INVESTIGATION OF THERMAL AND PHYSICAL PROPERTIES OF CROSS-LINKED LLDPE/WAX BLENDS IN THE PRESENCE OF DIBENZOYL PEROXIDE

by

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DECLARATION

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

Signature: ....

"During the last century, and part of the one before, it was widely held that there was an unreconcilable conflict between knowledge and belief. The opinion prevailed among advanced minds that it was time that belief should be replaced increasingly by knowledge; belief that did not itself rest on knowledge was superstition, and as such had to be opposed. According to this conception, the sole function of education was to open the way to thinking and knowing, and the school, as the outstanding organ for the people's education, must serve that end exclusively."

Isaac Newton

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SYNOPSIS

In this work, the thermal and mechanical properties of uncross-linked and cross-linked LLDPE/wax blends were investigated. The mechanically mixed samples were melt-pressed into sheets, from which the analyses were done. The thermal analyses were determined using DSC, TGA, and melt flow extrusion plastometer. It was found that wax is apparently miscible with LLDPE in both the crystalline and molten states. It was also found that changes in wax and the cross-linking agent contents result in changes in (i) the degree of crystallinity of the blends, (ii) melting and cooling temperatures of the blends, and (iii) the thermal stability of the blends.

The cross-linking of the blends induced by DBP significantly affects the mechanical properties. It was found that the ultimate properties of LLDPE/wax blends deteriorated in the presence of wax. Stress at break increased as a function of DBP content, whereas elongation at break decreased. The yield point properties also resulted in interesting changes as the concentrations of wax and DBP were varied. Elongation at yield increased with increasing wax content and decreased with increasing DBP content. It was further found that higher concentrations of wax improved Young's modulus of blends, while higher cross-linking efficiency showed the opposite.

LIST OF ABBREVIATIONS

PE	Polyethylene
LLDPE	Linear low density polyethylene
HDPE	High density polyethylene
LDPE	Low density polyethylene
PS	Polystyrene
PP	Polypropylene
DBP	Dibenzoyl peroxide
DCP	Dicumyl peroxide
X_c	Degree of crystallinity
ΔH_m	Specific enthalpy of melting
ΔH_c	Specific enthalpy of crystallization
ΔH_m^*	Specific enthalpy of melting for 100% crystalline PE
$\Delta H_{m,PE}$	Enthalpy of PE
$\Delta H_{m,w}$	Enthalpy of wax
ΔH_m^{add}	log additive rule
w_{PE}	Weight portion of PE
w_w	Weight portion of wax
T_m	Melting temperature
$T_{o,m}$	Onset temperature of melting
T_c	Crystallization temperature
$T_{o,m}$	Onset temperature of crystallization
T_g	Glass transition temperature
A_a	Percentage area with respect to LLDPE
A_b	Percentage area with respect to wax
R_t	Retention times
FR	Flow rate
DSC	Differential scanning calorimetry
TGA	Thermogravimetric analysis
FTIR	Fourier–transform-infrared
GPC	Gel permeation chromatography
MFI	Melt flow index

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CHAPTER 1

INTRODUCTION

1.1 Polyethylene

Polyethylene is one of the groups of semi-crystalline polymers. These polymers comprise of a crystalline phase, amorphous phase, and a partially ordered phase [1]. Amorphous polymers do not contain any crystalline regions, and randomly coiled chains characterise this state. In crystalline polymers an ordering of the chains or part of them occurs. As a result, chains can be organized into a regular three-dimensional crystalline state [2]. Polymers are said to derive their usefulness from the obtainable mechanical properties, such as stress–strain (or tensile–elongation) and stress–relaxation behaviour [3]. Amorphous polymers above their T_g show low stress values (low tensile strength) accompanied by low elongation. In contrast, an amorphous polymer below its T_g shows moderate tensile strength but very low elongation. Cold drawing of PE is accompanied by the formation of a *neck*, wherein the contraction of the cross-section of the specimen occurs abruptly. During drawing, oriented chains as well as crystalline structures are responsible for the high strength of the material [2]. Hardness is related to T_g, whereas elasticity depends upon the ability of disordered chain segments to be straightened out under the influence of stress. Elasticity is usually observed above T_g. Highly crystalline materials are expected to show less elasticity [3].

PE can be categorised according to the extent of its chain branching: HDPE, LDPE and LLDPE. HDPE has a density of about 0.96 g cm^{-3} and a melting temperature of about 133 °C; LDPE has a density of about 0.92 g cm^{-3} and a melting temperature of about 108 °C; LLDPE has a density of about 0.94 g cm^{-3} and a melting temperature of about 123 °C [4].

The homopolymer, LDPE, was the first commercialised polyolefin and is prepared by radical polymerisation using traces of oxygen or peroxide as the initiator at high pressure (3000 atm) and temperature (350 °C). The branch content is greater than for other PE's by an order of magnitude and the branches are of varying length. Short chain branching is assumed to affect morphological and solid state properties, while long-chain branching is mostly manifested in viscoelastic properties [1,2]. LDPE has high impact strength, low brittleness temperature, flexibility, film transparency and outstanding electrical properties. It was used during World

War II to insulate radar cables. It is currently mostly used for power and communication cable insulation, and food packaging [5]. Molecular weights of LDPE fall in the range between 6000 and 40000 g mol^{-1}. High molecular weight crystalline polymers are hard and tough. The crystalline regions provide high strength.

HDPE is produced by Ziegler–Natta catalysis or by metal oxide catalysis (Phillips). It has a high crystallinity of up to 90 %, low to medium stiffness and hardness, medium to extremely high toughness, and unrestricted usage in contact with food [5]. It has a melting range of 130 to 138 °C, and is used in electrical, film, pressure pipe, and extruded sheet applications.

LLDPE is a copolymer of ethylene and 5–12 % by weight of an α–olefin such as 1–butene, 1–hexene or 1–octene. The copolymer is produced by either a solution process, where polymerisation is carried out at 7–20 atm and 100 °C, or gas phase processes where polymerisation is carried out at 25–100 atm and 25–300 °C [6]. It has low to medium density (0.94 g cm^{-3}) and linear alkane branches that are shorter than those of LDPE [7]. It has good mechanical properties [3]. The linearity provides strength, while the branching provides toughness. The modulus and ultimate tensile properties are significantly improved over branched LDPE [8,9]. Like conventional LDPE, the polymer contains short carbon chain side groups, which reduce structural regularity and hence crystallisation. Overall the polymer has similar properties to LDPE, but it has better strength properties in films, which is its major area of use. However, the polymers are less pseudoplastic than LDPE, so that melt viscosities are higher during processing [9]. There is some evidence that LLDPE may phase separate in the melt. Various authors [10,11] have analysed LLDPE materials and have found that they contain molecules of very different molecular weights and branch content. One advantage of LLDPE over LDPE is a faster cycling time during the moulding of containers and lids [12]. Today, LLDPE's represent approximately one-third of the total world production of LDPE and LLDPE [13].

In general, for PE, the crystal-to-liquid transformation is a first order transition [2]. The melting process is not absolutely sharp and occurs over a small but finite temperature range. The melting temperature is reproducible and the experimental determination of melting temperature can be carried out by various methods including DSC. Polyolefins possess a higher thermal stability than most other polymers including paraffin waxes. Mechanical stress of such polymers has a dominant effect over thermal effects because polyolefins undergo thermo-mechanical degradation in the range of temperatures where they are practically unaffected by thermal treatment alone [14].

1.2 Wax

Waxes are low-melting organic mixtures or compounds of high molecular weight, solid at room temperature and generally similar in composition to fats and oils except that they contain no glycerides. Some are hydrocarbons, others are esters of fatty acids and alcohols. They are classed among lipids. They are thermoplastic, but since they are not high polymers, they are not considered part of the family of plastics. Common properties are water repellency, smooth texture, low toxicity, and freedom from objectionable odour and colour. They are combustible and have good dielectric properties. They are soluble in most organic solvents and insoluble in water. Uses: polishes, candles, crayons, sealants, cosmetics, paper coating, packaging food products, and electrical insulation [9]. Low molecular weight PE waxes (molecular weight of about 2000 g mol^{-1}) are sometimes used as internal lubricants in PE in order to raise the melt index of the polymer or to standardise regrind materials when they do not conform to specifications [10]. Mixtures of micro- and macro-crystalline waxes and PE waxes are used in poultry processing for the wax picking of poultry. Waxy products containing synthetic rubbers, PIB, PE waxes and other copolymers are used for direct coating of cheese and fruits because they prevent desiccation, reduce loss in flavour substances, and protect the surface of cheese from undesired mold. PE waxes are used as substitutes for natural waxes in shoe cream formulations that contain solids and solvents (white spirits and turpentine) colorants [15].

Waxes are fundamentally categorized into two types, viz type I and type II. Type I is for highly crystalline waxes (e.g. hard paraffin wax), whereas type II is for waxes with much lower crystallinity (e.g. oxidized wax). For this study, a type I wax was chosen for some of its special characteristics such as, (i) its molecules do not differ too much from each other, so that they can easily crystallize out together, (ii) movement of molecules within the crystallites, and (iii) cleaving of crystallites through weak regions [16].

Paraffin wax is a white, translucent solid, tasteless and odourless. It is a class of aliphatic hydrocarbons characterised by straight or branched carbon chains with generic formula C_nH_{2n+2}, with a density of 0.880–0.915 g cm^{-3} and a melting point of about 90 °C. It is soluble in benzene, ligroin, warm alcohol, chloroform, turpentine, carbon disulphide and olive oil, but insoluble in water and acids. It is also combustible [8]. Paraffin wax is useful as a processing aid and lubricant at about 1 % in rubber and plastics. Hard, high molecular mass grades are also used as an ozone protectant in rubbers [9].

1.3 Polymer blends

The founder of the polymer blends industry is Alexander Parkes (an artist), who mixed two isomers of polyisoprene, amorphous *cis* natural rubber and semi-crystalline *trans* gutta–percha. Owing to the difference in stiffness of the two isomers and their relative miscibility, this immediately offered a range of materials with different performance [17]. As a result, the use of polymer alloys and blends is increasing from year to year. Many polymers can be improved by adding polyolefins to them. This is an area of major commercial importance, and one in which both theoretical research and practical development are currently very active. This is because the polyolefin family of polymers offers a broad spectrum of structures, properties and applications, which can be broadened further by blending individual polyolefins with other polymers [18]. The combination of more than one different polymer to have a new material with desirable features is not new in chemistry. In the past, different monomers were chemically combined by means of random, block, and even graft co-polymerisation methods with this goal in mind [13]. However, the idea of blending is viewed as a way of solving existing problems and creating new products without synthesising new chemical structures.

The possibilities of blending of the major polymers are infinite, and the market place will dictate the tailoring of blends. The principle reason for blending is to improve the product/cost performance for a polymer of a specific end-use application. In supporting this idea, Paul and Barlow [13] found that the blending of polymers A and B for commercial applications depends on more than one factor for the success of a new material. The first is the combination of properties where, for example, polymer A may have a desirable high thermal resistance, but its processing characteristics may be very poor. Polymer B, however, may have very good processability but poor thermal resistance. Therefore it may be of interest to combine polymers A and B, although there will generally be a compromise involved. The blend may have the desirable attributes for certain applications that neither pure A nor pure B alone could meet. A second reason is cost dilution. Here polymer A may have excellent properties and greater levels of some properties needed for certain applications. However, the price of polymer A may prohibit its use in these applications. Dilution of this polymer with a cheaper polymer B may reduce the properties to a level still acceptable for the particular application, but still bring the price of the blend to a competitive level in the market. As a result, blending can be a means of producing a material that is value for money. Typical examples of LLDPE/polyolefin blends are LLDPE/LDPE (50/50) for ice bags, (40/60) for produce bags and merchandise bags, and (30/70) for shirt sacks [2]. LDPE/LLDPE blends showed improved stiffness, abrasion resistance and reduced water vapor permeability. PE/PS blends, on the other hand, showed improved impact, elongation, and tensile strength [17].

Miscibility and compatibility of component polymers in blends are important material properties [19]. Most pairs of polymers are thermodynamically immiscible, but some polymer blends are compatible and exhibit excellent physical properties that offer advantages over either of the individual polymers. When a polymer blend is immiscible, it separates into two or more phases, and gives poor physical properties. It is generally assumed that either the particle size of the dispersed domains is not optimum, or that the immiscibility of the two phases produces weak interfaces between them, which fail easily under stress. Partial miscibility, on the other hand, is observed when the system displays practical compatibility without any further treatment. It is probably because they form a third, mixed inter-phase, which modulates between the two separate phases [20]. For example, the blends of PE/modified polyamide were found to be immiscible [21].

In the relatively rare cases of miscible (or compatible) polymers, the blend properties are intermediate between those of the individual unblended polymers. Useful blends represent a compromise among the properties of the individual polymers. For example, ethylene/styrene copolymer blends show partial miscibility in the region of 9–10 wt % in styrene content [22], and bisphenol-A polycarbonate/poly(styrene-co-methacrylic acid) is also found to be miscible

[23]. HDPE/LLDPE blends have limited miscibility [17]. Blends of poly(benzoyl paraphenylene) and polycarbonate were found to be immiscible [24]. LLDPE/wax blends mixed in the molten state showed a lower degree of miscibility than those thoroughly mechanically mixed [25,26,27]. Mechanically mixed LDPE/wax blends also showed mutual immiscibity at 20 % and more wax [28].

Properties that polyolefins generally contribute to polymer blends include high melt strength and elasticity. Mechanical properties, such as tensile strength, tensile elongation and impact strength, for a particular polymer, vary with its morphology and crystallinity [4,11]. The tensile strength is the highest for glassy liquids (e.g. polystyrene), intermediate for crystallizable polymers (e.g. PE), and the lowest for cross-linked polymers. Blending of a crystallizable polymer with another crystallizable polymer can change the tensile strength [29]. For example, PP/elastomer blends become more rigid and stable as PP increases, and a noticeable increase in tensile and flexural modulus and strength, as well as a sensible decrease in tensile elongation were observed [30]. Enhanced crystallization behaviour in branched PE when blended with linear PE was observed [7]. In a more relevant study of mechanically mixed LLDPE/oxidized paraffin wax [31], an increase in wax content of the blends showed no significant influence on the melting and crystallization temperatures, as well as the melting and crystallization enthalpies, of the blends. The trends are similar to those observed for LLDPE/hard paraffin wax blends [32]. It is therefore evident that the oxygen containing components does not cause the wax to interact differently with the LLDPE. In both cases, (i) a small increase in Young's modulus of the blends with an increase in wax content was observed, (ii) wax content does not influence the elongation at yield and yield stress of the blends, and (iii) an increase in wax content decreases both stress and elongation at break.

1.4 Cross-linking

Cross-linking is a method used to modify the properties of polymers. Modification of polymers is an extremely useful tool that further increases the applications of polymers. This is done to obtain desired properties in the new modified material. PE is said to cross-link in three ways: radiation, thermo-chemical, and moisture cross-linking [33]. In this study the thermo-chemical method that requires an added chemical, typically a peroxide, was used. A peroxide initiator is an organic compound containing the peroxide link (-O-O-) that cleaves on heating or on UV light irradiation to produce free radicals capable of initiating the formation of cross-links [10]. The wide variety of peroxy compounds available, with differing activities, make them the most widely used group of initiators capable of giving cross-links at 30–150 °C, depending on activity [10]. The choice of peroxide for cross-linking of a polymer depends particularly on the thermal stability of the peroxide related to the temperature of polymer processing [34]. In this study, dibenzoyl peroxide was used as the peroxide initiator for cross-linking. Dibenzoyl peroxide ($(C_6H_5CO)_2O_2$) is a white, granular, crystalline solid, tasteless, and has the faint odour of benzaldehyde. It has a melting point of 103-105 °C, decomposes explosively above 105 °C, and is soluble in nearly all organic solvents, as well as slightly soluble in alcohols, vegetable oils, and water [9]. It may explode spontaneously when dry (< 1 % of water), and is therefore handled damped in water. It is a diacyl peroxide and one of the most widely used free radical polymerisation initiators. It decomposes on heating as shown in Table 1.1.

Table 1.1 Decomposition half live times of DBP

Temperature/ °C	Time/ h
50	220
70	13
92	1
100	0.36
136	0.017

DBP has the following uses: (i) polymerisation initiator in the range 70-100 °C at various concentrations, (ii) cross-linking initiator for many elastomers, especially silicone rubbers at about 125 °C, (iii) bleaching agent for flour, fats, oils, and waxes, (iv) polymerisation catalyst, (v) drying agent for unsaturated oils, (vi) pharmaceutical and for cosmetic purposes, (vii) rubber vulcanisation without sulphur, and (viii) production of cheese [8].

Peroxides initiate the cross-linking of polyolefins through the homolytic cleavage of the O-O bond to alkoxy radicals

$$ROOR' \rightarrow RO^{\bullet} + R'O^{\bullet}$$

which abstract/remove hydrogens from the surrounding molecules:

$$RO^{\bullet} + \sim CH_2CH_2CH_2\sim \rightarrow ROH + \sim CH_2{}^{\bullet}CHCH_2\sim$$

This produces alkyl macro-radicals, which recombine to form a cross-link. The choice of peroxide for cross-linking of a polymer depends on the thermal stability of the peroxide related to the temperature of polymer processing [34]. Processing of polyolefins takes place at relatively high temperatures (> 100 °C), which involves high frictional and shearing forces at high speed, leading to deterioration of materials [18,35].

The number of cross-links formed in a polymer may be calculated from the amount of decomposed peroxide and from the cross-linking efficiency. If the reaction conditions are chosen so that about 5 half-lives of peroxide decomposition are reached, then the amount of non-decomposed peroxide (about 3 % of its original concentration) may be ignored. For the decomposition of peroxide in PE at 210 °C, the efficiency of peroxide was about 80 % [36].

