

**INVESTIGATION OF PHASE CHANGE CONDUCTING MATERIALS
PREPARED FROM POLYETHYLENES, PARAFFIN WAXES
AND COPPER**

by

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DECLARATION

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

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DEDICATION

Ho bana ba thari e ntsho. Hlomelang ka thuto, hoba ntwana e ntse e loana. Ho mesuwe le mesuwetsana yohle e mphahlollotseng mahlo thutong, setsong le bononong, peo ya lona ha e a wela majweng. O na ke moputso wa lona bohle.

ABSTRACT

Phase change materials based on polyethylene (LDPE, LLDPE and HDPE) and copper (micro and nano) blended with soft paraffin wax were studied in this work. The purpose of this study was to form composites that can store energy as well as conduct heat. The influence of wax content, as well as copper content and copper particle size, on the morphology and thermal, mechanical and conductivity properties was investigated. The scanning electron microscopy results show that both the Cu micro- and nano-particles were well dispersed in the matrix. The nano-particles, did, however, also form agglomerates. The results also show that the Cu micro-particles have a greater affinity for the wax than for the polyethylenes, giving rise to preferable crystallization of the wax around the Cu particles. The differential scanning calorimetry results show that the Cu micro- and nano-particles influence the crystallization behaviour of the polyethylenes in different ways. The extent to which the copper particles influence the crystallization behaviour of the polyethylenes also depends on the respective morphologies of the different polyethylenes. All the polyethylene/wax blends are immiscible or only partially miscible at wax contents of 30, 40 and 50%. The presence of wax in the polyethylene/wax blends reduces the melting temperatures of all three polyethylenes, indicating the plasticizing effect of the molten wax in the polyethylene matrix. The thermogravimetric analysis results show observable influence of both the presence of copper and the sizes of the copper particles, as well as the presence and amount of wax, on the thermal stabilities of the blends and composites. The thermal conductivities of the composites show a non-linear increase with an increase in Cu particle content. The presence of wax slightly decreases these values, confirming the preferable crystallization of wax around the Cu particles. The thermal conductivities of the Cu nano-particle containing composites, at the same copper contents, are almost the same as those of the micro-particle containing composites. Young's moduli increased with an increase in copper content in both the polyethylene composites and the polyethylene/wax blend composites, except in the case of HDPE where a decrease was observed. The dynamic mechanical analysis storage moduli determined through dynamic mechanical analysis show the same trends as the Young's moduli. The tensile strengths show variable behaviour, but mostly these values decrease with increasing Cu and wax contents. The energy storage results show that the heat transport is faster in the case of the blend composites compared to the polyethylene/wax blends, and the heat transport in the polyethylene/wax blends is also faster than in the neat polyethylene

OPSOMMING

Faseveranderingsmateriale (PCMs), gebaseer op poliëtileen (LDPE, LLDPE en HDPE) en koper (mikro en nano) gemeng met sagte paraffienwas is in hierdie werk bestudeer. Die doel van hierdie studie was om komposiete te berei wat energie kan stoor en hitte kan gelei. Die invloed van washoeveelheid, sowel as die koperhoeveelheid en koper deeltjiegrootte, op die morfologie en termiese, meganiese en geleidingsvermoë eienskappe is ondersoek. Die skandeer elektronmikroskopie resultate wys dat beide die Cu mikro- en nanodeeltjies is goed versprei in die matriks. Die nanodeeltjies het egter ook agglomerate gevorm. Die resultate wys ook dat die Cu mikroneeltjies 'n groter affiniteit vir die was as vir die poliëtilene het, wat aanleiding gee tot verkieslike kristallasie van die was om die Cu deeltjies. Die differensieel skandeer kalorimetrie resultate wys dat die Cu mikro- en nanodeeltjies die kristallasiegedrag van die poliëtilene op verskillende maniere beïnvloed. Die mate waartoe die koperdeeltjies die kristallasiegedrag van poliëtilene beïnvloed hang ook af van die onderskeidelike morfologieë van die verskillende poliëtilene. Al die poliëtileen/wasmengsels is nie- of slegs gedeeltelik mengbaar by washoeveelhede van 30, 40 en 50%. Die teenwoordigheid van was in die poliëtileen/wasmengsels verlaag die smelttemperatuur van al drie poliëtilene, wat dui op 'n plastiserings effek van die gesmelte was in die poliëtileenmatriks. Die termograwimetrie resultate wys opvallende invloed van beide die teenwoordigheid van koper en die grootte van die koperdeeltjies, sowel as die teenwoordigheid van en hoeveelheid was, op die termiese stabiliteite van die mengsels en komposiete. Die termiese geleidingsvermoë van die komposiete wys 'n nie-liniêre toename met toenemende hoeveelhede Cu. Die teenwoordigheid van was verminder hierdie waardes effens, wat die verkieslike kristallasie van was om die Cu deeltjies bevestig. Die termiese geleidingsvermoë van die nanodeeltjie bevattende komposiete is byna dieselfde as dié van die mikroneeltjie bevattende komposiete. Young's moduli het toegeneem met toenemende koper inhoud in beide die poliëtileen komposiete en die poliëtileen/wasmengsel komposiete, behalwe in die geval van HDPE waar 'n afname opgemerk is. Die dinamiese meganiese analise stoormoduli wys dieselfde neigings as die Young's moduli. Die treksterktes wys veranderlike gedrag, maar meestal neem die waardes af met toenemende Cu en was inhoud. Die energie storingsresultate wys dat die hitte vervoer is vinniger in die geval van die mensel komposiete vergeleke met die poliëtileen/wasmengsel komposiete, en die hitte vervoer in die poliëtileen/wasmengsel komposiete is ook vinniger as in die suiwer poliëtileen.

LIST OF ABBREVIATIONS

3APTES	3-aminopropyl triethoxysilane
AEAPS	<i>N</i> -(2-aminoethyl)-3-aminopropyl-trimethoxysilane
Ag	Silver
Al	Aluminum
ASTM	American society for testing and materials
CENG	Compressed expanded natural graphite
CNT	Carbon nano-tube
CRYSTAF	Crystallization analysis fractionation
Cu	Copper
DBP	Dibenzoyl peroxide
DCP	Dicumyl peroxide
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimetry
EDS	Energy dispersive spectroscopy
EG	Expanded graphite
HB-PUPCM	Hyper-branched polyurethane
HDPE	High density polyethylene
LDPE	Low-density polyethylene
LLDPE	Linear low-density polyethylene
MFI	Melt flow index
MWCNT	Multi-walled carbon nano-tube
PA	Polyamide
PANI	Polyaniline
PCMs	Phase change materials
PE	Polyethylene
PEG	Polyethylene glycol
PP	Polypropylene
PPC	Polyethylene–paraffin compound
PPS	Poly (phenylene sulphide)
PS	Polystyrene
PU	Polyurethane

PVA/SBN	Polyvinyl alcohol/soybean nano-fibre
SBS	Styrene-butadiene-styrene
S-EG	Ultrasonicated-expanded graphite
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis
VGCF	Vapour-grown carbon fibres
Wax FT	Oxidized or un-oxidized Fischer-Tropsch paraffin wax
Wax S	Soft paraffin wax
Zn	Zinc

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CHAPTER 1

INTRODUCTION

1.4 Background

Recently material scientists have anticipated a prominent role for intelligent phase change materials (PCMs). The term phase change materials denotes substances with a high heat of fusion which, through melting and solidifying at certain temperatures, are capable of storing and gradually releasing large amounts of energy [1]. Latent heat thermal energy storage is one of the most efficient ways of thermal energy storage and is largely considered a feasible approach for renewable energy realization in solar thermal systems. Heat is stored mostly by means of the latent heat of phase change of the medium. The temperature of the medium remains largely constant during the phase transition. High latent heat is required to provide higher thermal storage per unit weight, while a high density is desirable to allow a smaller size for the storage container. A higher specific heat is preferred to provide for better sensible heat storage [2].

PCMs can be divided according to the character of the phase change into solid-solid, solid-liquid or liquid-gas PCMs. The most commonly used phase change materials are solid-liquid ones. Liquid-gas PCMs are not considered to be practical for use as thermal storage materials due to the large volumes or high pressures required to store the materials when in the gas phase. However, liquid-gas PCMs have a higher heat of transformation than solid-liquid PCMs. Initially, solid-liquid PCMs perform like conventional storage materials; their temperature rises as they absorb heat. Unlike conventional storage materials, however, when PCMs reach the phase-change temperature (melting point), they absorb large amounts of heat without a significant rise in temperature. When the ambient temperature around the molten material falls, the PCM solidifies, releasing its stored latent heat. As a result, activities in the development of PCMs mainly focus on solid-liquid transitions. Solid-liquid PCMs are often used for heat storage applications. Examples include water, salt hydrates, paraffins, certain hydrocarbons and metal alloys. Salt hydrate phase change materials used for thermal storage

in space heating and cooling applications have low material costs, but high packaging costs [3].

Among the solid-liquid PCMs, paraffins offer some significant advantages over other PCMs. They have mass based latent heats and varied phase change temperatures giving a flexibility to choose proper PCMs for different latent heat thermal energy storage applications. They do not show phase separation after repeated cycling across the solid-liquid transition. Vapor pressures of paraffins are very low. When paraffins are microencapsulated, the convection heat transfer caused by molten paraffin is negligible. Paraffins are produced in substantial quantities by the industry and are thus readily available and inexpensive [4].

Thermal energy storage is one of the most important applications of PCMs. They can be applied conveniently in many fields such as peak shift of electrical demands, solar energy utilization, waste heat recovery, intelligent air-conditioned buildings, and temperature-controlled greenhouses, electrical appliances with thermostatic regulators, energy-storage kitchen utensils, insulation clothing and season storage [5,6].

Blending paraffin waxes with polymers provides an opportunity to utilize phase change materials with a unique, controlled structure. A polymeric matrix keeps a phase change material in fixed shape, even after its melting, and suppresses leaching. Such materials are easily shaped and the polymeric phase provides its own specific properties [5]. A variety of polymer matrices, based on both thermoplastics and thermosetting resins, are available with a large range of chemical and mechanical properties [6].

Polymers can also be made conductive by adding conductive filler such as metallic powders [7,8]. Metal filled polymers are used in many fields of engineering and the interest of these composites arises from the fact that the electrical behaviour of such materials is close to that of metal fillers whereas the other physical properties typical of polymers are preserved [7]. In addition, these composites show improved thermal properties that are strongly dependent on the filler concentration, the ratio between the properties of the two components, and the size and the shape of the particles dispersed in the polymer matrix [8-10].

Blending an insulating polymer matrix with conductive fillers or metal particles exhibit several interesting features due to their resistivity variation with thermal, mechanical and

chemical treatments [11-14]. The key parameters determining the conductivity of polymer composites are their morphology and the structure of the conductive pathway within the composites. The problem with heating applications is the optimization of conductivity properties; heat dissipation is difficult in most polymers which results in poor thermal conductors.

It is often desirable to increase thermal conductivity with thermally conductive fillers [15]. High performance thermally conductive PCM's are designed by combining organic component (polymer and wax) and dispersed conductive fillers as several inorganic materials, graphite or metallic powders are frequently used as thermally conductive fillers [10,16,17,18].

However, due to experimental difficulties to precisely control several parameters such heat loss, temperature, thermal contact resistance; thermal conductivity value determination may depend on the methods used. The controlled heat flow [8], hot wire, [19] and periodical [20,21] and laser flash methods are the most frequently used methods for determination of thermal conductivity and/or thermal diffusivity.

The industrial applications of thermal conductivity are linked with requirements for levels of thermal conductance in circuit boards, heat exchangers, appliances and machinery [22], and a very important issue is the improvement of thermal conductivity of phase change materials [23]. Polymeric materials, including polymeric PCM are widely used in the electronics industry for packaging to protect device from environmental effects. This is associated with the need for heat dissipation and therefore thermally conductive packaging is necessary [24].

In recent years, much attention has been focused on studying polymer composites containing nanoparticles. The importance of using nanoparticles in composites is that they have special size-dependant specific properties, while the favorable properties of the polymer remain preserved in the composites [25, 26]. Incorporating particulate inorganic fillers into polymeric materials improves the mechanical, electrical, thermal and processing properties suitable to replace metals and other composite materials in many industries. Nano-sized fillers have capabilities to improve these properties even more on account of much larger interface areas and stronger interfacial interaction with the adjacent polymer phase [27,28]. A lot of research is focused on inorganic quantum dots or polymer nanocomposites for several applications like

photovoltaic devices [29], electroluminescent devices [30], white light sources [31] temperature probes [32], and optical fibers [33].

Traditional composite materials, like metal and ceramic composites, are widely used in industrial applications. They are used at high loading levels to increase modulus and to improve dimension stability, while significantly increasing weight and viscosity, and decreasing toughness, optical properties, and surface quality.

Generally their cost and performance ratio is high. In polymer nano-composite materials, nano-scale fillers can be very useful with proper treatment at loadings under 5% by weight. These materials can present an improvement in composite properties, thermal stability, dimensional stability and heat deflection temperature [34].

By gradually increasing the filler content in metal polymer composite, the most significant changes in the electrical properties occur in a certain, relatively narrow, critical region of filler content. At low filler content, the conducting fillers are dispersed within the polymeric matrix as isolated clusters. Beyond a critical concentration of conductive filler known as the percolation threshold, and filler clusters begin to connect with each other to form a filler network throughout the entire composite. This results in a several orders of magnitude increase in the conductivity properties of the composite. This transition from isolated cluster to connected network of conducting filler is known as a percolation transition [20,35,36].

1.5 Objectives

The overall objective of this study was to study phase change conducting polymer composites based on polyethylenes (PE) and copper powder (nano and micro particles respectively) blended with soft paraffin wax. In this study different polyethylenes (low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE) and high density polyethylene (HDPE)) were blended with soft paraffin wax. Different amounts of micro-and nano-sized copper particles were mixed into these blends. The copper powder was used as filler for the improvement of the thermal conductivities of the composites, and to control the rate of absorption and release of heat energy by the PCM. Soft paraffin wax was selected as the phase change material (PCM) due to its excellent thermal stability and ease of handling.

The reason for using both micro- and nanosized copper particles in this investigation is because it is known that nano-particles generally have a stronger effect on polymer properties at lower contents than the micro-particles. The specific objectives of this project were as follows:

- Preparation of polyethylene/wax phase change blends, containing different amounts of wax, in the absence and presence of different amounts of nano- and micro-sized copper. The wax was the phase change material and the copper was added to improve the thermal conductivities of the systems.
- Determination of the morphologies of the different samples using scanning electron microscopy (SEM).
- Determination of the melting and crystallization behaviour of the samples using differential scanning calorimetry (DSC).
- Determination of the influence of the presence of wax and copper on the tensile properties of the samples.
- Determination of the influence of the presence of wax and copper on the thermal stability of the samples using thermogravimetric analysis (TGA).
- Determination of the influence of the presence of wax and copper on the dynamic mechanical behaviour of the samples using dynamic mechanical analysis (DMA).
- Determination of the influence of copper (amount and particle size) on the thermal conductivity and heat absorption characteristics of the samples.
- Explaining of the observed properties in terms of the sample morphologies.

1.3 Outline of the thesis

This manuscript comprises of five chapters.

Chapter 1: Background and objectives

Chapter 2: Literature survey

Chapter 3: Experimental

Chapter 4: Results and discussion

Chapter 5: Conclusions

1.4 References

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CHAPTER 2

LITERATURE SURVEY

2.1 Introduction

In order to obtain a final product with the desired properties, polymers are often processed by adding various kinds of fillers [1], such as graphite [2], copper [3,4], and metallized organic/inorganic fillers [5]. These polymers are of interest in many fields of science and engineering [6,7]. The mixing of polymers with metal particles is one of the most widely used methods because the resulting compounds are malleable or ductile [8]. Processing methods include internal mixing, as well as extrusion and injection molding. Generally, the literature tends to focus on the thermal and electrical conductivities of graphite or metal containing polymers. However, studies of the mechanical properties of such composites are conspicuously lacking [9,10].

The importance of thermal conductivity studies of polymer composites is associated with the need for improved thermal conductance in many applications, such as circuit boards, heat exchangers, appliances and other machinery [11]. Self-regulated heating ability can be obtained for conductive polymer composites that have sharp positive temperature coefficient effects. The characterization of electrical and thermal conductivity as a function of temperature is therefore instructive in heating device design. The factors influencing conducting polymer composites have been studied in previous works [12,13]. The morphology and structure of conductive pathways within the composites have been established as the key influential factors governing conductivity of metal filled polymers. For heating applications, heat dissipation that is generally poor, must also be considered. Hence, it is often desirable to increase the thermal conductivity by using thermally conductive fillers.

Significant enhancement of thermal conductivity of metal filled polymers has been reported in the literature. For example, the introduction of 7% w/w of carbon black particles into an epoxy matrix was reported to increase the thermal conductivity to $1 \text{ W m}^{-1} \text{ K}^{-1}$ [14], while an increase to $0.7 \text{ W m}^{-1} \text{ K}^{-1}$ was reported for polyethylene with copper powder [9]. The most commonly used metal fillers in polymers are silver, copper, nickel and aluminum. Silver has a high electrical conductivity, even as an oxide. Copper and aluminum are also conductive, but their oxides are insulators. This limits the use of copper and aluminum as electro-conductive fillers [15-17].

The preparation of polymer composites by the dispersion of small loadings of nano-sized fillers in a polymer matrix has recently attracted much attention in research and industry for its potential to improve the performance of macro-molecular materials [18]. Nano-particles provide the polymer matrix with improved physical properties, unlike traditional micron-sized fillers, due to a significant increase in polymer to filler interfacial regions [19,20]. This greatly reduces the required filler content in the composites, making them lighter in weight and easier to be processed. Nano-composites also lead to a lower thermal coefficient of expansion and gas permeability, higher swelling resistance and enhanced ionic conductivity compared to the pristine polymers, presumably due to the nano-scale structure of the hybrids and the synergism between the polymer and the silicate [21,22].

A lot of work has been done by our group to investigate the thermal and mechanical properties of polyethylene/wax blends [23-37]. Unfortunately there is not much available information from other authors concerning the mutual miscibility or compatibility of polyethylenes and paraffin wax, despite the fact that it has a crucial influence on the morphology of the blends and also on all the final properties. Apart from the work cited above, not much is known about the static or dynamic mechanical properties of such materials.

Phase change materials (PCMs) received much attention in energy storage materials research, in thermal protection systems, and in actively and passively cooled electronic devices [36]. Different inorganic and organic substances were used in the past as phase change materials; paraffin waxes belong to the most prospective ones. Latent heat thermal energy storage is one of the most promising ways of storing energy in renewable form as an alternative to solar-photo-thermal systems. Heat is stored mostly by means of the latent heat of phase change of

the medium. The temperature of the medium remains more or less constant during the phase transition [38]. One of the most attractive properties of PCMs is a stable latent heat without degeneration. In order to measure the degree of latent heat degeneration, the phase change process must be assessed repeatedly [39].

Paraffin waxes have desirable properties as PCMs, but they have a low thermal conductivity ($0.24 \text{ W m}^{-1} \text{ K}^{-1}$). This reduces the rate of heat storage and extraction during melting and solidification cycles, and therefore the overall power of the phase change material decreases. It is important that the storage unit can be charged and discharged very fast with thermal energy, and therefore materials that provide good thermal conductivity are attractive for encapsulated PCMs. In order to improve the thermal conductivity of an alkane-based PCM, its container must be designed with an adequate surface-to-volume ratio and the container material must have a suitable heat transfer coefficient [40].

2.2 Preparation and morphologies

2.2.1 Polymer/wax blends

In previous research it was found that the morphologies of blends and composites depend on the processing conditions and this has an influence on the final properties [41]. In this section a summary the processing methods used in previous research, and the influence of the different processing methods on the respective morphologies of the blends and composites will be given.

Luyt and co-workers published several papers [26,27,29,31,35] where they discussed the thermal and mechanical properties of uncrosslinked and crosslinked polyolefin/wax blends. In all these papers they had prepared the blends by initially mixing the polyolefin and wax powders in a coffee mill, followed by melt pressing of the powder mixtures into 1 mm thick sheets. They generally used wax contents of 10, 20, 30 and 40%. For their studies on crosslinked blends they had also included dicumyl peroxide (DCP) in their powder mixtures. In this summary of their work, their results on crosslinked polyolefin/wax blends is excluded since crosslinking did not form part of the scope of current study.

In their investigation of LDPE/wax blends they used LDPE with a melting point of 111-115 °C, density of 0.91-0.94 g cm⁻³, MFI of 20 g/10 min and a hard, brittle straight hydrocarbon-chain paraffin wax with a melting point of 90 °C, carbon distribution of C28 – C120, density of 0.94 g cm⁻³, and average molar mass of 0.785 kg mol⁻¹ [26]. When 10% of wax was used in the blends, the blends were miscible, but from 20% and especially for 30 and 40% of wax, LDPE and wax were not miscible. They also investigated LLDPE/wax blends, where they used LLDPE with an MFI of 3.5 g/10 min and a density of 0.938 g cm⁻³. These blends were found to be miscible up to wax contents of 40% [27,29,31]. Miscibility of the blends was also observed when the same polymer was blended with an oxidized paraffin wax at wax contents of 10, 30 and 50% [35].

They also prepared the same blends using an industrial extruder [24,28,33,40]. LLDPE blended with a hard Fischer-Tropsch paraffin wax was prepared in a Bandera film blower at 100 rpm at 180 °C and then pressed for 3 min at the same temperature [24]. When prepared in this way, the LLDPE/wax blends showed complete miscibility only for samples containing up to 10% wax, while partial miscibility or complete immiscibility were observed for higher wax contents. In the case of an oxidized Fischer-Tropsch paraffin wax [35] blended with LDPE [26], partial miscibility or immiscibility were also observed at wax contents higher than 10% [28]. From this it is clear that the sample preparation method to a large extent determines the PE/wax blend morphology.

Krupa and Luyt [41] used the same wax, previously blended with LDPE and LLDPE [24,27,29,31], in an investigation of the thermal properties of polypropylene/wax blends. In this study, isotactic PP with an MFI of 12 g/10 min and a density of 0.9 g cm⁻³ was used. The blends were prepared through melt extrusion. In this case miscibility was only observed for the 5% wax containing blend, while partial miscibility or immiscibility were observed for the blends containing more than 5% wax.

The morphology of polyethylenes blended with two types of Fischer-Tropsch paraffin wax was investigated by of Luyt and Hato using thermal fractionation experiments [34]. They investigated the influence of un-oxidized and oxidized Fischer-Tropsch paraffin waxes on the properties of their blends with LDPE, LLDPE and HDPE. They used the same hard paraffin wax referred to in the previous paragraphs, while the oxidized paraffin wax had a molecular weight of 669 g mol⁻¹, and a density of 0.95 g cm⁻³. The blends were melt-mixed in a

Brabender Plastograph, followed by compression molding into 1 mm thick sheets. Blending HDPE with both waxes gave rise to completely miscible blends for 10 and 20% wax contents, while it gave rise to a partially miscible blend for 30% wax content. This suggests that at high wax contents there is not enough space for the wax to co-crystallize with the HDPE, and therefore the wax crystallized separately. These results are in line with the work done by Krump *et al.* [30]. In the case of LLDPE blended with the oxidized hard paraffin wax, complete miscibility was observed at all compositions investigated. The same behaviour was observed for most LLDPE/wax blends [27,29,31,35] prepared in different ways. LDPE blended with hard paraffin wax gave rise to partially miscible blends for all the wax contents, while complete miscibility was observed for the 10% wax-containing blend when oxidized hard paraffin wax was used. This is in line with observations in another study by the same group [26].

In an effort to obtain more concrete evidence of possible co-crystallization, crystallization fractionation (CRYSTAF) analysis was performed on different polyethylenes blended with a hard, brittle, oxidized straight-hydrocarbon chain paraffin wax [33]. These blends were prepared through melt extrusion. The same LLDPE used in previous investigations [27,29,31], LDPE with MFI of 1.7 g/10 min, a density of 0.916 g cm⁻³ and HDPE with an MFI of 8 g/10 min, and a density of 0.963 g cm⁻³ were used. When 30 and 50% of wax was used in the LDPE/wax blends, the LDPE and wax crystallized separately, while co-crystallization was observed for the LLDPE/wax blends. The co-crystallization observed for the LLDPE/wax blends, even for samples with high wax contents, is in line with observations discussed in other papers [35,36]. Since no CRYSTAF results were reported for LLDPE blended with unoxidised wax, there is no confirmation yet of co-crystallization in these blends. In the case of LDPE/wax blends, these results are in complete agreement with other work done on the same systems [28], but results on HDPE/wax blends have not been reported before.

