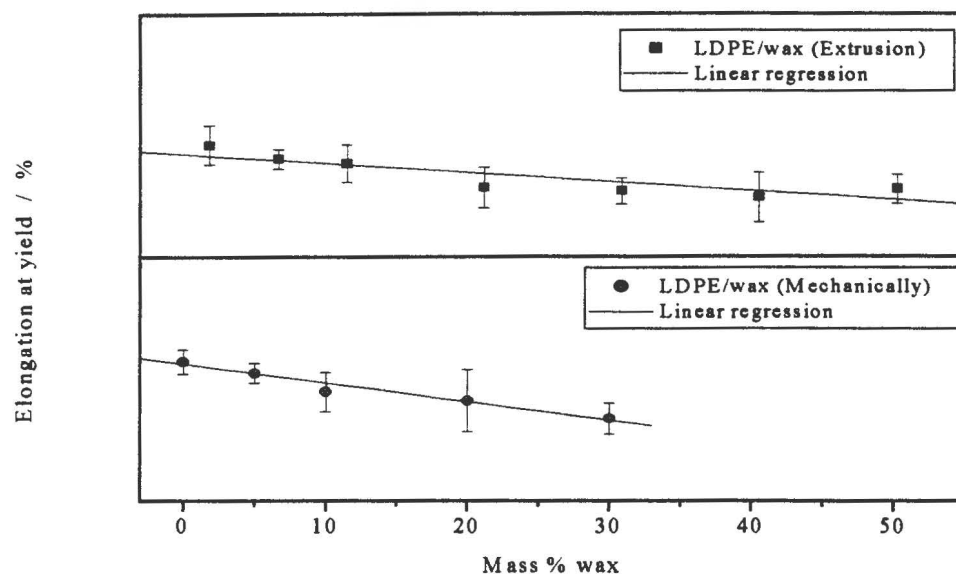


Figure 3.36 Elongation at yield vs mass % wax for LDPE/wax blends.

Yield stress for mechanically and extrusion mixed LLDPE/wax and LDPE/wax blends are shown as a function of wax content in Figures 3.37 and 3.38.

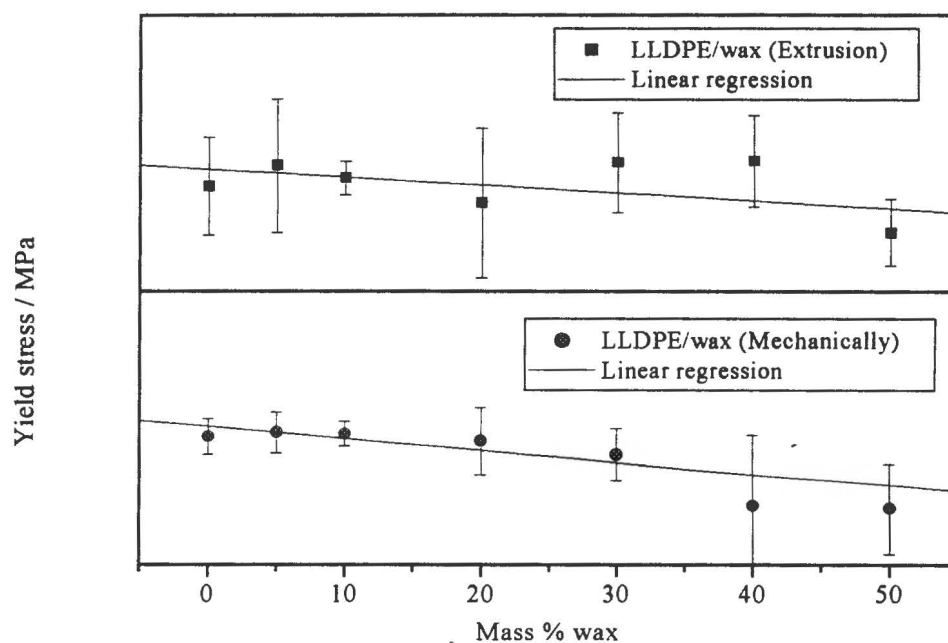


Figure 3.37 Yield stress vs mass % wax for LLDPE/wax blends

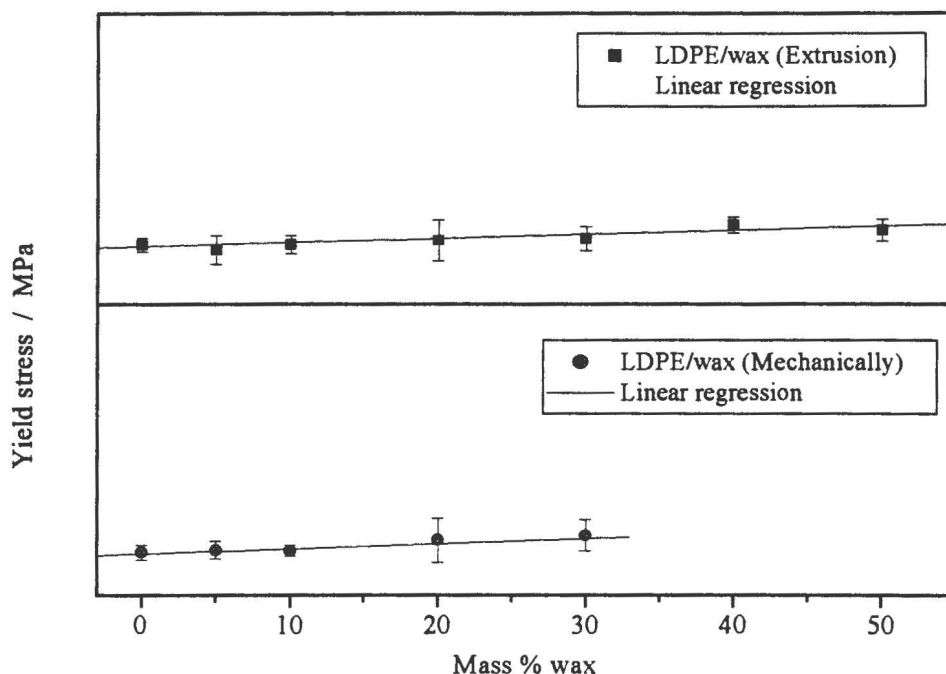


Figure 3.38 Yield stress vs mass % wax for LDPE/wax blends

The yield stress shows an equal decrease with increase in wax content for both types of LLDPE/wax blends (Figure 3.37). The LDPE/wax blends show an increase in yield stress with increasing wax content (Figure 3.38). The mechanically mixed blends containing 30 % and more wax show no yield point, but brittle rupture was observed.