Cross-linking involves the formation of tri–dimensional gels causing changes in the properties of materials [37]. It reduces the polyolefin crystallinity and the sizes of the lamellar crystals [10]. The reduction of the lamellar thickness of crystallites leads to a decrease of T_m. It is said that this results in a sharp reduction in the polymers' drawability [36]. Their ultimate elongation decreases by a factor 2-5, leading to much lower tensile strength values. Cross-linking leads to an increase in the tensile strength and stability of PE. The yield stress of PE is directly related to its degree of crystallinity, whereas the tensile stress at break depends on the polymer drawability, where strain hardening is in effect. In order to crystallize the polymer, it is necessary to have intermolecular cross-links, introduced by irradiation [38] or by a peroxide initiator [34]. Regulated cross-linking of e.g. low-density polyethylene (LDPE) can enhance physical, mechanical, and processing properties of polyolefins. Since LDPE is suitable for many applications but has high flexural modulus, softens around 105 °C and is permeable to gases, the presence of cross-links improves stability, creep resistance, and stress cracking [39].

Cross-linking is also a suitable tool in modifying the properties of higher paraffin waxes. It was found that the cross-linking of wax in the presence of dicumyl peroxide (DCP) produces hard, insoluble and infusible gels. The cross-linked structure of waxes is more stable against the formation of gaseous products on heating [40,41]. The increase in elasticity (elongation at break) of cross-linked waxes is directly proportional to the molecular weight of wax. When the DCP concentration was increased beyond 1:1 mole per mole of hard wax, insoluble and infusible hard brittle gels were obtained [40]. Upon introducing cross-links to HDPE, Kim & Kim [33] observed an increase in the amorphous domain and cross-link density.

The introduction of cross-linking to blends of incompatible polymers may result in interesting changes. For example, peroxide-initiated cross-linking of LDPE/PP blends was investigated to enhance dispersive mixing of the components by modifying their rheological properties. It was found that the yield and modulus values of LDPE/PP blends are improved in the presence of low amounts of cross-linking agent. The properties of these blends also depend on both the concentration of the initiator and the ratio of the blend components [36]. Cross-linking of PE/PP blends in the presence of DCP resulted in the high temperature resistance of the polymer system being improved. However, the heat resistance of the polymer blend became worse as the PP content increased [42].

In the case of polyolefin/wax blends, our research group has published recent data and it was found that, for mechanically mixed LLDPE/hard paraffin wax blends in the presence of DCP as cross-linking agent [25], Young's modulus increases with an increase in DCP content. It was further observed that cross-linking caused an increase in elongation at yield and stress at break, as well as a decrease in elongation at break and yield stress. For the thermal properties of mechanically mixed LLDPE/wax blends, Krupa & Luyt [25] observed a decrease in melting and crystallization temperatures, as well as the melting and crystallization enthalpies, with an increase in DCP content. A higher degree of crystallinity with an increase in cross-linking agent (DCP) content was also observed. Generally, during cross-linking of LLDPE/wax blends, it was further found that only PE cross-linked, while wax only grafted onto the PE chains at higher wax concentrations. It was also found that when using DCP as the cross-linking agent, the gel content of the PE phase exceeds 100 % for 20 % and more wax. When estimating the gel content using the wax phase of the LLDPE/wax blends, they found that the wax contained 0 % gel [25,26].

The molecular mass of a polymer increases during cross-linking and this is interrelated with the properties in the polymer connected with the sample deformability. Cross-linking leads to an increase in the tensile strength, and improved creep properties [43]. The stabilisation effect of chemical cross-links on entanglements and crystallites may be the direct cause of differences in the determination of mechanical properties and the sol–gel analysis of the cross-linked polymer [18]. Several procedures may be used to determine the concentration of cross-links in a cross-linked polymer. The most frequently used are equilibrium swelling, stress-strain measurements and sol-gel analysis. The proportionality between gel content and concentration of peroxide, however, does not exist at large concentrations [43,44]. It was further found that at 0.5 % peroxide there is maximum crystallinity and in the range of 2 % peroxide there is a regular network.

1.5 Degradation

The commercial importance of polymer blends implies an interest in the knowledge of their degradation behaviour [19]. For example, polymer waste recycling is a major problem, because huge amounts of synthetic polymers are manufactured every year for many different purposes. Within those wastes there are several different polyolefins, such as PE and PP [45]. To categorize these different materials is a lengthy and costly process. Therefore the study of the thermal degradation of blends containing such materials will be a major contribution in finding the solution. Moreover, blending of recycled plastics is said to be a promising technique in plastics waste management [19].

The degradation of polymers involves several physical and/or chemical processes accompanied by small structural changes that lead to significant deterioration of the quality of the polymeric material and loosening of its functionality. Degradation must be carefully monitored in order to evaluate the usefulness of polymers in different applications [46]. Thermal degradation is important, especially when polymers are processed and fabricated for use. The study of thermal degradation is important in the design of materials with improved properties for particular applications [47]. For polyurethane/elastomer blends, the pre-blended samples degrade at a lower temperature compared to the pre-heated pre-blended samples [48]. In general, PEs degrade by random scissions of the chains [49].

It is well known that an increase in temperature increases the number of cross-links formed as well as the amount of hydrogen, number of main chain scissions, and end-chain methyl groups, respectively. An increase in the number of hydrogens and cross-links may correspond to the higher yield of free radicals at higher temperatures [45]. The scission of the main chain may also occur as a parallel process. The cross-linking would have to be even higher in order to compensate for it. The scissions of the polymer main chain are due to oxygen that is always present in trace quantities in polyethylene even in a high vacuum [49]. In a physical mixture of two polymers, however, frequently some grafting of one polymer on to the other is also present as a result of the method of blend preparation, due to scission of polymer chains during melt mixing [17]. During degradation, the sample environment may influence the behaviour in various ways. Degradation in air is usually more complex than in nitrogen due to additional oxidation reactions that ultimately make the material to be less thermally stable [50,51].

1.6 Objectives of the study

The basic objectives of this study is to investigate and explain the influence of wax and DBP content on the thermal, rheological and mechanical properties of LLDPE/wax blends. The ideal blend will have improved flow properties, essential for higher productivity per time unit, and reduction of shear stress during processing. It should also have improved crack resistance, with reduced permeability. The good mechanical properties of LLDPE should, however, be conserved.

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CHAPTER 2

MATERIALS AND METHODS

2.1 Materials

The hard, brittle, crystalline, straight hydrocarbon–chain paraffin wax, used in this study, was supplied by Schümann-Sasol. It has a melting point of 90 °C, decomposes at 250 °C, and has an average molar mass of 785 g mol^{-1}. It is white with exceptional opacity and consists of saturated hydrocarbons from C_{33} upwards averaging about C_{50}. It has an iso-paraffin content of approximately 10 %, is chemically inert, inhibited against oxidation and free of aromatics.

Dibenzoyl peroxide (DBP) supplied by Sigma Aldrich Co. Ltd. was used as the cross-linking agent. It has a melting point of 105 °C, and decomposes at temperatures above 105 °C.

LLDPE was supplied in powder form by Sasol Polymers. It has a particle size less than 600 µm, a melt flow index of 3.5 g/10min, a density of 0.938 g cm^{-3}, and an average molecular weight of 191600 g mol^{-1}.

2.2 Methods

Different LLDPE/wax/DBP m/m ratios (see Table 2.1) were mechanically mixed in a coffee mill for about 2 minutes to form a homogeneous mixture. The samples were melt pressed into 100 x 80 x 0.7 mm shapes at 160 °C for 3 minutes using a 10-ton hot-melt press.

Table 2.1 Samples used in this study

LLDPE/wax/DBP	LLDPE/wax/DBP	LLDPE/wax/DBP	LLDPE/wax/DBP
100/0/0	99/0/1	98/0/2	97/0/3
98/2/0	97/2/1	96/2/2	95/2/3
95/5/0	94/5/1	93/5/2	92/5/3
90/10/0	89/10/1	88/10/2	87/10/3
80/20/0	79/20/1	78/20/2	77/20/3
70/30/0	69/30/1	68/30/2	67/30/3
60/40/0	59/40/1	58/40/2	57/40/3

Gel content was determined through xylene extraction of the uncross-linked part of the samples. 0.2 g samples, wrapped in fine stainless steel mesh and tied with a string, were placed in a roundbottomed flask half filled with xylene and refluxed for 12 hours, changing xylene at 3-hour intervals. After extraction, the wrapped samples were washed with chloroform and first dried at room temperature for 24 hours and then at about 50 °C in an oven for 4 hours. The samples were re-weighed and the gel content was determined by calculating the percentage ratio of the mass of xylene-insoluble gel to that of the sample before extraction, using Equation 2.1.

$$\% \text{ gel} = [m_3 - (m_2 - m_1)/m_1] \times 100 \qquad \textbf{[2.1]}$$

where m_1 = mass of sample before extraction, m_2 = mass of sample + mesh + copper wire (before extraction), and m_3 = mass of sample + mesh + copper wire (after extraction).

Thermogravimetric (TGA) analyses were carried out on a Perkin–Elmer TGA7 thermogravimetric analyzer. Samples ranging between 5 and 10 mg were heated from 25 to 600 °C at a heating rate of 10 °C min^{-1} under flowing nitrogen and synthetic air atmospheres respectively.

Differential scanning calorimetry (DSC) analyses were carried out on a Perkin–Elmer DSC7 thermal analyzer under flowing nitrogen atmosphere. The instrument was calibrated using the onset temperatures of indium and zinc standards as the melting temperatures, and the melting enthalpy of indium. Polymer samples (between 5 and 10 mg) were initially heated from 25 to 150 °C at 20 °C min^{-1}, held at 150 °C for one minute to eliminate thermal history effects, and then cooled to 25 °C at 20 °C min^{-1}. They were maintained at 25 °C for one minute, heated again up to 150 °C at 10 °C min^{-1}, and then cooled to 25 °C 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. The degree of crystallinity, X_c, was calculated using Equation 2.2.

$$X_c = (\Delta H_m/\Delta H_m^*) \times 100 \qquad \textbf{[2.2]}$$

where ΔH_m is the melting enthalpy of the samples calculated from the main melting peak, and $\Delta H_m^* = 288 \text{ J g}^{-1}$ is the melting enthalpy of 100 % crystalline PE [52]. The same value for ΔH_m^* was also used for the blends because wax has the same orthorhombic crystal structure as PE.

Fourier transform infrared (FTIR) spectroscopic analyses were carried out on a Nicolet Impact 410 FTIR spectrometer at a resolution of 8 cm^{-1}, a scan range of 4000 – 400 cm^{-1}, and a total of

200 scans per analysis. Samples with dimensions 50 x 20 mm from the melt-pressed disks were directly placed in front of the beam for each analysis.

Flow rates of uncross-linked blends were determined using a Ceast Melt Flow Junior extrusion plastometer at 190 °C and under a 1 kg mass.

The mechanical properties were determined using a Hounsfield W5K tensile tester at a cross–head speed of 50 mm min^{-1}. Dumbbell shaped specimens with cross-sectional area of 75 x 15 mm and gauge length of approximately 21.0 mm, were used for measurements. In total, six dumbbells per blend sample were used for each analysis and the average was taken as the reported value. The respective values at yield point were calculated as shown in Equations 2.3 and 2.4.

Yield stress: $\sigma_y = F_y/w.t$ [Mpa] **[2.3]**

Elongation at yield: $\varepsilon_y = 100\ x_y/x_o$ [%] **[2.4]**

where F_y = force at yield, w = width at center of dumbbell, t = thickness of sample, x_y = extension at yield, and x_o = gauge length.

The ultimate properties were calculated as shown in Equations 2.5 and 2.6.

Elongation at break: $\varepsilon_b = 100\ x_b/x_o$ [%] **[2.5]**

Stress at break: $\sigma_b = F_b/w.t$ [MPa] **[2.6]**

where x_b = extension at break, and F_b = force at break.

Young's modulus of elasticity was calculated by firstly determining the linear regression (F = A + B.x) of the first 5 – 6 points, and then using Equation 2.7.

Young's modulus: $E = B.x_o/w.t$ [MPa] **[2.7]**

Molecular weight distribution of the respective samples was determined from the xylene soluble parts of the blends. Sample concentrations of 0.1 g sample / 4.0 ml xylene were analysed in a

Waters 150-C ALC/GPC equipped with a refractive index detector and two Waters styragel HR 4E (7.8 x 300 mm) columns. The following conditions were used:

Solvent	: o-xylene
Injection volume	: 100.0 ml
Run time	: 59 minutes
Column temperature	: 120 °C

The presented values were calculated by firstly adding all peak areas to get the total peak area, Equation 2.8.

$$A_{tot} = \sum A_i \qquad \textbf{[2.8]}$$

where A_{tot} = total peak area, A_i = individual peak areas.

The individual peak areas were then divided by the total peak area to get the respective percentage area (A), Equation 2.9.

$$A = (A_i/A_{tot}) \times 100 \qquad \textbf{[2.9]}$$

The percentage area with respect to LLDPE or wax content was calculated by dividing the obtained percentage area by the mass ratio of the respective components, Equations 2.10 and 2.11.

$$A_a = A/w_{PE} \qquad \textbf{[2.10]}$$

$$A_b = A/w_w \qquad \textbf{[2.11]}$$

where A_a = percentage area with respect to LLDPE content, and A_b = percentage area with respect to wax content.

CHAPTER 3

RESULTS

3.1 Characterisation of materials and blends

3.1.1 Extent of cross-linking

The gel content results are summarised in Table 3.1.

Table 3.1 Gel content of cross-linked LLDPE/wax blends

PE/W/DBP	% gel	% gel/w_{PE}	PE/W/DBP	% gel	% gel/w_{PE}	PE/W/DBP	% gel	% gel/w_{PE}
99/0/1	46.1	46.5	98/0/2	88.6	90.4	97/0/3	88.2	90.9
97/2/1	41.3	42.6	96/2/2	87.5	91.1	95/2/3	86.0	90.5
94/5/1	42.9	45.6	93/5/2	85.3	91.7	92/5/3	84.6	92.0
89/10/1	10.9	12.3	88/10/2	75.3	85.6	87/10/3	79.5	91.4
79/20/1	14.1	17.8	78/20/2	75.7	97.1	77/20/3	74.6	96.9
69/30/1	0.19	0.28	68/30/2	68.9	100.9	67/30/3	71.9	107.3
59/40/1	0.040	0.075	58/40/2	60.5	104.3	57/40/3	68.3	119.8

PE/W/DBP = percentage composition of LLDPE/wax/dibenzoyl peroxide, % gel = gel content, and % gel/w_{PE} = gel content with respect to LLDPE content

It can be seen in Table 3.1 that for 1 % DBP, the gel content decreases significantly with an increase in wax content. For 2 and 3 % DBP, the decrease in gel content with increasing wax content is less pronounced. Figure 3.1 shows that for 1 % DBP, the gel content at wax contents ≤ 5 % ranges between 40 and 50 %. At wax contents ≥ 10 %, the gel content is between 0 and 15 %. However, the gel content at higher DBP concentrations is significantly higher than that for 1 % DBP. At lower wax contents 2 and 3 % DBP give similar values for gel content, but 3 % DBP seems to be more effective at high wax contents.

The gel content with respect to LLDPE content in the blends was also determined (Table 3.1). The calculated values show that at the lower DBP concentration, the gel content relative to

LLDPE content has similar values than those of the overall gel content. At the higher DBP concentrations, the increase in wax content causes an increase in gel content with respect to LLDPE content. This increase exceeds 100 % at 30 % and more wax.

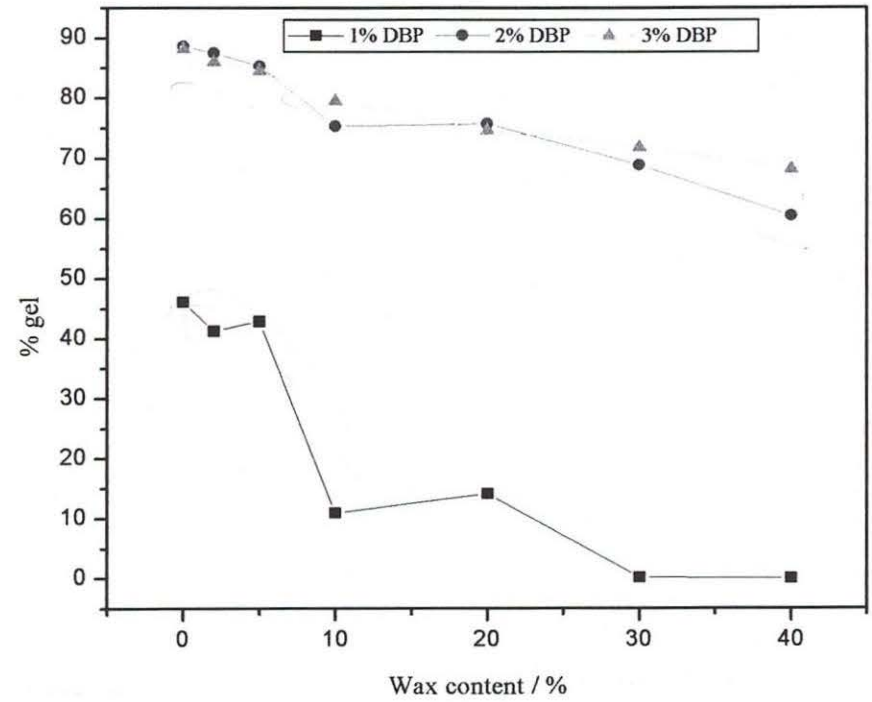

Figure 3.1 Gel content of cross-linked LLDPE/wax blends as function of wax content

3.1.2 Determination of structure

The infrared spectra of the different samples are presented in Figures 3.2 – 3.5, and the vibration intensity values for the characteristic vibrations are listed in Tables 3.2 – 3.4. The intensity of the C-H out-of-plane bending or wagging vibrations at 883.98 cm^{-1}, which are characteristic of C-H bending vibrations of hydrogen attached to unsaturated carbons [53], increases with increase in wax content for both uncross-linked and cross-linked LLDPE/wax blends (Table 3.2).