Mpanza and Luyt studied LDPE blended with three different Fischer-Tropsch paraffin waxes at low wax contents [23]. Apart from the hard paraffin wax (H1 wax) used in a previous study [34], they also looked at a soft paraffin wax (M3 wax) normally used for candle-making, with a melting point of about 58 °C and a high melting point fraction (EnHance) of the hard paraffin wax (melting point 117 °C). The main purpose of the study was to investigate the use of the different waxes as processing agents for LDPE. They found LDPE and EnHance wax to

be miscible up to 10% wax content, but LDPE and the other two waxes were miscible only at much lower wax contents.

2.2.2 Phase change materials

Phase change materials (PCMs) are prepared by several different methods such as melt-mixing [37,42,43,45], a polymerization-filling technique and a two-roll mill mixing [43]. Phase change materials based on PP and LDPE blended with respectively a soft paraffin wax and a hard, oxidized paraffin wax were studied by Krupa *et al.* [42,43]. Isotactic PP [41], LDPE [33], a hard, brittle, oxidized straight-hydrocarbon chain paraffin wax and a soft paraffin wax with a carbon number of C18-C40, an average molar mass of 374 g mol^{-1} , and a density of 0.919 g cm^{-3} were used in these studies. All the blends were prepared in a Brabender Plasticorder at 190°C , followed by compression molding at the same temperature. They were prepared in polymer/wax ratios of between 10 and 60 weight %. When PP was blended with 10% of soft paraffin wax, the blends were partially miscible, while they were immiscible at higher wax contents. In the case of PP/oxidized hard paraffin wax blends, immiscibility was observed from 40% of wax, with partial miscibility at lower wax contents. Immiscibility of LDPE/wax blends was also observed for both waxes at higher wax contents.

A phase-change composite based on exfoliated graphite, ethylene glycol (EG) and polystyrene was prepared by a polymerization-filling technique. Xiao *et al.* [44] used this method and a two-roll mill to prepare the exfoliated graphite/polystyrene composites. The expanded graphite, with an average particle size of $300 \mu\text{m}$ and prepared with H_2SO_4 as an intercalant and HNO_3 as an oxidant, were dried to remove any moisture before heat treatment. Heat treatment was performed for 30 s in a furnace at 800°C in an air atmosphere. Expansion and exfoliation occurred during the heat treatment. Purified styrene was mixed with the expanded graphite, and polymerized using benzoyl peroxide as initiator. The mixture was continuously stirred under nitrogen while the temperature was increased from ambient to 85°C to 150°C . The floating system was then centrifuged and the solids were dried at 60°C under vacuum. EG-filled polystyrene composites were prepared by blending EG and polystyrene at 170°C on

a two-roll mill. For the radical polymerization of styrene, the molecular weight and molecular weight distribution of polystyrene synthesized in the presence of 2.8, 5.6 and 11.1% of EG, showed that the molecular weight increased and the molecular weight distribution broadened. In the polymerization-filled composites, the EG layers were interconnected to form conductive nets, with the polystyrene chains in the interspaces of the nets.

The same expanded graphite [44] was used to prepare paraffin/expanded graphite PCM composites [47]. A paraffin (*n*-docosane) with a melting temperature of 42-44 °C and a density of 0.785 g cm⁻³ was used. The composite PCMs were prepared by mixing 2%, 4%, 7% and 10% of EG into the molten paraffin. The composites containing up to 10% EG were found to be form-stable and no leakage of molten paraffin was observed during the solid-liquid phase change, and the paraffin was distributed uniformly in EG due to its structural compatibility. The surface area of the expanded graphite had a wide pore size distribution, which mainly consisted of mesopores and macropores. The expanded graphite had a worm-like structure, and absorbed paraffin was uniformly distributed in the paraffin/EG composite PCMs.

A two-roll mixer [44] was also used to investigate the thermal performance of a highly conductive, shape-stabilized thermal storage material [44]. The shape-stabilized PCM was prepared by mixing a technical grade paraffin, with a melting point range of 56-58 °C, with a styrene-butadiene-styrene (SBS) triblock copolymer on a two-roll mixer at a temperature of 100 °C. Three parts by weight of exfoliated graphite were added to 100 parts by weight of a 80/20 w/w paraffin/SBS composite. The same technical grade paraffin (P1) was used, together with a technical grade paraffin (P2) with a melting point ranging from 42-44 °C, as a PCM in HDPE with a density of 0.942 g cm⁻³ [45]. The form-stable HDPE/P1 and HDPE/P2 composite PCMs were prepared by melt-mixing the paraffin with the HDPE. The composite ratios were 50, 60, 70, 75 and 77 wt. %. The results showed that both composite PCMs were immiscible at contents above 50 wt. % paraffin. The paraffins were dispersed into a network of solid HDPE, and both the composite PCMs seemed to have similar rough textures.

HDPE and paraffin were also used to prepare a polyethylene-paraffin compound (PPC) as a form-stable solid-liquid phase change material [38]. The form-stable PPC consisted of the paraffin as the dispersed PCM in HDPE as the supporting material. The same procedure as discussed in the previous paragraph was used to prepare the PCM blends. When the

temperature was between the melting point of the HDPE and that of the paraffin, the HDPE solidified while the paraffin was still a liquid in the three-dimensional netted structure of the solidified HDPE. Since HDPE has a high crystallinity, the form-stable PPC showed appropriated strength, even when the paraffin was liquid. A number of HDPEs with different melt indices and densities were comparatively used as supporting materials in the form-stable PPCs. They were blended in different ratios with refined and semi-refined paraffins with different melting points. SEM images showed that these PPCs all had similar rough textures.

Xing *et al.* [49] prepared form-stable paraffin phase change materials composed of paraffin and HDPE. They first prepared a silica gel polymer by an *in situ* polymerization method, and then microencapsulated the form-stable paraffin PCMs with silica gel as coating material. The main purposed of this investigation was to solve the problem of leakage, frosting and fast thermal properties deterioration. They managed to effectively prevent the leakage of paraffin and thus to keep the paraffin content higher, to turn the lipophilicity of the form-stable PCMs completely into good hydrophilicity, and to improve the flame-retardant properties of the PCMs.

2.2.3 Thermally conductive polymer composites

Conducting polymer composites, especially polyethylenes filled with graphite and polyamide particles coated with silver, were studied by Krupa *et al.* [10,49,52,54]. In their study of polymer/graphite composites [10,52], they used LDPE and HDPE [34], as well as polystyrene (PS) as supporting materials and two types of graphite as fillers. All the composites were prepared in a Brabender mixer at 170 °C, followed by compression molding of the mixtures. They only used a graphite content of 60 wt. %, and this value was chosen because graphite has an influence on the degree of crystallinity of polyethylene, and in semi-crystalline polymers the portion of the crystalline phase has an important influence on almost all the physical (especially mechanical) properties of the polymers. It was observed that both fillers had little influence on the degree of crystallinity of the polymers in the composites. The SEM images showed that the graphite particles of both types were irregularly shaped and contained many sharp edges, and that this had an influence on the mechanical properties of the composites. Moreover, the graphite particles were not uniformly distributed in the HDPE matrix.

The same group investigated silver containing composites based on polyethylene mixed with silver coated polyamide (PA6) [50,54]. They used high density polyethylene (HDPE) with a melting temperature of 129 °C and a melting enthalpy of 199 J g⁻¹ as the matrix. The metallization of PA6 particles was carried out using an electro-less metallization method, prepared in two solutions. Their fillers were in volume fractions of 0.023, 0.051, 0.084, 0.125, 0.173, 0.244 and 0.334 of silver. SEM images showed that, when a filler volume fraction of 0.023 was used in the composites, the conductive network was not yet developed, but when the filler content was increased to a volume fraction of 0.173, the conductive network was fully developed. They further observed that not all the PA particles were well covered by a silver shell, and that the thickness of the silver shell was lower than 1 µm. They also investigated polyurethane-based adhesives with silver-coated basalt particles [53]. The particle diameter was less than 15 µm, and the metallic layer had a thickness of 1 µm. The formation of an internal network of irregularly shaped silver-coated basalt particles within the matrix was observed. They compared these composites with composites prepared by using graphite instead of silver-coated basalt particles. Apart from also being irregularly shaped, the graphite particles displayed a significant anisotropy.

Metal filled polymers were prepared by mixing a polymer and copper powder particles in a Brabender mixer [3], a Rheomix mixer [51] and a single-screw extruder [55]. LDPE, LLDPE [34] and copper powder were used to prepare the PE/Cu composites [3]. The composite ratios ranged between 0 and 24 v/v of copper powder particles. Optical microscopy showed that the copper powder distribution was relatively uniform at all copper contents. Two different sizes of copper particles (with a geometric standard deviation of 2.08 and 1.65) were used to prepare polypropylene/Cu composites [51]. The composites were prepared in a Rheomix mixer until the stabilization of the torque indicated good filler dispersion in the matrix, followed by compression molding. The SEM images showed random dispersion of the copper particles surrounded by the polymer matrix. The Cu particles had different sizes and were not perfectly spherical, and the same was observed for the composites containing the smaller Cu particles. The Cu particles had an irregular geometry and were entirely dispersed in the polymeric matrix.

The incorporation of different copper powder particles (micro- and nano-particles) into a polymer was also investigated by Xia *et al.* [56], where LDPE/Cu micro- and nano-composites were prepared by compounding the LDPE with 2, 4, 6, 10 and 13 wt. % of

respectively micro (5 μm) and nano (50 nm) copper particles in a single screw extruder. The temperature of the extruder was maintained at respectively 145, 160 and 180 $^{\circ}\text{C}$ from the hopper to the die. SEM images, SEM-EDS Cu-mapping photographs and energy dispersive spectroscopy (EDS) images showed copper nano-particle aggregates uniformly distributed in the matrix. The crystalline morphologies of pure LDPE and the LDPE/Cu nano-composite containing 13 wt. % of copper nano-particles showed different crystalline structures and the same orientation characteristics, but no spherulitic crystalline morphology was observed. An important feature observed in the nano-composites was the long and twisted nature of the lamellar morphology, which was not observed in the pure LDPE. The intertwined lamellae constituted an interlocked lamellar assembly instead of well separated rows.

The effect of a silane-based coupling agent on the properties of silver nano-particles filled epoxy composites was studied by Tee *et al.* [57]. The epoxy resin was used as the matrix and polyether-amine as curing agent, while the nano-sized silver particles were used as the metallic conductive filler in the production of the composites. The silver nano-powder was treated by a silane-based coupling agent called 3-aminopropyl triethoxysilane (3APTES). In order to avoid agglomeration and to facilitate the dispersion of silver nano-powder in the matrix, chloroform was used as dispersing agent and ethanol to dilute the 3APTES silane coupling agent. The loadings of silver nano-powders varied from 2 to 8% by volume and the silver nano-powder was mixed with the epoxy in an ultrasonic bath, followed by adding the curing agent into the mixture. The filler dispersity in the treated composites improved compared to the untreated system. Optical microscopy showed that the nano-particles were generally uniformly dispersed in the epoxy matrix.

To achieve excellent dispersion of conductive nanoparticles in a polymer matrix, the competition between polymer/polymer and polymer/nano-particle interactions has to be balanced to avoid clustering of particles in polymer nano-composites. Alam *et al.* [58] addressed this problem by investigating the effect of ferro-fluid concentration on the properties of the Fe_3O_4 /polyaniline (PANI) nano-composites. They used ammonium hydroxide solution without purification and double distilled aniline. The preparation of the ferro-fluid was carried out at room temperature by adding an NH_4OH solution to an aqueous solution of different concentrations of ferric chloride (2, 6 and 8 wt. %). The SEM images of Fe_3O_4 /PANI with 6 wt.% of Fe_3O_4 showed a homogeneous nano-porous structure with a uniform particle distribution.

2.3 Thermal properties

2.3.1 Melting and crystallization

2.3.1.1 Polymer/wax blends

LLDPE was mechanically mixed with a hard, brittle, straight-hydrocarbon chain paraffin wax, with and without crosslinking agents dibenzoyl peroxide (DBP) [27] and dicumyl peroxide (DCP) [31]. The authors wanted to establish whether or not it is possible to improve the blend properties by crosslinking, but this discussion will concentrate only on the uncrosslinked blends. The uncrosslinked blends, containing up to 40% of wax for both studies, showed melting behaviour similar to that of pure LLDPE, despite the fact that pure wax showed three significant peaks, which suggested the co-crystallization of PE and wax components. Since the wax has linear hydrocarbon chains of low molecular weight, these chains probably co-crystallize with the linear sequences of the LLDPE chains, which favours the crystallization process. The melting temperature of the blends decreased, while the melting enthalpy increased with an increase in wax content [27]. In the other paper [31], which was published 3 years earlier, it was reported that an increase in wax content did not influence the melting peak temperatures of the blends, but that the melting enthalpies of the blends increased with increasing wax content. It is interesting that the authors of the second paper [27] made no comment about the fact that their observations of the influence of wax content on the melting temperatures of LLDPE (for apparently the same system) were different from those reported in [31].

The same authors studied the thermal behaviour of the same LLDPE, discussed in the previous paragraph, as well as an LDPE (referred to before in [28]), blended with an oxidized wax [36]. The blends, that were prepared through mechanical mixing (using a coffee mill) and melt-pressing, were compared with the same blends prepared by extrusion. The melting peak temperatures of the extruded LLDPE/wax blends were similar to those of the mechanically

mixed blends. These observations show that the dependence of melting temperatures on wax content for LLDPE is almost the same and is not affected by the type of mixing. However, the melting enthalpies of the mechanically mixed LLDPE/wax blends remained the same, while those of the extruded blends decreased with an increase in wax content. This shows that the melting enthalpies, and therefore the total crystallinity of the blends, depend on the preparation conditions. In the case of LDPE the presence of oxidized wax also did not significantly influence the polymer melting behaviour. It was suggested that the wax crystallized together with the linear sequences of the LDPE chains. In this case the enthalpy values, and therefore the crystallinity, increased with increasing wax content. This was observed for both mechanically mixed and extruded blends, but the extruded blends showed higher crystallinities than the mechanically mixed blends. In a similar study [34] the blends were prepared by melt mixing. The melting enthalpies of the LLDPE/wax blends decreased with increasing amount of wax in the blends, which are in line with the observation on extruded LLDPE/wax blends [36]. The melting enthalpies of the LDPE/wax blends prepared by melt mixing decreased with increasing wax content, whereas the melting enthalpies of the same blends, respectively prepared through extrusion [36] and mechanical mixing followed by melt pressing [28], increased with increasing wax content. The extruded blends were found to have higher crystallinities than both the mechanically and melt mixed blends. For all the investigated blends the presence and amount of wax did not significantly influence the melting peaks, and therefore the lamellar thickness, of the PE crystallites. The crystallization trends for all the investigated blends were similar to those of melting.

In a related study [24] an un-oxidized wax was blended with LLDPE by extrusion, and the melting peak temperatures decreased with an increase in wax content. Compared to this, the melting peak temperatures of the same blends prepared through mechanical mixing remained the same [27,31]. The melting enthalpies of both extruded and mechanically mixed blends increased with increasing wax content, which implies that the crystallinity of the blends increased in both cases. However, the melting enthalpies of the extruded blends were higher than those of the mechanically mixed blends, which is in line with observations on LLDPE blended with an oxidized wax [36].

Mpanza and Luyt [23] blended LDPE with three Fischer-Tropsch paraffin waxes of different average molar masses (very high, high and medium) at fairly low wax concentrations. In these cases, the blends were prepared by melt-mixing. They found that the melting enthalpies of the

LDPE blended respectively with the very high and high average molar mass waxes increased with increasing wax content, while those for LDPE blended with the medium average molar mass wax decreased with increasing wax content. Since this wax has a higher crystallinity than LDPE, this observation was attributed to the possibility that the wax did not co-crystallize with LDPE, or that it acted as a plasticizer and inhibited LDPE from crystallizing. For all the investigated blends the presence and amount of wax did not significantly influence the melting peak temperatures, and therefore the lamellar thickness, of the LDPE crystallites.

The influence of thermal fractionation on the melting behaviour of different polyethylenes and paraffin waxes, and their blends, were investigated by Hato and Luyt [34]. For most of the systems the DSC curves showed a series of melting peaks that were attributed to the melting of crystallites of specific branching density. The oxidized hard paraffin wax showed more peaks than the un-oxidized wax, which was attributed to the oxygen containing groups found on the backbone chain of the oxidized wax. After thermal fractionation the HDPE showed only one melting peak, which was attributed to the un-branched nature of the polymer. LDPE showed seven melting peaks, and LLDPE eleven. This indicated that LDPE displayed a narrower crystallization temperature range than LLDPE, which suggested a narrower size distribution of the crystallites for LDPE in comparison with LLDPE. In this study the influence of blending was determined by comparing the observed curves, after thermal fractionation, with the calculated curves. The calculated curves were obtained by mathematically adding the DSC curves, obtained after fractionation, of the individual components in the same proportion in which they were present in the blend. The experimental curves of HDPE/un-oxidized wax blends, after thermal fractionation, differed from the calculated curves in the temperature range of 60-100°C. This indicated a possible co-crystallization of the low-melting fractions. Similar behaviour was observed for the HDPE/oxidized wax blends, but in this case a slight indication of phase separation was observed, even at low wax contents. Both oxidized and un-oxidized wax seemed to have the same influence on the crystallization of the main polymer fraction. Complete miscibility was observed for all the LLDPE/oxidized wax blends. This indicated possible co-crystallization of oxidized wax with LLDPE, which was also evident from the thermal fractionation curves. The thermal fractionation analyses of the LLDPE/un-oxidized wax showed partial miscibility and an indication that the shorter wax chains co-crystallized with LLDPE, while the longer wax chains crystallized separately in the amorphous phase of the LLDPE. In the case of the LDPE/un-oxidized wax blends partial miscibility for all the investigated blends was observed,

while complete miscibility was observed at low oxidized wax content, but not for the blends containing higher oxidized wax contents. The reason for this behaviour was that the wax probably crystallized mostly in the amorphous part of LDPE, although there may have been some co-crystallization.

2.3.1.2 Phase change materials

The specific melting enthalpy, related to wax melting, in PP/soft paraffin wax blends (that are regarded as shape-stabilized phase change materials) increased with an increase in wax content [42,43]. Although energy is also absorbed during the solid-solid phase transition, the authors only evaluated the melting endotherm of the soft paraffin wax. The experimental values were also higher than the theoretically expected values. This was due to the inhomogeneity of the samples, since the blends were significantly phase separated. Another reason given was the apparent leakage of paraffin wax from the matrix during sample preparation. The specific melting enthalpy of LDPE/soft paraffin wax blends increased with an increase in wax content, and it was explained as being the result of the higher crystallinity of the wax. This increase in the melting enthalpy was in agreement with the additive rule used for the calculation of the total melting enthalpy from the individual melting enthalpies of LDPE and wax, and this indicated that there was no wax leakage during the preparation of the blends. Oxidized, hard paraffin wax also displayed multiple endothermic peaks, and the authors could not conclusively relate the first peak to a solid-solid transition between different crystalline wax structures. However, in a later study done by the same authors [64], it was proved that for the soft paraffin wax the first peak was a solid-solid transition, whereas for the oxidized hard paraffin wax there was no evidence of a solid-solid transition. It was concluded that the multiple endothermic peaks were due to the melting of different molar mass fractions. The specific melting enthalpy of the oxidized hard paraffin wax blends increased with an increase in wax content. This increase was similar to that observed in the soft paraffin wax blends.

Solid-solid and solid-liquid transitions were also observed by Xiao *et al.* in shape stabilized composite PCMs, where styrene-butadiene-styrene rubber (SBS) served as supporting material for the paraffin [46,47]. The paraffin underwent a solid-liquid phase change in the polymer network, and no leakage of paraffin in the molten state was observed. The shape stabilized composite PCMs exhibited the same phase transitions as those of the pure paraffin,

and all of their DSC curves showed a sharp principal peak as well as a supplementary peak between 40 and 60 °C, which is in line with the observations by Krupa *et al.* [42,43]. The heat transfer rate of the 80/20 w/w paraffin/SBS composite was higher for the solidification and lower for the melting processes compared to that of the pure paraffin. This behaviour was attributed to the thermal conductivity of SBS which was higher than that of the paraffin, and the heat transfer was enhanced in the conduction dominated solidification process.

When two different paraffins (P1 and P2) were mixed with HDPE to form composite PCMs with different percentages of paraffin, the DSC results showed three peaks, the main peak being the solid-liquid phase change of the paraffin, and the minor peaks on both sides of the main peak being the solid-solid phase transition of the paraffin and the melting peak of HDPE, respectively. Both types of PCM exhibited the same thermal characteristics, because there was no chemical reaction between HDPE and the paraffin in the preparation of the form-stable composite PCMs. A paraffin was also mixed with EG by Sari and Karaipekli [48] to form composite PCMs. Their DSC curves showed two melting peaks that were also attributed to solid-solid and solid-liquid phase changes, and the total latent heat capacity of the composite PCMs was lower than that of the pure paraffin. The melting peaks associated with solid-liquid and solid-liquid transitions were also observed by Alkan [65]. DSC analysis revealed that sulfonated paraffin samples absorbed and dissipated more energy than pure paraffin samples during melting and solidification. This was explained as being the result of sulfonic acid interactions.

2.3.1.3 Thermally conductive polymer composites

The thermal properties of polyethylenes filled with copper particles were investigated by several groups [3,52,56]. One study compared composites that contained respectively micro- and nano-sized particles [56]. The authors showed that incorporation of micro- or nano-sized Cu particles into LDPE reduced the melting temperature, increased the crystallization temperature, and lowered the degree of crystallinity of the matrix of the composites. Similar effects were observed for the melting peak temperatures, melting enthalpies and crystallinities of LDPE and LLDPE filled with copper particles [3]. In both studies the authors showed that the increase in crystallization temperature was due to Cu particles acting as nucleating agents. The decrease in degree of crystallinity was due to the immobilization of polymer chain segments by Cu particles, resulting in reduced crystal growth rates. The degree of crystallinity

of the matrix of the nanocomposites was lower than that of the microcomposites, indicating that the Cu nano-particles have a much stronger influence on the nucleation and the motion of the polymer chains than the Cu micro-particles [56]. Two different copper particle sizes (larger and smaller) were also used as fillers in a PP matrix [52]. This study showed an insignificant change in matrix crystallinity. The crystallinity increased slightly more for the composite containing the larger particles. It was concluded that the crystallinity did not depend on the filler concentration or particles size. Zhao *et al.* [61] studied the thermal properties of poly(phenylene sulphide) (PPS)/EG and PPS/ultrasonicated-EG (S-EG) nanocomposites. For both EG and S-EG in PPS the crystallization temperature increased with an increase in filler content. The melting temperature, as well as the melting enthalpy, also increased with the introduction of EG or S-EG into PSS, indicating an increase in crystallinity of the nanocomposites.

For semi-crystalline polymers it was shown that the crystalline content had an important influence on almost all the physical properties of the polymer, and therefore it is important to investigate the influence of graphite on the change in the degree of crystallinity of HDPE [10]. The specific melting enthalpy of the pure HDPE, as well as of the composites filled with 60 wt. % of graphite, did not show significant differences. A slight decrease in the melting temperature of the composite was observed, which suggested that the filler reduced the lamellar thickness of the crystallites. The same behaviour was observed in a previous study [53], where both HDPE and PS were filled with 60 wt. % of graphite. Silver-coated polyamide (PA6) particles were also used as a filler for HDPE [55]. In this case a slight decrease in the degree of crystallinity with an increase in silver-coated PA6 particle content was observed. This showed that the filler particles represent defect centers, which inhibit the folding of macromolecular chains.

Chunyan *et al.* [59] investigated nano-carbon/PMMA composite materials using pulsed laser ablation deposition. The glass transition temperatures of the nano-carbon/PMMA composites decreased with an increase in nano-carbon particle content. This was the result of the large surface areas of the polar surface groups on the nanoparticles, giving rise to improved dispersion within the PMMA matrix. The strong interaction between the polar side groups in the PMMA macromolecules and the adsorbed polar groups on the surfaces of the nanocarbon particles weakened the interaction between the PMMA macromolecules. The incorporation of nano-carbon particles increased the free volume of the composites and there was more inter-

space for the movement of the PMMA macromolecules, leading to a reduction in the activation energy for the movement of PMMA chain segments and a decrease in the glass transition temperature.