Elongation at break for mechanically and extrusion mixed LLDPE/wax and LDPE/wax blends is shown as a function of wax content in Figures 3.39 and 3.40. A decrease in elongation at break was observed for mechanically and extrusion mixed LLDPE/wax and LDPE/wax blends with increase in wax content. For mechanically mixed 60/40 and 50/50 m/m LDPE/wax blends, the elongation at break is very small (Table 3.10).

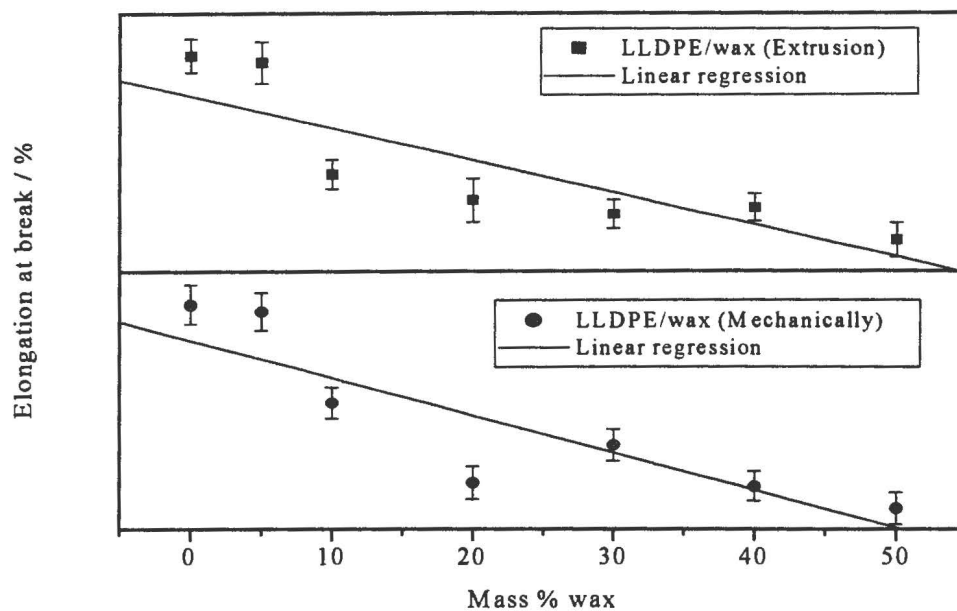


Figure 3.39 Elongation at break vs mass % wax for LLDPE/wax blends

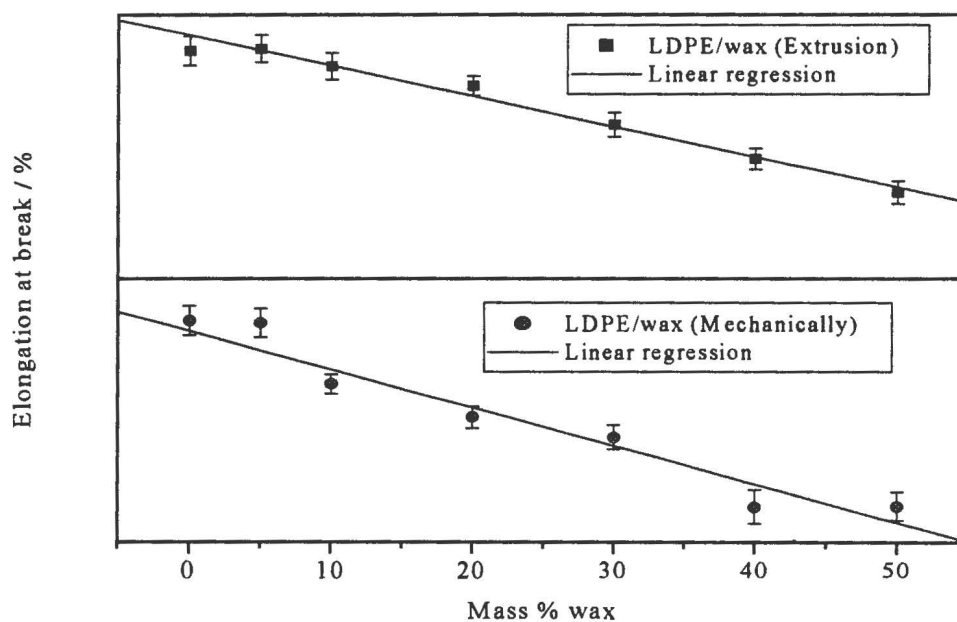


Figure 3.40 Elongation at break vs mass % wax for LDPE/wax blends

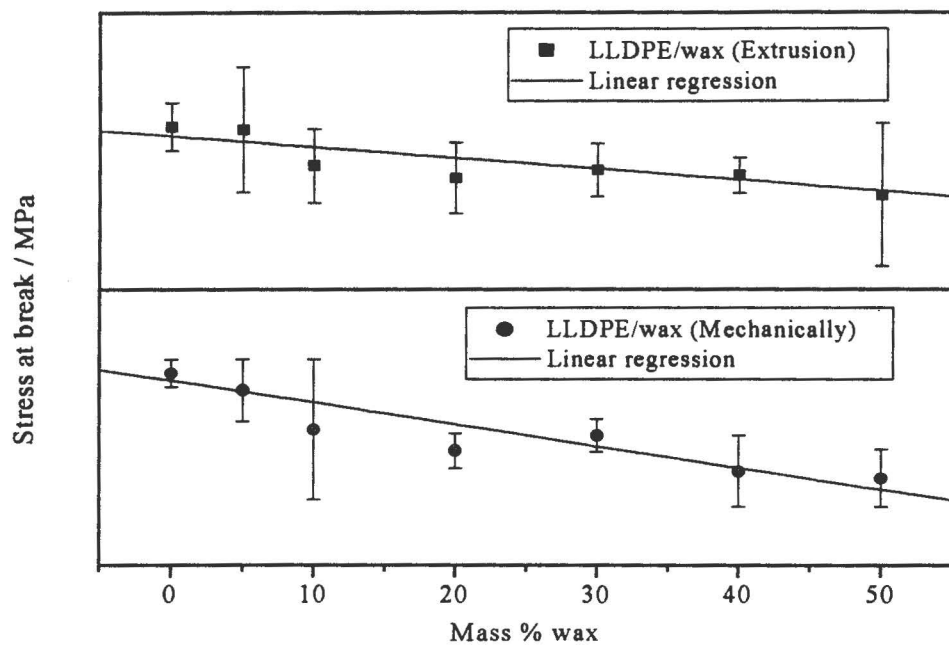


Figure 3.41 Stress at break vs mass % wax for LLDPE/wax blends

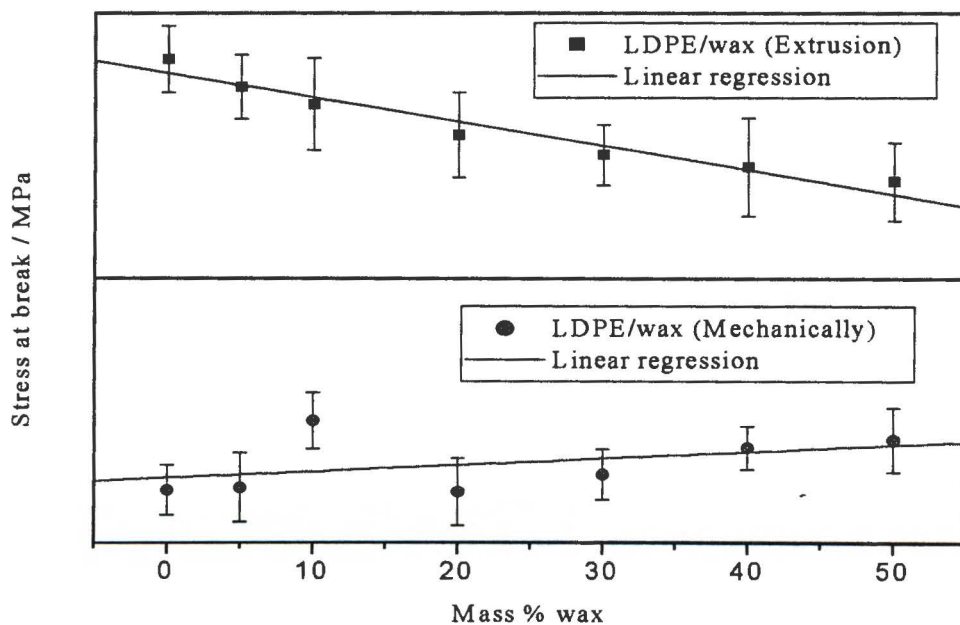


Figure 3.42 Stress at break vs mass % wax for LDPE/wax blends

The stress at break for mechanically and extrusion mixed LLDPE/wax blends decreases with increase in wax content, but a slightly stronger decrease is observed for extrusion mixed samples (Figure 3.41). For LDPE/wax blends two trends are observed. A decrease in stress at break is observed for extrusion mixed blends, while stress at break slightly increases with an increase in wax content for mechanically mixed blends (Figure 3.42).

CHAPTER 4

DISCUSSION AND CONCLUSIONS

4.1 Discussion

4.1.1 Mechanically mixed LLDPE/wax blends

In Figure 3.2 and Table 3.1 it can be seen that the C=O vibration, observed from the IR-spectra of pure wax, decreases with an increase in wax content. There is also a decrease in the -CH₂- and -CH₃ bending vibrations with an increase in wax content. This means that there may be a reaction between the wax and LLDPE at the C=O sites. This is confirmed by a decreasing (-CH₂)_n long chain structure with an increase in wax content, which suggests that some degradation occurs when C=O groups react with -CH₂- groups, giving rise to shorter main chains. Possible linking between -CH₃ and C=O does not have an influence on the length of the main chains, because -CH₃ terminates the side branches. The degradation of the main chains will affect the ultimate mechanical properties of the blends, as discussed later.