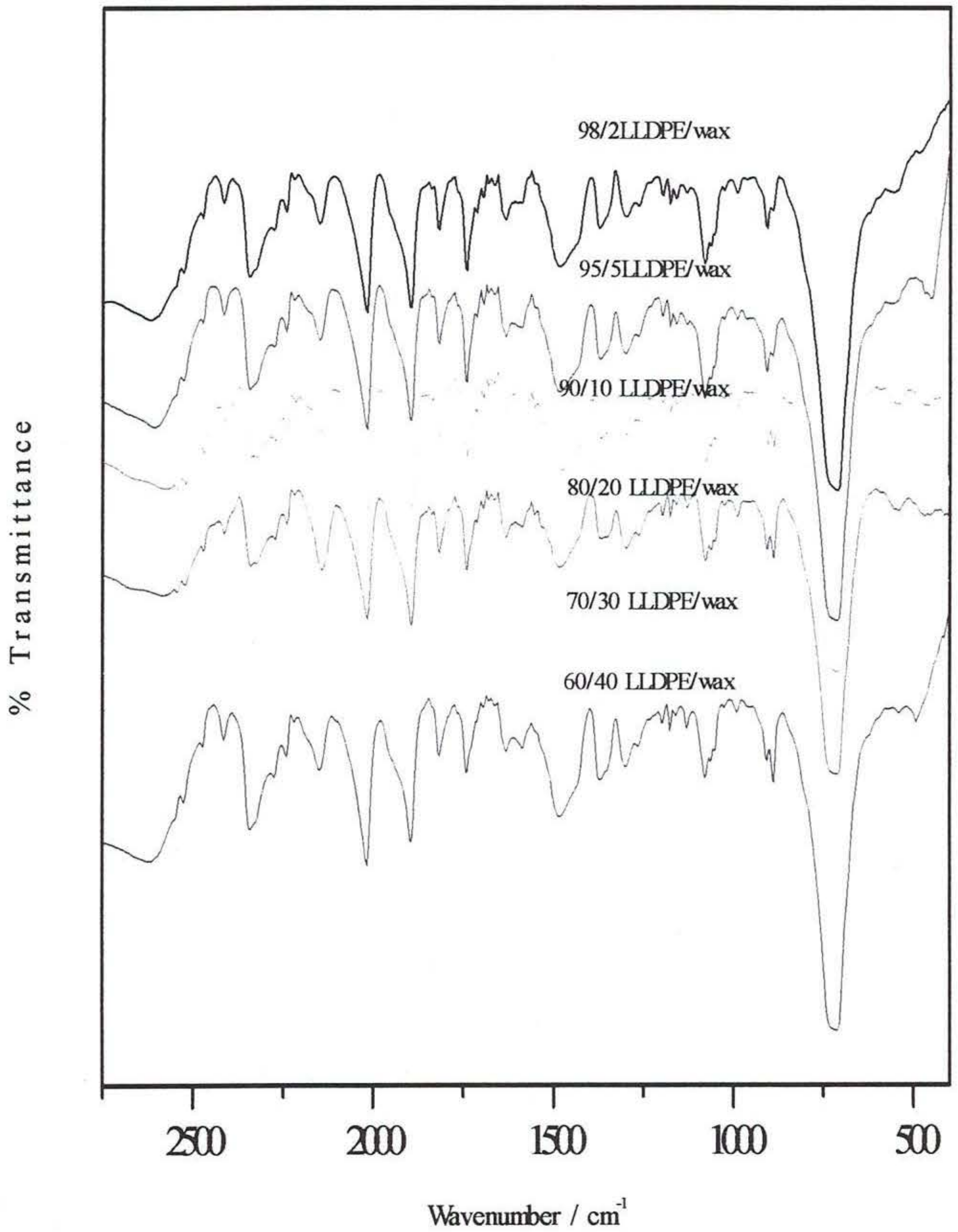

Figure 3.2 **FTIR spectra of uncross-linked LLDPE/wax blends**

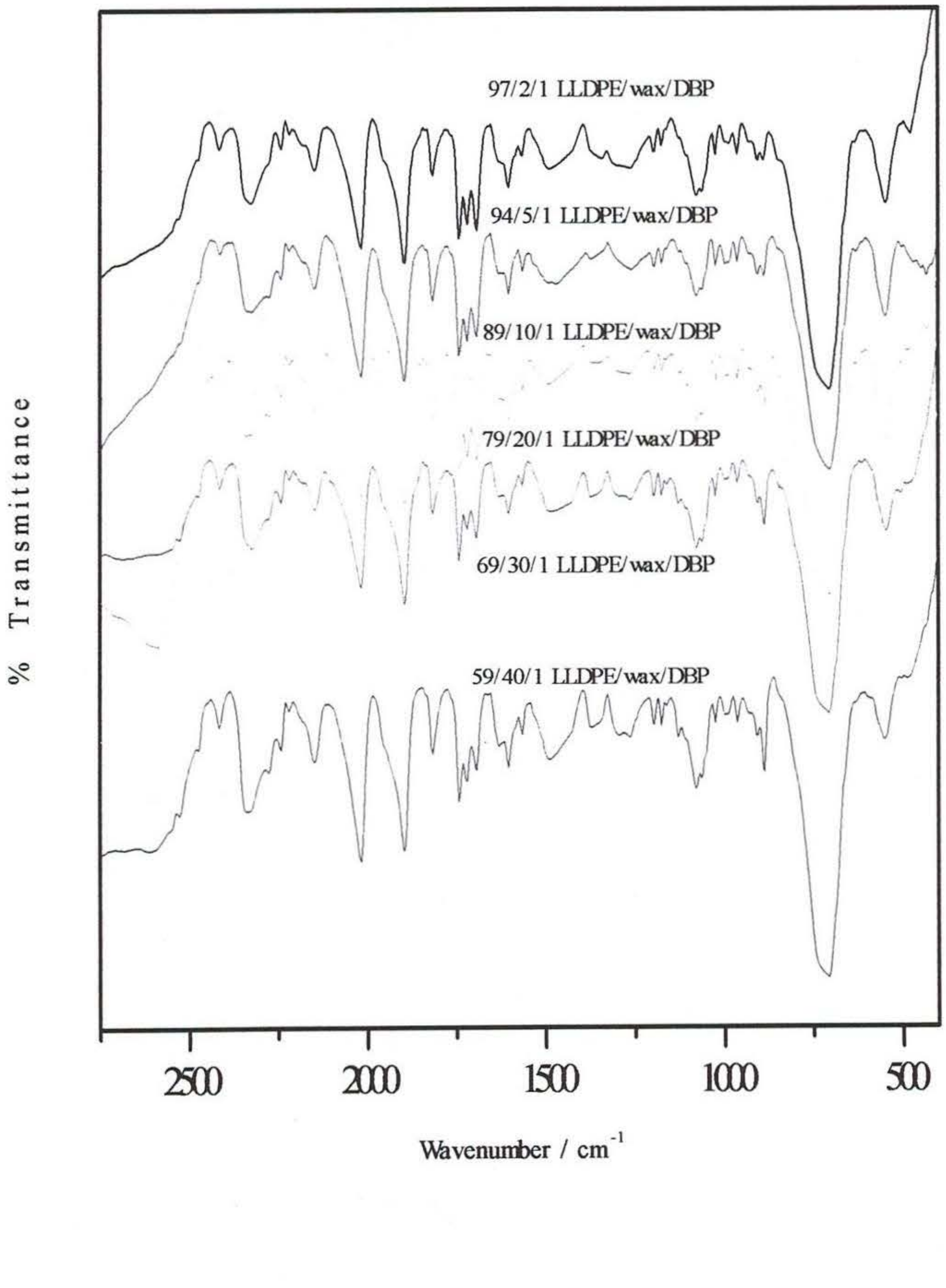

Figure 3.3 **FTIR spectra of LLDPE/wax/DBP blends cross-linked in the presence of 1 % DBP**

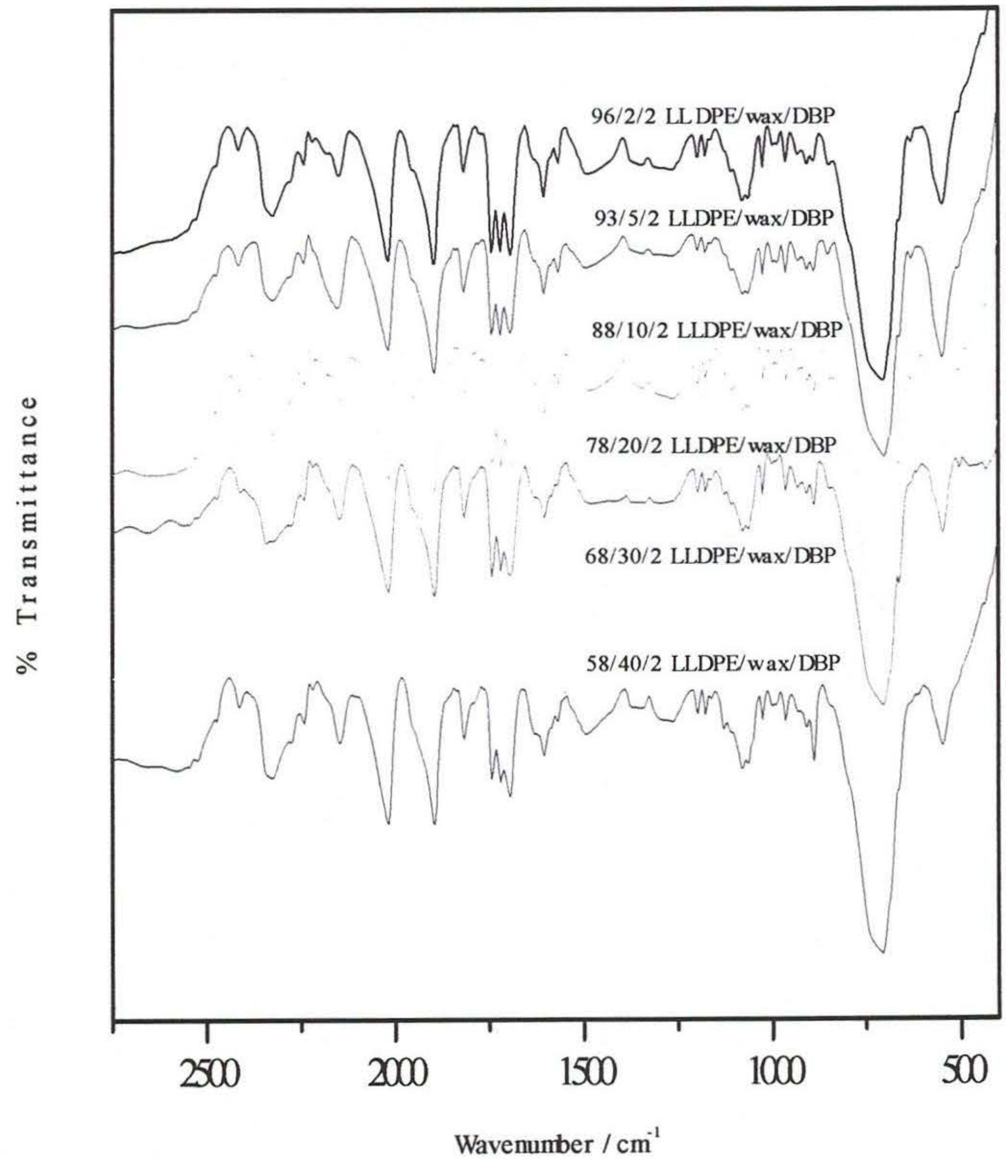

Figure 3.4 **FTIR spectra of LLDPE/wax/DBP blends cross-linked in the presence of 2 % DBP**

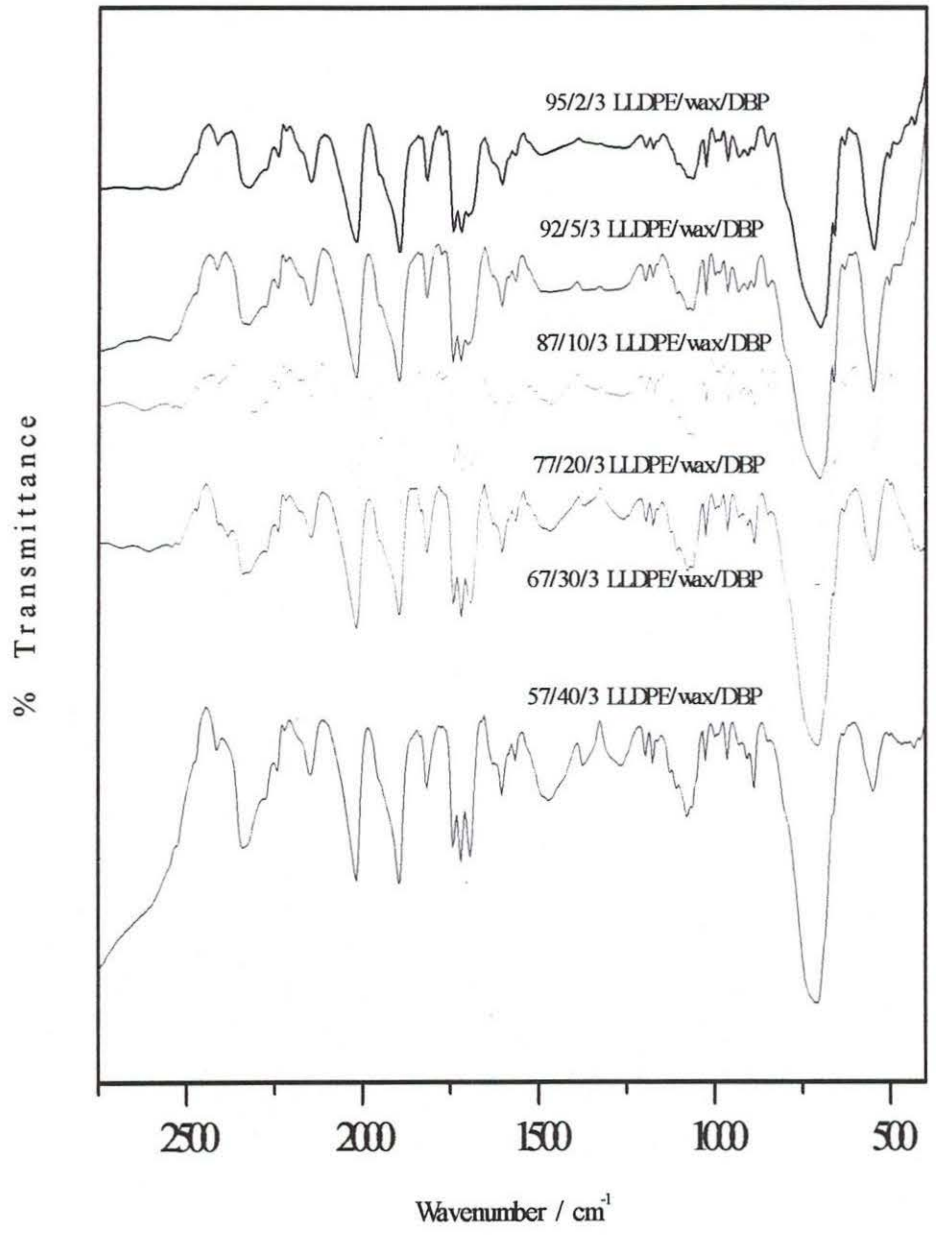

Figure 3.5 **FTIR spectra of LLDPE/wax/DBP blends cross-linked in the presence of 3 % DBP**

The intensity of this vibration is higher at lower DBP concentrations and decreases as DBP content increases.

Table 3.2 Effect of wax concentration on the =C-H bending vibrations in the region 1000 – 800 cm^{-1} for uncross-linked and cross-linked blends

% Wax	(0 % DBP) Intensity	(1 % DBP) Intensity	(2 % DBP) Intensity	(3 % DBP) Intensity
2	6.0	5.4	2.3	2.7
5	6.6	4.9	3.5	4.3
10	8.7	4.9	7.0	4.7
20	9.9	9.8	7.3	7.9
30	9.9	11.6	10.1	9.2
40	12.3	14.2	12.6	9.7

The effect of both wax and DBP contents on the intensity of the CH_2 characteristic vibration in the region 800 – 650 cm^{-1} is shown in Table 3.3. An increase in wax content results in a general increase in the intensity of this vibration for both uncross-linked and cross-linked LLDPE/wax blends. There is a decrease in the intensity of this vibration as the DBP content increases. A small vibration appears next to the main vibration in this region as the DBP concentration increases.

The appearance of a triplet peak in the region 1740-1706 cm $^{-1}$, characteristic of the C=O group stretching vibration, is observed for cross-linked blends. The vibrations become more pronounced as the concentration of DBP increases. Uncross-linked blends show only one significant vibration, independent of the wax content, in this region.

CH_3 has a deformation vibrational mode at 1375 cm^{-1} [53]. Table 3.4 shows a general increase in the intensity of this vibration as wax content in both uncross-linked and cross-linked LLDPE/wax blends increases. There is a strong decrease in vibration intensity with increasing DBP concentration.

A typical C-H bending vibration at around 1480 cm^{-1} generally increases in intensity as wax concentration in the blends becomes larger. An increase in DBP content results in a decrease in the intensity of this vibration.