Anantha and Hariharan [62] studied the physical and ionic transport in a poly(ethylene oxide)-NaNO₃ polymer electrolyte system. In the presence of NaNO₃ the glass transition temperature increased and this was attributed to ion–dipole interactions reducing the segmental motion of the PEO, which in turn affected the flexibility of the chains. This indicated that complexation with oxygen in the polyether side chains of the polymer had occurred. The melting temperature of the polymer did not vary much with the addition of NaNO₃. The degree of crystallinity decreased significantly for the PEO-complexed material with O/Na = 3:1.

Yang *et al.* [75] studied the thermal properties of aligned vapour grown carbon nano-fibre reinforced (VGCNF) polyethylene. DSC analysis was used to determine the changes in crystallization behaviour of drawn HDPE and its nano-composites. It is known that nano-fibres or nano-tubes act as either nucleating agents or obstacles to crystallization, depending on the type of matrix [76-79]. The heating curves of the HDPE and the VGCNF-composites, prepared at different take-up speeds, showed that the crystal structure of the samples changed with take-up speed. For pure HDPE, the pressed sample showed a single peak with a shoulder at the low temperature side, indicating an orthorhombic phase. As the take-up speed increased, the presence of secondary and tertiary pronounced peaks were observed. These peaks were associated with transformations from folded-chain to extended-chain crystals. The shape of the curves sharpened with windup speed, indicating the destruction of the less perfect crystals, while fibrillar transformation occurred. In the case of the nano-fibres, the melting peak also sharpens as the take-up speeds were increased. The difference was explained as being the result of the hindering of the structural transformations by the nano-fibres. The addition of nano-fibres into the HDPE matrix lowered the crystallinity of both the pressed and drawn composites. This is consistent with the qualitative observation that nano-fibres hindered the crystallization transformation of pure HDPE.

2.3.2 Thermal stability

2.3.2.1 PE/wax blends

In several studies the thermal stability of LDPE/wax blends were investigated using thermogravimetric analysis (TGA) [26-28,31,35,36]. In all these cases high wax contents were mixed into the polymer, which generally reduced the thermal stability of the blends. However, one study showed that at low soft paraffin wax contents, the thermal stability of the LDPE/wax blends was improved [23], despite the lower thermal stability of wax. The TGA curves of LDPE [26] and LLDPE [27], both mechanically mixed with un-oxidized wax and melt-pressed, showed a reduction in thermal stability with increasing wax content. This was a logical consequence of the lower thermal stability of the wax. Similar behaviour was observed when LLDPE was mechanically mixed with oxidized wax [31,35]. The thermal stability of extruded LDPE/oxidized wax blends was improved for small wax contents, and this was explained as being the result of co-crystallization of LDPE and wax at these wax levels [28]. In the case of the mechanically mixed LDPE/oxidized wax blends, the 10 wt.% wax containing blends were less thermally stable than the pure LDPE. However, the thermal stability gradually improved with increasing wax content [36]. This was the result of the increase in crystallinity, attributed to co-crystallization of wax chains with linear sequences of LDPE. The extruded blends showed better thermal stability than the mechanically mixed blends, because mixing in the molten state gave rise to better co-crystallization of the components. Extruded LLDPE/oxidized wax blends showed better thermal stability than pure LLDPE at lower wax content [36], while the mechanically mixed blends showed the opposite behaviour in all LLDPE/wax ratios.

2.3.2.2 Phase change materials (PCM)

The TGA curves of PP/wax and LDPE/wax PCMs showed a decrease in thermal stability with an increase in wax content [42,43], which is a logical consequence of the lower thermal stability of the wax. The blends containing a hard, oxidized paraffin wax showed higher thermal stability than those containing a soft paraffin wax. A two-step degradation was observed for the soft paraffin wax containing PCMs, indicating less co-crystallization with the respective polymers. No char yield was observed at temperatures higher than 500 °C for all these blends.

A two-step degradation was also observed, by Cia *et al.* [62], where the flammability and thermal properties of HDPE/paraffin hybrids as form stable phase change materials were investigated. The first step was associated with the degradation of the flame-retardant and the

paraffinic molecular chain, while the second step was associated with the degradation of HDPE. The flame-retardant containing form-stable PCMs showed a larger char residue at 700°C. The amounts of residue increased due to the higher content of melamine phosphate (MPP) in the PCMs. Cao and Liu [63] also observed a two-step degradation when they investigated hyper-branched polyurethane (HB-PUPCM) as novel solid-solid phase change materials for thermal energy storage. At high temperatures, the polyurethane degraded first through decomposition of the urethane bonds, followed by rupture of the soft segment phase.

2.3.2.3 Conductive polymer composites

Generally, the literature focuses on the thermal conductivities of metal containing polymers. However, a few papers are devoted to the thermal stability of polyethylene filled with metals [3,56,60]. When LDPE/Cu nano- and micro-composites were compared [56], the thermal decomposition temperatures of the nano-composites increased sharply at low Cu nano-particle contents, and reached an optimum value at 2 wt.% Cu, after which it decreased with further increase in nano-Cu content. In the case of the LDPE/Cu micro-composites, the optimum thermal stability was reached only after addition of 6 wt.% Cu, but higher Cu contents did not reduce this thermal stability. The difference was attributed to the influence of the difference in surface area and surface energy of the different Cu particles on the diffusion of volatile decomposition products within the LDPE/Cu composites.

Luyt *et al.* [3] also investigated PE/Cu composites containing Cu micro-particles. They found that the thermal stability of LDPE/Cu micro-composites increased, whereas the thermal stability of LLDPE/Cu micro-composites decreased, with increasing Cu content. Both LDPE and LLDPE were filled with Cu micro-particles up to 24 vol.%. At Cu contents above 16 vol.%, the thermal stability of the LLDPE/Cu composites decreased due to the Cu particles situated in the inter-lamellar spaces, which brought them in close contact with the lamellar surface. The high heat capacity and thermal conductivity of the Cu then caused these particles to quickly reach higher temperatures than the surroundings matrix, which caused the degradation of the LLDPE to start at lower overall temperatures.

The thermal stability of aligned vapour grown carbon nano-fibre reinforced polyethylene was studied by Yang *et al.* [76]. They investigated nano-composite samples drawn at different take-up speeds, and all these composites showed higher thermal stability than pure HDPE.

Differences in the take-up speed did not seem to change the thermal degradation behaviour of the samples. This was due to the higher thermal stability of the nano-fibres and the restriction effect of the nano-fibres on the polymer chain mobility.

2.4 Mechanical properties

2.4.1 Polymer/wax blends

The use of wax-based processing agents is a well-known practice in the polyolefin industry. However, there were only a few publications on the influence of wax on the mechanical properties of PE/wax blends, except for a number of studies done by Luyt and co-workers [24,28,29,34,36]. LLDPE and LDPE were blended with an oxidized wax to establish the reason for the detrimental effects of wax on the ultimate mechanical properties of the blends [28,36]. The authors compared the tensile properties of mechanically mixed and extruded blends. Young's modulus increased while elongation at break decreased with an increase in oxidized wax content for both mechanically mixed and extruded blend systems. This is in line with results obtained by investigating the same blends prepared through melt mixing followed by compression molding [34]. For both LDPE and LLDPE, the extruded blends showed higher Young's moduli than the mechanically mixed blends, probably as a result of higher lamellar perfection obtained by extrusion. The stress at break decreased with an increase in wax content for the mechanically mixed and extruded blends, except for the mechanically mixed LDPE samples, which showed brittle transitions. This was due to the introduction of low molecular weight wax, which affected the blend structure in such a way so as to favour fracture propagation. The relatively low molecular weight of LDPE was given as another possible reason for the observed brittle fracture.

The same group studied both mechanically mixed [29] and extruded [24] LLDPE/un-oxidized wax blends. The blends showed an increase in Young's modulus and a decrease in elongation at break with an increase in wax content for both systems. These observations were expected, since the wax was harder and had a higher modulus than the LLDPE matrix. The stress at break showed a decrease for mechanically mixed blends, whereas for extruded blends an increase in tensile strength with an increase in wax content was observed. In the extruded blends three different types of behaviour were observed [24]. The first was that the materials underwent strain hardening during stretching. The second was that, for the samples consisting

of 10 and 20% wax, strain softening was observed after the yield point. Thirdly the samples that consisted of 30% or more wax did not show a yield point, but instead they showed brittle rupture.

Hato and Luyt [34] also investigated HDPE melt-blended with un-oxidized and oxidized waxes. The Young's moduli of the blends increased with increasing wax content, and this was attributed to the higher degree of crystallinity of the material in the presence of un-oxidized wax and co-crystallization in the case of oxidized wax. Both un-oxidized and oxidized waxes reduced the stress at break of these blends, with the oxidized wax having a more significant influence. This was due to the lower crystallinity of the oxidized wax, which reduced the total crystallinity and the ultimate strength of the blend.

2.4.2 Thermally conductive polymer composites

Rusu *et al.* [9] investigated the mechanical properties of HDPE filled with zinc powder. They calculated the tensile elongation of HDPE/Zn composites using several models that were based on the basic model given by Equations 2.1 and 2.2

$$\frac{\varepsilon_c}{\varepsilon_p} = \left(1 - \Phi^{1/3}\right) \quad (2.1)$$

$$\frac{\varepsilon_c}{\varepsilon_p} = \left(1 - K_5 \Phi^{2/3}\right) \quad (2.2)$$

where ε_c is the elongation of the composites, ε_p the elongation of the polymer, Φ the volumetric fraction of filler, and K_5 a constant depending on the dimensions of the dispersed particles and on the treatments applied to them ($K_5 = 1.21$). For low metal powder contents in the composites, the experimental plot of the evolution of relative tensile elongation at yield was superimposed on the plot obtained from Equation 1. With increasing filler content a decrease in the experimental curve was observed compared to model predictions. Similar results were reported for the relative tensile elongation at break, with the difference that Equation 2 better predicted the experimental data. Young's modulus as a function of the filler content was also predicted by different theoretical models for composites with dispersive fillers. Amongst the most frequently used from both historical and technical viewpoints, were those of Einstein (Equation 2.3), Guth (Equation 2.4) Thomas (Equation 2.5) and Quemada (Equation 2.6), and others (Equations 2.7 and 2.8) [73].

$$\frac{E_c}{E_p} = (1 + 2.5\Phi) \quad (2.3)$$

$$\frac{E_c}{E_p} = (1 + 2.5\Phi + 14.1\Phi^2) \quad (2.4)$$

$$\frac{E_c}{E_p} = [1 + 2.5\Phi + 10.05\Phi + 0.00273\exp(16.6\Phi)] \quad (2.5)$$

$$\frac{E_c}{E_p} = \frac{1}{(1 - 0.5K_6\Phi^2)} \quad (2.6)$$

$$\frac{E_c}{E_p} = (1 - \Phi^{2/3}) \quad (2.7)$$

$$\frac{E_c}{E_p} = \frac{(1 - \Phi^{2/3})}{1 - \Phi^{2/3} + \Phi} \quad (2.8)$$

where E_c is the Young's modulus of the composite materials, E_p that of the polymer, and Φ the volume fraction of the filler. This shows that, according to both the theoretical predictions and the experimental results, the elongation decreased with an increase in filler content. Equation 2.3 was applied to polymers charged with low amounts of non-interactive spherical particles. Equation 2.4 was a development of the Einstein equation and takes into account the interactions between particles at higher filler contents. Equation 2.5 represents an experimental relation based on the results produced by a system with mono-dispersed spherical particles, and Equation 2.6 introduces a coefficient (usually $K_6 = 2.5$) that models the contact between particles and the differences in particle geometry. The experimental and theoretical dependence of Young's modulus of HDPE composites filled with zinc powder show that up to 4% zinc content, the theoretical curve corresponding to Equation 2.7 fits well with the experimental data. Above this value none of the present models was able to fit the experimental data. A general analysis of the mechanical properties indicated that incorporation of metal filler into a polymer caused a deterioration of the mechanical properties. For most composites a pronounced deterioration occurred in the area in which the filler particles were dispersed, both individually and as agglomerates.

Brito and Sanchez [66] investigated epoxy-amine filled with metal (Zn, Cu, and Al) particles. The breaking strength decreased as a function of filler content, and this behaviour was more pronounced for the composites with Zn and Al. Since the mechanical behaviour of the

composite depends on the quality of adhesion between the matrix and the filler, these factors account for the differences observed in the stress at break of the studied composites. According to Kunori and Geil [67] a strong interfacial adhesion between the dispersed and continuous phases produces a high breaking strength in the composites. However, in the study by Brito and Sanchez the composites with Al showed the lowest breaking strength and the non-filled matrix presented the highest breaking strength. The composites with Cu and Al had similar breaking strengths up to 10% filler content. Between 10 and 20% a pronounced decrease in the breaking strength was observed, which was related to poor ductility of the matrix.

The mechanical properties of thermoplastic/graphite composites were studied by Krupa *et al.* [10,53]. An increase in Young's modulus of HDPE and LDPE, filled with different types of graphite, was observed with an increase in graphite content. This increase was more pronounced for composites containing particles with higher specific surface areas. Generally the HDPE composites had higher Young's modulus values than the LDPE composites because of the higher crystallinity of HDPE. All the composites showed an initial decrease followed by an increase in stress at break. The initial decrease was more pronounced when HDPE was used as matrix, also because of the higher degree of crystallinity of HDPE. A general decrease in elongation at break for all the investigated systems with an increase in graphite content was observed. Chodák and Krupa [68] suggested a relationship between the decrease in elongation at break and the increase in electrical conductivity, which was probably the result of the formation of internal networks within the matrix.

In another study by Krupa *et al.* [54], a decrease in elongation at break for polyurethane (PU)/Ag composites with an increase in Ag-coated polyamide particles was observed. The authors tried to apply the models, discussed above [9], on their system, but they were not successful because their fillers did neither have a perfect spherical shape nor a perfect adhesion. The authors found it difficult to estimate the influence of irregularity and quality of adhesion on the final values of elongation at break. In the only available study on the influence of Cu particles on the mechanical properties of polyethylenes [3], it was found that the presence of copper powder in LDPE and LLDPE matrices reduces chain mobility, and gives rise to a rapidly decreasing elongation at break. The stress at break of the LDPE/Cu composites slightly decreased with an increase in Cu content, while the decrease in the case of

LLDPE/Cu composites was much more significant. An increase in Young's modulus for both types of composites with an increase in Cu content was also observed.

Silver nanoparticles were used as metallic conductive filler in epoxy composites [57]. When 3-aminopropyl triethoxysilane (3APTES) was introduced, the flexural modulus and strength significantly improved in comparison with the untreated Ag/epoxy system. The presence of the 3APTES silane coupling agent gave rise to a significant improvement in the filler-matrix interfacial bonding, leading to an increase in the efficiency of stress transfer from the matrix to the filler. According to Tan *et al.* [69], the coupling agent functions as a molecular bridge at the interface of dissimilar polymer binder and fillers. This results in the formation of covalent bonds across the interface, that subsequently improve the flexural properties of the composites. However, the incorporation of treated Ag into the epoxy matrix reduced the strain at break. The decrease in strain at break for the treated Ag filled composites might have been due to the good interfacial bonding existing between the constituent phases. This interfacial bonding, as well as well-distributed rigid nano-particles, resulted in brittle fracture, which was indirectly shown by the low strain at break values.

2.5 Dynamic mechanical properties

2.5.1 Phase change materials

Krupa *et al.* [54] used dynamic mechanical analysis (DMA) to follow changes in the modulus and the thermal expansion of PP/wax and LDPE/wax blends as function of temperature, as well as their dimensional stability during cycling [42,43]. When a soft paraffin wax was used, the decrease in storage modulus above the melting point of the wax was more pronounced at higher wax contents for both PP/wax and LDPE/wax blends, which suggested plasticizing of the polymer matrices by the wax components in their molten state. The soft paraffin wax in its solid state was found to reinforce the LDPE matrix, and this did not depend on the wax concentration in the studied concentration range. The wax acted as a highly crystalline filler which immobilized the polymer chains at the crystal surface, leading to a higher modulus of the polymeric matrix. The dimensional expansion of the phase change blends were practically independent, or at least minimally dependent, on the wax concentration from 40 to 60 wt.%. After wax melting, lower wax concentrations gave rise to less contraction, which was due to molten wax chain motion which was separated from the polymer domains and consequently

due to a rearrangement of the molecules in the amorphous region of the polymers. The dimensional expansion of the PP/soft paraffin wax blends increased with increasing wax content up to 30 wt.% wax. Dimensional contraction of the PP/hard paraffin wax blends above the melting point of the wax was observed. This was due to the rearrangement of the molecular chains, which were probably connected to the formation of separate hard paraffin wax domains after heating. In comparison to blends containing soft paraffin wax, PP blends containing oxidized hard paraffin wax formed more compact and stronger materials. In the case of LDPE/oxidized hard paraffin wax blends the dependence of the elastic modulus and loss factor of the blends on temperature showed similarly behaviour to that of soft paraffin wax containing blends.

The DMA results of a hyper-branched polyurethane copolymer (HB-PUPCM) with 80% polyethylene glycol (PEG) soft segment content [63] showed a peak in the $\tan \delta$ curve at about 64 °C and a rapid shift in the storage modulus, which indicated that melting has occurred. In contrast with pure PEG, PEG in HB-PUPCM did not influence the liquid state even at a temperature much higher than the melting point of pure PEG. The DMA curve showed that the PEG segments in HB-PUPCM remained in the solid state even when the temperature was 100 °C, over 33 °C above the melting point of pure PEG. These observations imply that the hard segment domain served as a skeleton which restricted the free movement of the soft PEG segments at temperatures above the melting point of PEG.

2.5.2 Thermally conductive polymer composites

Yang *et al.* [75] studied the dynamic mechanical properties of aligned vapour grown carbon-nanofibres (VGCNFs)-reinforced HDPE. The storage modulus of the polymer decreases rapidly with increasing temperature, whereas the loss modulus and $\tan \delta$ reached a maximum when the polymer was heated through the glass transition (T_g) region. The drawn nanocomposites showed much higher storage moduli than pure HDPE, especially at low temperatures, which was the result of the reinforcing effect of the nanofibres on the matrix and the reinforcing effect of orientation upon drawing. The presence of carbon nanofibres also enabled the matrix to sustain high modulus values at high temperatures. Post-drawing after extrusion improved the dynamic mechanical properties of the nanofibre reinforced composites as a result of the orientation of the nanofibres and the polymer chains. With an increase of the temperature to the melting temperature, the storage moduli tended to converge to that of pure

HDPE, indicating that at high temperatures the modulus of the composites were dominated by the matrix' intrinsic modulus. When the composites were subjected to an external stress, energy was dissipated by friction as a result of fibre–fibre and fibre–polymer interactions. Similar to the storage modulus results, when approaching the melting temperature of HDPE, the storage modulus curves of the VGCN-reinforced HDPE composites tended to converge and exhibit the intrinsic properties of the HDPE matrix [80]. The damping factor is the ratio of the loss modulus to the storage modulus. It is obtained as the ratio of the real part to the imaginary part of the complex viscosity. It was found that the composites showed a slightly higher damping than pure HDPE, owing to the viscoelastic energy dissipation as a result of fibre–fibre friction and fibre–HDPE interaction [80,81]. The post-drawing process showed negligible effect on the damping of the composites. The composites with different take-up speeds showed the same $\tan \delta$ and they all exhibited damping peak at values close to 90 °C.

The DMA properties of LDPE/multiwalled carbon nano-tube (MWCNT) nano-composites were studied by Liang and Tjong [82]. The storage moduli of the LDPE/CNT nano-composites increased with an increase in CNT content. This indicated the effectiveness of the reinforcing effect of the CNT on the LDPE matrix. The maximum value of the storage modulus was obtained with 0.52 vol.% of CNT. The $\tan \delta$ curves of pure LDPE and its nano-composites showed a broader peak located between ~ -20 °C for LDPE and ~ -10 °C for the LDPE/CNT nanocomposites, and this was ascribed to the glass transition of LDPE. The authors did not give a specific explanation for this increase in the value of T_g , but somewhere else in the paper they mention the immobilization of the polymer chains in the presence of CNT.

The storage moduli of polyvinyl alcohol (PVA)/soybean nano-fibre (SBN) composites improved with increasing SBN content [71]. This improvement was more significant at lower temperatures, and was explained as being the result of the increased total surface area of the nano-fibre and the resultant increased interaction and adhesion between the nano-fibre and the matrix. The storage modulus of the PVA showed a significant drop after 42 °C, and for the nano-composite films it occurred at 49 °C. The $\tan \delta$ curves also showed a slight shift in peak maxima to higher temperatures with increasing SBN content. This indicated restricted molecular movement due to the interaction between the filler and the polymer.

2.6 Thermal conductivity

2.7.1 Phase change materials

Since thermal conductivity is important in phase change materials, and since it has been identified as one of the problems in organic phase change materials, several studies were conducted on thermal conductivities and heat transfer rates in these materials. Highly conductive composites made of PCMs and graphite were studied by Pincemin *et al.* [83]. Nitrates (NaNO_3 , KNO_3), hydroxides (NaOH , KOH) and chlorides (ZnCl_2 , NaCl , KCl) were used as PCMs in this investigation. The low thermal conductivity of the PCMs leads to low and decreasing heat storage and discharge powers. This major drawback had severely inhibited their applications in industrial or domestic fields. In this study, the thermal conductivity enhancement was obtained by addition of three different types of graphite to the PCMs. The authors wanted to prepare materials with a thermal conductivity of at least $8 \text{ W m}^{-1} \text{ K}^{-1}$. The thermal conductivity of composite PCMs increased with increasing amount of graphite. At 20 wt.% graphite content, different sizes and types of graphite gave rise to a significant variation in conductivity, from 3.5 to $9 \text{ W m}^{-1} \text{ K}^{-1}$. This was due to the fact that the larger particles formed better conductive networks within the PCM. Moreover, lower particle density led to a larger number of dispersed particles and consequently to a better conductive network. The authors also compared the effect of particle size at lower graphite content for two different types of graphite. For both types of graphite the thermal conductivity linearly decreased with increasing particle size.

Several authors investigated the effect of exfoliated graphite (EG) on the heat transfer rates of different phase change material systems. Xiao *et al.* [46,47] showed that the heat transfer rate of paraffin/SBS increased for the solidification process, but decreased for the melting process when compared to those of pure paraffin. However, the presence of EG in this system dramatically improved the heat transfer rates for both the melting and solidification processes.

The time for complete solidification and complete melting of the paraffin/SBS/EG composites was two-ninths and two-fifths respectively of that of the paraffin.

Sari [45] studied form-stable paraffin/HDPE composites as solid-liquid phase change materials for thermal energy storage. The study of the improvement in thermal conductivity was performed only on samples containing 77% paraffin. Expanded and exfoliated graphite were added to these composites and the thermal conductivity of the composites was found to significantly improve. Sari and Karaipekli [48] also studied the thermal conductivity of paraffin/expanded graphite (EG) composites in the absence of the HDPE matrix. They found that the thermal conductivity increased with increasing mass of EG, indicating a strong association between the two components. However, further increase in EG content leads to a decrease in wax content, which is not a desirable fact, because the wax is the active substance in the PCM. For this reason they arbitrary decided to use only 10 % of EG, since it was found that this content was high enough to significantly improve the thermal conductivity of the PCM.

Paraffin/expanded graphite composites, that were prepared by absorbing the paraffin into the EG, was studied by Zhang and Fang [50]. In this composite the paraffin served as a latent heat storage material and the EG acted as the supporting material, which prevented leakage of the molten paraffin from its porous structure due to capillary and surface tension forces. The solid-liquid phase change temperature of the composite PCM was the same as that of the paraffin, and the latent heats of the paraffin/expanded graphite composite materials were equivalent to the calculated values based on the mass ratios of the paraffins in the composite. The heat transfer rate of the composites was higher than that of the paraffin due to the combination with the EG, which has a high thermal conductivity. The samples had a large thermal storage capacity and improved thermal conductivity, and they did not experience liquid leakage during the solid-liquid phase change.