The GPC results in Figure 3.6 show that the percentage peak area of the second peak increases with an increase in wax content, and an increase in wax content has no apparent influence on the other two peaks. This indicates that there is an increase in the number of small molecules. Since both wax and PE has shorter molecules in their structure, an increase in wax content will probably lead to an increase in the number of shorter molecules. Another observation is that an increase in wax content causes a slight shift of the first and second peaks to a lower retention time. This suggests an increase in the MW of the material, indicating the possibility of a linking reaction. There is also an increase in the area of the wax related peak (which is not observed in LLDPE and LDPE chromatogram) with an increase in wax content in the blends, which is to be expected. An increase in wax content has no significant influence on the percentage peak area of the other two peaks observed from the pure wax chromatogram.

The DSC curves in Figure 3.8 show two endothermic melting peaks for pure wax, while LLDPE has only one endothermic melting peak. Figure 3.9 shows that, for the blends containing up to 40 % wax, a single endothermic peak is present in the melting range of LLDPE. This indicates that wax and LLDPE are miscible in the crystalline phase in these concentration regions. Another more probable explanation is that wax crystallizes onto the LLDPE crystallites. However, for the blend containing 50 % wax, another small peak is present in the same melting range as that of wax. The appearance of this small peak indicates the presence of phase separation between wax and LLDPE. It is also possible that in this case wax may have leached out of the matrix. The poorer miscibility of the components will have an influence on the thermal degradation of the material and on the mechanical properties. This will be discussed later. These results are not very different from the previous investigation by Krupa and Luyt [46]. They found that mechanically mixed LLDPE and oxidized wax are miscible up to 50 % wax, and concluded that both components are miscible in the crystalline phase.