Table 3.3 **Effect of wax concentration on the CH_2 vibration in the region 800 – 650 cm^{-1} for uncross-linked and cross-linked LLDPE/wax blends**

% Wax	(0 % DBP) Intensity	(1 % DBP) Intensity	(2 % DBP) Intensity	(3 % DBP) Intensity
2	56.9	44.1	41.7	32.4
5	57.3	38.9	37.1	35.2
10	51.0	40.8	43.0	35.9
20	52.0	43.6	40.3	40.4
30	51.0	49.8	44.0	40.9
40	58.2	50.7	44.6	45.6

Table 3.4 **Effect of wax concentration on the CH_3 vibration at 1375 cm^{-1} for uncross-linked and cross-linked LLDPE/wax blends**

% Wax	(0 % DBP) Intensity	(1 % DBP) Intensity	(2 % DBP) Intensity	(3 % DBP) Intensity
2	9.7	2.8	2.9	0.28
5	9.5	1.5	1.5	0.89
10	7.3	2.3	2.2	0.85
20	6.9	4.2	1.0	1.6
30	7.0	5.6	2.0	2.1
40	12.6	6.3	2.8	3.1

3.1.3 Molecular weight distribution

The GPC results of the unblended components showed that LLDPE has three significant peaks, with the first peak at a retention time of 11.8 minutes, the second at about 21.0 minutes, and the third at 29.6 minutes. Wax has two significant peaks, with the first at 16.0 minutes and the second at about 21.0 minutes. The summaries of the GPC retention times (R_t) as function of the change in wax and cross-linking agent contents are shown in Tables 3.5 – 3.8. The obtained data is for the extracted or sol parts of the blends, and the non-extracted or gel part of the blends will show inverse trends. Both uncross-linked and cross-linked LLDPE/wax blends show a shift of the first LLDPE characteristic peak at about 11.0 min to lower R_t values as the concentrations of wax and DBP increase (Table 3.5). It does not seem as if the R_t values of the other peaks are influenced by the amount of wax or extent of cross-linking (Tables 3.6 – 3.8).

Table 3.5 Retention times (R_t) of the peak at about 11.0 min for uncross-linked and cross-linked LLDPE/wax blends

% Wax	0 % DBP	1 % DBP	2 % DBP	3 % DBP
2	11.2	10.7	10.5	10.6
10	10.9	10.7	10.5	10.5
30	10.8	10.9	10.5	10.8
40	10.8	10.6	10.6	10.6

Table 3.6 Retention times (R_t) of the peak at about 16.0 min for uncross-linked and cross-linked LLDPE/wax blends

% Wax	0 % DBP	1 % DBP	2 % DBP	3 % DBP
2	16.2	16.1	15.3	16.2
10	16.2	16.2	16.2	16.1
30	16.6	16.1	16.2	16.4
40	16.2	16.3	16.4	16.3

Table 3.7 **Retention times (R_t) of the peak at about 21.0 min for uncross-linked and cross-linked LLDPE/wax blends**

% Wax	0 % DBP	1 % DBP	2 % DBP	3 % DBP
2	21.0	21.7	21.5	21.7
10	21.0	21.2	21.6	21.6
30	21.5	21.7	21.8	21.9
40	21.9	21.2	21.9	21.8

Table 3.8 **Retention times (R_t) of the peak at about 29.5 min for uncross-linked and cross-linked LLDPE/wax blends**

% Wax	0 % DBP	1 % DBP	2 % DBP	3 % DBP
2	29.7	29.7	29.7	29.5
10	29.8	29.8	29.5	29.6
30	29.9	29.6	29.8	29.9
40	29.8	29.6	30.1	29.7

The percentage area of the first peak at 11.0 min shows a general decrease with an increase in wax content for both uncross-linked and cross-linked LLDPE/wax blends (Table 3.9). The % area of this peak as a function of DBP content shows a general increase with increasing DBP content. The % area of the wax characteristic peak at 16.0 min increases with increasing DBP content and generally increases with increase in wax content (Table 3.10). Table 3.11 shows the % area of the peak at an R_t of 21.0 minutes. Values for uncross-linked blends are fairly constant. Values for blends cross-linked in the presence of 1 % DBP are too scattered to indicate a trend, whereas those cross-linked in the presence of 2 % DBP show a general decrease. A slight increase is also observed for blends cross-linked in the presence of 3 % DBP.

The % area of the peak at 29.5 min decreases as a function of wax content for uncross-linked blends, and blends cross-linked in the presence of 1 % DBP. The values remain fairly constant for blends cross-linked in the presence of 2 % DBP, and increase for blends cross-linked in the presence of 3 % DBP (Table 3.12).

Table 3.9 **% Area of the peak at an R_t of about 11.0 min as a function of wax and DBP contents**

% Wax	0 % DBP	1 % DBP	2 % DBP	3 % DBP
2	6.2	80.9	38.2	35.8
10	4.9	5.8	29.3	20.2
30	2.7	8.5	9.1	20.9
40	3.3	7.6	28.7	7.5

Table 3.10 **% Area of the peak at an R_t of about 16.0 min as a function of wax and DBP contents**

% Wax	0 % DBP	1 % DBP	2 % DBP	3 % DBP
2	1.3	2.2	7.4	12.5
10	3.9	7.5	8.3	11.5
30	29.0	3.1	31.3	31.5
40	11.1	34.6	42.6	17.3

Table 3.11 **% Area of the peak at an R_t of about 21.0 min as a function of wax and DBP contents**

% Wax	0 % DBP	1 % DBP	2 % DBP	3 % DBP
2	8.4	31.4	42.5	39.7
10	7.2	82.2	34.2	46.5
30	5.3	12.4	36.5	28.6
40	12.5	43.9	17.6	45.9

Table 3.12 **% Area of the peak at an R_t of about 29.5 min as a function of wax and DBP contents**

% Wax	0 % DBP	1 % DBP	2 % DBP	3 % DBP
2	84.1	35.6	11.8	11.9
10	83.9	4.5	28.1	21.8
30	62.9	76.1	23.1	19.0
40	72.9	13.8	11.1	29.2

The percentage areas with respect to both LLDPE and wax contents were also determined. Tables 3.13 – 3.16 show the percentage areas (A_a) of the respective peaks with respect to the weight content of LLDPE in the blends. The A_a values of the first peak at about 11.0 min generally decrease as a function of wax content and increase with an increase in DBP content (Table 3.13). Although the results are scattered, the A_a values of the other peaks at about 16.0, 21.0 and 29.5 min generally increase with an increase in both wax and DBP contents (Tables 3.14 – 3.16).

The percentage areas (A_b) of the peak at an R_t of about 11.0 min as a function of wax content remain virtually the same for uncross-linked blends and for those cross-linked in the presence of 1 % DBP. The A_b values of blends cross-linked in the presence of 2 and 3 % DBP generally increase with an increase in wax content (Table 3.17). A general increase in A_b as a function of DBP content is observed.

The A_b values of the peak at an R_t of about 16.0 min increase as a function of wax content (Table 3.18). The values remain the same at ≤ 10 % wax and increase for > 10 % wax with an increase in DBP content. The A_b values of the peak at 21.0 min as a function of wax content generally increase. It can be seen in Table 3.19 that at lower wax concentrations, an increase in DBP content does not significantly affect the A_b values, whereas at higher wax contents a general increase with an increase in DBP content is observed.

The A_b values of the peaks at 21.0 and 29.5 min as a function of wax content show relatively similar behaviour (Tables 3.19 - 3.20). A_b as a function of wax content generally increases. The A_b values of the peak at an R_t of 21.0 min generally increase with increasing DBP concentration. For the peak at an R_t of about 29.5 min, A_b decreases with an increase in DBP content (Table 3.20).

Table 3.13 % Area (A_a) of the peak at an R_t of about 11.0 min with respect to the weight content of LLDPE in the LLDPE/wax blends as a function of wax and DBP contents

% Wax	0 % DBP	1 % DBP	2 % DBP	3 % DBP
2	6.3	31.8	39.8	36.5
10	5.4	6.5	33.3	23.2
30	3.8	12.3	13.4	31.2
40	5.5	12.9	49.5	13.2

Table 3.14 % Area (A_a) of the peak at an R_t of about 16.0 min with respect to the weight content of LLDPE in the LLDPE/wax blends as a function of wax and DBP contents

% Wax	0 % DBP	1 % DBP	2 % DBP	3 % DBP
2	1.3	2.3	7.7	12.7
10	4.3	8.4	9.4	13.2
30	41.4	4.5	46.0	47.0
40	18.5	58.6	73.4	30.4

Table 3.15 % Area (A_a) of the peak at an R_t of about 21.0 min with respect to the weight content of LLDPE in the LLDPE/wax blends as a function of wax and DBP contents

% Wax	0 % DBP	1 % DBP	2 % DBP	3 % DBP
2	8.6	32.4	44.3	40.5
10	8.0	92.4	38.9	53.4
30	7.6	18.0	53.7	42.7
40	20.8	74.4	30.3	80.5

Table 3.16 % Area (A_a) of the peak at an R_t of about 29.5 min with respect to the weight content of LLDPE in the LLDPE/wax blends as a function of wax and DBP contents

% Wax	0 % DBP	1 % DBP	2 % DBP	3 % DBP
2	85.8	36.7	12.3	12.1
10	93.3	5.0	31.9	25.1
30	89.9	110.3	34.0	28.4
40	120.8	23.4	19.1	51.2

Table 3.17 % Area (A_b) of the peak at an R_t of about 11.0 min with respect to the weight content of wax in the LLDPE/wax blends as a function of wax and DBP contents

% Wax	0 % DBP	1 % DBP	2 % DBP	3 % DBP
2	0.12	0.62	0.76	0.72
10	0.49	0.58	2.9	2.0
30	0.81	2.5	2.7	6.3
40	1.3	3.0	11.5	3.0

Table 3.18 % Area (A_b) of the peak at an R_t of about 16.0 min with respect to the weight content of wax in the LLDPE/wax blends as a function of wax and DBP contents

% Wax	0 % DBP	1 % DBP	2 % DBP	3 % DBP
2	0.026	0.097	0.15	0.25
10	0.39	0.75	0.83	1.1
30	8.7	0.93	9.4	9.4
40	4.4	13.8	17.0	6.9

Table 3.19 % Area (A_b) of the peak at an R_t of about 21.0 min with respect to the weight content of wax in the LLDPE/wax blends as a function of wax and DBP contents

% Wax	0 % DBP	1 % DBP	2 % DBP	3 % DBP
2	0.17	0.63	0.85	0.79
10	0.72	8.2	3.4	4.6
30	1.6	3.7	10.9	8.6
40	5.0	17.6	7.0	18.4

Table 3.20 % Area (A_b) of the peak at an R_t of about 29.5 min with respect to the weight content of wax in the LLDPE/wax blends as a function of wax and DBP contents

% Wax	0 % DBP	1 % DBP	2 % DBP	3 % DBP
2	1.7	0.17	0.24	0.24
10	8.4	0.45	2.8	2.2
30	18.9	22.8	6.9	5.7
40	29.2	5.5	4.4	11.7

3.1.4 Degree of crystallinity

The calculated values for the degree of crystallinity (X_c) are shown in Table 3.21.

Table 3.21 Degree of crystallinity (X_c) of cross-linked and uncross-linked LLDPE/wax blends

Sample PE/W/BP	X_c / %	Sample PE/W/BP	X_c / %	Sample PE/W/BP	X_c / %	Sample PE/W/BP	X_c / %
100/0/0	55.2	99/0/1	49.6	98/0/2	54.1	97/0/3	58.0
98/2/0	50.4	97/2/1	48.6	96/2/2	50.2	95/2/3	45.2
95/5/0	55.4	94/5/1	50.5	93/5/2	46.4	92/5/3	46.0
90/10/0	52.1	89/10/1	51.4	88/10/2	51.6	87/10/3	42.6
80/20/0	55.6	79/20/1	53.4	78/20/2	56.4	77/20/3	54.6
70/30/0	63.4	69/30/1	50.2	68/30/2	57.1	67/30/3	43.8
60/40/0	59.9	59/40/1	51.3	58/40/2	61.8	57/40/3	45.2
0/100/0	71.7	-	-	-	-	-	-

PE/W/BP = percentage ratios of LLDPE/wax/DBP, and X_c = degree of crystallinity

For the uncross-linked LLDPE/wax blends there seems to be a general increase in the crystallinity with increasing wax content. The crystallinity values of blends cross-linked in the presence of 1 and 2 % DBP are scattered, but show a generally increasing trend as a function of wax content. However, blends cross-linked in the presence of 3 % DBP do not show any particular trend, but the values for these blends are generally lower than that for unblended LLDPE. Although the results are scattered, the crystallinity values generally decrease with an increase in DBP content.

3.2 Properties of blends

3.2.1 Thermal properties

The DSC heating curves of unblended LLDPE and wax are shown in Figure 3.6 and the temperatures are summarized in Table 3.22. LLDPE shows only one endotherm with the peak maximum at 132 °C. Wax shows a triple endothermic peak. The first peak is at 75 °C, the second is a shoulder at 90 °C and the third is at 105 °C.

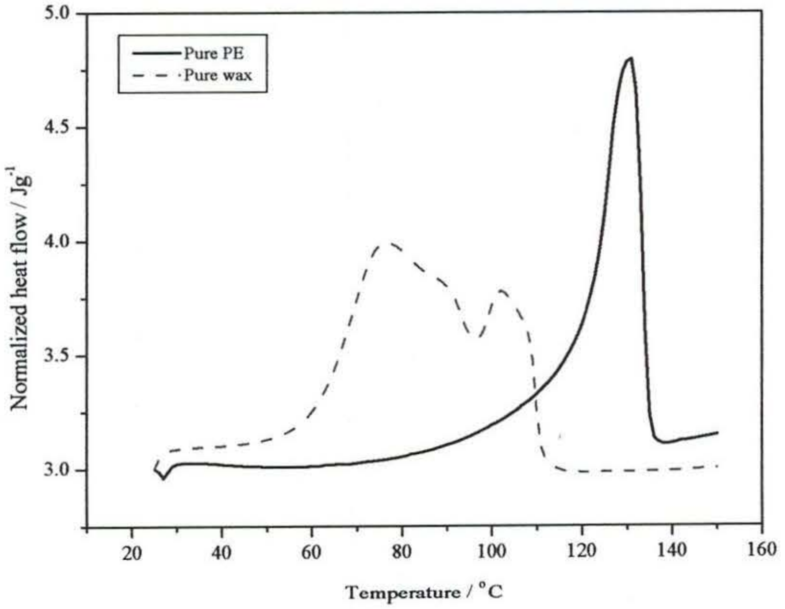

Figure 3.6 DSC heating curves of unblended LLDPE and wax

The effect of wax content on the thermal properties of uncross-linked blends is shown in Figure 3.7. All the DSC curves show only one endothermic peak. The onset and peak temperatures are summarized in Table 3.23. There is a slight decrease in onset and peak temperatures of melting with increasing wax content. The ΔH_m values of the blends increase with an increase in wax content. These values are in line with those calculated according to the additive rule (Equation 3.1).

$$\Delta H_m^{add} = \Delta H_{m,PE}\, w_{PE} + \Delta H_{m,w} w_w \qquad [3.1]$$

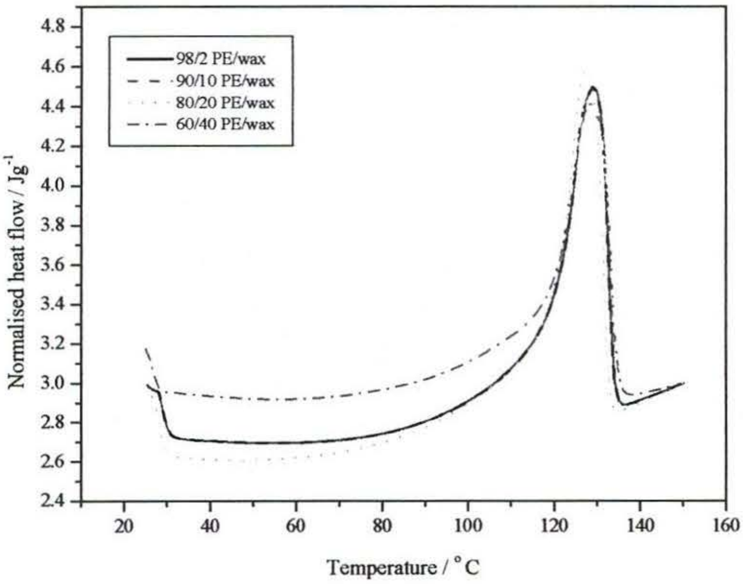

Figure 3.7 DSC heating curves of uncross-linked LLDPE/wax blends

Table 3.22 Summary of DSC data for uncross-linked LLDPE/wax blends

LLDPE/wax/DBP	$T_{o,m}$ [° C]	$T_{p,m}=T_m$ [° C]	ΔH_m [Jg^{-1}]	$T_{o,c}=T_c$ [° C]	$T_{p,c}$ [° C]	ΔH_c [Jg^{-1}]	ΔH_m^{add} [Jg^{-1}]
100/0/0	119.9	131.2	159.1	113.0	110.5	-171.6	159.1
98/2/0	119.9	130.4	145.3	112.0	109.3	-184.8	160.3
95/5/0	118.7	128.9	159.5	112.0	109.5	-185.1	162.1
90/10/0	118.3	128.7	150.0	111.6	109.0	-187.2	165.2
80/20/0	119.7	126.4	160.1	111.9	109.3	-214.5	171.2
70/30/0	118.8	129.2	182.5	111.8	108.8	-216.1	177.3
60/40/0	118.8	128.0	172.4	111.4	108.3	-212.1	183.4
0/100/0	60.6	77.2	206.5	94.9	91.8	-219.2	219.8