A supported PCM made of paraffin impregnated by capillary forces in a compressed expanded natural graphite (CENG) matrix was studied by Py *et al.* [40]. The thermal conductivity of the porous graphite matrix improved when its bulk density was increased. The thermal conductivity of porous graphite in the axial the direction is in the range of 4-10 W m⁻¹ K⁻¹ and in the radial direction in the range of 5-100 W m⁻¹ K⁻¹. The experimental conductivities of the paraffin/CENG composites and the calculated conductivities of the raw

CENG with respect to the axial and radial directions showed thermal conductivities similar to that of the pure graphite matrix. Therefore, the low thermal conductivity of the paraffin did not affect the overall performance of the composites.

2.7.2 Conducting polymer composites

Polymers are materials that have low thermal conductivity ranging from $0.15 \text{ W m}^{-1} \text{ K}^{-1}$ for amorphous polymers such as PS, to $0.5 \text{ W m}^{-1} \text{ K}^{-1}$ for crystalline polymers such as HDPE. Krupa *et al.* [51] demonstrated that metal-coated particles can be effectively used to improve the thermal conductivity of, for example, HDPE. The study was based on HDPE filled with silver-coated polyamide (PA). It was found that very low silver content, if deposited on the PA particles, significantly improved thermal conductivity of composites.

The study of the thermal transport in composite materials requires a model of the thermal conductivity of heterogeneous materials that considers the influence of various parameters. Many different models have been devised that account for the geometry or orientation of the filler particles in the matrix, the concentration of filler, and the ratio between the thermal conductivity of the filler to the thermal conductivity of the matrix. However, none of these models have general validity [11]. The upper or lower bounds of effective thermal conductivity represent the simplest models and were given when materials were arranged in parallel or series with respect to heat flow. The parallel conduction model is described by Eq. 2.9,

$$\lambda_c = \lambda_f \Phi_f + \lambda_m \Phi_m \quad (2.9)$$

and the series conduction model by Eq. 2.10,

$$\frac{1}{\lambda_c} = \frac{\Phi_f}{\lambda_f} + \frac{\Phi_m}{\lambda_m} \quad (2.10)$$

where λ_c , λ_m , λ_f are the thermal conductivities of the composites, matrix and filler respectively, and Φ_f and Φ_m are the volume fractions of the filler and the matrix. According to Bujard *et al.* [72] the only thorough lower bounds was the Hashin and Shtrikman bounds [73]. This was the best possible bounds when no information about particle distribution in the matrix was available. The lower bound was expressed as

$$\lambda_m = \frac{\lambda_m + \Phi_g}{\left[\frac{1}{\lambda_f} - \lambda_m + 1 - \frac{\Phi_g}{3\lambda_m} \right]} \quad (2.11)$$

Self-consistent calculation of thermal conductivity of the composites was predicted by Budiansky [74]. The model enables the determination of thermal conductivity of an N-component system only from the knowledge of thermal conductivities of pure components and their volume fractions according to Eq. 2.12,

$$\lambda_c = -b + \sqrt{\frac{(b^2 - 4ab)}{2a}} \quad (2.12a)$$

$$a = 2 \quad (2.12b)$$

$$b = \lambda_f - 2\lambda_m - 3(\lambda_m - \lambda_m)\Phi_g \quad (2.12c)$$

$$c = \lambda_f \lambda_m \quad (2.12d)$$

This model describes experimental data up to 25 vol. % of the filler. This range was broader than in the Hashin-Shtrikman model. Generally, no additional parameters beside the thermal conductivities of pure components were required. When the filler content was higher, the model failed and gave unrealistically high predictions of composites' thermal conductivity.

Boudenne *et al.* [52] investigated the thermal conductivity of polypropylene filled with two different sizes of copper particles (1.65 and 2.08 μm). A non-linear increase in the thermal conductivity was observed with an increase in the volume fractions of both fillers. At a given filler concentration, a higher thermal conductivity was observed in the composite filled with the smaller Cu particles. This difference was more significant at higher filler concentrations. This result was also reported by several authors for metallic particles and polymeric matrices [53,54,84,85].

2.8 References

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CHAPTER 3

EXPERIMENTAL

3.1 Materials

3.1.1 Introduction

Polyethylene (PE) is produced in different forms, each of which has different properties resulting from variations in structure. Low-density polyethylene (LDPE) contains both short chain and long chain branches. Linear low-density polyethylene (LLDPE) contains only short-chain branches, but can have a wide range of branch contents, depending on the catalyst and concentration of α -olefin co-monomer. High-density polyethylene (HDPE) is the most crystalline form, because the chains contain very little branching [1]. Based on ASTM D-1238, the densities of polyethylenes vary. Since the content and length of the side chain branching dominate the degree of crystallinity, the melting temperature of polyethylenes can be varied by controlling the crystallinity [2-6]. LLDPE is produced in either gas-phase or slurry-reactor processes by copolymerizing ethylene with α -olefin monomers under low pressure conditions (2 to 7.5 MPa), and a temperature of up to 250 °C in the presence of a catalyst such as the Ziegler-Natta type. The type of monomer such as 1-butene, 1-hexene or 1-octene [7], also influences the characteristics of this polymer. LDPE is produced from an ethylene monomer using high pressures ranging from 100 to 135 MPa at 150 to 300 °C in the presence of a small amount of oxygen or an organic peroxide [8]. Both stirred autoclave and tubular reactor processes are used. The crystallinity of the resulting polymer is determined by the reaction temperature. The lower the reaction temperature, the higher the crystallinity and the density. HDPE is produced as a homopolymer using reaction processes, catalyst systems, as well as pressure and temperature conditions similar to those used for the production of LLDPE. Small amounts of co-monomer can be used to produce polymers at the lower end of the density range. The type of catalyst used determines the molecular weight distribution, whereas weight is controlled by the proportion of hydrogen included.

Soft paraffin wax was selected as the phase change material (PCM) because of its high specific enthalpy of melting and low melting temperature. It is a white, translucent, tasteless

and odourless solid consisting of a mixture of solids of straight hydrocarbons chains. It is soluble in benzene, ligroin, hot alcohol, chloroform and carbon disulfide, but insoluble in water and acids. It is primarily used for the preparation of candles, paper coating, and protective sealants for food products and beverages, biodegradable mulch, stoppers for acids bottles and electric insulations [9].

Copper nano- and micro particles were used as fillers for the improvement of the thermal conductivity of the composites, and to control the rate of absorption and release of heat energy by the PCM. Metal fillers play an important role in the production of polymeric materials. They are widely used for electromagnetic interference shielding. Such composites are lighter than metals and are inexpensive [6]. The thermal conductivity of polymers can be improved by addition of metal fillers [10,11,12].

3.1.2 Low-density polyethylene (LDPE)

LDPE was supplied in pellet form by Sasol Polymers. It has an MFI of 7.0 g/10 min (ASTM D-1238), a melting point of 106 °C, a molecular weight of 96 000 g mol⁻¹, and a density of 0.918 g cm⁻³.

3.1.7 Linear low-density polyethylene (LLDPE)

LLDPE was supplied in pellet form by Sasol Polymers. It has an MFI of 1.0 g/10 min (ASTM D-1238), a molecular weight of 191 600 g mol⁻¹, a melting point of 124 °C, and a density of 0.924 g cm⁻³.

3.1.8 High-density polyethylene (HDPE)

HDPE was supplied in pellet form by DOW Chemicals. It has an MFI of 8 g/10 min (ASTM D-1238), a molecular weight of 168 000 g mol⁻¹, a melting point of 130 °C, and a density of 0.954 g cm⁻³.

3.1.9 Soft paraffin wax (M3 wax)

Soft paraffin wax (M3 wax) was supplied in powder form by Sasol Polymers. It is a paraffin wax consisting of approximately 99% of straight chain hydrocarbons and few branched chains, and it is primarily used in the candle-making industry. It has an average molar mass of 440 g mol^{-1} and a carbon distribution between C15 and C78. Its density is 0.90 g cm^{-3} and it has a melting point range around 40-60 °C.

3.1.10 Copper powder

Merck Chemicals in South Africa supplied the copper powder, which was used as one of the conducting fillers. It has a melting point of 1083 °C and a density of 8.96 g cm^{-3} , and the particles sizes were less than 38 μm determined by using a laboratory test sieve with a pore sizes of 38 μm . The copper nano-particles were supplied by Lawrence Packaging Supply Corp., Moonachie, New Jersey, USA, Lot # R402 and the particle size was 50 nm.

3.2 Methods

3.3.1 Preparation of the blends and composites

Materials in this work were used as received from the suppliers. Samples were weighed according to the desired ratios (Table 3.1) to make up a total volume of 40 mL (which is the volume required to thoroughly mix the different components). The samples were initially melt mixed in a Brabender Plastograph 50 mL internal mixer at a temperature of 160 °C (screw speed of 70 rpm for 15 min). This was followed by melt pressing of the samples at a pressure of 100 bar into 1 mm thick sheets in a hot-melt press at the same temperature and for the same time.

3.3.2 Scanning electron microscopy (SEM)

The surface structure and morphology of the samples were characterized by scanning electron microscopy (SEM). SEM creates images by focusing a high energy electron beam onto the surface of a sample, and detecting signals from the interaction of the incident electrons with the sample surface. Types of signals gathered in SEM are different and can include secondary

electrons, characteristic x-rays and back-scattered electrons. These signals not only come from the primary beam impinging upon the sample, but also from other interactions within and near the surface of the sample. SEM is capable of producing high-resolution images of a sample surface, but it requires that the specimens be conductive for the electron beam to scan the surface and that the electrons have a path to ground. The manner in which images are created gives great depth of field yielding a characteristic three-dimensional appearance useful for understanding the structure of a sample [13,14].

A Shimadzu model ZU SSX - 550 Superscan scanning electron microscope was used in this study. All the samples were frozen in liquid nitrogen, then fractured by simply breaking the specimens in an appropriate size to fit in the specimen chamber, and then mounted onto the holder. The surfaces of the samples were coated with gold by an electro-deposition method to impart electrical conduction before recording the SEM micrographs. This was done to prevent the accumulation of static electric charge on the specimen during electron irradiation.

Table 3.1 Sample compositions used in this study

PE/Cu micro-composite (v/v)	PE/Cu nano-composite (v/v)	PE/wax blend (v/v)	PE/wax/Cu micro-composite (v/v)
100/0	100/0	100/0	100/0/0
99/1	99/1	70/30	59/40/1
97/3	97/3	60/40	57/40/3
95/5	95/5	50/50	55/40/5
90/10	-	0/100	50/40/10
85/15	-	-	0/100/0
80/20	-	-	-
75/25	-	-	-

3.3.3 Differential scanning calorimetry (DSC)

Differential scanning calorimetry is widely used to characterize the thermal properties of polymers. The most measured important properties are melting, crystallization and oxidation temperatures and enthalpies, glass transition temperatures, as well as the composition and compatibility plasticized polymers and polymer blends. It is a technique in which the

difference in the amount of heat required to increase the temperature of a sample and a reference is measured as a function of temperature. Both the sample and the reference are maintained at nearly the same temperature throughout the experiment. The temperature programme for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The reference material should have a well-defined heat capacity over the range of temperatures to be scanned. The basic principle underlying this technique is that, when the sample undergoes a physical transformation such as a phase transition, more or less heat will need to flow to it than to the reference to maintain both at the same temperature. Whether more or less heat must flow to the sample depends on whether the process is exothermic or endothermic. For example, when a solid sample melts to a liquid, it will require more heat flowing to the sample to increase its temperature at the same rate as the reference. This is due to the absorption of heat by the sample as it undergoes the endothermic phase transition from solid to liquid. Similarly, as the sample undergoes exothermic processes (such as crystallization) less heat is required to raise the sample temperature. By observing the difference in heat flow between the sample and reference, DSC is able to measure the amount of heat absorbed or released during such transitions [15,16,17].

In this study, DSC analyses were done in a Perkin-Elmer Pyris-1 differential scanning calorimeter under flowing nitrogen (flow rate 20 mL min⁻¹). The instrument was computer controlled and calculations were done using Pyris software. It was calibrated using the onset temperatures of melting of indium and zinc standards, as well as the melting enthalpy of indium. Samples (5-10 mg) were sealed in aluminium pans and heated from -40 to 160 °C at a heating rate of 10 °C min⁻¹, and cooled at the same rate. For the second scan, the samples were heated and cooled under the same conditions. The peak temperatures of melting and crystallization, as well as melting and crystallization enthalpies were determined from the second scan. All DSC measurements were repeated three times for each sample. The melting and crystallization temperatures, as well as enthalpies, are reported as average values with standard deviations.

3.3.4 Thermogravimetric analysis (TGA)

TGA provides additional information to the more commonly used DSC. TGA measures the amount and rate of change in the mass of a sample as a function of temperature or time in a controlled atmosphere. The measurements are used primarily to determine the thermal

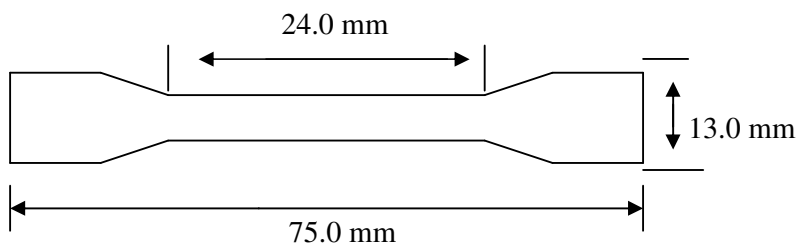
stabilities of materials as well as their compositional properties. The technique can analyze materials that exhibit either mass loss or gain due to decomposition, oxidation or loss of volatiles. It is useful for the study of polymeric materials, including thermoplastics, thermosets, elastomers, composites, films, fibers, coatings and paints. TGA measurements provide valuable information that can be used to select materials for certain end-use applications predict product performance and improve product quality. The technique is particularly useful for compositional analysis of multi-component materials or blends, thermal stabilities, oxidative stabilities, estimation of product lifetimes, decomposition kinetics, and effects of reactive atmospheres on materials, filler content of materials, as well as moisture and volatiles contents [18].

TGA analysis was carried out on a Perkin-Elmer TGA7 thermogravimetric analyser. Samples ranging between 5 and 10 mg were heated from 30 to 650 °C at a heating rate of 20 °C min⁻¹ under flowing nitrogen (flow rate 20 mL min⁻¹). A sample was placed into a pan which is attached to a sensitive microbalance assembly. The sample holder part of the TGA balance assembly was then placed into a high temperature furnace. The balance assembly measured the initial sample mass at room temperature and then continuously monitored changes in sample mass as function of temperature. The mass-temperature profile was analysed for the amount or percent mass lost at any given temperature, for any non-combusted residue at the final temperature, and for temperatures of various sample degradation processes. The maximum analysis temperature was selected so that the specimen mass was stable at the end of the experiment, meaning that all chemical reactions were completed. In this study, the TGA technique was mainly used to evaluate the thermal degradation behaviour of the samples used in this study.

3.3.5 Tensile testing

Tensile testing are normally used to determine the initial (or Young's) modulus, as well as the tensile strengths, and sample elongations, at yield and break. In a typical tensile test, a sample of known dimensions is firmly tightened between two grips. The tensile tester pulls the sample from both ends, and measures the force required to pull the specimen apart, as well as the elongation of the sample. This data is then used to construct a stress-strain curve, from which the required tensile values are determined [19].

A Hounsfield H5KS universal testing machine was used for the tensile analysis of the samples. The dumbbell samples were stretch at a speed of 50 mm min^{-1} under a cell load of 250.0 N . About nine test samples were cut using a dumbbell cutter and they were all tested. Stress-strain curves that indicated sample deficiencies were ignored during the final calculations of the tensile properties. The dimensions of the dumbbell shaped sample were as follows:



The instrument settings for the analyses were as follows:

Load range	250.0 N
Extension range	300.0 mm
Gauge length	24.0 mm
Speed	50.0 mm min^{-1}
Approach speed	0.02 mm min^{-1}

3.3.6 Dynamic mechanical analysis (DMA)

DMA properties, such as the storage modulus, loss modulus and loss factor ($\tan \delta$), of polymer blends and composites depend on the structure, crystallinity and the extent of branching. It is most useful for observing the viscoelastic nature of polymers, for measuring solid state transitions. It can be simply described as applying an oscillating force to a sample and analyzing the material's response to that force. These transitions, caused by molecular motions and free volume changes, define how a polymer will behave at a certain temperature. The thermal transitions in polymers can be described in terms of free volume changes or relaxation times. They are classified as γ -, β - and α -transitions by their types of motion [20]. Going from a very low temperature where the molecules are tightly compressed, to higher temperatures, the free volume starts increasing so that localized bond movements (bending and stretching) occur. This transition is called the γ -transition. As the temperature continues to

increase, the free volume increases to such an extent that whole side chains and localized groups of 4-8 backbone atoms begin to have enough space to move, and the material starts to develop toughness. This transition is called the β -transition. The α -transition is associated with the chain segment mobility in the crystalline phase, probably as a result of the reorientation of defect areas in crystals. The α -transition appears to be a composite process of two transitions labeled α and α' [21,22,23].

The dynamic mechanical properties of the blends and composites were investigated using a Perkin Elmer Diamond DMA. The settings for the analyses were as follows:

Frequency	1 Hz
Amplitude	20 μm
Temperature range	-140 to - 80 $^{\circ}\text{C}$
Heating rate	5 $^{\circ}\text{C min}^{-1}$
Preloading force	0.02 N
Length	20 mm
Width	12.0 – 12.5 mm
Thickness	1.0 – 1.3 mm

3.3.7 Thermal conductivity and thermal energy storage

In this study, the thermal conductivity was measured using a multi-purpose apparatus ISOMET, (Applied Precision, Bratislava, Slovakia) for non-steady measurements of thermal properties. The thermal conductivity values were calculated automatically from a time dependence of the thermal flow in the material. Samples were melt-pressed into spherical (7 cm diameter) 1 mm thick sheets in a hot-melt press at 160 $^{\circ}\text{C}$ for 5 min at a pressure of 100 bar. Thereafter, measurements were made at 25 ± 2 $^{\circ}\text{C}$ with a flat probe. For thermal energy storage and release measurements, a sensitive Testo recording thermometer was used. Testo 177-T3 (Testo AG, Germany) is temperature logger with display and switch for continual temperature monitoring. The Testo 177 data loggers are used to save and read out separate readings and measurements sequences. The device has two probes, a reference and a sample probe. 5-20 g samples of some of the blends and composites were molded into cylinders of diameter 3 cm. The sharp end of the sample probe was inserted into a sample which was immersed into a water bath kept at 93 $^{\circ}\text{C}$. The samples were heated for 20 min and cooled in

open air for another 20 min, and the heating and cooling curves were recorded. The experimental setup for the thermal storage and release experiments is shown diagrammatically in Fig. 3.1.

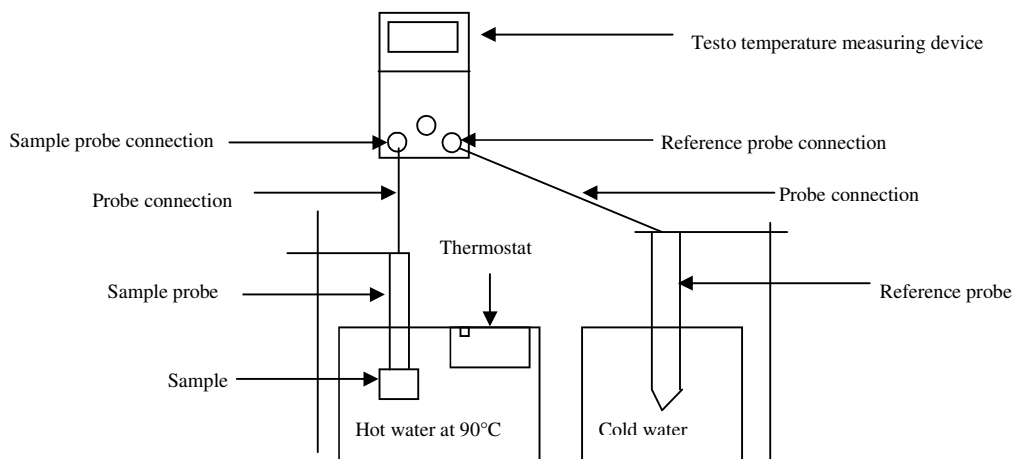


Figure 3.1 Setup for heat absorption measurements

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CHAPTER 4

RESULTS AND DISCUSSION

4.1 Scanning electron microscopy (SEM)

The overall morphology of the composites was studied by SEM analysis of the fracture surfaces of the composites. Fig. 4.1(a) shows a fair dispersion of micro-particles, with no obvious agglomeration. As can be seen in Figs. 4.1(b) and (c), the Cu nano-particles are fairly well dispersed, but also form agglomerates. To optimally improve the conductivity of the composites, it is important for the particles to form a percolation network within the polymer and blend matrices. No such network formation was observed in the SEM images of the investigated samples. In Fig. 4.1(a) there seem to be voids around the Cu particles, which indicate that the interaction between the polymer and the Cu particles is weak. The lack of adhesion between the polymer and filler indicates poor interfacial interaction. As the content of Cu particles is increased, the agglomeration of the particles also increased.

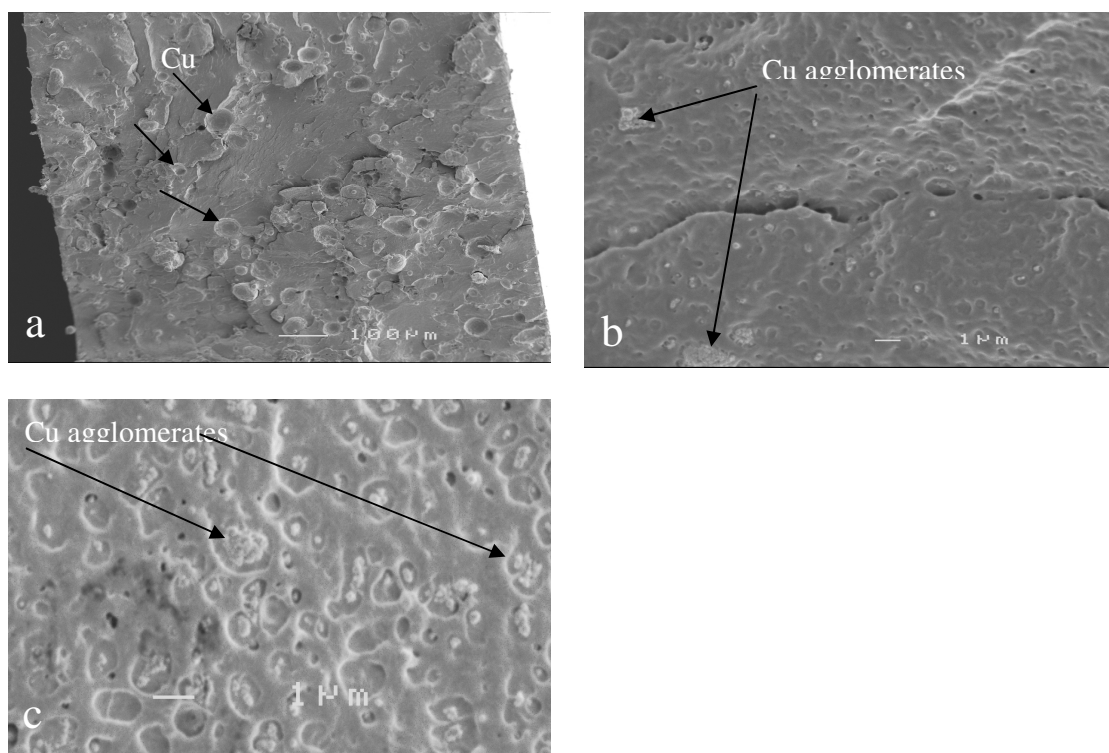


Figure 4.1 SEM images of (a) 90/10 v/v LDPE/Cu micro-composite (b) 99/1 v/v LDPE/Cu nano-composites, (c) 95/5 v/v LDPE/Cu nano-composites

Fig. 4.2 (a) and (b) show the micrographs of an LDPE/wax/Cu composite containing 1 vol.% Cu powder at a constant 40 vol. % of wax. The composite shows a two-phase morphology, implying the immiscibility of LDPE and wax. The Cu particles are not visible in these pictures, probably because they are covered by wax. This affinity between Cu and wax is clearly visible in Figs.4.2 (c) and (d), where it can be clearly seen that the Cu particles are covered by wax, as indicated by the arrows.