The DSC cooling curves in Figure 3.14 for the blends containing up to 40 % wax show a single exothermic peak in the melting region of LLDPE. This indicates that both components are probably miscible in the molten state. The blend containing 50 % wax shows another low intensity peak in the same region than that of the wax main peak. The observed behaviour indicates phase separation in the melt.

The onset and peak temperatures of melting depend on the lamellar thickness of the crystals. It can be seen in Figure 3.18 that an increase in wax content has no significant influence on the onset temperature of melting, while the peak temperature of melting shows a decrease with an increase in wax content (Figure 3.19). The onset temperatures of crystallization for mechanically mixed LLDPE/wax blends also remain virtually constant (Figure 3.21), while the peak temperature of crystallization decreases with an increase in wax content (Figure 3.22). This indicates that the lamellar thickness decreases as the wax content is increased, because wax has shorter chains that reduce the lamellar thickness. Literature [67] shows that the shift of the melting process to a lower temperature signifies a decrease in the stability of the lamellae. According to the expression for the thermodynamic melting temperature

$$T_m = T_m^\circ [1 - 2 / H_m^\circ (\delta_f / L + 2\delta_s / D)] \quad [4.10]$$

where T_m° is the equilibrium melting temperature and δ_f and δ_s are the crystal surface free energies per unit area of fold surface and inside surface respectively, the melting temperature will decrease by reducing the width D and the thickness L of the lamellae. This reduction in lamellar thickness has an influence on the ultimate mechanical properties of the blends, as will be discussed later.

Figure 3.20 shows that the specific melting enthalpy decreases with an increase in wax content. Since the specific melting enthalpy is closely associated with the degree of crystallinity of the materials, this observation indicates a decrease in the crystallinity of the blends. The crystallinity also has an influence on the ultimate mechanical properties of the blends, which will be discussed later. However, an increase in wax content has no significant influence on the specific enthalpy of crystallization (Figure 3.23). This is in agreement with the previous work by Krupa and Luyt [46] on mechanically mixed LLDPE/oxidized wax blends.

The degradation by random chain scission along the chain produces radicals or other reactive species. These reactive species may continue to break down into progressively smaller species, which becomes volatile and are lost, or they may attack other polymer chains leading to linking of the polymers, which are less prone to degradation. Ultimately, this will lead to a higher temperature residue referred to as a char. Pure wax and LLDPE undergo decomposition in a single step (Figure 3.24). The thermal stability of wax is much lower than that of pure LLDPE. Mechanically mixed LLDPE/wax blends start to decompose at temperatures below that of LLDPE (Figure 3.29). This indicates that the presence of wax decreases the thermal stability of the blends, which further decreases with an increase in wax content. No char yield was observed at a temperature higher than 500 °C.

Figure 3.33 shows that Young's modulus increases with an increase in wax content. This is contrary to the decrease in crystallinity observed from the DSC specific enthalpy values, which can be seen in Figure 3.20. The only possible explanation for this behaviour is that more perfect crystals were formed under these conditions. These results are in agreement with the previous findings by Krupa and Luyt [46-48].

The elongation at yield decreases with an increase in wax content (Figure 3.35). Since wax has much shorter molecules than LLDPE, the amorphous fraction of the blend will start to flow at much lower strains. The number of short chains increases with increasing wax content, which consequently leads to the decreasing of elongation at yield. Yield stress decreases with an increase in wax content, because of an increase in crystallinity (Figure 3.37). The presence of phase separation at high wax content can also affect the elongation as well as the yield stress. Krupa and Luyt [46], however, found that wax content does not significantly influence the yield point (elongation at yield and yield stress) of LLDPE/oxidized wax blends.

The elongation at break decreases with an increase in wax content (Figure 3.39). This means that the ultimate properties deteriorate in the presence of wax. In order to break the material, the tie-molecules must be pulled from the lamellae. Since wax has lower molecular weight, it can be assumed that only polyethylene chains form the tie-molecules. Because of that, the number of tie chains will decrease with increase in wax content of the blends. As a result ultimate properties of the blends will deteriorate. The number of tie-molecules will therefore allow the sample to break at lower elongation. Stress at break also decreases with an increase in wax content (Figure 3.41). This is probably because the lower number of tie-molecules will carry the applied load. Stress at break also decreases because of decreasing lamellar thickness, which can be seen as a decrease in melting temperature with an increase in wax content (Figure 3.19). If the lamellae are thinner, it will be easy to pull out the molecules from the lamellar defect points. Therefore, less strain energy will be needed to break the material.

4.1.2 Extrusion mixed LLDPE/wax blends

The FTIR spectra of extrusion mixed LLDPE/wax blends are shown in Figure 3.3. The intensity of the C=O vibration decreases with an increase in wax content. There is also a decrease in intensity of the -CH₂- and -CH₃ bending vibrations with an increase in wax content (Table 3.1). These observations are similar to those for mechanically mixed LLDPE/wax blends and can be explained in a similar way.

For extrusion mixed LLDPE/wax blends containing up to 20% wax, only one endothermic peak appears in the same melting range than that of LLDPE, while blends containing 30 % wax show another small peak in the same melting range than that of wax. The DSC cooling curves in Figure 3.14, for the blends containing up to 20 % wax, also show a single exothermic peak in the melting region of LLDPE, while those for the blends containing 30 % and more wax show a second, low-intensity peak in the same region than that of the wax main peak. The appearance of these small peaks indicates the presence of phase separation for these blends, while the blends containing smaller amounts of wax were completely miscible. The poorer miscibility will have an influence on the thermal degradation of the material and on the mechanical properties. This will be discussed later. These results are not very different from those observed by Krupa and Luyt [47]. They found that the extrusion mixed LLDPE/un-oxidized wax blends show only one melting peak for the blends containing up to 10 % wax, and the blends containing 20 % and more wax showed another small peak in the same temperature region than that of the wax main peak.