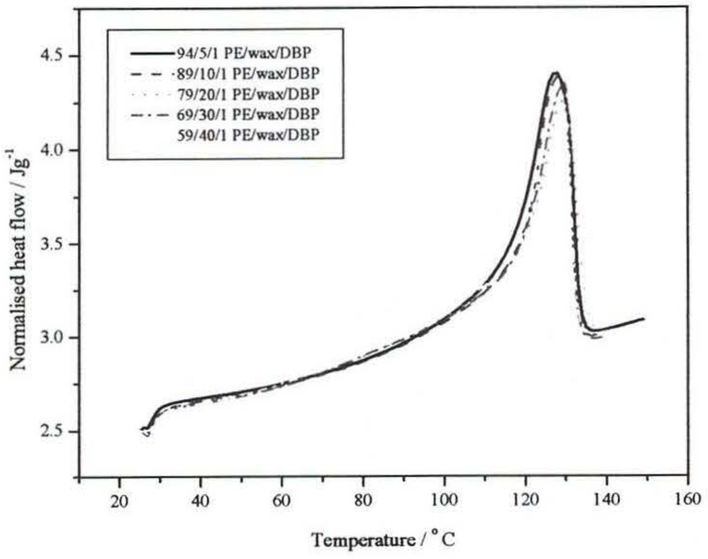

Figure 3.8 **DSC heating curves of LLDPE/wax blends cross-linked in the presence of 1 % DBP**

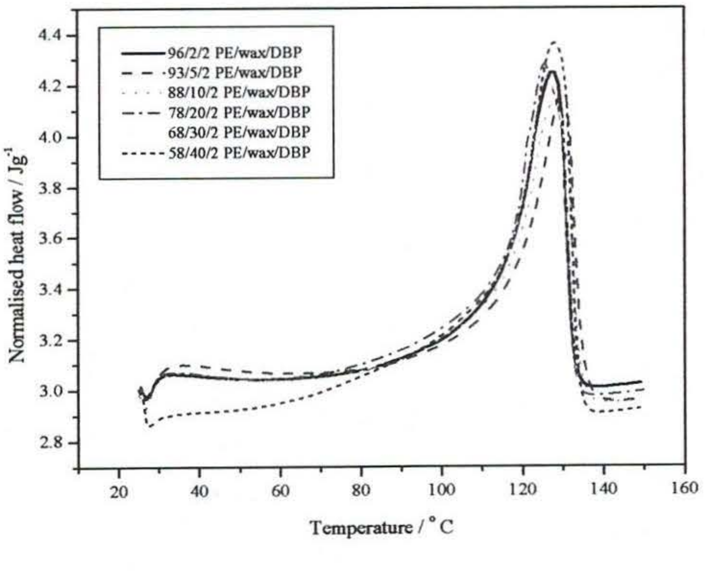

Figure 3.9 **DSC heating curves of LLDPE/wax blends cross-linked in the presence of 2 % DBP**

Figure 3.8 shows the DSC heating curves of blends cross-linked in the presence of 1 % DBP. Although there is a slight decrease in $T_{o,m}$ with increasing wax content, the change in wax content does not affect the shape of the melting peaks or the values of T_m (Table 3.23). The DSC curves of blends cross-linked in the presence of 2 % DBP show virtually no change in $T_{o,m}$ and T_m (Figure 3.9 and Table 3.23). It can be seen in Figure 3.10 that 3 % DBP does not affect the shape of the curves, but in this case both $T_{o,m}$ and T_m shift to lower temperatures with increasing wax content. Generally a slight decrease in both $T_{o,m}$ and T_m as a function of cross-linking agent is observed (Table 3.23).

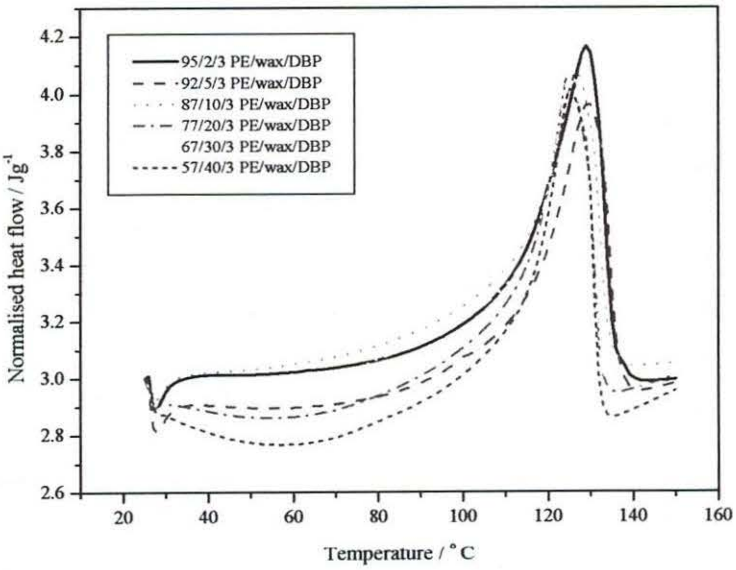

Figure 3.10 **DSC heating curves of LLDPE/wax blends cross-linked in the presence of 3 % DBP**

With respect to the melting enthalpies (Table 3.23), blends cross-linked in the presence of 1 and 2 % DBP show some scattering of results, which generally increase with increasing wax content. For blends cross-linked in the presence of 3 % DBP, they remain virtually constant with an increase in wax content. For cross-linked blends they generally decrease with increasing DBP content. The melting enthalpies of cross-linked blends differ from those calculated using the log additive rule (Equation 3.1).

Table 3.23 Summary of DSC data for cross-linked LLDPE/wax blends

LLDPE/wax/DBP	$T_{o,m}$ [° C]	$T_{p,m}=T_m$ [° C]	ΔH_m [Jg^{-1}]	$T_{o,c}$ [° C]	$T_{p,c}=T_c$ [° C]	ΔH_c [Jg^{-1}]	ΔH_m^{add} [Jg^{-1}]
97/2/1	118.6	129.0	140.1	112.6	107.3	-181.8	158.7
89/10/1	118.9	128.4	148.1	111.7	108.0	-176.4	163.6
69/30/1	117.1	129.0	144.6	111.1	106.8	-185.0	175.7
59/40/1	115.4	128.5	147.8	111.3	107.3	-167.6	181.8
96/2/2	114.5	127.4	144.6	110.8	105.1	-177.4	157.1
88/10/2	112.9	128.0	148.7	110.7	103.8	-192.1	162.0
68/30/2	113.2	126.4	164.5	110.6	107.5	-185.3	174.1
58/40/2	114.3	127.9	177.9	110.8	106.6	-208.9	180.2
95/2/3	114.8	129.2	130.2	113.2	103.2	-156.1	155.5
87/10/3	112.1	126.7	122.7	110.7	102.5	-147.1	160.4
67/30/3	114.7	125.4	126.3	110.0	105.5	-153.9	172.5
57/40/3	113.5	125.2	130.1	110.2	106.7	-241.4	178.6

The DSC cooling curves of the unblended LLDPE and wax are shown in Figure 3.11. Wax shows two significant peaks, with the first at 92 °C and the second at 70 °C. LLDPE shows one high intensity peak at 110 °C. It is clear that wax crystallizes at a lower temperature than LLDPE. The onset and peak temperatures of crystallization of uncross-linked blends slightly decrease as a function of wax content (Figure 3.12 and Table 3.22). The DSC curves of blends cross-linked in the presence of 1 % DBP show virtually no change in $T_{o,c}$ and $T_{p,c}$ with an increase in wax content (Figure 3.13 and Table 3.23). $T_{o,c}$ of blends cross-linked in the presence of 2 % DBP remains fairly constant as a function of wax content (Figure 3.14 and Table 3.23), while $T_{p,c}$ slightly increases. $T_{o,c}$ slightly decreases while $T_{p,c}$ slightly increases with an increase in wax content for blends cross-linked in the presence of 3 % DBP (Figure 3.15 and Table 3.23).

From Figures 3.12 - 3.15 it can be seen that the change in wax and DBP concentrations does not change the shape of the curves.

The crystallization enthalpy (ΔH_c) of uncross-linked blends significantly increases with an increase in wax content (Table 3.22). Although the crystallization enthalpy values of the cross-linked blends are somewhat scattered, a generally increasing trend with an increase in wax content is observed for all DBP concentrations (Table 3.23).

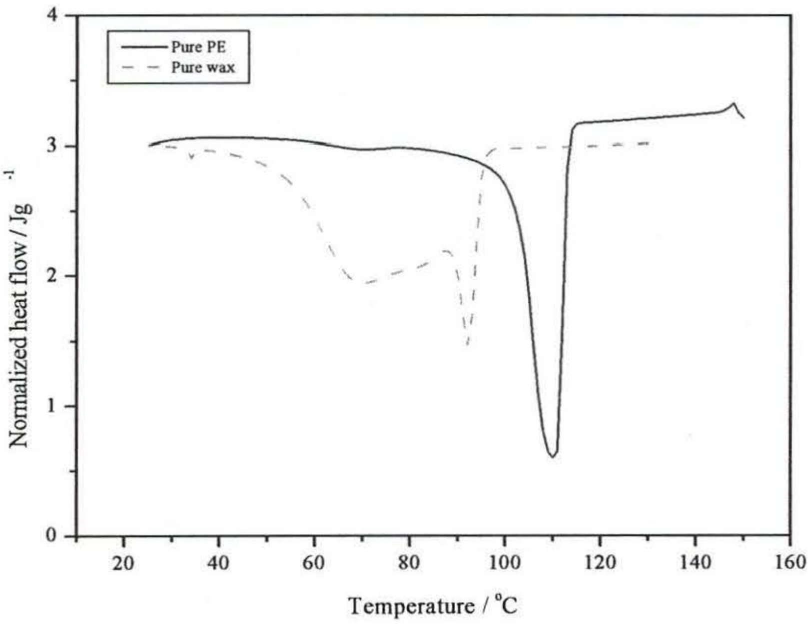

Figure 3.11 DSC cooling curves of unblended LLDPE and wax

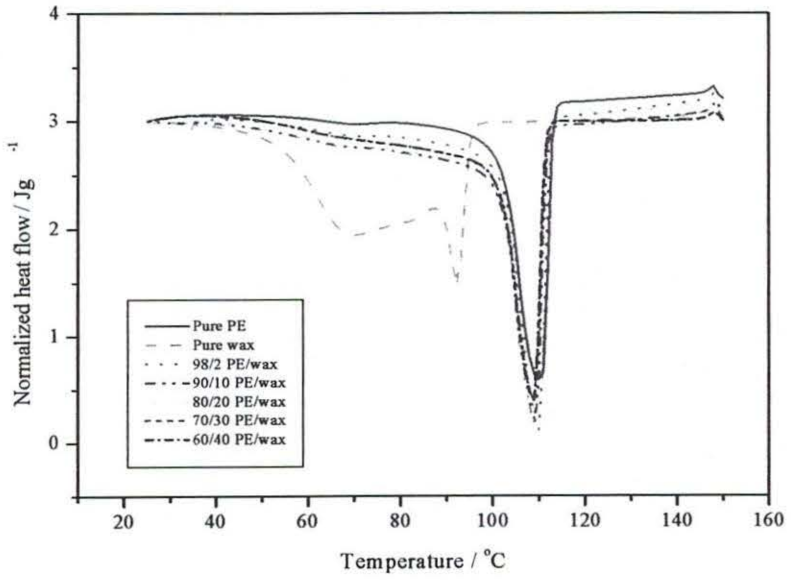

Figure 3.12 DSC cooling curves of uncross-linked LLDPE/wax blends

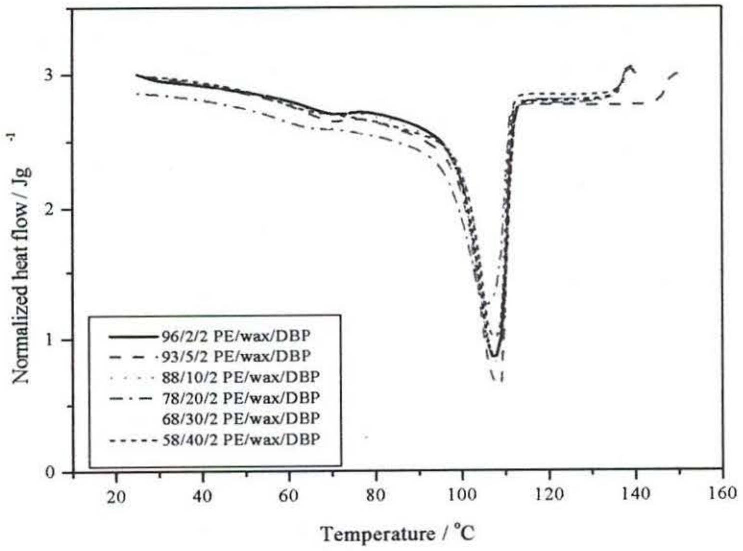

Figure 3.13 DSC cooling curves of LLDPE/wax blends cross-linked in the presence of 1 % DBP

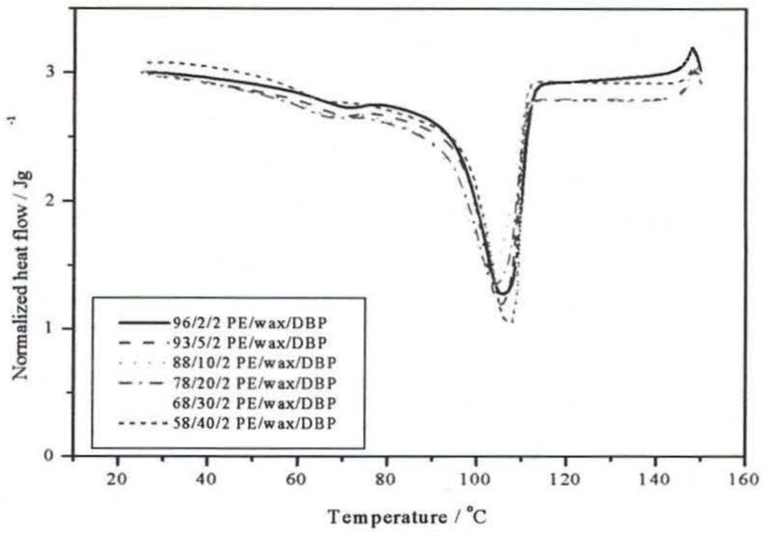

Figure 3.14 DSC cooling curves of LLDPE/wax blends cross-linked in the presence of 2 % DBP

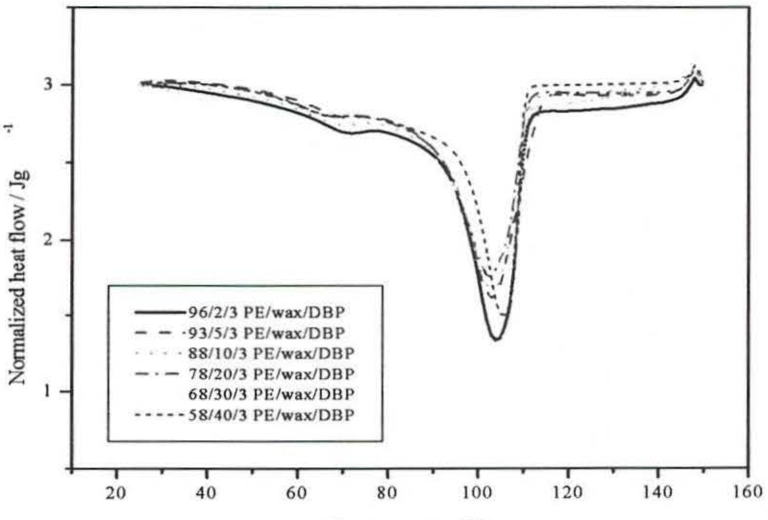

Figure 3.15 DSC cooling curves of LLDPE/wax blends cross-linked in the presence of 3 % DBP

The TGA curves and onset of decomposition temperatures for uncross-linked blends, analysed under nitrogen atmosphere, are shown in Figure 3.16 and Table 3.24, respectively. Unblended LLDPE starts to decompose at 458.1 °C and unblended wax at 332.1 °C. Decomposition temperatures for uncross-linked blends decrease with increasing wax content, but are still significantly higher than that of unblended wax.

Figures 3.17 – 3.19 show the TGA curves of blends cross-linked in the presence of 1, 2 and 3 % DBP respectively, analysed under nitrogen atmosphere. The onsets temperatures of decomposition of these blends are shown in Table 3.24. These temperatures generally decrease with an increase in wax content. It can be seen in Table 3.25 that the 5 and 10 % degradation temperatures of uncross-linked blends decrease with an increase in wax content.

Table 3.24 TGA onset temperatures of decomposition for uncross-linked and cross-linked LLDPE/wax blends

% Wax	0 % DBP	1 % DBP	2 % DBP	3 % DBP
2	458.5	459.5	451.3	451.3
5	459.7	457.7	456.2	456.2
10	453.6	467.9	456.2	463.3
20	430.0	463.3	453.6	446.5
30	439.3	467.8	429.9	444.2
40	434.5	465.5	437.1	441.6

Table 3.26 shows that in an inert atmosphere, 5 and 10 % degradation temperatures of blends cross-linked in the presence of different concentrations of DBP decrease with an increase in wax content. An increase in DBP content also results in a decrease in the 5 and 10 % degradation temperatures of blends.