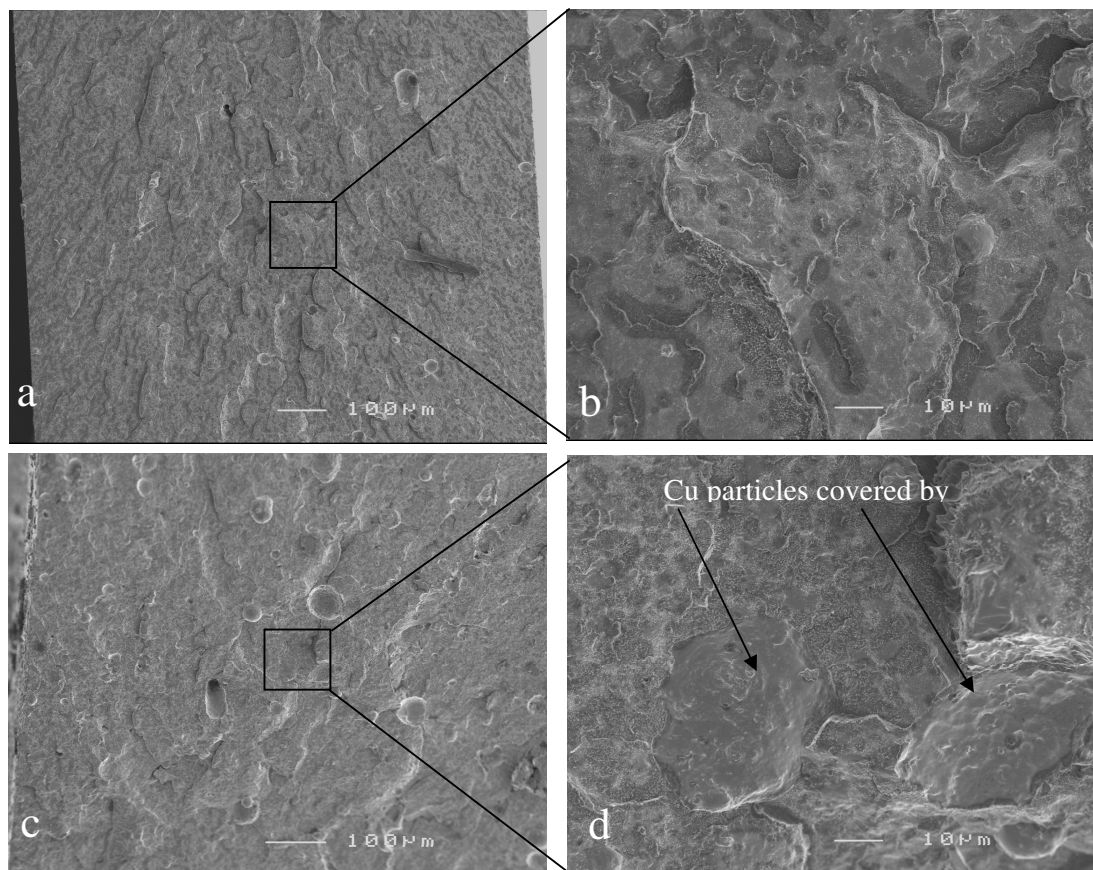


Figure 4.2 SEM images (a) 59/40/1 v/v LDPE/wax/Cu micro-composite (low magnification), (b) 59/40/1 v/v LDPE/wax/Cu micro-composite (high magnification), (c) 55/40/5 v/v LDPE/wax/Cu micro-composite (low magnification), (d) 55/40/5 v/v LDPE/wax/Cu micro-composite (high magnification)

4.2 Differential scanning calorimetry (DSC)

4.2.6 Polyethylenes filled with copper micro-particles

Fig. 4.3 shows the DSC heating curves for pure LDPE, LLDPE, and HDPE. The curves show endotherms with melting peak temperatures at 106.8, 127.7 and 134.7 °C for respectively LDPE, LLDPE and HDPE. Pure HDPE has a relatively high enthalpy value of 149.3 J g⁻¹, while LLDPE and LDPE respectively have enthalpies of 86.9 and 75.4 J g⁻¹. These values are in line with the known crystallinities of the respective polyethylenes.

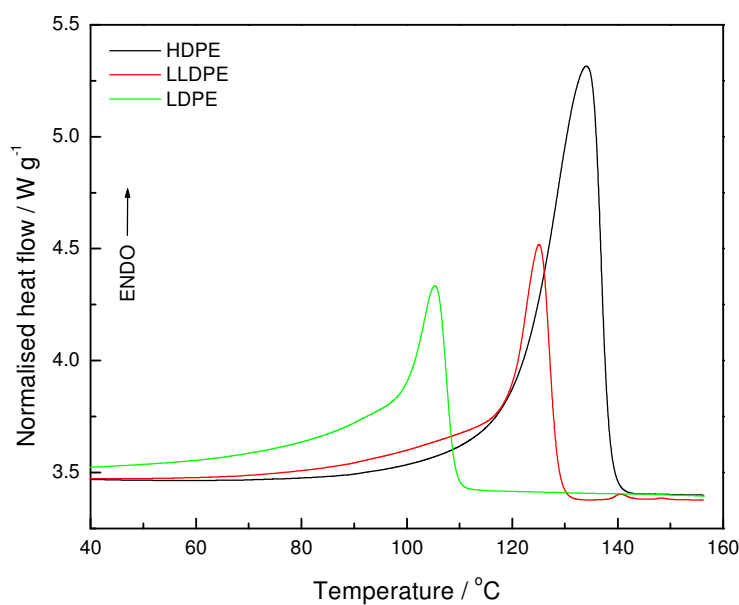


Figure 4.3 DSC heating curves of pure polyethylenes

Figs. 4.4-4.6 show the DSC heating curves of the different polyethylenes and their Cu micro-composites. For the LDPE/Cu micro-composites the peak temperatures of melting did not significantly change and are within experimental error. From this it is clear that the presence of up to 20 vol. % of Cu micro-particles in LDPE had little influence on the crystallite sizes. However, if the enthalpy values in Table 4.1 are compared (also see Fig. 4.7), it is clear that the Cu micro-particles reduce the LDPE chain mobility which gives rise to a lower crystallinity. When the measured melting enthalpy values (ΔH_m^{obs}) are compared with the calculated values (ΔH_m^{calc}), it can be seen that the LDPE in the composites had significantly lower enthalpy (or crystallinity) values than would be expected if it was assumed that the Cu

micro-particles had no influence on the LDPE crystallization behaviour. The ΔH_m^{calc} values were calculated from the melting enthalpy of pure LDPE and the weight fractions of LDPE in the respective composites.

Table 4.1 DSC results for polyethylene/Cu micro-composites

v/v	$T_{p,m} / ^\circ\text{C}$	$\Delta H_m^{\text{obs}} / \text{J g}^{-1}$	$\Delta H_m^{\text{calc}} / \text{J g}^{-1}$	$T_{p,c} / ^\circ\text{C}$	$\Delta H_c^{\text{obs}} / \text{J g}^{-1}$
LDPE/Cu					
100/0	106.8 ± 1.5	75.4 ± 6.2	-	91.7 ± 0.6	-63.7 ± 7.6
99/1	107.1 ± 1.4	61.5 ± 6.3	68.8 ± 5.6	91.5 ± 1.0	-57.0 ± 6.9
97/3	106.6 ± 1.7	51.3 ± 8.3	58.1 ± 4.7	91.4 ± 0.7	-41.2 ± 4.1
95/5	106.3 ± 1.2	39.9 ± 2.6	49.8 ± 4.1	91.8 ± 1.1	-43.5 ± 4.9
90/10	106.4 ± 1.1	23.4 ± 1.8	36.2 ± 6.4	91.8 ± 0.9	-27.6 ± 3.2
85/15	105.8 ± 0.8	18.6 ± 1.6	27.8 ± 4.6	92.8 ± 0.9	-21.3 ± 3.9
80/20	106.0 ± 0.9	14.4 ± 0.4	21.9 ± 3.4	92.2 ± 0.8	-16.0 ± 3.1
75/25	105.5 ± 1.2	10.4 ± 2.7	17.9 ± 1.5	92.9 ± 1.1	-12.4 ± 2.2
LLDPE/Cu					
100/0	127.7 ± 2.1	86.9 ± 1.0	-	109.6 ± 0.9	-50.1 ± 0.8
99/1	127.9 ± 1.2	69.4 ± 4.5	79.3 ± 0.9	110.2 ± 1.0	-45.2 ± 2.0
97/3	126.8 ± 1.3	58.8 ± 4.5	66.6 ± 0.8	110.0 ± 1.3	-37.7 ± 4.1
95/5	126.2 ± 0.5	45.3 ± 9.7	57.4 ± 0.6	110.3 ± 1.3	-32.7 ± 2.5
90/10	126.5 ± 1.3	30.9 ± 7.0	41.7 ± 0.5	110.9 ± 1.7	-22.2 ± 3.4
85/15	125.4 ± 1.4	19.6 ± 4.3	31.9 ± 0.4	111.6 ± 1.2	-17.1 ± 4.5
80/20	125.5 ± 1.4	15.2 ± 3.4	25.3 ± 0.3	111.0 ± 1.3	-14.3 ± 3.1
75/25	125.4 ± 1.6	10.2 ± 2.5	20.6 ± 0.3	112.5 ± 1.3	-10.4 ± 4.2
HDPE/Cu					
100/0	134.7 ± 0.5	149.3 ± 11.7	-	113.9 ± 1.1	-134.8 ± 2.6
99/1	134.1 ± 1.3	138.1 ± 3.1	136.2 ± 10.6	114.3 ± 0.1	-132.1 ± 2.1
97/3	133.6 ± 0.1	110.4 ± 7.3	115.0 ± 9.0	115.0 ± 0.9	-110.4 ± 0.4
95/5	132.6 ± 0.3	101.8 ± 0.8	98.5 ± 7.6	114.7 ± 0.6	-97.0 ± 2.3
90/10	131.6 ± 0.2	67.4 ± 6.7	71.7 ± 5.6	115.3 ± 0.3	-72.0 ± 1.6
85/15	131.4 ± 0.2	52.3 ± 8.0	54.8 ± 4.3	115.7 ± 0.2	-53.3 ± 0.3
80/20	130.8 ± 0.5	41.4 ± 1.6	43.4 ± 3.1	116.0 ± 0.4	-43.9 ± 0.3
75/25	130.2 ± 0.2	27.2 ± 9.8	35.2 ± 2.8	116.3 ± 0.6	-34.3 ± 0.4

$T_{p,m}$, ΔH_m^{obs} , ΔH_m^{calc} , $T_{p,c}$ are melting peak temperature, observed melting enthalpy, calculated melting enthalpy, and crystallization peak temperature

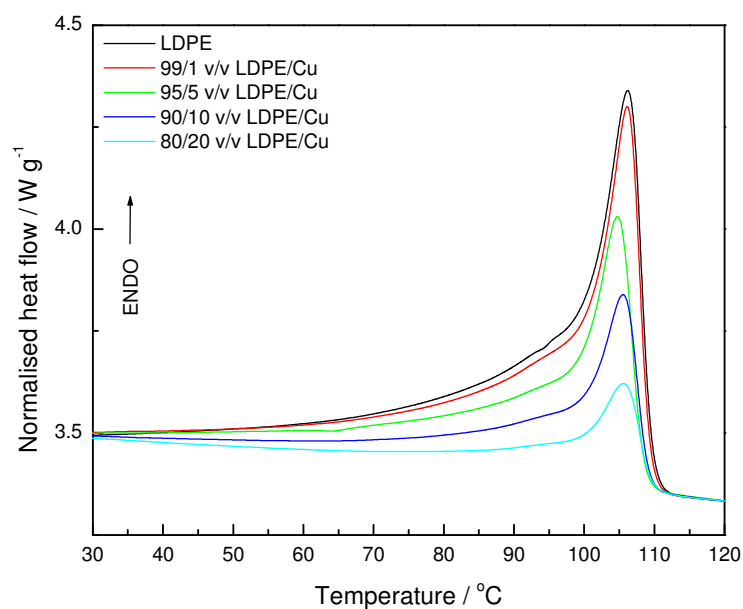


Figure 4.4 DSC heating curves of LDPE and LDPE/Cu micro-composites

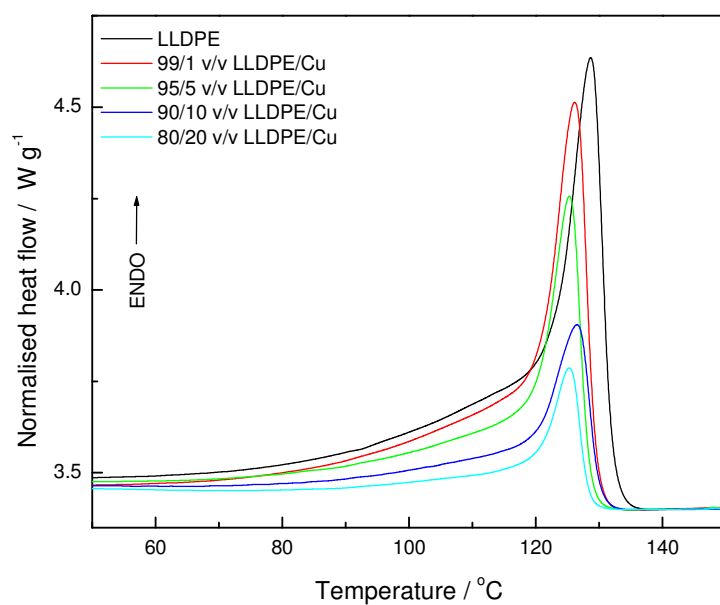


Figure 4.5 DSC heating curves of LLDPE and LLDPE/Cu microcomposites

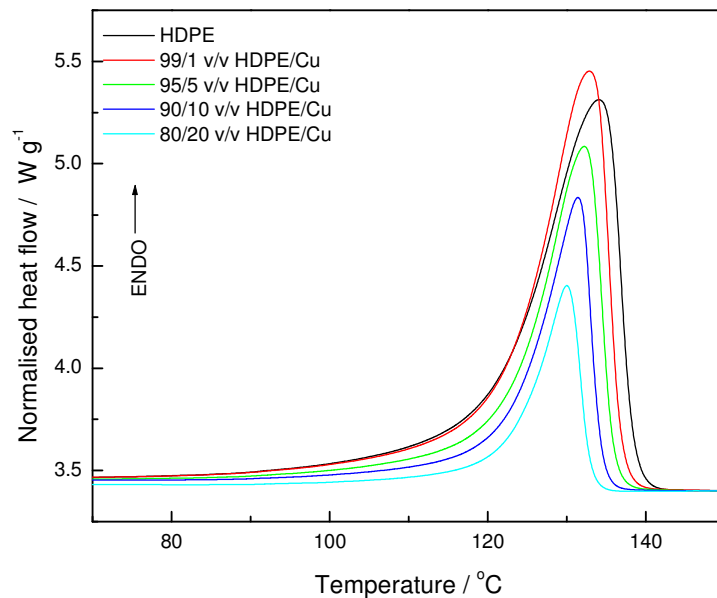


Figure 4.6 DSC heating curves of HDPE and HDPE/Cu micro-composites

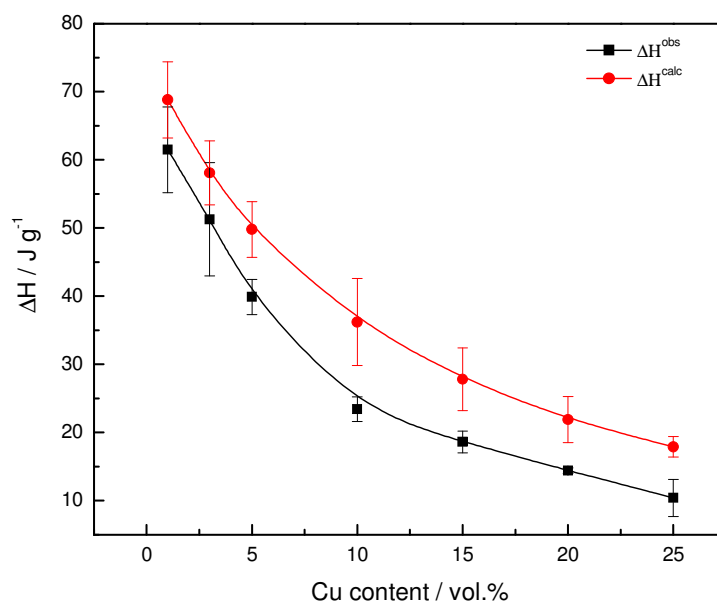


Figure 4.7 Comparison of observed and calculated melting enthalpies of LDPE and LDPE/Cu micro-composites

A slight decrease in the melting temperature of LLDPE with an increase in Cu content is observed for the LLDPE/Cu micro-composites. It seems as if the presence of Cu slightly reduces the LLDPE chain mobility which gives rise to smaller crystallites and a lower crystallinity. The latter is clear from a comparison of the ΔH_m^{obs} and ΔH_m^{calc} values in Table 4.1 and Fig. 4.8. In the case of the HDPE/Cu micro-composites, a more observable decrease in the melting temperature of the composites with an increase in Cu content is observed. It seems as if the influence of Cu micro-particles on the crystallite size of polyethylene becomes more significant with decreasing branching and increasing crystallinity of the polymer. Another reason may be that the presence of highly thermally conductive Cu causes a faster heat distribution through the polymer, which will result in a lower melting temperature. Table 4.1 and Fig. 4.9 show that the ΔH_m^{obs} and ΔH_m^{calc} values are almost the same for all the HDPE/Cu micro-composites, and therefore the presence and amount of Cu had very little influence on the HDPE crystallization behaviour.

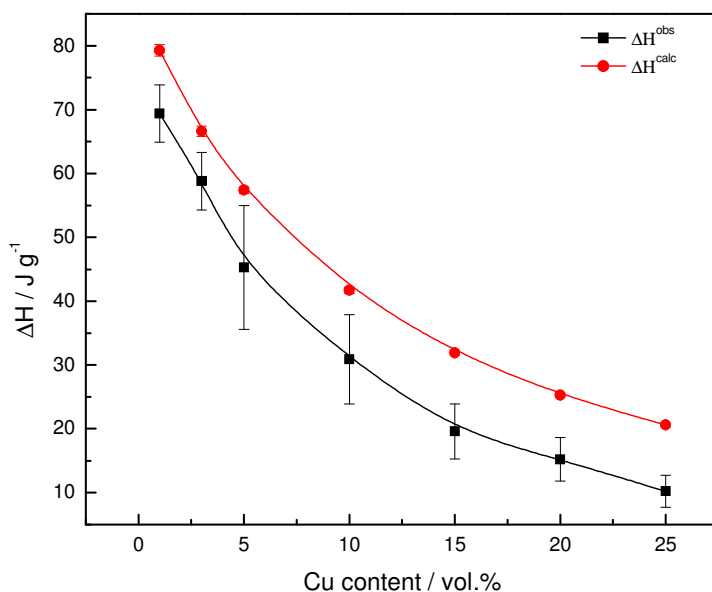


Figure 4.8 Comparison of observed and calculated melting enthalpies of LLDPE and LLDPE/Cu micro-composites

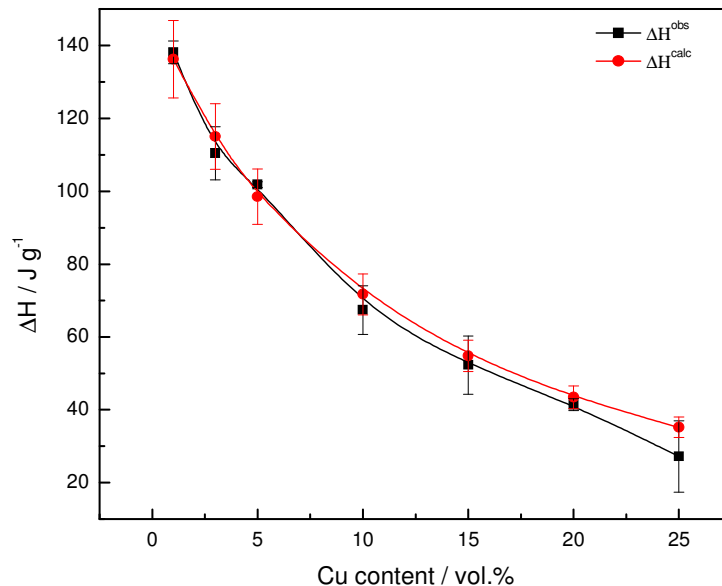


Figure 4.9 Comparison of observed and calculated melting enthalpies of HDPE and HDPE/Cu micro-composites

The observations described in the previous paragraphs may be explained if it is accepted that the Cu particles will either reduce polymer chain mobility (giving rise to reduced crystallinity) or act as nucleation points for polymer crystallization (giving rise to increased crystallinity). It seems as if the chain structure (and the resultant degree of crystallinity) of the polymer determines which of the two effects will be dominant. Since LDPE and LLDPE are branched, and therefore have significantly lower crystallinities than HDPE, which confirms that the Cu particles are located in the amorphous regions of the polymers. Chain immobilization will then be the more dominant effect, and therefore these polymers show reduced crystallinity in the presence of Cu micro-particles. Since HDPE is much more crystalline, the amorphous regions are much smaller and it is possible that crystallization will start at the Cu surfaces and that Cu particles will act as nucleation points for HDPE crystallization. This explains the slight lowering in HDPE melting temperature (indicating the presence of smaller crystallites). This is consistent with a study done by Xia *et al.* [1]. When they added 13 wt. % of Cu micro-particles into an LDPE matrix, the melting peak temperatures of pure LDPE and the LDPE/Cu micro-composites were the same within experimental error. Pure LDPE had a melting enthalpy of 87.8 J g^{-1} which reduced to 76.2 J g^{-1} when 13 wt. % of Cu micro-particles was

introduced, and the crystallization temperature increased for the same composition. The increased crystallization temperature was explained as being due to the presence of the Cu micro-particles, which acted as nucleating agents. However, the Cu particles at the same time seemed to have immobilized the LDPE chains, giving rise to reduced crystallinity, as can be seen from the smaller melting enthalpy values.

The observations from the cooling curves are in line with those from the heating curves, and the figures are presented in the appendix (Figs. A1-A3).

4.2.7 Polyethylenes filled with copper nano-particles

Figs. 4.10-4.12 show the DSC heating curves of the different polyethylenes and their Cu nano-composites. For the LDPE/Cu nano-composites the peak temperatures of melting did not significantly change and are within experimental error. From this it is clear that the presence of up to 5 vol. % of Cu nano-particles in LDPE had a negligible influence on the crystallite sizes. On the other hand, if the enthalpy values in Table 4.2 are compared, it is clear that the presence of the Cu nano-particles restricts the LDPE chain mobility which leads to a lower crystallinity. When the observed melting enthalpy values (ΔH_m^{obs}) are compared with the calculated values (ΔH_m^{calc}), it can be seen that the LDPE in the composites had significantly lower enthalpy (or crystallinity) values than would be expected if it was assumed that the Cu nano-particles had no influence on the LDPE crystallization behaviour.

Similarly, the copper nano-particles in the LLDPE/Cu and HDPE/Cu nano-composites had no significant influence on the melting peak temperatures of the respective polyethylenes. The observed melting enthalpies of these polyethylene composites were also lower than the calculated values. However, the differences between the observed and calculated values seem to decrease with increasing crystallinity from LDPE to LLDPE to HDPE. Since LDPE and LLDPE are branched, and therefore have lower crystallinities than HDPE, the Cu particles are situated in the amorphous regions of these polymers. Chain immobilization will then be the more dominant effect. Since HDPE is much more crystalline, the amorphous regions are much smaller and therefore the decrease in total crystallinity is less significant.