An increase in wax content has no significant influence on the onset temperatures of melting, but the peak temperatures of melting show a decrease with an increase in wax content (Figure 3.19). The same is observed for the onset and peak temperatures of crystallization, which is similar to that observed for mechanically mixed blends, and can be explained in the same way. The specific melting enthalpy decreases with an increase in wax content, indicating a decrease in the crystallinity of the material, which will have an influence on the ultimate mechanical properties of the blends, as will be discussed later.

The TGA results in Figure 3.26 show that the decomposition of the blends occurs in two steps. The onset of decomposition for the first step is in the same temperature region than that for pure wax and the % decomposition during the first step correlates well with the amount of wax initially mixed into the blend. Decomposition of the blends, after the first step, generally proceeds at a higher temperature than that of pure LLDPE. On the one hand it seems as if the poorer miscibility causes the wax to decompose separately from the LLDPE, but on the other hand the presence of wax seems to retard LLDPE decomposition. The degradation process occurs through chain scission by producing radicals or other reactive species. For this reason, it is

probable that wax decomposes first, initiating a transfer reaction onto the LLDPE chains, thus leading to an initial degradation of the blends at a lower temperature. Char yield was observed at a temperature higher than 500 °C.

Young's modulus increases with an increase in wax content (Figure 3.33). This is contrary to the decrease in crystallinity observed from the DSC specific enthalpy values. The only possible explanation for this behaviour is that more perfect crystals were formed under these conditions. The observed behaviour is in agreement with that for the mechanically mixed LLDPE/wax blends and with previous findings by Krupa and Luyt [46-48]. They also found that Young's modulus of the blends increased with an increase in wax content.

The elongation at yield and yield stress decreases slightly with an increase in wax content (Figures 3.35 and 3.37). The same explanation applies as in the case of mechanically mixed LLDPE/wax blends. These results are not in agreement with previous work by Krupa and Luyt [46], who found for extrusion mixed LLDPE/un-oxidized wax blends that an increase in wax content caused a decrease in elongation at yield. They also observed a small increase in yield stress for blends containing up to 20 % wax, but for the blends containing 30 % and more wax, no yield point, but brittle rupture was observed.

The elongation and stress at break decrease with an increase in wax content, which can be explained in the same way than for mechanically mixed LLDPE/wax blends. These results are not in agreement with the results by Krupa and Luyt [47], who found that stress at break was much smaller than yield stress, and that the blends consisting of 30 % and more wax, did not have a yield point, but exhibited brittle rupture giving rise to an increase in stress at break. They also observed that an increase in wax content resulted in a decrease in elongation at break in the whole concentration region.

4.1.3 Mechanically mixed LDPE/wax blends

The intensity of the C=O and $-\text{CH}_3$ vibration observed in the IR-spectrum of the blends in Table 3.2 decreases with an increase in wax content, which further has no significant influence on the intensity of the $-\text{CH}_2-$ bending vibrations. There is also a decrease in intensity of a long chain structure $(-\text{CH}_2-)_n$ with an increase in wax content in the blends. In this case it seems as if linking is more pronounced than degradation. These observations are not very different to those for LLDPE/wax blends, and therefore the explanation will be the same as that of mechanically and extrusion mixed LLDPE/wax blends.

The GPC results are similar to those for mechanically mixed LLDPE/wax blends, and can be interpreted in the same way (Figure 3.7).

The DSC heating curves show a single endothermic melting peak in the same melting region than that of pure LDPE for the blends containing up to 20 % wax, but for the blends containing 30 % and more wax another small broad peak is present in the same melting region than that of the main wax peak (Figure 3.11). These observations can also be explained in terms of miscibility at lower wax concentrations, and some phase separation at higher wax concentrations. The DSC cooling curves show similar behaviour (Figure 3.16).

The onset temperatures as well as the peak temperatures of melting decreases with an increase in wax content, but this decrease is very slight for the onset temperature of melting (Figure 3.18 and 3.19). This behaviour indicates a reduction in lamellar thickness. The specific enthalpy of melting of mechanically mixed LDPE/wax blends increases with an increase in wax content (Figure 3.20). This indicates an increase in the degree of crystallinity of the material. This will also have an influence on the mechanical properties such as Young's modulus and the yield stress of the blends. In contrary to the onset and peak temperatures of melting, an increase in wax content does not seem to influence the onset and peak temperatures of crystallization (Figure 3.21 and 3.22.). However, a slight increase in the specific enthalpy of crystallization with an increase in wax content was observed (Figure 3.23), which also indicates an increase in crystallinity.

The TGA results in Figure 3.27 show that the decomposition of the blends containing 40 % and more wax occur in two-step, indicating an initial decomposition of wax followed by that of LDPE. Similar behaviour was observed for extrusion mixed LLDPE/wax blends and can be explained in the same way. Furthermore, it can be seen that at higher wax content the decomposition of the blends, after the first step, proceed to a higher temperature than that of pure LDPE. Char yield was observed at a temperature higher than 500 °C.

Young's modulus increases with an increase in wax content (Figure 3.34). This increase is probably a consequence of the increasing crystallinity. During the application of force, mechanical energy is spread uniformly over the sample volume. Since the crystal modulus is at least three magnitudes of order higher than the amorphous, the crystal part will take more of the strain energy, which will increase the overall modulus of the blend. This effect will be more pronounced in samples with higher crystallinity. The observed behaviour is in agreement with previous findings by Krupa and Luyt [46-48]. They also found that Young's modulus of the blends increased with an increase in wax content.