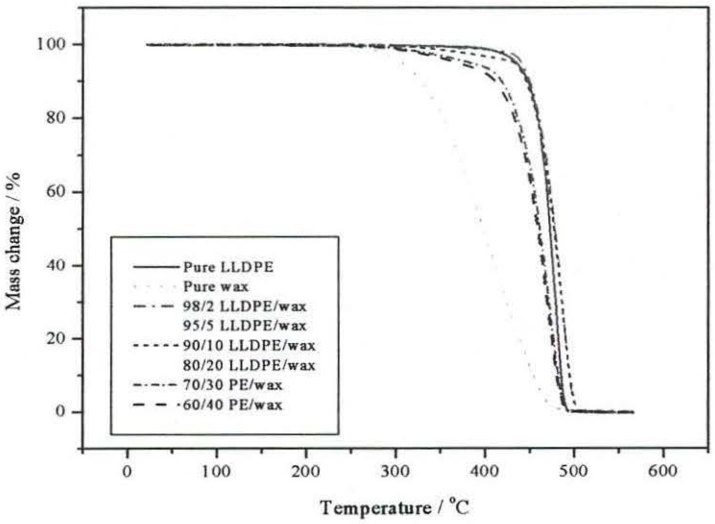

Figure 3.16 TGA curves of uncross-linked LLDPE/wax blends analysed under nitrogen atmosphere

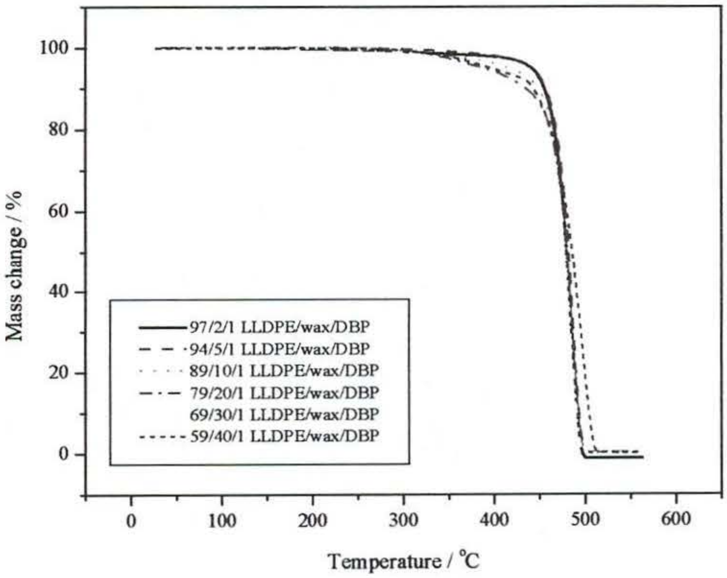

Figure 3.17 TGA curves of LLDPE/wax blends cross-linked in the presence of 1% DBP, analysed under nitrogen atmosphere

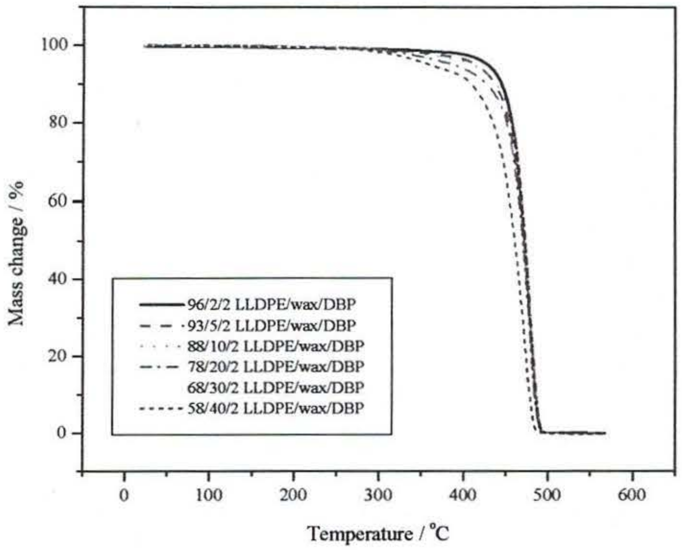

Figure 3.18 **TGA curves of LLDPE/wax blends cross-linked in the presence of 2% DBP, analysed under nitrogen atmosphere**

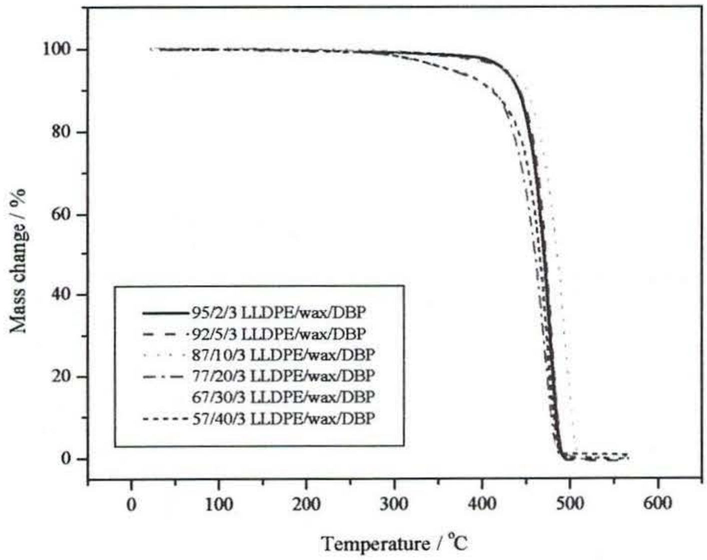

Figure 3.19 **TGA curves of LLDPE/wax blends cross-linked in the presence of 3% DBP, analysed under nitrogen atmosphere**

Table 3.25 Temperatures at 5 and 10 % decomposition of uncross-linked LLDPE/wax blends analysed under nitrogen and synthetic air atmospheres

Sample (PE/W/DBP)	$T_{5\%}$, nitrogen [°C]	$T_{10\%}$, nitrogen [°C]	$T_{5\%}$, synth. air [°C]	$T_{10\%}$, synth. air [°C]
100/0/0	435.2	448.4	345.7	370.2
98/2/0	440.7	450.4	367.9	405.7
95/5/0	431.1	444.2	333.2	362.8
90/10/0	431.7	445.7	338.6	435.2
80/20/0	397.6	419.5	333.7	427.2
70/30/0	380.7	417.9	319.1	348.9
60/40/0	367.8	410.5	311.1	356.5
0/100/0	305.9	326.9	256.4	270.3

Thermo-oxidative degradation of both uncross-linked and cross-linked LLDPE/wax blends was also determined. Figure 3.20 shows the thermo-oxidative degradation of uncross-linked blends. All the blends show a two-step decomposition process, with the first step at about 250 °C and the second at temperatures above 350 °C. There is a general decrease in temperatures at 5 and 10 % decomposition with increase in wax content (Table 3.25). The influence of the different concentrations of the cross-linking agent on the thermal oxidative stability of the blends is shown in Figures 3.21–3.23. Temperatures at 5 and 10 % decomposition generally decrease with increasing wax and DBP contents, respectively.

Table 3.26 Temperatures at 5 and 10 % decomposition of cross-linked LLDPE/wax blends analysed under nitrogen and synthetic air atmospheres

Sample (PE/W/DBP)	$T_{5\%}$, nitrogen [°C]	$T_{10\%}$, nitrogen [°C]	$T_{5\%}$, synth. air [°C]	$T_{10\%}$, synth. air [°C]
99/0/1	444.1	455.4	346.8	393.1
97/2/1	440.4	455.2	396.7	429.8
94/5/1	440.1	456.6	334.4	404.0
89/10/1	414.2	447.9	329.8	392.6
79/20/1	386.9	433.6	303.5	347.4
69/30/1	375.8	426.2	302.4	343.5
59/40/1	395.2	443.0	297.2	338.3
98/0/2	433.9	447.9	329.6	432.4
96/2/2	429.4	445.2	333.6	430.1
93/5/2	415.4	437.2	324.8	381.5
88/10/2	407.8	438.3	320.0	368.4
78/20/2	388.6	427.9	316.9	378.9
68/30/2	339.4	395.3	305.5	353.4
58/40/2	376.8	428.1	303.6	354.2
97/0/3	432.5	445.6	323.8	390.9
95/2/3	425.2	440.9	328.3	432.2
92/5/3	421.9	441.2	307.3	345.7
87/10/3	426.5	449.3	304.2	339.9
77/20/3	397.8	441.5	302.1	345.0
67/30/3	366.9	413.2	295.8	337.0
57/40/3	360.4	410.1	299.3	347.3

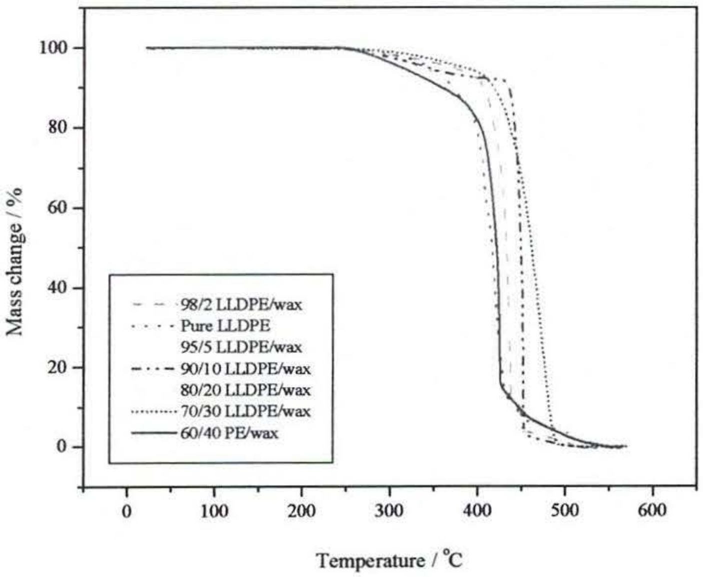

Figure 3.20 **TGA curves of uncross-linked LLDPE/wax blends analysed under synthetic air atmosphere**

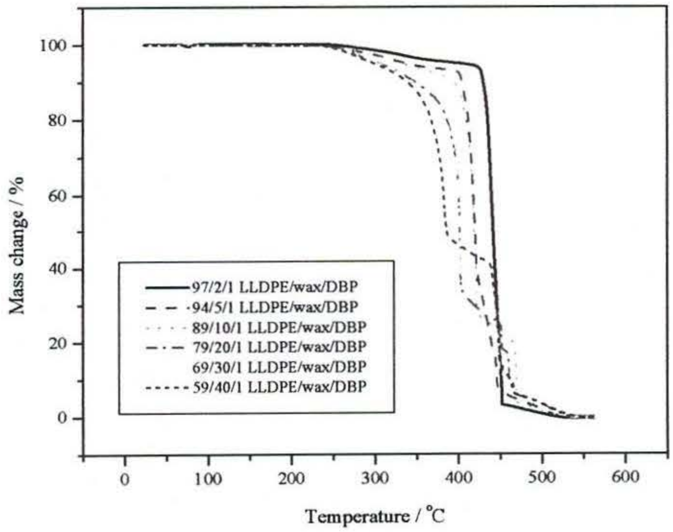

Figure 3.21 **TGA curves of LLDPE/wax blends cross-linked in the presence of 1% DBP, analysed under synthetic air atmosphere**

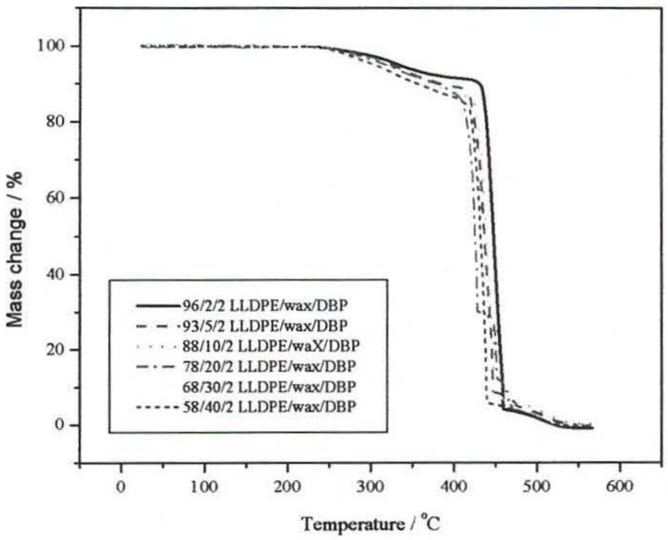

Figure 3.22 **TGA curves of LLDPE/wax blends cross-linked in the presence of 2% DBP, analysed under synthetic air atmosphere**

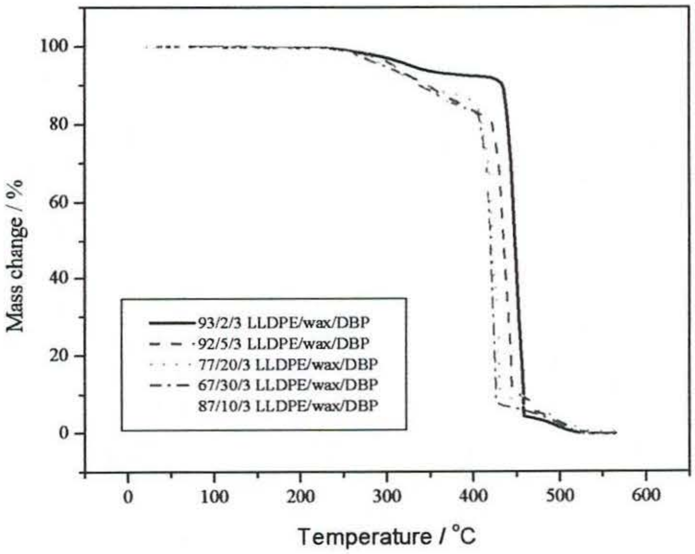

Figure 3.23 **TGA curves of LLDPE/wax blends cross-linked in the presence of 3% DBP, analysed under synthetic air atmosphere**

3.2.2 Mechanical properties

A summary of all the mechanical properties is shown in Table 3.27. The plot of the effect of wax content on the elongation at yield for both cross-linked and uncross-linked LLDPE/wax blends is shown in Figure 3.24. Uncross-linked blends show a general increase in elongation at yield with increase in wax content, while cross-linked blends show a decrease. The elongation at yield values of blends, cross-linked in the presence of 1 % DBP, seem higher at lower wax contents than those of blends cross-linked in the presence of 2 and 3 % DBP respectively. At the highest wax content the elongation at yield values are similar for the uncross-linked and different cross-linked blends (Table 3.27).

Figure 3.25 shows the effect of the cross-linking agent content on the elongation at yield of blends containing different wax contents. It can be seen that, although the results are scattered, the elongation at yield is higher for blends containing lower concentrations of wax. The elongation at yield also increases more with increasing DBP content at low wax contents.

The dependence of the yield stress on the wax concentration of LLDPE/wax blends is shown in Figure 3.26. An increase in the values of the yield stress with an increase in wax content for both cross-linked and uncross-linked blends is observed. Generally these values reach a maximum at a wax content of about 20 %. Figure 3.27 shows that the yield stress of LLDPE/wax blends is dependent on the amount of cross-linking agent and that it decreases with increasing DBP concentration.

Table 3.27 Mechanical properties of uncross-linked and cross-linked LLDPE/wax blends

Sample LLDPE/wax/DBP	$\varepsilon_y \pm s\varepsilon_y$ [%]	$\sigma_y \pm s\sigma_y$ [MPa]	$\varepsilon_b \pm s\varepsilon_b$ [%]	$\sigma_b \pm s\sigma_b$ [MPa]	$E \pm sE$ [%]
100/0/0	24.3 (4.5)	18.8 (1.4)	1355.5 (364)	20.4 (3.5)	118.5 (35.9)
95/5/0	14.5 (2.5)	19.2 (1.3)	849.4 (71.0)	20.3 (0.82)	232.0 (46.7)
90/10/0	20.7 (5.7)	21.5 (1.3)	1145.6 (358)	20.1 (2.8)	184.2 (5.7)
80/20/0	16.5 (3.1)	21.9 (0.85)	163.6 (69.7)	14.8 (1.9)	169.9 (51.9)
70/30/0	22.2 (7.3)	21.8 (0.34)	540.0 (67.7)	13.4 (0.52)	129.6 (34.2)
60/40/0	22.8 (3.6)	21.7 (1.5)	163.4 (68.0)	12.9 (0.55)	130.4 (25.2)
94/5/1	35.3 (3.8)	18.0 (0.65)	1380.7 (422)	26.7 (1.6)	103.5 (35.2)
89/10/1	25.7 (6.0)	18.9 (0.32)	1241.6 (347)	24.1 (4.1)	121.0 (12.2)
79/20/1	24.7 (5.9)	20.7 (0.55)	1204.4 (229)	22.6 (2.2)	154.8 (40.4)
69/30/1	26.2 (6.4)	20.4 (0.25)	767.1 (131.8)	16.5 (1.7)	124.1 (47.4)
59/40/1	21.4 (1.8)	21.7 (0.56)	596.5 (30.5)	14.1 (1.0)	122.9 (26.8)
93/5/2	28.2 (1.5)	17.6 (0.62)	769.6 (89.9)	21.4 (1.8)	127.3 (30.0)
88/10/2	23.5 (4.3)	18.3 (0.55)	764.1 (213.8)	21.8 (4.5)	125.3 (7.7)
78/20/2	23.5 (9.5)	18.3 (0.60)	1017.2 (556)	23.6 (2.9)	127.7 (52.9)
68/30/2	20.4 (7.6)	19.5 (0.60)	908.7 (152.8)	23.5 (2.1)	166.6 (58.6)
58/40/2	20.5 (2.5)	21.2 (0.90)	506.2 (202.1)	18.1 (16.0)	164.1 (87.2)
92/5/3	23.5 (2.4)	16.2 (1.3)	746.0 (169.9)	21.0 (2.1)	118.7 (18.4)
87/10/3	24.6 (5.4)	17.6 (0.60)	813.9 (245.6)	23.4 (2.5)	122.8 (17.2)
77/20/3	21.5 (5.8)	19.0 (1.1)	569.9 (280.4)	17.3 (3.1)	127.4 (39.5)
67/30/3	22.8 (6.2)	18.6 (0.70)	793.0 (305.2)	21.4 (3.9)	158.1 (27.1)
57/40/3	22.8 (10.2)	19.3 (0.40)	1025.1 (237)	22.4 (2.1)	167.1 (90.0)