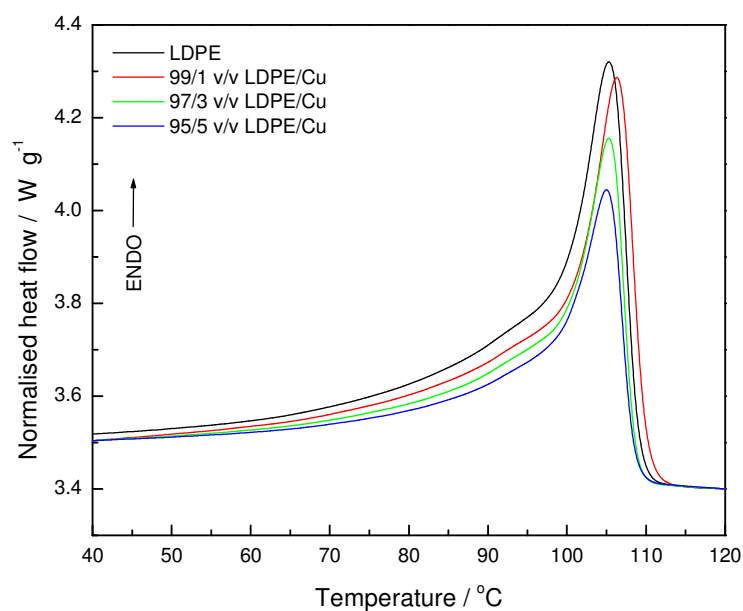


Figure 4.10 DSC heating curves of LDPE and LDPE/Cu nano-composites

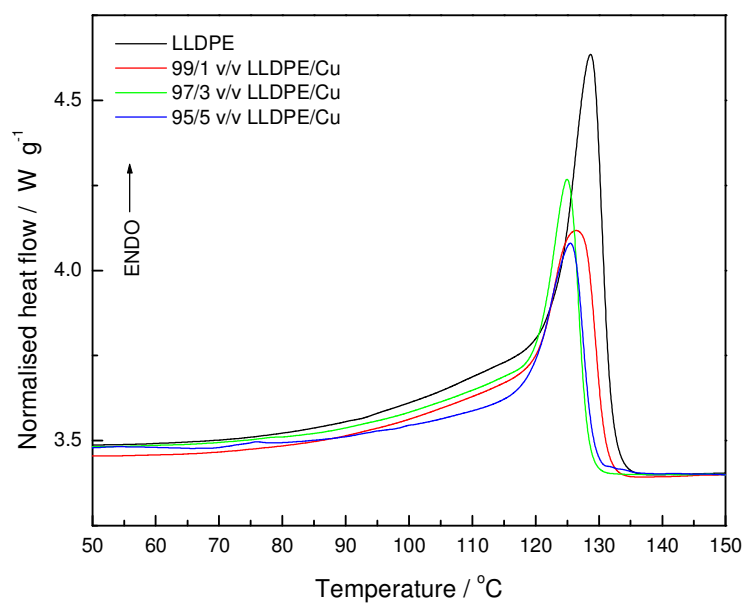


Figure 4.11 DSC heating curves of LLDPE and LLDPE/Cu nano-composites

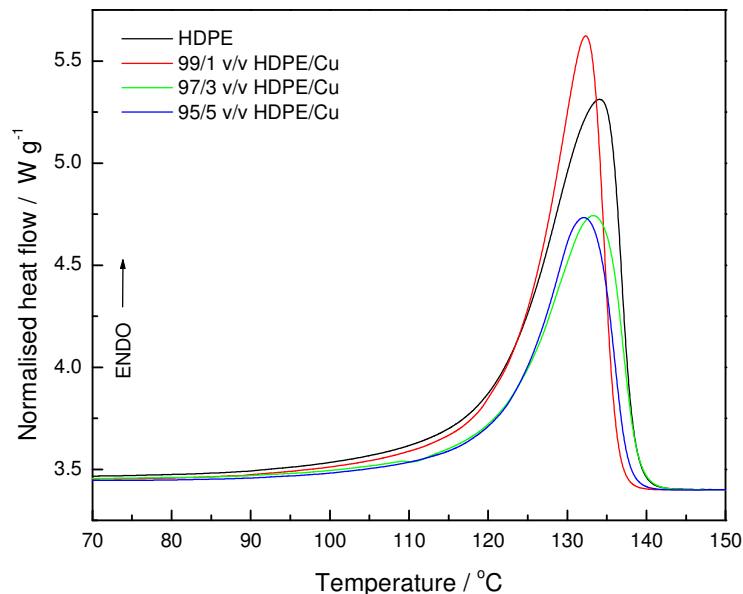


Figure 4.12 DSC heating curves of HDPE and HDPE/Cu nano-composites

Xia *et al.* [1] showed that the introduction of 13 wt. % of Cu nano-particles into an LDPE matrix decreased the melting peak temperature and crystallinity of the nano-composites. The decreased crystallinity was due to the Cu nano-particles hindering the motion of the polymer chain segments and slowing down crystal growth. In contrast the crystallization temperature was increased at the same Cu nano-particle content. This was explained as being due to the presence of Cu nano-particle aggregates, which acted as nucleating agents. Xiao *et al.* [2] investigated the independent effect of different crystallization conditions (rapid and slow crystallization) on LDPE/TiO₂ and LDPE/*N*-(2-aminoethyl)-3-aminopropyl-trimethoxysilane (AEAPS) nano-composites. When TiO₂ and AEAPS were incorporated into LDPE, all the DSC results displayed similar melting temperatures. This indicated that the addition of TiO₂ nano-particles did not significantly change the lamellar thickness. When comparing the two crystallization conditions, the DSC curves of the rapidly crystallized samples were broader than those of the slowly crystallized ones. This was seen as an indication that more defective crystals are formed under rapid crystallization conditions. They suggested that the presence of nano-particles inhibited the spherulitic organization of the LDPE crystals under rapid crystallization conditions. In this study cooling occurred at a rate of 10 °C min⁻¹, which is

fairly slow. Even so, the presence of the nano-particles caused a observable decrease in total crystallinity of LDPE.

The observations from the DSC cooling curves correspond to those from the heating curves, and the cooling curves are presented in the appendix (Figs. A4-A6).

Table 4.2 DSC results for polyethylene/Cu nano-composites

v/v	$T_{p,m} / ^\circ\text{C}$	$\Delta H_m^{\text{obs}} / \text{J g}^{-1}$	$\Delta H_m^{\text{calc}} / \text{J g}^{-1}$	$T_{p,c} / ^\circ\text{C}$	$\Delta H_c^{\text{obs}} / \text{J g}^{-1}$
LDPE/Cu					
100/0	106.8 ± 1.5	75.4 ± 6.2	-	91.7 ± 0.6	-63.7 ± 7.6
99/1	105.9 ± 0.3	49.4 ± 2.3	68.8 ± 5.6	90.8 ± 0.1	-54.3 ± 1.9
97/3	105.7 ± 0.1	38.8 ± 0.9	58.1 ± 4.7	91.7 ± 0.3	-48.3 ± 0.8
95/5	105.3 ± 0.1	35.5 ± 1.9	49.8 ± 4.1	91.9 ± 0.1	-41.5 ± 0.6
LLDPE/Cu					
100/0	126.7 ± 2.1	86.9 ± 1.0	-	109.6 ± 0.9	-50.1 ± 0.8
99/1	126.9 ± 0.4	62.6 ± 1.4	79.3 ± 0.9	109.3 ± 0.1	-47.0 ± 4.0
97/3	125.6 ± 0.2	56.6 ± 2.3	66.6 ± 0.8	110.7 ± 0.1	-38.3 ± 2.1
95/5	126.0 ± 0.1	43.9 ± 0.7	57.4 ± 0.6	111.7 ± 0.1	-31.0 ± 2.7
HDPE/Cu					
100/0	134.7 ± 0.5	149.3 ± 9.7	-	113.9 ± 1.1	-134.8 ± 2.6
99/1	133.2 ± 0.2	132.1 ± 2.5	136.2 ± 10.6	113.8 ± 0.2	-126.2 ± 2.2
97/3	133.1 ± 0.1	106.8 ± 1.5	115.0 ± 9.0	113.9 ± 0.3	-109.5 ± 3.2
95/5	134.4 ± 1.0	82.9 ± 0.8	98.5 ± 7.6	114.7 ± 0.3	-90.0 ± 1.6

$T_{p,m}$, ΔH_m^{obs} , ΔH_m^{calc} , $T_{p,c}$ are melting peak temperature, observed melting enthalpy, calculated melting enthalpy, and crystallization peak temperature

4.2.8 Comparison of the melting and crystallization behaviour of the PE/Cu micro- and nano-composites

Tables 4.1 and 4.2 show that both micro- and nano-particles did not significantly influence the LDPE melting temperature, and therefore had a negligible influence on the crystallite sizes. Fig. 4.13 shows the experimental melting enthalpies as function of Cu content for LDPE/Cu nano- and micro-composites. It can be seen that the experimental melting enthalpies of the

LDPE/Cu micro-particles are higher than those of LDPE/Cu nano-composites at the same volume percentages of copper. This clearly shows that the crystallinities of the LDPE/Cu nano-composites are observably lower than those of the LDPE/Cu micro-composites, indicating that Cu nano-particles had a stronger influence on the motion and nucleation of the polymer chain segments. This behaviour indicates that the Cu nano-particles restricted the polymer chain mobility to a larger extent than the Cu micro-particles, probably because the Cu micro-particles counteract this effect through their ability to act as nucleating agents that promote the crystallization process of LDPE.

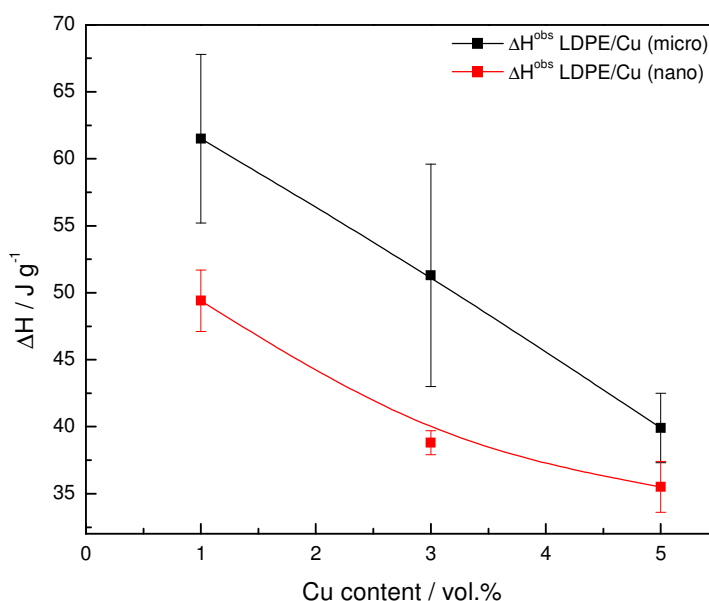


Figure 4.13 Comparison of ΔH^{obs} for the melting of LDPE in LDPE/Cu micro- and nano-composites

It seems as if the influence of Cu micro-particles on the crystallite size of polyethylene becomes more significant with decreasing branching and increasing crystallinity of the polymer. Tracz *et al.* [3] found that the nucleating and ordering effects of fillers on polyethylene crystallization depend to a larger extent on the nano-structure of its surface. Nano-particles do not have any nucleating effect, but they act as obstacles for the crystallization of polyethylene. Even though some nano-particle agglomerates may nucleate PE crystallization, the overall influence of the nano-particles on the crystallization of LDPE can be considered to be a retardant effect. Therefore, the degree of crystallinity of LDPE in

the nano-composites is lower than that of pure LDPE. Micro-particles can nucleate PE crystallization, because they can provide sufficiently large flat domains. However, the sizes of the micro-particles are comparable to the spherulite size of LDPE, and thus the micro-particles also hinder spherulite growth, so that the degree of crystallinity of LDPE in the presence of micro-particles is not significantly higher than that of the pure LDPE. Huang *et al.* [4] found that the addition of 2 and 4% of Al nano-particles can either facilitate or hinder the crystallization of LDPE, depending on the dispersion of the nano-particles in the polymer. The well-dispersed Al nano-particles did not have a nucleating effect and mainly acted as obstacles, but the agglomerates of Al nano-particles acted as nucleating agents and slightly improved the crystallization. The micro-particles had a nucleating effect and facilitated the crystallization process. These observations and explanations are in line with the results of this study, although here the presence of Cu micro-particles was found to reduce the total LDPE crystallinity, but to a smaller extent than the Cu nano-particles. In LDPE/Al micro- and nano-composites and in LDPE/TiO₂ nano-composites the melting behaviour indicated that the lamellar thickness distribution of both nano- and micro-composites did not significantly change compared to that of pure LDPE [3,4].

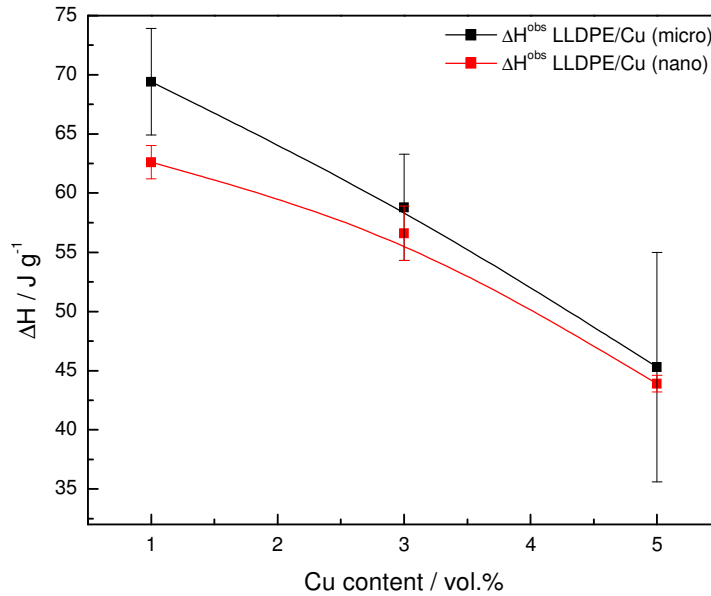


Figure 4.14 Comparison of ΔH^{obs} for the melting of LLDPE in LLDPE/Cu micro- and nano-composites

The Cu nano- and micro-particles in the LLDPE/Cu and HDPE/Cu composites did also not show a significant influence on the melting peak temperatures, and therefore they had a negligible influence on the crystallite sizes. The measured enthalpy values of the LLDPE/Cu and HDPE/Cu nano-composites are also lower than those of the micro-composites, and the differences are more significant (Figs. 4.14 and 4.15). This is probably the result of higher restriction of polymer chain mobility, because of much the higher surface areas of the nanoparticles. Another reason may be the fact that the distances between the adjacent nanoparticles are much smaller than between the micro-particles, which can also restrict movement and folding of the polymeric chains between the particles. Although the Cu nano-particles may have restricted the polymer chain mobility more effectively than the Cu micro-particles, the Cu nano-particle agglomerates may have counteracted this effect because of its ability to act as nucleating agents that promotes the crystallization process of the polyethylenes.

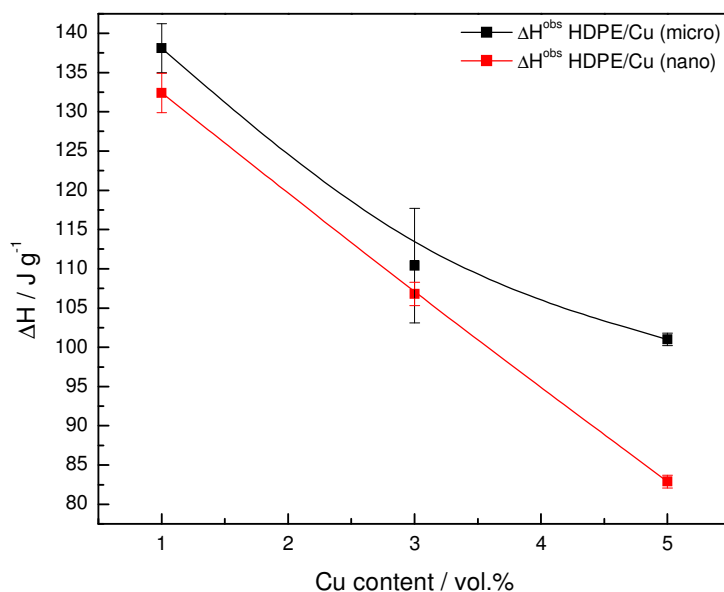


Figure 4.15 Comparison of ΔH^{obs} for the melting of HDPE in HDPE/Cu micro- and nano-composites

4.2.9 Polyethylene/wax blends

The DSC heating curves obtained for the different PEs and the wax are presented in Fig. 4.16, while those for the different PE/wax blends are shown in Figures 4.17 - 4.19. The melting peak temperatures, as well as melting and crystallization enthalpies are summarized in Table 4.3. The wax shows a melting peak at 58 °C, with a peak shoulder at 33 °C. The DSC heating curves of the LDPE/wax blends show two clearly defined endothermic events. The first event between 30 and 70 °C consists of a peak shoulder at about 33 °C and two overlapping peaks between 45 and 70 °C. The first event is in the same temperature region as the melting peak of pure wax, but its shape is different. When the wax content in the blend is lower, the peaks between 45 and 70 °C shows clearly defined peak maxima. However, at higher wax contents, the lower temperature peak becomes more dominant, reducing the higher temperature peak to a peak shoulder. This indicates that the shorter LDPE chains and/or branches probably co-crystallized with the wax, but that this effect becomes less pronounced with increasing wax content. The melting enthalpy values of the LDPE/wax blends are the same within experimental error than those calculated using the additive rule in Equation 4.1. This confirms that there was no wax leakage from the LDPE matrix, which is a good observation for shape-stabilized phase change materials. The explanation of the DSC results in terms of co-crystallization of LDPE/wax blends, at low wax contents, is in line with that given by Hato and Luyt [5]. They envisaged co-crystallization of LDPE with both un-oxidized and oxidized hard paraffin wax in their study of the thermal fractionation of PE/wax blends. The second thermal event in Fig. 4.17 is associated with the melting of LDPE crystallites. The melting peak temperatures of LDPE in the blends are significantly lower than that of pure LDPE (Table 4.3 and Fig. 4.17), and the temperatures further decrease with increasing wax content. This behaviour is probably the result of the molten wax which acts as a plasticizer in the LDPE matrix.

$$\Delta H_m^{add} = \Delta H_{m,PE} w_{PE} + \Delta H_{m,w} w_w \quad (4.1)$$

where $\Delta H_{m,PE}$, $\Delta H_{m,w}$, ΔH_m^{add} are the specific enthalpies of melting of PE, wax and blends, and w_{PE} , w_w are the weight fractions of PE and wax in the blends.

Table 4.3 DSC results for polyethylene/wax blends

v/v	T _{p,m} / °C	ΔH _m ^{obs} / J g ⁻¹	ΔH _m ^{add} / J g ⁻¹	T _{p,c} / °C
LDPE/wax				
100/0	106.8 ± 1.5	75.4 ± 6.2	75.4	91.7 ± 0.6
70/30	58.2 ^a ± 5.0 59.7 ^b ± 1.2 100.4 ^c ± 2.8	104.7 ± 3.7	104.4	55.6 ^a ± 0.9 87.4 ^b ± 0.9
60/40	55.5 ^a ± 0.7 96.9 ^b ± 3.2	114.0 ± 10.9	113.6	55.8 ^a ± 0.2 87.8 ^b ± 1.8
50/50	55.0 ^a ± 0.6 97.6 ^b ± 2.1	111.0 ± 8.6	106.3	56.0 ^a ± 0.6 86.0 ^b ± 0.5
0/100	58.4 ^a ± 1.2	172.2 ± 0.1	172.2	53.1 ± 0.4
LLDPE/wax				
100/0	126.7 ± 2.1	86.9 ± 1.0	86.9	109.6 ± 0.9
70/30	57.3 ^a ± 1.6 121.8 ^b ± 0.9	108.5 ± 10.3	111.7	53.2 ^a ± 0.9 105.7 ^b ± 0.9
60/40	54.5 ^a ± 1.1 119.8 ^b ± 1.1	104.9 ± 15	120.6	49.8 ^a ± 0.7 105.2 ^b ± 1.1
50/50	57.2 ^a ± 0.6 120.8 ^b ± 1.1	130.3 ± 8.2	130.0	49.8 ^a ± 0.9 103.8 ^b ± 0.6
0/100	58.4 ^a ± 1.2	172.2 ± 0.1	172.2	53.1 ± 0.4
HDPE/wax				
100/0	134.7 ± 0.5	149.3 ± 9.7	149.3	113.9 ± 1.1
70/30	56.1 ^a ± 0.1 124.6 ^b ± 1.8	150.9 ± 15	156.2	51.1 ^a ± 0.1 110.2 ^b ± 1.8
60/40	56.4 ^a ± 0.4 124.1 ^b ± 2.3	153.2 ± 9.9	158.5	51.1 ^a ± 0.6 110.2 ^b ± 0.4
50/50	57.1 ^a ± 0.1 124.1 ^b ± 0.3	148.4 ± 8.9	160.8	50.8 ^a ± 0.9 109.6 ^b ± 1.1
0/100	58.4 ^a ± 1.2	172.2 ± 0.1	172.2	53.1 ± 0.4

T_{p,m}, ΔH_m^{obs}, ΔH_m^{calc}, T_{p,c} are melting peak temperature, observed melting enthalpy, calculated melting enthalpy, and crystallization peak temperature, while a and b indicate the first and second peak maxima in the wax melting peak

The results of the DSC analyses of LLDPE/wax blends are summarized in Table 4.3 and presented in Fig. 4.18. The DSC heating curve of pure wax shows a melting peak at 58 °C, with a peak shoulder at 33 °C. The DSC heating curves of the blends show two clearly defined endothermic events. The first event consists of a peak shoulder at about 33 °C and a single peak at about 58 °C. The second event is associated with the melting of LLDPE crystallites. The melting peak temperatures of LLDPE in the blends are lower than that of pure LLDPE (Table 4.3 and Fig. 4.18), and the temperatures further decrease with increasing wax content. This behaviour is probably the result of the molten wax which acts as a

plasticizer in the LLDPE matrix. Looking at Figs. 4.17 and 4.18 it seems as if there are smaller decreases in the melting temperatures of LLDPE than in the case of LDPE. The reason is most probably that the paraffin wax, which has been found to have a much lower miscibility with LDPE than with LLDPE [5-7], probably crystallizes separately in the amorphous phase of LDPE, while part of the wax may co-crystallize with the LLDPE chains. The wax that crystallizes separately will melt before the polyethylene, and the molten wax will act as a plasticizer. However, the wax that is co-crystallized with the polyethylene chains will melt at the same temperature as the polyethylene, and can therefore not contribute to the plasticizing effect of the wax. Since the wax probably has a higher miscibility (more co-crystallization) with LLDPE than with LDPE, there will be less crystalline wax in the amorphous regions of LLDPE and therefore the plasticizing effect and reduction in melting temperature of the polymer will be less obvious.