The elongation at yield decreases with an increase in wax content (Figure 3.36). This behaviour can be explained in a similar way than for mechanically mixed LLDPE/wax blends. The blends containing 40 % and more wax have no yield point, but brittle rupture was observed. However, yield stress shows an increase with increasing wax content (Figure 3.38). Presumably, this behaviour is a consequence of the increased crystallinity of the material. It is well known that the amorphous fraction transfers strain energy to the crystals during the flow of the material. For this reason, as wax content increases, crystals will somehow preserve or stabilise the flow of the material, which will need more stress energy from the applied force. The presence of phase separation at high wax contents can also affect the elongation at yield, as well as the yield stress.

The elongation at break decreases with an increase in wax content (Figure 3.40), while the stress at break increases with an increase in wax content (Figure 3.42). The

decrease in the elongation at break may be explained in the same way than for the other systems. Stress at break, however, will only increase if there is lamellar thickening, or higher crystal perfection. Since the DSC results indicate lamellar thinning, the most probable explanation is that the effect of crystal perfection is more pronounced than the effect of lamellar thinning.

4.1.4 Extrusion mixed LDPE/wax blends

The IR-spectra in Figure 3.5 show the same changes in the intensities of a long chain structure ($-\text{CH}_2-$)_n, C=O, $-\text{CH}_2-$ and $-\text{CH}_3$ bending vibrations as in the mechanically and extrusion mixed LLDPE/wax blends, and the explanation of these observations can also be explained in the same way.

The extrusion mixed LDPE/wax blends containing up to 10 % wax show only one DSC endothermic peak in the same melting range than LDPE (Figure 3.12), while the blends containing 20 % and more wax show another low-intensity peak, besides the main peak observed in all the blends, in the same melting range than that of the main wax peak. The DSC cooling curves (Figure 3.17) show similar behaviour. This indicates complete miscibility only at very low wax contents. Comparison of the present and previous results shows that the PE/oxidized wax blends have better miscibility than the PE/un-oxidized wax blends. The reason for this is probably degradation occurring in this system as can be seen from the FTIR results (Figure 3.2-3.5 and Tables 3.1-3.2), giving rise to shorter chains that will mix and crystallize together more effectively.

An increase in wax content causes a decrease in the onset and peak temperatures of melting (Figure 3.18). This behaviour can be explained in a similar way than for mechanically mixed LDPE/wax blends. The onset temperature of crystallization remains virtually constant (Figure 3.21), while the peak temperature of crystallization initially increases at low wax content followed by a decrease with increase in wax content (Figure 3.22). The decrease in T_c indicates a decrease in lamellar thickness.

The TGA results in Figure 3.28 show that, at low wax contents, the blends decompose in a single step and these blends seem to be thermally more stable than pure LDPE. At high wax contents the decomposition of the blends occurs in two steps. The onset of decomposition for the first step is in the same temperature region than that for pure wax and the % decomposition during the first step correlates well with the amount of wax initially mixed into the blend. Decomposition of the blends, after the first step, generally proceeds at a higher temperature than that of pure LDPE. On the one hand it seems as if the poorer miscibility at high wax contents causes the wax to decompose separately from the LDPE, but on the other hand the presence of wax seems to retard LDPE decomposition. The degradation process occurs through chain scission by producing radicals or other reactive species. For this reason, it is probable that wax decomposes first, initiating a transfer reaction onto LDPE chains, thus leading to an initial degradation of the blends at a lower temperature. Char yield was observed at a temperature higher than 500 °C.

Young's modulus increases and the elongation at yield decreases with an increase in wax content (Figure 3.33), and the explanation for this behaviour is the same as for the mechanically mixed LDPE/wax blends. The yield stress increases with an increase in wax content (Figure 3.38). Presumably this behaviour is a consequence of the increased crystallinity of the material. The explanation is similar to that in mechanically mixed LDPE/wax blends. The presence of phase separation at high wax contents can also affect the elongation at yield as well as the yield stress.

The elongation and stress at break decrease with an increase in wax content (Figures 3.40 and 3.42). This observation is similar to that for mechanically mixed LLDPE/wax blends, and can be explained in the same way.

4.2 Conclusions

The following conclusions were reached:

1. The FTIR results for all four systems indicated that linking and degradation occur. The decrease in the intensities of the C=O, -CH₂-, -CH₃, and the long chain

structure $(-\text{CH}_2-)_n$ bending vibrations with an increase in wax content confirm this conclusion. This was found to have an effect on the elongation at break of the blends.

2. It was hoped that the GPC results would also support the conclusions on linking and degradation. There was, unfortunately, an increase in the peak area of only one peak (Peak 2) with an increase in wax content, and a slight shift of the first and second peaks to lower retention times, which may indicate an increase in MW of the material. This is, however, not conclusive enough to support any conclusions on linking and/or degradation.
3. The DSC analyses showed that during melting mechanically and extrusion mixed LLDPE/wax samples containing up to 40 % and 30 % wax respectively as well as the mechanically and extrusion mixed LDPE/wax samples containing up to 30 and 20 % wax respectively, a single melting peak is present in the same melting region than that of PE. This indicates that both components are miscible in the crystalline phase. In this case it is possible that wax crystallizes onto PE (LLDPE and LDPE) crystallites. At higher wax content phase separation is observed through an indication of a small low-intensity peak in the same temperature region than that of pure wax. In both cases it can be seen that the samples prepared mechanically are more miscible than extrusion mixed samples. Furthermore, the LLDPE/wax blends in both systems show higher miscibility than the LDPE/wax blends.
4. An increase in wax content causes a slight decrease in onset temperature of melting for mechanically and extrusion mixed LDPE/wax blends. Furthermore, the peak temperature of melting of all the blends also decreases with an increase in wax content. This behaviour indicates that the lamellar thickness decreases. This was also found to have an effect on the ultimate mechanical properties of the blends. The specific enthalpy of melting for the LLDPE/wax blends decreases with an increase in wax content, which indicates a decrease in the degree of crystallinity. For LDPE/wax blends ΔH_m increases with an increase in wax content, indicating an increase in the degree of crystallinity. This will affect the Young's modulus of the material. The onset temperatures of crystallization remain virtually constant for all four systems with an increase in wax content. However, the peak temperature of crystallization for extrusion mixed LLDPE/wax

blends decreases with an increase in wax content, while for other systems it remains virtually constant with an increase in wax content. The specific enthalpy of crystallization shows different trends for the different systems.