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

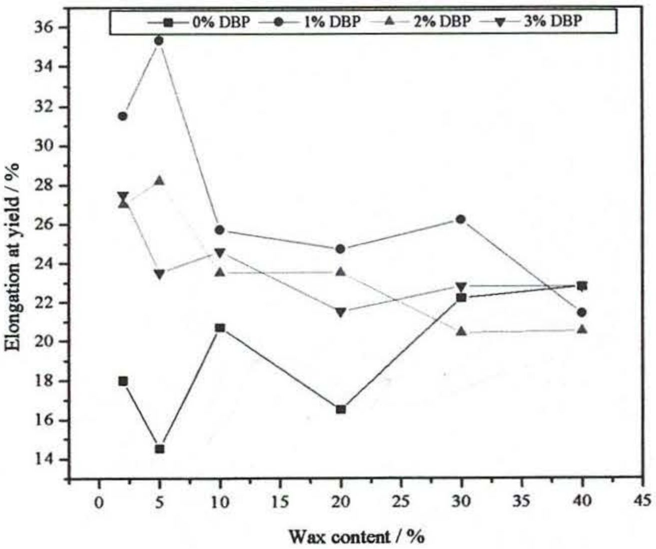

Figure 3.24 Effect of wax content on the elongation at yield of LLDPE/wax blends

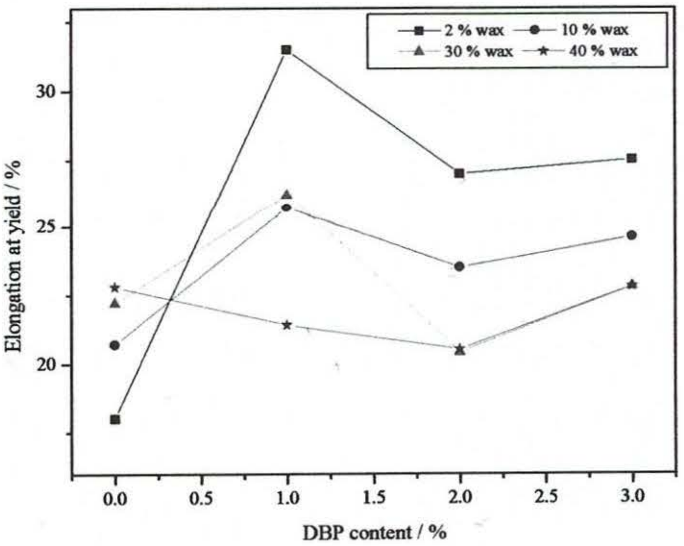

Figure 3.25 Effect of DBP content on the elongation at yield of LLDPE/wax blends

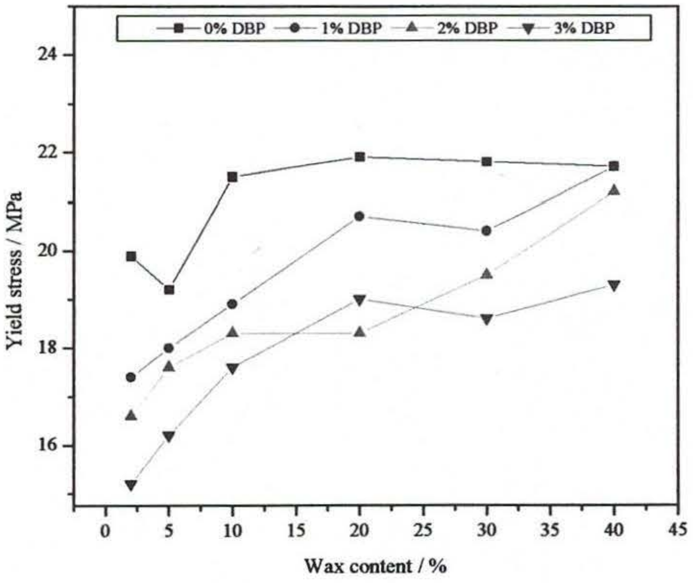

Figure 3.26 **Effect of wax content on the yield stress of LLDPE/wax blends**

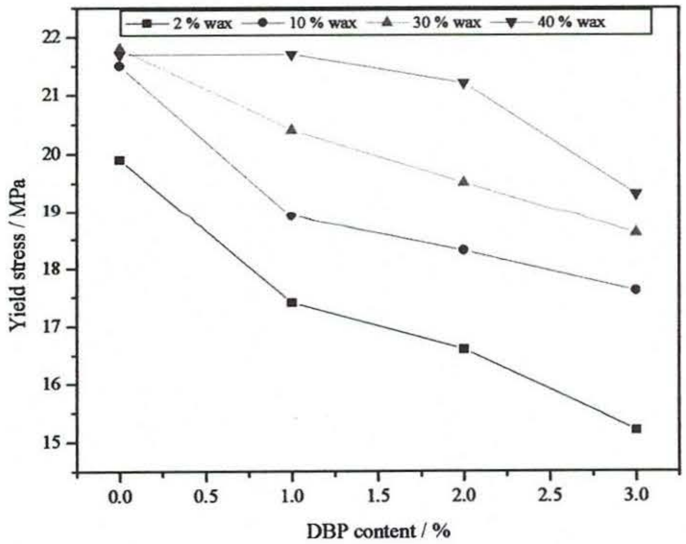

Figure 3.27 **Effect of DBP content on the yield stress of LLDPE/wax blends**

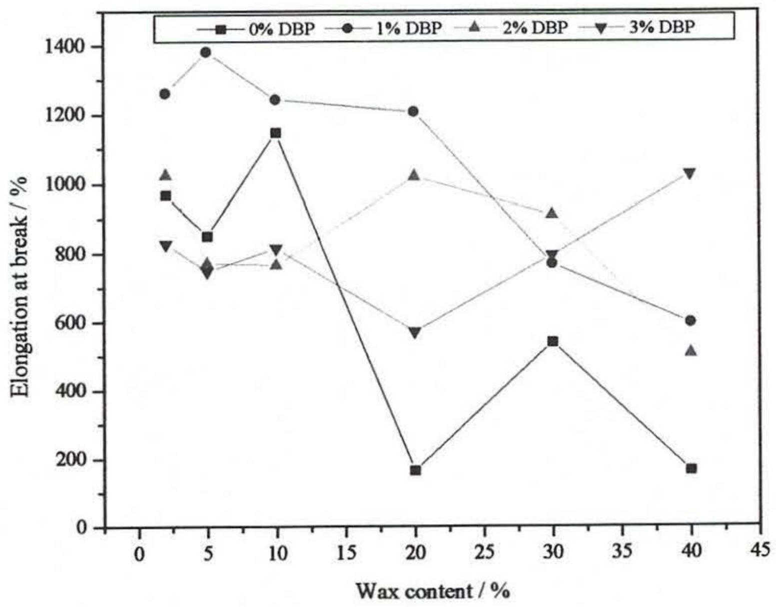

Figure 3.28 Effect of wax content on the elongation at break of LLDPE/wax blends

The influence of wax content on the elongation at break of both cross-linked and uncross-linked LLDPE/wax blends is shown in Figure 3.28. Although the results are scattered, a general decrease in elongation at break with increasing wax content is observed for uncross-linked blends and blends cross-linked in the presence of 1 and 2 % DBP contents. The effect of an increase in the cross-linking agent content on the elongation at break of LLDPE/wax blends is shown in Figure 3.29. Blends with low wax contents show an initial increase in the presence of 1 % DBP, but the elongation at break substantially decreases in the presence of higher DBP contents. Higher wax contents give rise to increasing elongation at break with increasing DBP content.

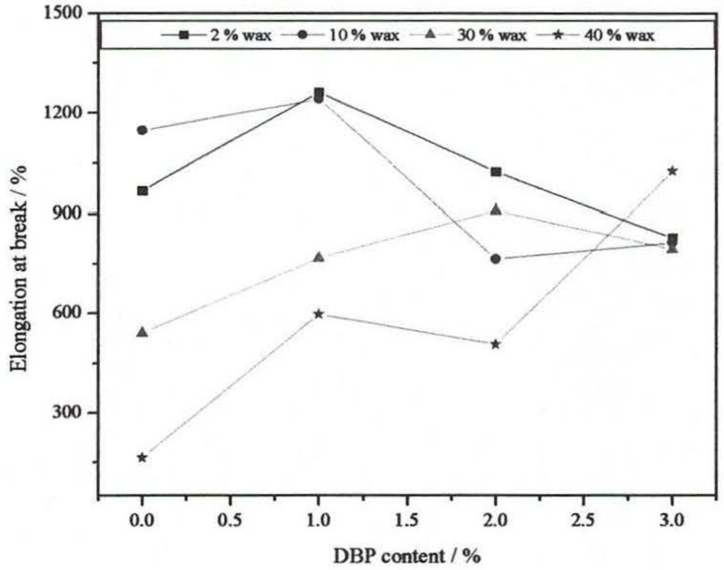

Figure 3.29 Effect of DBP content on the elongation at break of LLDPE/wax blends

The effect of wax content on the stress at break of blends is shown in Figure 3.30. The stress at break generally decreases with increasing wax content for uncross-linked blends and blends cross-linked in the presence of 1 % DBP. The stress at break values of blends cross-linked in the presence of 2 and 3 % DBP remain virtually constant with increasing wax content (see also Figure 3.31), except for 2 % DBP where there is a decrease in stress at break for wax contents above 30 %.

It can be seen in Figure 3.31 that the blends containing ≤ 10 % wax have high stress at break values, which slightly increases on cross-linking, but it does not seem as if DBP content has a major influence on these values. The stress at break of blends containing 30 % wax significantly increases with an increase in DBP content up to 3 % DBP, after which it stabilizes. For 40 % wax containing blends, the stress at break continuously increases with an increase in DBP content.

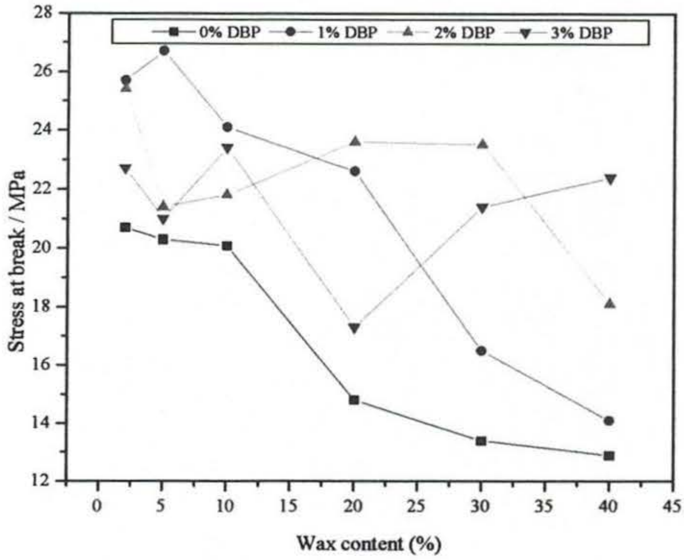

Figure 3.30 Effect of wax content on the stress at break of LLDPE/wax blends

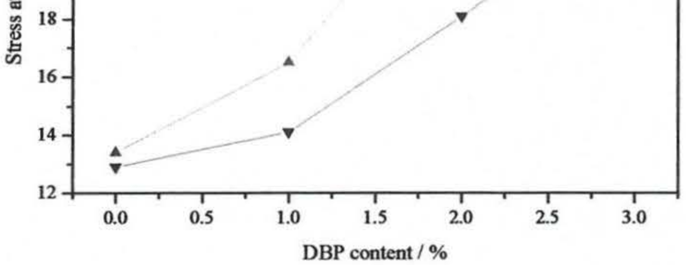

Figure 3.31 Effect of DBP content on the stress at break of LLDPE/wax blends

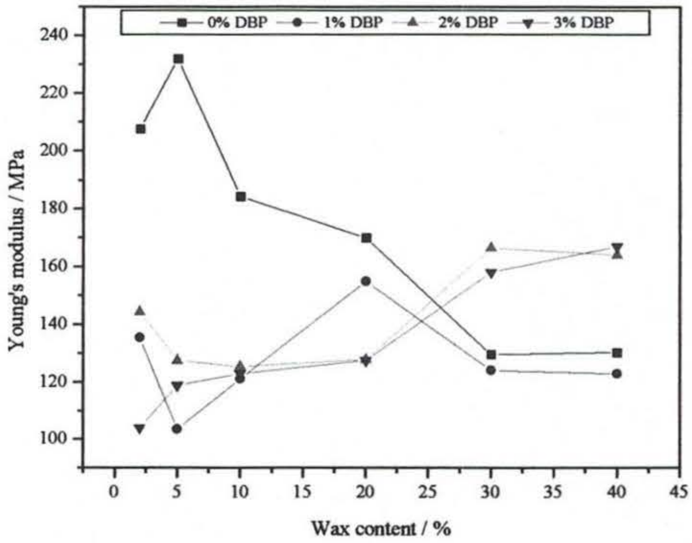

Figure 3.32 Effect of wax content on Young's modulus of LLDPE/wax blends

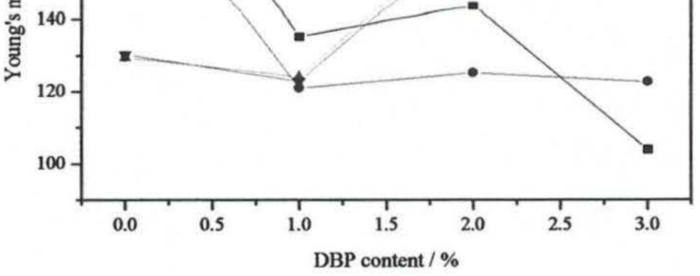

Figure 3.33 Effect of DBP content on Young's modulus of LLDPE/wax blends

The influence of wax content on Young's modulus of LLDPE/wax blends is shown in Figure 3.32. At low wax concentrations, the uncross-linked LLDPE/wax blends have high Young's modulus values, which decrease as wax concentration increases. However, cross-linked blends have lower Young's modulus values that slightly increase as the wax content in the blends increases, except for 1 % DBP where the values remain fairly constant. The influence of the cross-linking agent content on Young's modulus is shown in Figure 3.33. Blends containing lower concentrations of wax have high Young's modulus values, which initially decrease and then remain constant as the concentration of DBP increases. Young's modulus of blends containing higher wax content slightly increases as a function of DBP content.

3.2.3 Flow Properties

Table 3.28 Melt flow index values of uncross-linked LLDPE/wax blends

Wax content / %	FR / g min $^{-1}$	FR/FR$_{PE}$
0	3.5	1.0
2	3.7	1.06
10	5.1	1.46
20	7.1	2.03
40	19.3	5.51

FR = flow rates, FR/FR$_{PE}$ = flow rate of blends divided by the flow rate of unblended LLDPE

Table 3.28 shows the MFI values for the different uncross-linked blends, and these values are plotted in Figure 3.34. An exponential increase in flow rate with increasing wax content is observed. Using the log additive rule, Equation 3.2,

$$\log(FR_{blend}) = w_{wax}\log(FR_{wax}) + w_{PE}\log(FR_{PE}) \qquad \textbf{[3.2]}$$

and plotting log FR_{blends} as function of wax content, gives a linear graph (Figure 3.35). The linear regression coefficient has a value of 0.996 and extrapolation gives a flow rate value of 56.6 g/10 min. for unblended wax.

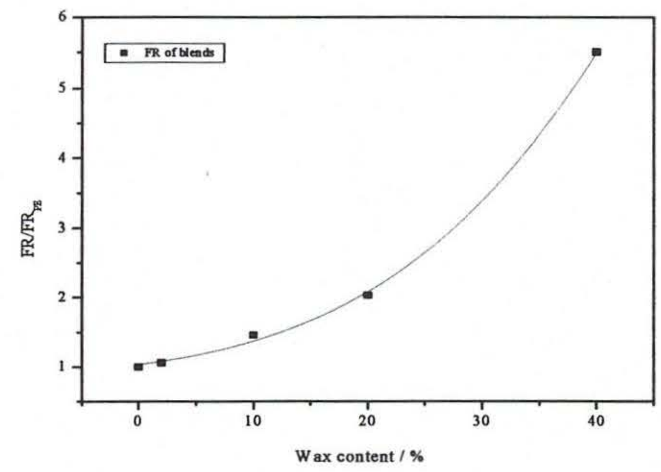

Figure 3.34 Melt flow index of uncross-linked LLDPE/wax blends as a function of wax content

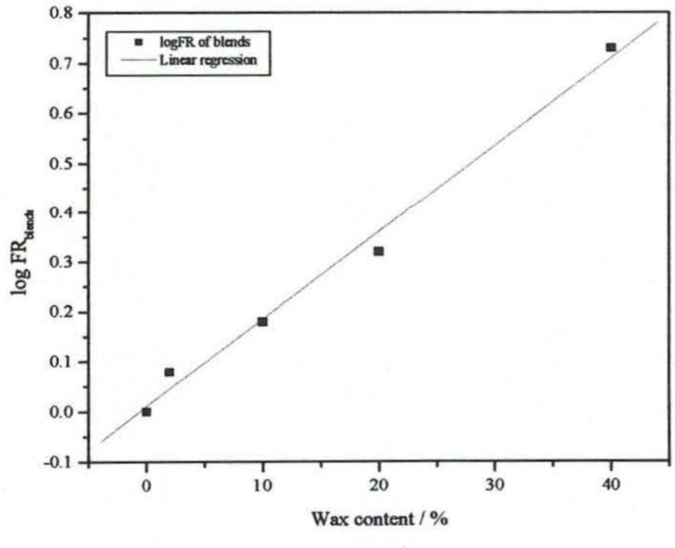

Figure 3.35 Logarithm of flow rates of LLDPE/wax blends as a function of wax content

CHAPTER 4

DISCUSSION AND CONCLUSIONS

4.1 Uncross-linked blends

The DSC heating curves of unblended LLDPE and wax in Figure 3.6 show a single endotherm for LLDPE, and a triple endotherm for wax. The triple endotherm for wax may indicate wax fractions melting at different temperatures. The existence of different wax fractions is clear from the GPC results (Section 3.1.3), which show more than one characteristic wax peak at different retention times. Despite the lower melting temperature of wax, the DSC heating curves of uncross-linked blends (Figure 3.7) show only one endothermic peak. This means that the chains of both LLDPE and wax crystallize together. This is also supported by the ΔH_m values that are in agreement with those calculated using the log additive rule (ΔH_m^{add}) (Table 3.22). However, it is not clear from these results how wax crystallizes with LLDPE. The single peak indicates that LLDPE and wax are probably miscible in the crystalline phase, and this conclusion is supported by the melt flow results (Figure 3.35) that show a linear dependence of logarithm of flow versus wax concentration in the uncross-linked blends. Utracki [18] showed that, if the melt viscosity of the blends behaves according to the log additive rule, the components are miscible with each other.