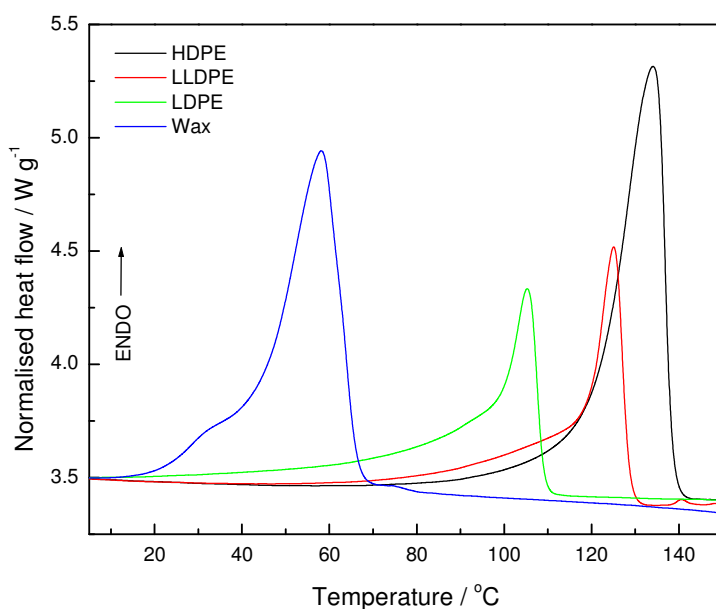


Figure 4.16 DSC heating curves of pure polyolefins and pure wax

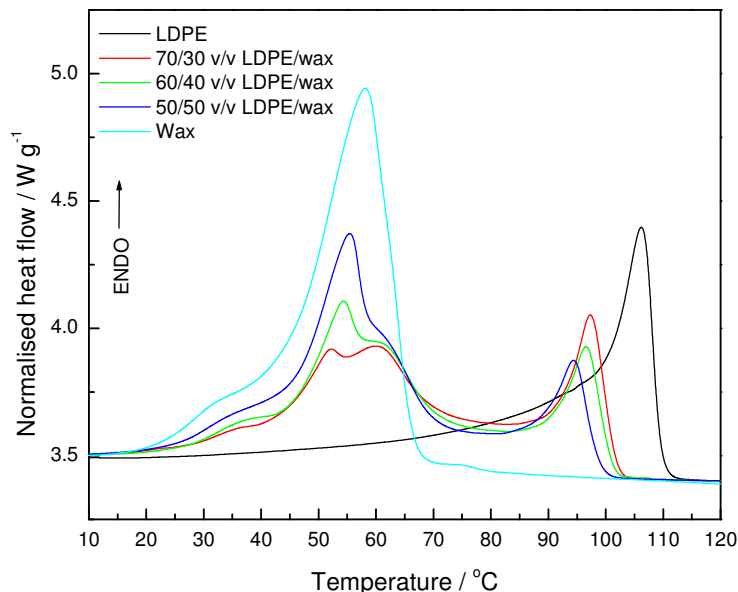


Figure 4.17 DSC heating curves of LDPE, wax and LDPE/wax blends

The melting peak temperatures, as well as the melting and crystallization enthalpies of the HDPE/wax blends are shown in Fig. 4.18 and summarized in Table 4.3. The curve for pure wax is the same than previously discussed. The DSC heating curves of the HDPE/wax blends show two clearly defined endothermic events. The first event consists of a peak shoulder at about 33 °C, and a single peak at about 58 °C. The second event is associated with the melting of the HDPE crystallites. In this case the decrease in melting peak temperature is higher than in the case of LDPE and LLDPE. According to Hato and Luyt [5] paraffin wax has the lowest miscibility with HDPE, and it will therefore have the strongest influence on the melting temperature of the polymer (see explanation above Table 4.3). As in the case of LDPE and LLDPE the observed and calculated (according to Eq. 4.1) melting enthalpies are the same within experimental error, indicating that no wax leakage occurred during sample preparation. Another possibility in case of LDPE might be that ethylene crystallization is disrupted by the wax which is less miscible and therefore forms a more segregated morphology with the wax dispersed in the polymer matrix.

The observations from the DSC cooling curves correspond to those from the heating curves, and the cooling curves are presented in the appendix (Figs. A.7-A.9).

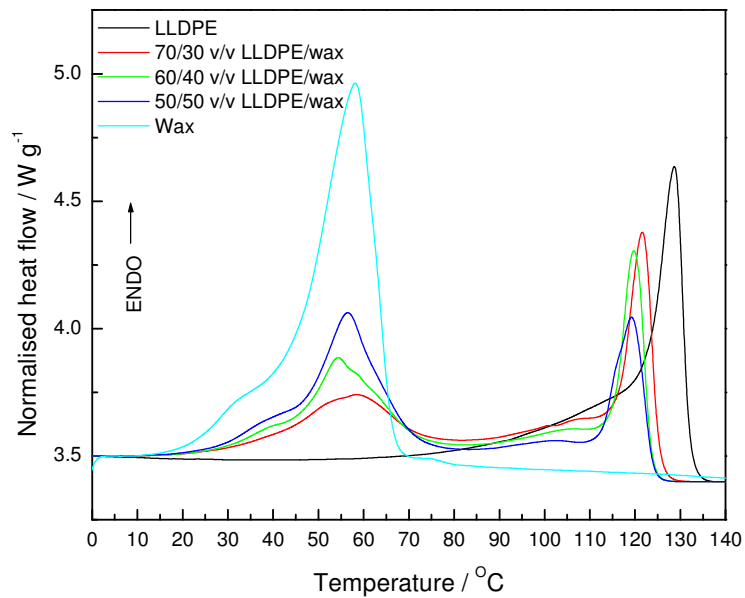


Figure 4.18 DSC heating curves of LLDPE, wax and LLDPE/wax blends

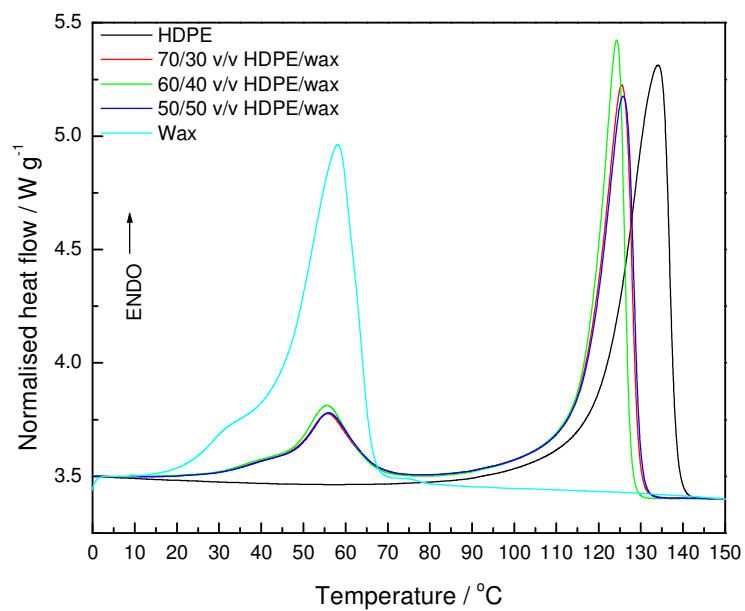


Figure 4.19 DSC heating curves of HDPE, wax and HDPE/wax blends

4.2.5 Polyethylene/wax/Cu micro-composites

The DSC heating curves of the PE/wax/Cu micro-composites are presented in Figs. 4.20 - 4.22. The peak temperatures, as well as the melting and crystallization enthalpies are summarized in Table 4.4. Table 4.4 also contains the enthalpies calculated according to the additive rule (Eq. 4.1). Inspection of the figures, as well as the tabulated values, show that the presence of Cu micro-particles did not significantly change the thermal behaviour of the PE/wax blends, despite the fact that the wax seems to have a higher affinity for the copper and preferably crystallizes on the copper surface (see discussion of SEM results in section 4.1). The melting temperatures for the wax as well as all three polymers show the same changes that were observed for the blends in the absence of copper, while the melting enthalpies in all cases correspond well with those calculated according to the additive rule. The observations from the DSC cooling curves correspond to those from the heating curves, and the cooling curves are presented in the appendix (Figs. A.10-A.12).

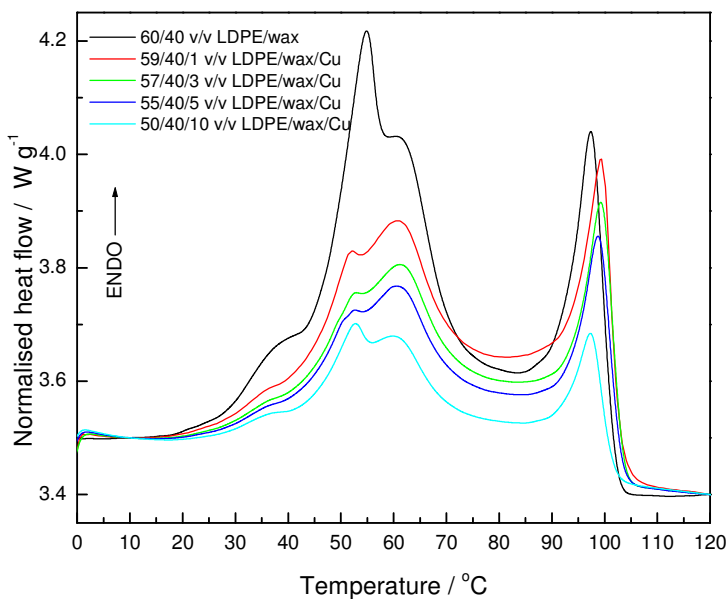


Figure 4.20 DSC heating curves of LDPE, wax and LDPE/wax/Cu micro-composites

Table 4.4 DSC results for polyethylene/wax/Cu micro-composites

v/v	T _{p,m} / °C	ΔH _m ^{obs} / J g ⁻¹	ΔH _m ^{add} / J g ⁻¹	T _{p,c} / °C
LDPE/wax/Cu				
100/0/0	106.8 ± 1.5	75.4 ± 6.2	75.4	91.7 ± 0.6
59/40/1	58.1 ^a ± 5.4 99.9 ^b ± 1.2	104.7 ± 6.8	104.0	55.6 ^a ± 0.9 87.4 ^b ± 0.9
57/40/3	61.3 ^a ± 0.9 100.6 ^b ± 1.1	87.8 ± 3.4	88.0	55.8 ^a ± 0.2 87.8 ^b ± 1.8
55/40/5	60.6 ^s ± 1.6 99.3 ^b ± 0.9	68.2 ± 9.0	79.3	56.0 ^a ± 0.6 86.0 ^b ± 0.5
50/40/10	53.2 ^a ± 1.6 98.4 ^b ± 1.6	48.3 ± 4.0	56.5	53.8 ^a ± 3.5 86.1 ^b ± 0.5
0/100/0	58.4 ^a ± 1.2	172.2 ± 0.1	172.2	53.1 ± 0.4
LLDPE/wax/Cu				
100/0/0	126.7 ± 2.1	86.9 ± 1.0	86.9	109.6 ± 0.9
59/40/1	54.9 ^a ± 1.6 120.4 ^b ± 1.8	113.5 ± 6.6	109.5	49.8 ^a ± 0.5 105.5 ^b ± 0.8
57/40/3	54.7 ^a ± 1.4 120.6 ^b ± 1.9	89.5 ± 10.4	92.5	49.8 ^a ± 0.6 105.7 ^b ± 0.8
55/40/5	54.6 ^a ± 1.6 119.9 ^b ± 1.6	74.3 ± 9.5	80.4	50.1 ^a ± 0.5 105.8 ^b ± 0.8
50/40/10	55.1 ^a ± 1.6 120.0 ^b ± 2.2	49.5 ± 12.0	59.6	50.1 ^a ± 0.5 106.0 ^b ± 1.0
0/100/0	58.4 ^a ± 1.2	172.2 ± 0.1	172.2	53.1 ± 0.4
HDPE/wax/Cu				
100/0/0	134.7 ± 0.5	149.3 ± 9.7	149.3	113.9 ± 1.1
59/40/1	56.5 ^a ± 0.6 123.8 ^b ± 0.7	150.0 ± 3.5	148.2	51.8 ^a ± 1.1 109.2 ^b ± 0.4
57/40/3	56.5 ^a ± 0.4 122.8 ^b ± 0.4	113.7 ± 5.0	122.2	51.9 ^a ± 0.6 109.7 ^b ± 0.4
55/40/5	56.9 ^a ± 0.4 123.5 ^b ± 0.2	91.7 ± 14.8	100.6	51.9 ^a ± 0.6 110.1 ^b ± 0.4
50/40/10	56.8 ^a ± 0.1 122.8 ^b ± 1.0	77.1 ± 5.7	78.0	51.7 ^a ± 0.1 110.1 ^b ± 0.3
0/100/0	58.4 ^a ± 1.2	172.2 ± 0.1	172.2	53.1 ± 0.4

T_{p,m}, ΔH_m^{obs}, ΔH_m^{calc}, T_{p,c} are melting peak temperature, observed melting enthalpy, calculated melting enthalpy, and crystallization peak temperature, while a and b indicate the first and second peak maxima in the wax melting peak

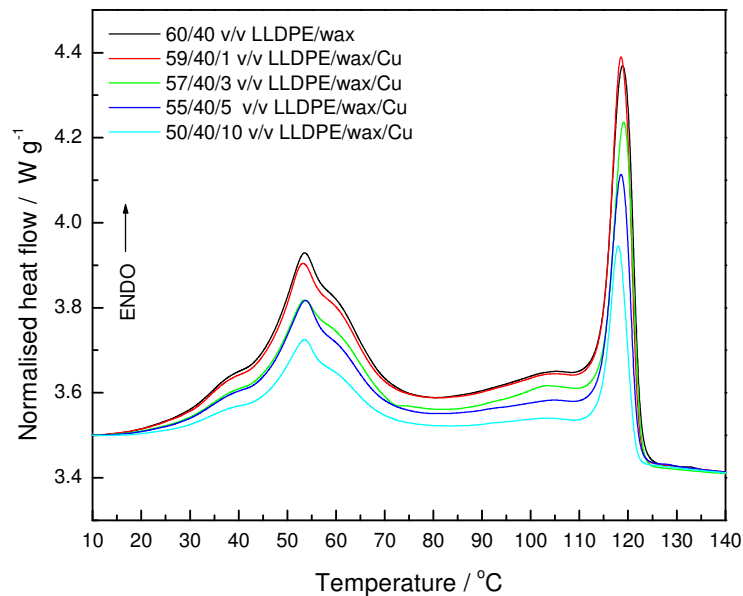


Figure 4.21 DSC heating curves of LLDPE, wax and LLDPE/wax/Cu micro-composites

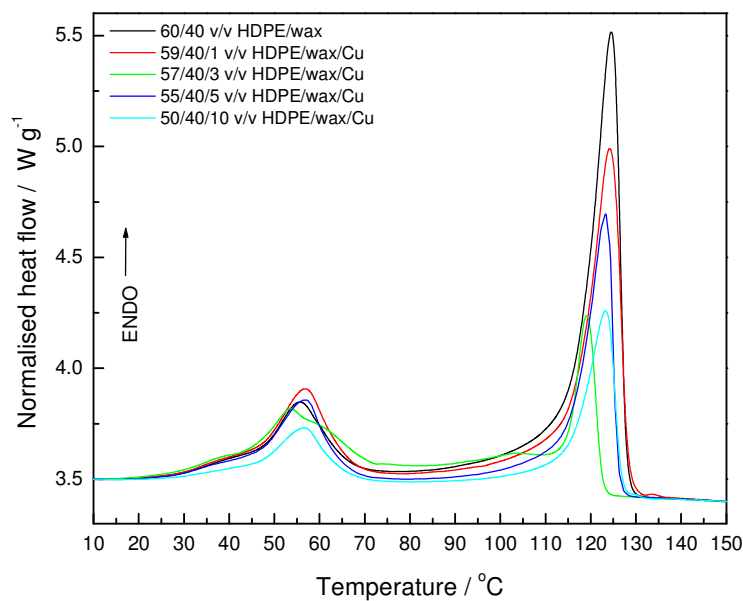


Figure 4.22 DSC heating curves of HDPE, wax and HDPE/wax/Cu micro-composites

4.3. Thermogravimetric analysis (TGA)

4.3.2 Polyethylenes

The thermal stability was characterized in terms of the temperatures at 10% of mass loss as well as the temperatures of the maximum mass loss rate (peak temperature in derivative TGA). The results are summarized in Table 4.5. The thermograms of pure LDPE, LLDPE and HDPE obtained under the nitrogen atmosphere, are shown in Figure 4.23. It can be seen that HDPE has the highest thermal stability followed by LLDPE and then LDPE. This is probably attributed to their difference in crystallinities, since HDPE has the highest crystallinity followed by LLDPE and LDPE. Linear chain polymers also seem to decompose with more difficulty than the branched chain ones, and the apparent activation energies for the thermal degradation of HDPE, LLDPE and LDPE were calculated to be 333-343, 219-230 and 188-199 kJ mol⁻¹ respectively [8]. Apparently decomposition by removal of side branches accelerates the overall degradation process [9].

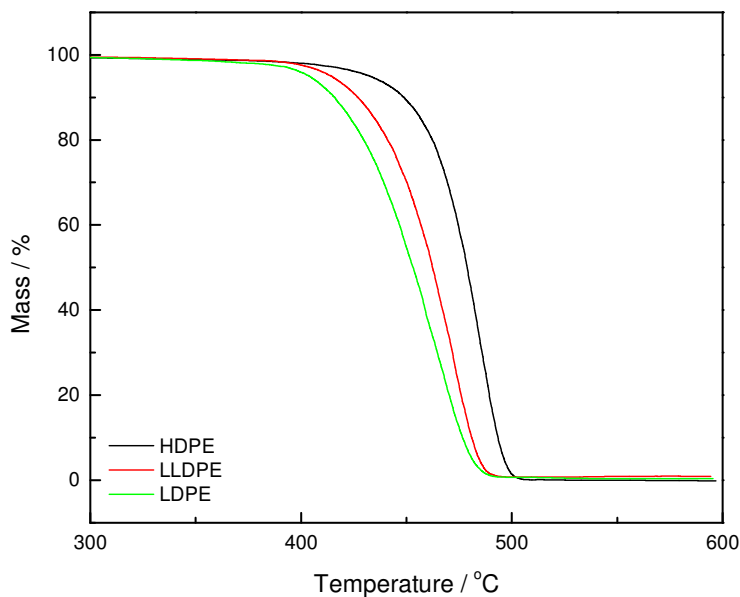


Figure 4.23 TGA curves of pure LDPE, LLDPE and HDPE

4.3.2 Polyethylenes filled with copper micro-particles

The TGA curves of PE/Cu micro-composites are presented in Figs. 4.24 to 4.26 and the corresponding data are summarized in Table 4.5. Figure 4.24 shows the TGA curves of pure LDPE and the influence of different Cu micro-particle contents on the thermal stabilities of the composites. There is a non-linear increase in thermal stability with an increase in Cu micro-particle content up to 20 vol. %. This is may be due to the inability of the polymer chains to move freely because of the presence of Cu micro-particles, which will retard the movement of free radical chains and inhibit the degradation process. Another reason may be that the diffusion of the volatile degradation products may be retarded by the presence of the copper particles, which will lead to these products only coming off at higher temperatures. In other studies [1,10] it was also found that an increase in conductive filler content enhances the thermal stability of LDPE. Krump *et al.* [10] found that the thermal stability of LDPE/Cu micro-composites increased with an increase in Cu micro-particle content. Xia *et al.* [1] showed that the optimum thermal stability was reached after addition of 6 wt. % Cu, but at higher Cu contents the thermal stability remained constant. Omastová *et al.* [11] showed that carbon black (CB) and modified CB in an LDPE matrix improved the thermal stability of the filled composites, with modified CB having a more significant effect.

The TGA curves of LLDPE and its Cu micro-composites are shown in Figure 4.25, and the TGA results are summarized in Table 4.5. The thermal stability improves with an increase in Cu micro-particles up to 1-3 vol. % Cu, and the temperature at maximum decomposition rate increases for 1 vol. % Cu, after which it decreases. This is in line with the observations by Xia *et al.* [1], but differs from the observations on the LDPE/Cu composites, probably because of the higher crystallinity of LLDPE which results in more intimate contact between the Cu and the LLDPE crystals (especially at higher Cu contents). The higher heat capacity and thermal conductivity of copper then causes more effective heat transfer to the LLDPE crystals.

The TGA curves of HDPE and its Cu micro-composites are shown in Figure 4.26, and the TGA results are summarized in Table 4.5. In this case there is no clear trend for the influence of Cu content on the thermal stability of HDPE and it seems that, within an observable experimental error, the Cu micro-particles did not significantly influence the thermal stability of HDPE. This is probably the result of a balance between thermal stability enhancement and thermal degradation initiation effects by the copper particles. The higher thermal conductivity

of the metallic Cu particles may override its stiffening effect. Since HDPE is highly crystalline and inherently less thermally conductive, the transfer of heat through the entire sample is delayed. When the Cu content is above 10 vol. %, there may be a strong interconnection between the Cu particles, resulting in increased thermal stability. This may also be attributed to the hindered polymer chain mobility enforced by the Cu micro-particles.

In all of these polyethylenes filled with Cu micro-particles, the shift towards higher temperature is in the order of their polymer chain regularity. There is an increase in residue with increasing Cu content for all the investigated samples, and these values are in line with the initial wt.% Cu mixed into the samples (Table 4.5). This indicates that the presence of Cu did not cause any char formation.

Table 4.5 **Temperatures of 10% degradation and DTG peak temperatures, as well as wt. % of residue, of PE/Cu micro-composites**

v/v	T ₁₀ / °C	T _{peak} / °C	Wt. % residue	Wt.% Cu in sample
LDPE/Cu				
100/0	443.3	485.5	-	
99/1	449.7	487.6	7.3	8.8
95/5	454.3	489.9	32.6	33.0
90/10	459.7	485.2	51.7	52.0
80/20	461.2	480.2	69.9	69.0
LLDPE/Cu				
100/0	454.1	492.9	-	
99/1	468.5	501.8	9.7	8.9
95/5	461.4	491.7	34.0	33.1
90/10	470.4	488.9	52.0	52.2
80/20	470.4	485.4	70.3	69.5
HDPE/Cu				
100/0	467.0	500.1	-	
99/1	463.6	496.3	8.8	8.5
95/5	469.2	497.3	32.3	33.0
90/10	455.2	485.7	50.4	51.0
80/20	458.4	471.4	69.4	69.7

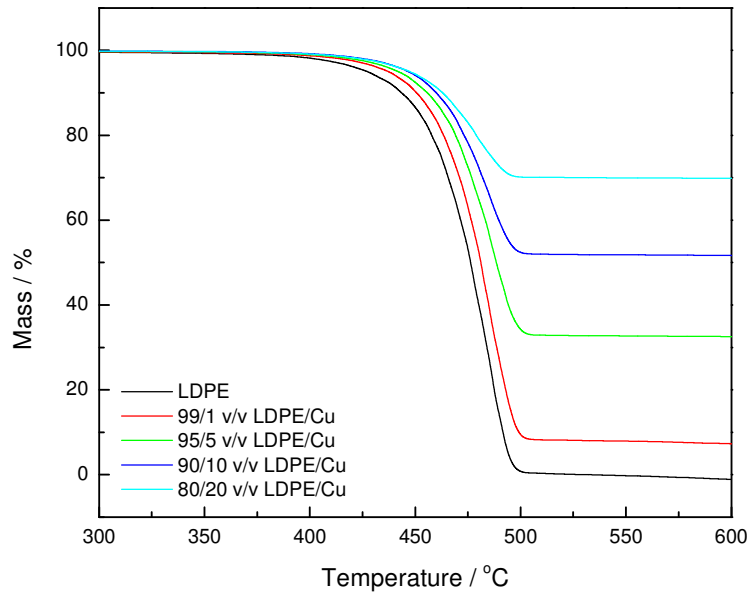


Figure 4.24 TGA curves of LDPE and LDPE/Cu micro-composites

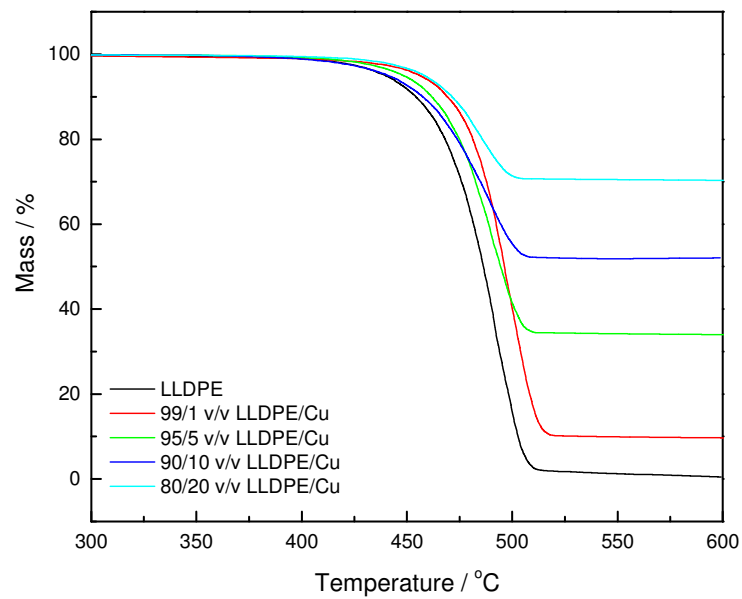


Figure 4.25 TGA curves of LLDPE and LLDPE/Cu micro-composites

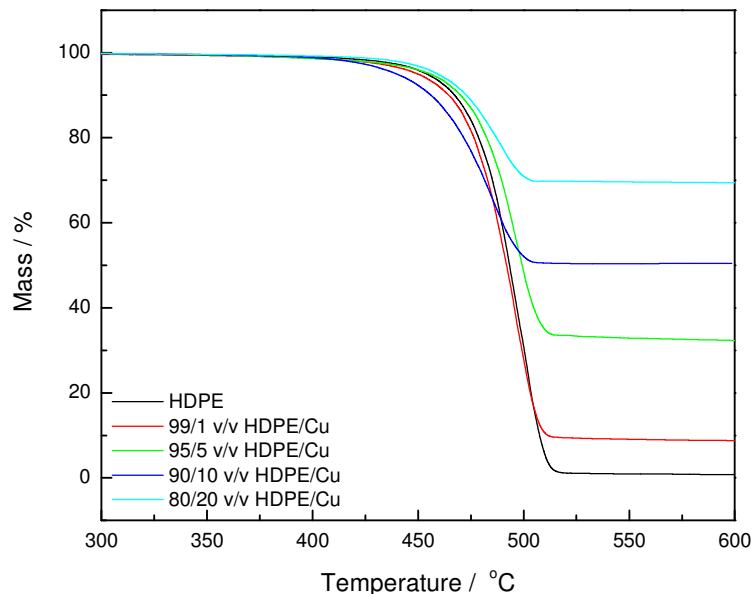


Figure 4.26 TGA curves of HDPE and HDPE/Cu micro-composites

4.3.3 PE/Cu nano-composites

The TGA curves of the PE/Cu nano-composites are shown in Figs. 4.27 to 4.29, and the results are summarized in Table 4.6. The thermal stability of LDPE and LLDPE generally increases with increasing Cu nano-particle content, but for LDPE a decrease is observed for the highest Cu content of 5 vol. %. This decrease in thermal stability is probably due to the presence of Cu nano-particle agglomerates that cause an increase in energy propagation. The formation of these agglomerates was observed in the SEM results (Fig. 4.1 (d)). The delayed thermal degradation for both LDPE/Cu and LLDPE/Cu nano-composites is due to the restricted chain and volatile degradation products mobility imposed by the Cu nano-particles. In both these sets of nano-composites there is also a good correlation between the % residue after complete decomposition and the wt. % Cu initially mixed into the sample. This confirms that the presence of Cu did not cause any char formation.