5. The TGA analyses showed that the thermal stability of the blends decreases with an increase in wax content. This is because the thermal stability of the wax is much lower than that of the PE (LLDPE and LDPE). The extrusion mixed LLDPE/wax, mechanically mixed LDPE as well as the 50/50 m/m extrusion mixed LDPE/wax blends show a two-step mass loss indicating initial decomposition of wax followed by that of PE at a higher temperature. This is because of poorer miscibility. The temperatures of 10 and 20 % decomposition of the extrusion mixed LLDPE/wax blends, as well as mechanically and extrusion mixed LDPE/wax blends containing up to 20 % wax, show that the blends have higher thermal stability than pure PE. This indicates that the presence of wax improved the thermal stability of the blends. In all the investigated systems the temperature of decomposition of the blends containing 40 % and more wax falls below that of pure PE. In this case the presence of wax decreases the thermal stability of the blends. This is because of the poorer miscibility of the blends.
6. All four systems show a general increase in Young's modulus with an increase in wax content. In the case of mechanically and extrusion mixed LLDPE/wax blends, it is a consequence of more perfect crystals, because the crystallinity decreases with increasing wax content. For mechanically and extrusion mixed LDPE/wax blends it is a consequence of an increase in crystallinity, where the crystals take more of the strain energy. A general decrease in elongation at yield with an increase in wax content was observed. This is associated with the amorphous fraction of the material, which will need less force for the material to flow. Yield stress for LLDPE/wax blends decreases with an increase in wax content. This is a consequence of the softening of the amorphous fraction due to the presence of wax, which will need less force for the material to flow. A decrease in ΔH_m for LLDPE/wax blends also affects the yield stress of the blends. For LDPE/wax blends yield stress increases with an increase in wax content. This indicates that the increase in the crystallinity of the material is more important than the softening of the amorphous fraction. A general decrease in elongation at break with an increase in wax content was observed. This is because of the short

taut tie-molecules, which will require less force to break the material. Degradation of the blends also affects the elongation at break. Stress at break of the blends decreases with an increase in wax content, except for mechanically mixed LDPE/wax blends. The decrease is a result of the decrease in lamellar thickness, but the increase is probably the result of more crystal perfection, which improves the stress at break despite the decrease in lamellar thickness.

4.3 Suggestions for future research

In this research, miscibility between the components was investigated by using DSC. However, it was found that at lower wax concentrations in the blends, both components are probably miscible in the crystalline phase. There are other techniques that can be used to verify miscibility of the materials, such as DMA. In this case the miscibility will be verified by the T_g . If only one T_g is observed, it will indicate good miscibility, but if two T_g 's are observed, this will indicate poor miscibility of the components. Furthermore, the following need to receive attention in future research: (i) the morphology of the material and (ii) the crystal structure. By using techniques such as electron microscopy and X-ray diffraction, morphology and crystal structure of the material can be investigated.

BIBLIOGRAPHY

1. H.H. Hatt and J.A. Lamberton, *Research*, **9**, 139 (1956)
2. G. Von Rosenberg, Freiher, *Vom Waschs*, Farbwerke Hoechst AG, Frankfurt a M, **2** (1), 18 (1967)
3. C. Campbel, G. Brink and L. Glasser, *J. Phys. Chem.*, **79**, 660 (1975)
4. Sasolchem Tech. Bulletin (1993)
5. J.H. Leroux, *J. Appl. Chem.*, **18**, 39 (1969)
6. R.D. Deanin in *Encyclopedia of Polymer Science and Technology*, John Wiley and Sons, New York, Supp., **2**, 458 (1977)
7. Sasolchem Bulletin, *Fischer-Tropsch Waxes*, 20 (1984)
8. A. Brink and F. Dressler, *Br. Polym. J.*, **1**, 37 (1969)
9. A.S. Luyt, N.S. Nhlapo and H.C.M. Vosloo, *J. Appl. Polym. Sci.*, **70**, 1551 (1998)
10. A.S. Luyt and K. Ishripersadh, *Thermochim. Acta*, **333**, 155 (1999)
11. L.A. Utracki, *Am. Chem. Symp.*, 163 (1989) (chapter 7)
12. V.R. Gowariker, N.V. Viswanathan and J. Sreedhar, *Polymer Science*, 7th ed., New Delhi Publisher, Bangalore, Bombay, 226-227 (1993)
13. S. Hashemi and J.G. Williams, *Polymer*, **27**, 384 (1986)
14. F. Defoor, G. Groenickx, P. Schouterden and Van der Heiden, *Polymer*, **33**, 3878 (1992)
15. Y.W. Mai and J.G. Williams, *J. Mater. Sci.*, **12**, 1376 (1997)
16. H. Ulrich, *Introduction to Industrial Polymers*, 2nd ed., Hanser Publishers, Munich, Viena, New York, Barcelona (1993)
17. L.A. Utracki, *Polymer Alloys and Blends: Thermodynamics and Rheology*, Hanser Publishers, New York, 472 (1989)
18. D.V. Bibee and K.K. Dohrer, *TAPPI Proc.*, 639 (1987)
19. M.R. Nyden, G.P.F. Dorney and J.E. Brown, *Macromolecules*, **25**, 1658 (1992)
20. L.A. Utracki, *Commercial Polymer Blends*, Chapman & Hall, London, Weinheim, New York, Melbourne, Madras, 85 (1998)
21. R.A. Shanks, J. Li and L. Yu, *Polymer*, **41**, 2133 (2000)
22. D.R. Poul and J.W. Barlow, *J. Macromol. Sci. -Rev. Macromol. Chem.*, **C18(1)**, 109 (1980)