Table 3.21 shows that an increase in wax content leads to an increase in the crystallinity of the blends. This is the result of more linear and shorter wax chains, which can easily be incorporated into the LLDPE crystal structure. The DSC heating curves of uncross-linked blends show that the wax content slightly decreases the melting temperature (T_m) of the blends (Table 3.22). Decreasing of the blends' melting temperature shows that, despite increasing of the crystallinity as wax content increases, the average lamellar thickness decreases. The short wax chains somehow cause the blend to form thinner lamellae, although they favour a higher extent of crystallization. The DSC cooling curves (Figures 3.11-3.12) also show a single exotherm for uncross-linked LLDPE/wax blends. The results show that wax has no significant influence on the crystallization temperature of the blends (Table 3.22). This is probably because LLDPE and wax are miscible in the molten state and that, when these blends are cooled from the melt, they tend to organize themselves into regular crystalline structures.

The FTIR spectra (Figure 3.2) show a decrease in the intensity of the CH_3 vibration with an increase in wax content. This is probably the result of the lower number of CH_3 groups in wax compared to LLDPE. Contrary to wax, the molecules of which are more linear, LLDPE has a number of short side chains that terminate into CH_3. The increase of wax content obviously leads to a decreasing number of CH_3 groups in the blends. An increase in the number of CH_2 groups with increasing wax content was also observed, and is explained in the same way. CH groups also increase with increasing wax content, probably because wax has more of the unsaturated sites than LLDPE.

GPC results (Table 3.5) show a slight shift of the peak at 11.0 min, which is characteristic of LLDPE's longer molecules, to lower R_t values for uncross-linked blends. The shift is, however, too small to put any meaning to it. A decrease in % area of the peak at 11.0 min with increasing wax content is also observed (Table 3.9). This indicates a decrease in the number of molecules that have this specific molecular weight distribution. However, when calculating the % peak area with respect to LLDPE content in the blends, the value remains fairly constant. The decrease in % peak area is therefore the result of wax dilution of the LLDPE chains.

In the case of the wax characteristic peak at 16.0 min, the % peak area increases with an increase in wax content in the blends (Table 3.10). This means that the number of molecules with this molecular weight distribution increases. This is supported by the values calculated with respect to the weight content of wax in the blends, which slightly increase with increasing wax concentration (Table 3.18).

The % peak area at an R_t of about 21.0 min, which is characteristic of both LLDPE and wax, is also not significantly affected by an increase in wax content (Table 3.11). This means that the number of molecules belonging to this molecular weight distribution does not change. When the % peak area is calculated with respect to the weight content of LLDPE in the blends, the values show a generally decreasing trend with an increase in wax content (Table 3.15). The values of the % peak area calculated with respect to the wax content in the blends generally increase as a function of wax content (Table 3.19). This clearly indicates wax dilution of the LLDPE chains.

The % peak area of the characteristic peak for the LLDPE's shorter molecules at an R_t of 29.5 min increases with an increase in wax content (Table 3.12). This means that the number of molecules corresponding to this molecular weight distribution increases. When calculating the % peak area with respect to the weight content of LLDPE, the values increase as a function of wax content (Table 3.16). It is thus possible that the short chains of wax with this specific molecular weight distribution easily mix with those of LLDPE.

Hlangothi & Luyt [54] found that hard paraffin wax has a low thermal stability. The thermal stability of uncross-linked LLDPE/wax blends, analysed in an inert environment, decreases at higher wax concentrations (Table 3.25). This is probably because wax has shorter chains and is thermally less stable than LLDPE. Thermo-oxidative degradation of uncross-linked blends resulted in a two-step process (Figure 3.20). It can be seen that this two-step process becomes more significant at high wax contents. A possible explanation for this behaviour is that the shorter chains of wax decompose first in the presence of oxygen, followed by the decomposition of LLDPE. It is clear from Figures 3.19-3.21 that the % decomposition in the first step is directly related to the wax percentage in the blends. Krupa & Luyt also observed a two-step process [32]. They found that the higher wax content decreased the thermal stability of the blends even more in an oxidative environment. A reason for this observation may be that the higher quantities of oxygen in the system facilitate the decomposition process. Oxygen attacks the chain atoms and removes hydrogen atoms to form carbonyl groups. These highly reactive carbonyl groups can react with other molecules and thus result into rupture. The thermal stability of the blends analysed in nitrogen atmosphere is higher than those analysed in synthetic air atmosphere, which is to be expected, since oxidative degradation normally leads to decomposition at lower temperatures [34].

Crystals prevent material flow in the solid state, because crystallinity stabilizes the material. An increase in wax content for uncross-linked blends shows a slight increase in elongation at yield (Figure 3.24), despite the fact that wax has shorter chains. A possible explanation is that shorter wax chains affects the amorphous phase in such a manner that complete stretching of amorphous phase prior to macroscopic yield point is finished at higher elongations. An increase in yield stress as a function of wax content is observed (Figure 3.26). Since wax increases the crystallinity of the blends, there must be a good interaction between the crystalline and amorphous regions, which restrict the movement of lamellae. This implies that more force is needed to make the material flow.

Shorter chains in the materials also imply that (i) low elongation is required to stretch all molecules, and (ii) it is easier to draw the chains from the lamellae. In order to break the material, the majority of the tie-molecules should be taut, and the taut tie-molecules should be pulled out from the lamellae. Although the results are scattered, the ultimate properties of the blends deteriorate in the presence of wax (Figures 3.28-3.31), which supports the idea that the shorter chains of wax affect the properties of blends. The decreasing stress at break as a function of wax content may also indicate a decrease in the thickness of the lamellae with increasing wax content, because less force is required to pull out the taut tie-molecules from the lamellae.

Young's modulus also decreases with increasing wax content in the blends despite the increase in crystallinity (Figure 3.32 and Table 3.27). Since Young's modulus normally depends on crystallinity, it should increase with increasing crystallinity of the material, because crystals take more strain energy on themselves that increases Young's modulus of the material. The interaction between the crystalline and amorphous regions is probably responsible for this behaviour, because the strain energy must be transferred from the amorphous to the crystalline phase. In this investigation the change in the interaction between the LLDPE and the wax can affect the transfer of energy to the crystalline phase, and that this is responsible for the increase in modulus of the blends.

4.2 Cross-linked blends

The gel content results show that the extent of cross-linking of LLDPE/wax blends is dependent on the amount of wax in the blends, as well as on the peroxide content (Table 3.1). More gel was obtained at higher DBP concentrations and this implies more cross-linking. On the other hand, the extent of cross-linking decreases with increasing wax content in the blends. The reason for this is probably that mostly LLDPE cross-links, because wax does not cross-link at such low peroxide concentrations [40, 54]. The gel content, with respect to the amount of LLDPE, of the blends cross-linked at high DBP concentrations, exceeds 100 % for 30 % and more wax. This indicates that cross-links must have formed between the LLDPE and wax chains, increasing the 3-dimensional network gel. Krupa & Luyt observed similar behaviour, where dicumyl peroxide (DCP) was used as the cross-linking agent [25,32]. They found that the gel content relative to the LLDPE content exceeded 100 % for blends containing 20 % and more wax. In comparing the two peroxides, it seems as if DCP is more effective in forming cross-links between the LLDPE and wax chains.

Table 3.21 shows a decrease in the degree of crystallinity with increasing DBP content. This is possible since cross-linking is said to reduce the extent of crystallinity [34]. Krupa & Luyt also observed a decrease in the degree of crystallinity with an increase in DCP [25]. Although there is a decrease in the crystallinity of cross-linked blends, cross-linking does not affect the shape of the DSC curves of blends cross-linked in the presence of different concentrations of DBP (Figures 3.8-3.10). However, the melting temperature (T_m) of the blends decreases with increasing DBP concentration (Table 3.23). Samples cross-linked in the presence of DCP also showed a decrease in the T_m of the blends with increasing DCP concentration [32]. This means that cross-linking reduces the thickness of the lamellae. The DSC cooling curves (Figures 3.13-3.15) also show a single exotherm for blends cross-linked in the presence of different DBP concentrations. It seems as if cross-linking may have an influence on the values of T_c, but not so much on those of $T_{o,c}$. This may be the result of the cross-links in the melt that hinder the process of crystallization [7, 24].

The structure determination by FTIR showed an increase in the C-H out-of-plane bending or wagging vibrations of hydrogens attached to unsaturated carbons for cross-linked LLDPE/wax blends as a function of wax content (Figures 3.3–3.5). This implies that more unsaturated sites are formed in the blends. An increase in DBP content results in a decrease in the intensity of these vibrations. It is therefore possible that although cross-linking occurs in the blends, chain scission and degradation also occurs. It can be seen in Table 3.3 that an increase in DBP content results in a decrease in the intensity of the CH_2 vibrations. Since the vibration intensities are high for uncross-linked blends, and low for cross-linked blends, it is clear that cross-linking reduces the number of CH_2 groups. Although this is the case, it seems as if cross-linking still affects the most reactive sites because the intensity of CH_3 bending vibration significantly decreases as the concentration of the cross-linking agent increases (Figure 3.3-3.5). It is therefore clear that cross-linking probably takes place in the middle of the chains as well as at the chain or branch ends.

For cross-linked blends, C=O stretching vibrations are observed. The intensity of this vibration increases with increasing DBP content. This vibration does, however, not exist in the uncross-linked blends. This clearly shows that the origin of this vibration is due to the presence of DBP in the blends, and is probably caused by traces of un-decomposed DBP that might be trapped in the matrix of the blends. Another possibility is that, instead of forming cross-links, reactive sites combined with traces of oxygen trapped in the blend matrix.

GPC results (Table 3.5) of blends cross-linked in the presence of different concentrations of DBP show a slight shift of the peak at 11.0 min to lower retention times. This peak is characteristic of LLDPE's longer molecules. The shift is, however, too insignificant to attach any real meaning to it. Since the analyses were done on the sol part of the extracted blends, the obtained results of % area of the peaks are discussed in terms of the inverse trends. A general decrease in the % area of the peak at about 11.0 min with an increase in DBP content is observed (Table 3.9). This is supported by the results calculated with respect to the weight contents of respectively LLDPE and wax in the blends, which show a general decrease with increasing DBP content (Tables 3.13-3.17). The decrease is less pronounced for the % area values with respect to wax content. These results seem to indicate that the longer LLDPE chains preferably cross-link.

The % area of the peak at an R_t of about 16.0 min, which is characteristic of wax, decreases with increasing cross-linking agent content (Table 3.10). The reason must be that wax does not cross-link at lower DBP concentrations and that more wax was extracted with the solvent. This is supported by a general decrease in the % area of this peak, calculated with respect to the weight content of wax in the blends (Table 3.18).

With respect to the peak characteristic of both LLDPE and wax, at an R_t of about 21.0 min, the % peak area decreases with increasing DBP content (Table 3.11). The % peak areas, calculated with respect to LLDPE and wax respectively, also decrease with increasing DBP content (Tables 3.15 and 3.19). This indicates that both LLDPE and wax chains must have been cross-linked.

The peak at an R_t of about 29.5 min is characteristic of LLDPE's shorter chains. The % area of this peak increases as a function of DBP content (Table 3.12). The % peak areas, calculated with respect to LLDPE and wax contents respectively, increase with increasing DBP content (Tables 3.16 and 3.20). This could be due to shorter chains that did not cross-link, and/or degradation of larger molecules taking place along with cross-linking.

The TGA curves in Figure 3.17 show that the blend containing 1 % DBP seems to have higher thermal stability in an inert environment than the uncross-linked blend, whereas 2 and 3 % DBP content decrease the thermal stability of the blends (Table 3.26). This is probably due to chain scission and degradation, which accompanies cross-linking. It is also possible that DBP acts as an oxidizing agent that further facilitates the decomposition process.

Thermo-oxidative degradation and decomposition of cross-linked blends resulted in a two-step process (Figures 3.21-3.23). This means that somehow LLDPE and wax decompose separately. The % decomposition of the first step is also in line with the wax content in the blends. With an increase in cross-linking agent content, the thermal stability of the blends decreases, because during cross-linking chain transfer can easily occur, forming highly reactive C=O groups which may initiate degradation.

Cross-linking reduces the elongation at yield of the blends (Figure 3.25). A probable explanation is that cross-links prevent the flow of molecules. Krupa & Luyt observed that the elongation at yield of LLDPE/wax blends, cross-linked in the presence of DCP as cross-linking agent, increased with extent of cross-linking. The yield stress decreases with an increase in DBP content because the crystallinity decreases (Figure 3.27). This implies that less force is needed to make the material flow. Krupa & Luyt, however, observed an increase in yield stress with an increase in DCP content [55].

In the presence of cross-links, the elongation at break of LLDPE/wax blends decreases (Figure 3.29). C=O groups probably cause degradation of the amorphous phase, which results in a smaller number of tie-molecules that are easy to break. Previous studies also showed that an increase in cross-linking agent (DCP) content resulted in a decrease in the elongation at break [55].

Despite the decrease of lamellar thickness with increasing DBP content, the formation of a three-dimensional network increases the stress at break (Table 3.31). The network caused by cross-links will absorb part of the mechanical energy, which is necessary for pulling out the tie-molecules. As a result a higher force is needed to break the material. Krupa & Luyt found that cross-linking had a small influence on the stress at break for LLDPE/wax blends cross-linked in the presence of lower concentrations of DCP, but caused a decrease in stress at break in the presence of higher DCP content [55].

It can be seen in Figure 3.33 that Young's modulus of cross-linked blends containing lower wax concentrations slightly increases with increasing DBP content. On the other hand, blends containing higher concentrations of wax show an opposite trend. It should also be noticed that highly cross-linked blends have high Young's modulus values at higher wax concentrations (Figure 3.32). Introducing the cross-links into the amorphous region somehow changes the interaction between the phases that leads to an increase in Young's modulus.

4.3 Conclusions and suggestions for future research

LLDPE and wax crystallize together and are miscible in both the crystalline and molten states. Uncross-linked and cross-linked LLDPE/wax blends showed only one peak for both the DSC heating and cooling curves, despite the fact that wax has more that one peak. The miscibility was also confirmed by the linear dependence of logarithm of flow as a function of wax content in the uncross-linked blends.

Crystallinity of LLDPE/wax blends increases with increasing wax content and decreases with increasing DBP content. This is clear from an increase in ΔH_c and ΔH_m with increasing wax content, but a decrease with increasing DBP content. The reason is because wax chains are more linear and shorter, and can easily be incorporated into the LLDPE crystal structure. However, cross-links hinder the process of crystallization and decrease the thickness of lamellae.

Changes in wax and DBP concentrations affect the lamellae of the blends. This results in some interesting properties. The average lamellar thickness decreases when the concentrations of wax and DBP in the blends are increased, even though an increase in wax content increases the extent of crystallinity. This is due to wax having short chains, which cause the blend to form thinner lamellae, and cross-linking that reduces the crystallinity. The effect of the change in lamellar thickness is observed in changes of the ultimate properties of the blends, as discussed previously in this chapter

Shorter wax chains further improve the flow rate of the blends, whereas cross-links prevent the flow. The flow rate of uncross-linked LLDPE/wax blends is exponentially dependant upon the wax content. These factors result in an increase in elongation at yield and yield stress of the blends as a function of wax content, and a decrease in both these properties with extent of cross-linking.

The interaction between the LLDPE and wax phases changes when the concentrations of wax and DBP are varied. These changes affect the transfer of energy from the amorphous to the crystalline region. As a result, Young' modulus slightly decreases with increasing wax content, and increases with cross-linking. Yield stress of blends also increases as a function of wax content, due to good interaction between the crystalline and amorphous regions, which restricts the movement of lamellae.

An increase in wax content decreases the thermal stability of the blends because wax has shorter chains than LLDPE. An increase in DBP content causes a significant decrease in the thermal stability of the blends, because of chain scission that accompanies the cross-linking process.

At lower wax and DBP concentrations only LLDPE chains cross-link, as is clear from the gel content results. The presence of more wax and DBP causes wax chains to also cross-link with or graft onto LLDPE chains.

This study revealed interesting changes in the thermal and mechanical properties of cross-linked and uncross-linked LLDPE/wax blends. Most of these could be linked to morphological changes as a result of wax apparently being completely miscible with LLDPE in the crystalline state, both for cross-linked and uncross-linked blends. This project did, however, not include techniques used to establish the morphology of the blends in comparison to that of unblended LLDPE and wax. Future research on these blends may involve electron diffraction and electron microscopic analyses to establish the exact morphology of these blends.

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