23. A. Aiji, *Polym. Eng. Sci.*, **35**(1), 64 (1995)
24. W.J. McGill and J. Fourie, *J. Appl. Polym. Sci.*, **19**, 879 (1975)
25. L. Yu, R.A. Shanks and H.Z. Stachurski, *J. Mater. Sci. Lett.*, **15**, 610 (1992)
26. C. Koning, M. van Duin, C. Pagnoulle and R. Jerome, *Prog. Polym. Sci.*, **23**, 707 (1998)
27. J. Pospisil, Z. Horak, Z. Krulis, S. Nespurek and S. Kuroda, *Polym. Degr. Stab.*, **65**, 405 (1999)
28. P. Van Ballegooie and A. Rudin, *J. Appl. Polym. Sci.*, **39**, 2097 (1990)
29. R. Mikkonen and A. Savolainen, *J. Appl. Polym. Sci.*, **39**, 1709 (1990)
30. H. Ismail and S. Suzaimah, *Polym. Testing*, **19**, 879 (2000)
31. K. Tashoro, K. Imanishi, Y. Izumi, M. Kabayashi, K. Kabayashi, M. Satoh and R.S. Stein, *Macromolecules*, **28**, 847 (1995)
32. R.A. Shanks and G. Amarasinghe, *Polymer*, **41**, 4579 (2000)
33. M. Maity, B.B. Khatau and C.K. Das, *Polym. Degr. Stab.*, **72**, 499 (2001)
34. L.A. Utracki and B.D. Favis, in *Handbook of Polymer Science and Technology*, Vol. 4, *Composites and Special Applications*, N.P. Ceremisinoff, Ed., Marcel Dekker, Inc., New York, 173 (1989)
35. D. Abraham, K.E. George and D.J. Francis, *Eur. Polym. J.*, **26**, 197 (1990)
36. F.P. Lamantia, Ed., *Recycling of Plastic Materials*, Chem. Tec. Publishing, Canada, 122 (1993)
37. R.S. Sandler, W. Karo, J. Bonesteel and E.M. Pearce, *Polymer Synthesis and Characterization*, Academic Press, 108-109 (1998)
38. H. Ismail and H.C. Leong, *Polym. Testing*, **20**, 509 (2001)
39. K. Nagdi, *Rubber as an Engineering Material: Guidelines for Users*, Hanser, Munich, 76 (1993)
40. R. Dell'Erba, G. Groeninckx, H. Reynaers and M.H.J. Koch, *Polymer*, **42**, 7831 (2001)
41. L.A. Utracki and B. Schuld, *Polym. Eng. Sci.*, **27**, 1512 (1987)
42. T. Kuy, S. Hu and R.S. Stein, *J. Polym. Sci. Phys.*, **25**, 89 (1987)
43. V. Balsamo and A.J. Muller, *J. Mater. Sci. Lett.*, **12**, 1457 (1993)
44. M. Lazar, R. Rado and J. Rychly, *J. Adv. Poly. Sci.*, **95**, 149 (1990)
45. B. Temperlay, *Polym. Eng. Sci.*, **32**, 65 (1992)
46. I. Krupa and A.S. Luyt, *Polymer*, **42**, 7285 (2001)
47. I. Krupa and A.S. Luyt, *J. Polym. Degr. Stab.*, **70**, 111 (2000)

48. I. Krupa and A.S. Luyt, *Polymer*, **42** (17), 47 (2001)
49. T.N. Mtshali, I. Krupa and A.S. Luyt, *Thermochim. Acta*, **380**, 47 (2001)
50. I. Krupa and A.S. Luyt, *J. Appl. Sci.*, **81** (1), 9773 (2001)
51. P. Hlangothi, I. Krupa and A.S. Luyt, *Thermochim. Acta*, **360**, 41 (2000)
52. J.R. Freid, *Polymer Science and Technology*, Prentice Hall PTR, USA, 369 (1995)
53. M Alger, *Polymer Science Dictionary*, 2nd Ed., Chapman and Hall, UK, 266 (1997)
54. M.J. Folkes and P.S. Hope, *Polymer Blends and Alloys*, London: Blackie academic and professional, 7 (1993)
55. N.I. Sax and R.J. Lweis, *Condensed Chemical Dictionary*, 11th Ed., Van Nostrand Reinhold, New York, 434 (1987)
56. H.W. Kammer, *Polym. Network Blends*, **5**, 69 (1995)
57. J.W. Teh, A. Rudin and J.C. Keung, *Adv. Polym. Tech*, **13**, 1 (1994)
58. J.M. Yang, H.L. Chen, J.W. You and J.C. Hwang, *Polymer*, **29**, 657 (1997)
59. S. Steinmann, W. Gronski and C. Friedrich, *Polymer*, **42**, 6619 (2001)
60. E.S. Sherman, *J. Mater. Sci.*, **19**, 4041 (1984)
61. Y. Liu and R.W. Truss, *J. Appl. Polym. Sci.*, **60**, 1461 (1996)
62. M. Rusu in *Handbook of Polyolefins*, edited by C. Vasile and R.B. Seymour, M Dekker, Inc., NY, Basel, Hong Kong, 243 (1993)
63. G. Capaccio and I.M. Ward, *Nature (Phy. Sci.)*, **243**, 143 (1973)
64. P.A. Irvine and P. Smith, *Macromolecules*, **19**, 240 (1986)
65. J.P. Penning, *Ph.D Thesis*, University of Groningen, (1994)
66. G. Dreezen, D.A. Ivanov, B. Nysten and G. Groeninckx, *Polymer*, **41**, 1395 (2000)
67. J.G. Fatou in *Handbook of Polyolefins*, edited by C. Vasile and R.B. Seymour, M Dekker, Inc., NY, Basel, Hong Kong, 142 (1993)