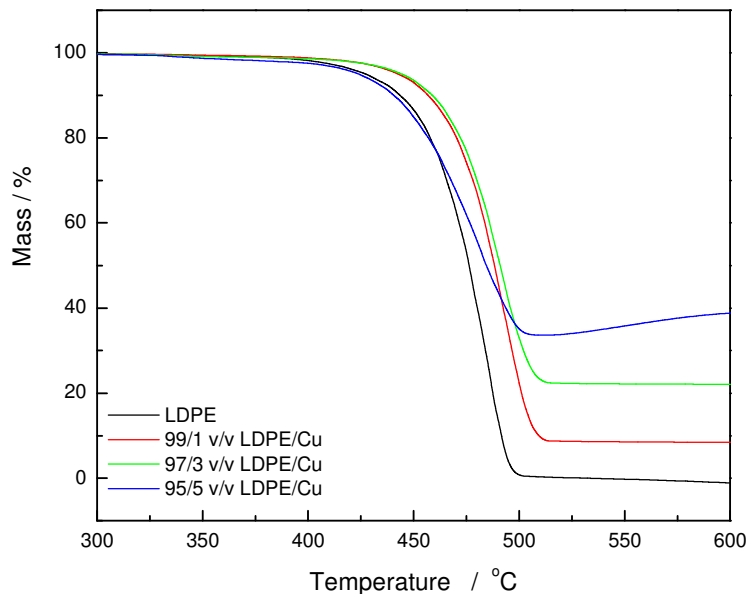


Figure 4.27 TGA curves of LDPE and LDPE/Cu nano-composites

Table 4.6 Temperatures of 10% degradation and DTG peak temperatures, as well as wt. % of residue, of PE/Cu nano-composites

v/v	T ₁₀ / °C	T _{peak} / °C	Wt. % residue	Wt.% Cu in sample
LDPE/Cu				
100/0	443.3	485.5	-	
99/1	456.0	480.7	8.4	8.8
97/3	458.0	491.4	22.0	23.1
95/5	440.2	480.9	33.4	33.0
LLDPE/Cu				
100/0	454.1	492.9	-	
99/1	441.8	491.7	10.5	8.9
97/3	464.6	495.9	22.5	23.0
95/5	468.1	495.6	33.4	33.1
HDPE/Cu				
100/0	467.0	500.1	-	
99/1	409.7	460.0	9.7	8.9
97/3	437.3	484.1	26.3	23.0
95/5	460.9	486.3	31.2	33.0

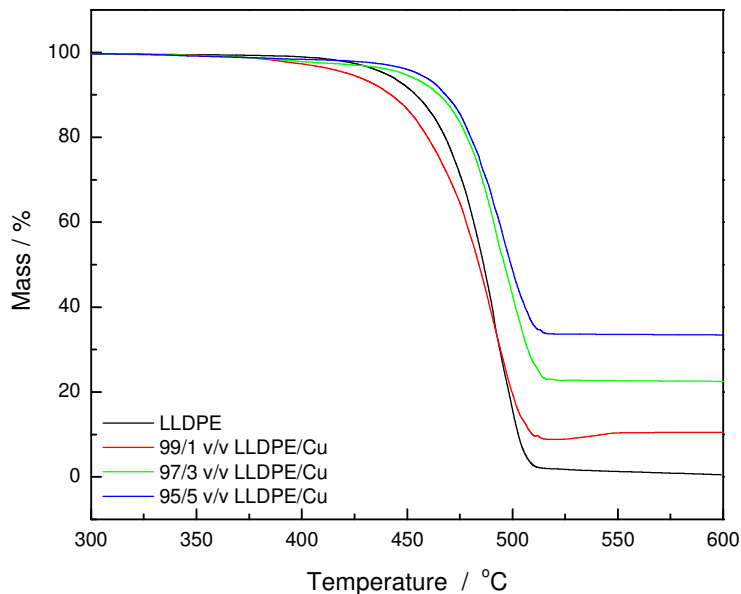


Figure 4.28 TGA curves of LLDPE and LLDPE/Cu nano-composites

In comparison, HDPE filled with the same amount of Cu nano-particles showed different behaviour. There is an initial decrease in the thermal stability of HDPE when 1 vol. % of Cu nano-particles are present. The reason for this is not entirely clear. When the Cu nano-particle content is increased, their influence on the polymer chain and volatile degradation products mobility increases. Hence, the HDPE/Cu nano-composites start degrading at higher temperatures. It is worth noting that the Cu nano-particles enhance the thermal stabilities of polyethylenes with lower crystallinities, and reduce and reduce those of highly crystalline polyethylenes. In this case also there is a good correlation between wt. % residue and wt. % of nano-Cu initially mixed into the samples.

Some TGA curves in Figs. 4.27-4.29 show a weight increase above 500 °C. These analyses were repeated with the same result. It was not possible, with the available techniques, to establish the reason for this behaviour.

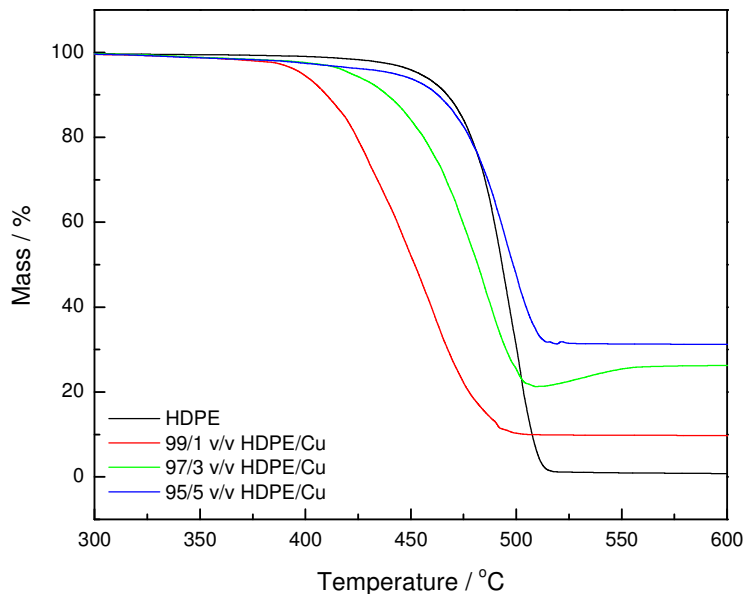


Figure 4.29 TGA curves of HDPE and HDPE/Cu nano-composites

4.3.4 Comparison between PE/Cu micro- and nano-composites

The TGA curves of pure LDPE and its Cu nano- and micro-composites are shown in Figure 4.30. The thermal stability of LDPE is higher in the presence of 3 vol. % Cu, but the nano-particles have a more significant influence. Because of their larger surface areas, and because of the higher amorphous content in LDPE, the nano-particles probably have a more significant effect on the immobilization of the polymer chains and free radicals formed during degradation. In the case of LLDPE (Figure 4.31) both micro- and nano-particles also improve the thermal stability of the polymer, but in this case the effect of particle size is not so obvious. In HDPE/Cu the micro-particles slightly enhances the thermal stability of HDPE, while the nano-particles significantly reduce its thermal stability (Figure 4.32). As discussed above, there probably is a fine balance between faster heat transfer within the polymer as a result of the presence of the Cu micro-particles, and immobilization of HDPE chains (including free radicals) and degradation volatiles. However, because of differences between size and structure of the nano-particles and those of the micro-particles, the balance is more towards effective heat transfer within the polymer in the case of the nano-composite.

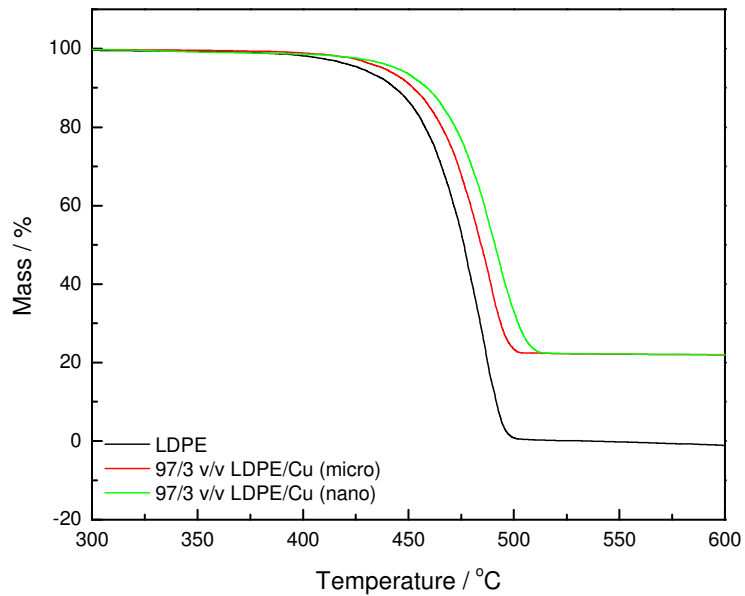


Figure 4.30 TGA curves of LDPE and 97/3 v/v LDPE/Cu composites

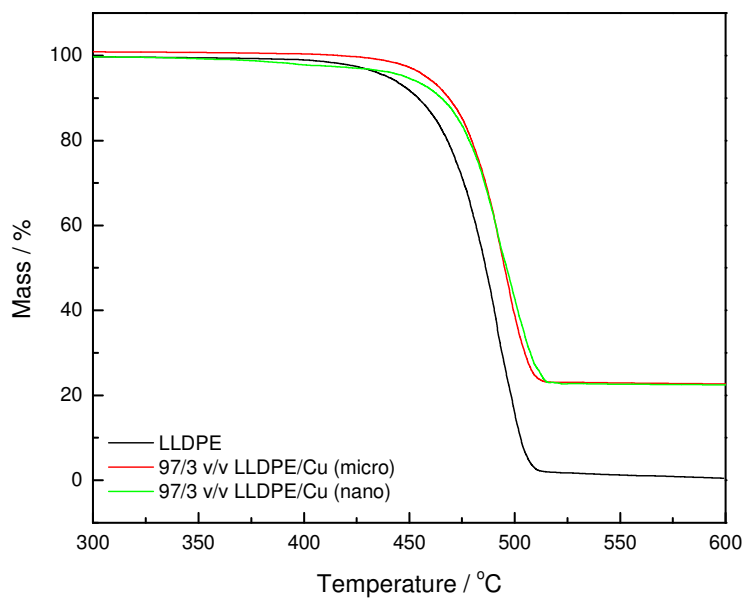


Figure 4.31 TGA curves of LLDPE and 97/3 v/v LLDPE/Cu composites

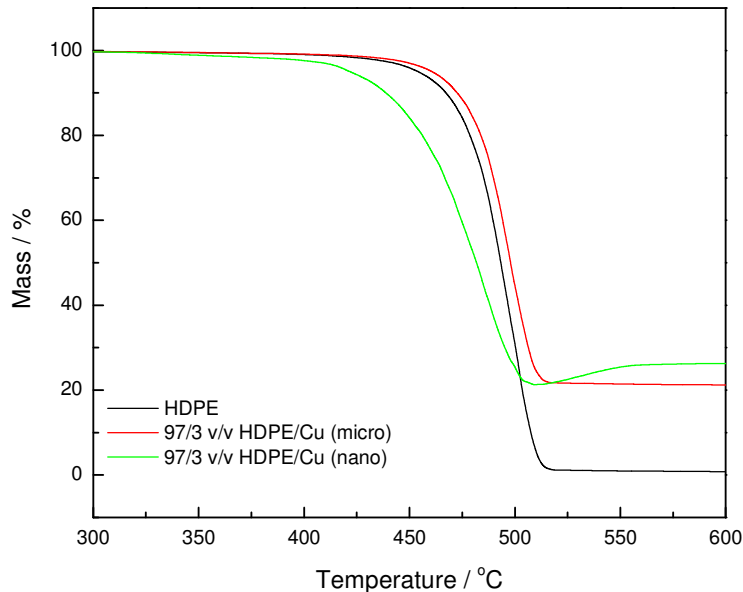


Figure 4.32 TGA curves of HDPE and 97/3 v/v HDPE/Cu composites

4.3.5 PE/wax blends

The TGA curves of the PE/wax blends are shown in Figs. 4.33 to 4.35, and the results are summarized in Table 4.7. For all the blends the thermal stability decreases with an increase in wax content, and the PE/wax blends degrade in two clearly distinguishable steps. Such degradation behaviour is typical for immiscible blends in which the constituents have different degradation temperatures. The first degradation step is that of wax, which has a lower thermal stability than any of the polymers. The second step is associated with the polymer degradation. As reported, the short-chain fractions of wax, as well as fragments formed by chain scission, will have enough energy to leave the matrix at a lower temperature [7,12-14]. Thus, introducing more of the low molecular weight wax induces a gradual decrease in the temperatures at which the degradation starts. For example, when 10% mass loss was selected as point of comparison, the thermal degradation of LDPE/wax samples with 30, 40, and 50 vol. % of wax are determined as 292, 282, and 271 °C respectively, that are 150, 161, and 172 °C lower than the 443 °C of pure LDPE.

Table 4.7 **Temperatures of 10 and 50% degradation of PE/wax blends**

v/v	T ₁₀ / °C	T ₅₀ / °C
LDPE/wax		
100/0	443.3	476.3
70/30	292.9	468.8
60/40	282.4	439.4
50/50	271.1	-
100/0	262.4	341.4
LLDPE/wax		
100/0	464.6	486.1
70/30	292.9	479.4
60/40	282.4	469.1
50/50	271.1	-
100/0	262.4	341.4
HDPE/wax		
100/0	467.0	493.0
70/30	290.8	478.8
60/40	294.8	478.8
50/50	271.9	-
100/0	262.4	341.4

At the same level of mass loss the thermal degradation temperatures for the LLDPE/wax blends were determined as 172, 182, and 192 °C lower than the 464 °C of pure LLDPE. The same is true for HDPE/wax blends, with thermal degradation temperatures for the HDPE/wax blends 176, 171 and 195 °C lower than pure HDPE. No char yield was observed at temperatures higher than 500 °C for all the PE/wax blends. The thermal stabilities of all the PE/wax blends therefore fall below that of the pure PEs, and gradually decreases with increasing wax content. This is because soft paraffin wax has much shorter chains and is thermally less stable than the pure PEs. The thermal stability of PE/wax blends gradually decreases with increasing wax content. In all investigated polyethylenes, it can be seen that wax does influence the decomposition of the polymer phase. It was, however, difficult to establish definite trends and therefore no conclusion can be drawn from this.

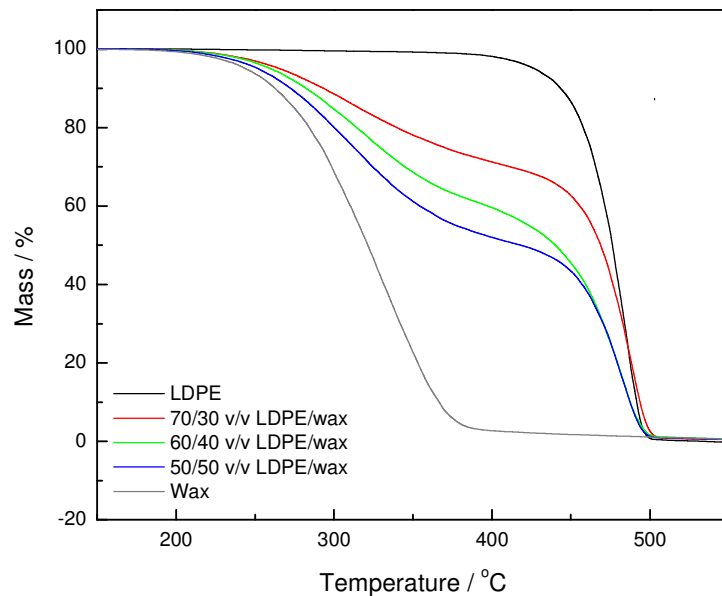


Figure 4.33 TGA curves of LDPE, wax and different LDPE/wax blends

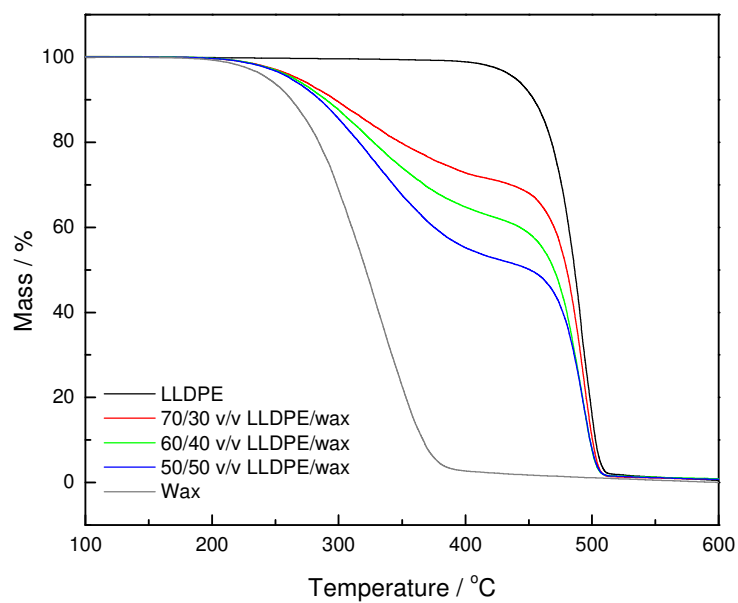


Figure 4.34 TGA curves of LLDPE, wax and different LLDPE/wax blends

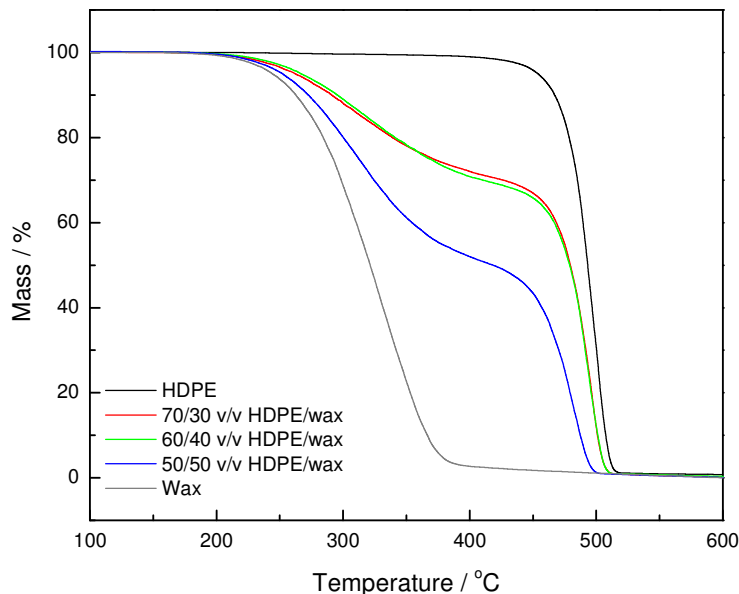


Figure 4.35 TGA curves of HDPE, wax and different HDPE/wax blends

4.3.6 PE/wax/Cu micro-composites

The thermal stability results of PE/wax/Cu micro-composites at constant 40 vol. % of wax are presented in Figs. 4.36 to 4.38 and are summarized in Table 4.8. The composites degraded in two clearly distinguishable steps, similar to those observed for the PE/wax blends. The thermal stabilities of the composites generally increase with increasing Cu content, and they are higher than those of the corresponding PE/wax blends, although this effect is less pronounced for the HDPE/wax/Cu micro-composites. The higher thermal stabilities are probably due to a combination of the immobilization of PE and wax free radicals and volatile degradation products, since the wax decomposes first, and since it is concentrated around the Cu particles.

Table 4.8 Temperatures of 10, 20 and 50% degradation, of PE/wax/Cu micro-composites

v/v	T ₁₀ / °C	T ₂₀ / °C	T ₅₀ / °C	Wt. % residue	Wt. % Cu in sample
LDPE/wax/Cu					
60/40/0	282.4	313.4	439.4	0.0	0.0
59/40/1	289.9	326.9	470.9	7.8	7.0
57/40/3	293.0	334.0	477.0	21.5	23.6
55/40/5	292.8	337.8	478.8	30.4	33.9
50/40/10	298.3	354.3	-	41.8	42.0
LLDPE/wax/Cu					
60/40/0	282.4	327.1	469.1	0.0	0.0
59/40/1	292.7	329.7	479.7	9.7	8.7
57/40/3	295.9	339.9	484.9	24.4	24.0
55/40/5	295.9	341.9	488.9	34.4	34.0
50/40/10	303.0	427.0	-	53.1	51.0
HDPE/wax/Cu					
60/40/0	294.8	340.8	478.8	0.0	0.0
59/40/1	294.7	333.7	478.7	9.1	8.9
57/40/3	289.2	329.2	484.2	22.7	21.0
55/40/5	292.8	340.2	487.2	31.7	30.3
50/40/10	298.3	404.0	-	53.7	51.9

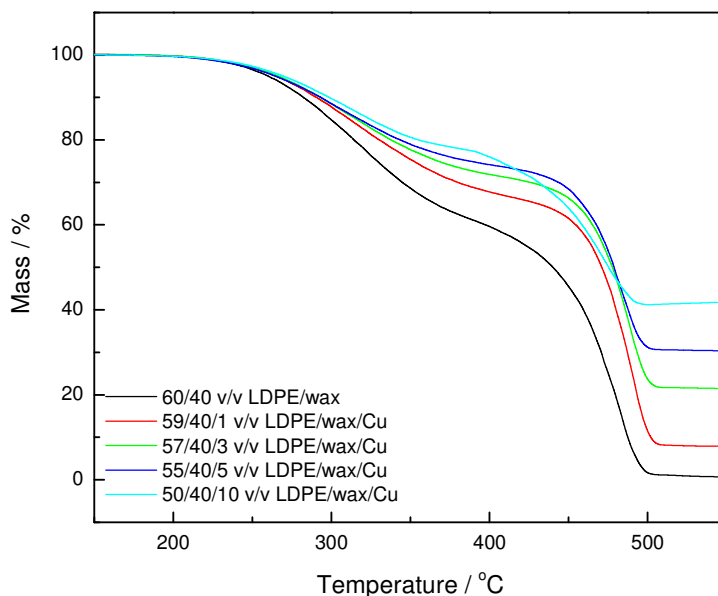


Figure 4.36 TGA curves for LDPE, wax and different LDPE/wax/Cu micro-composites

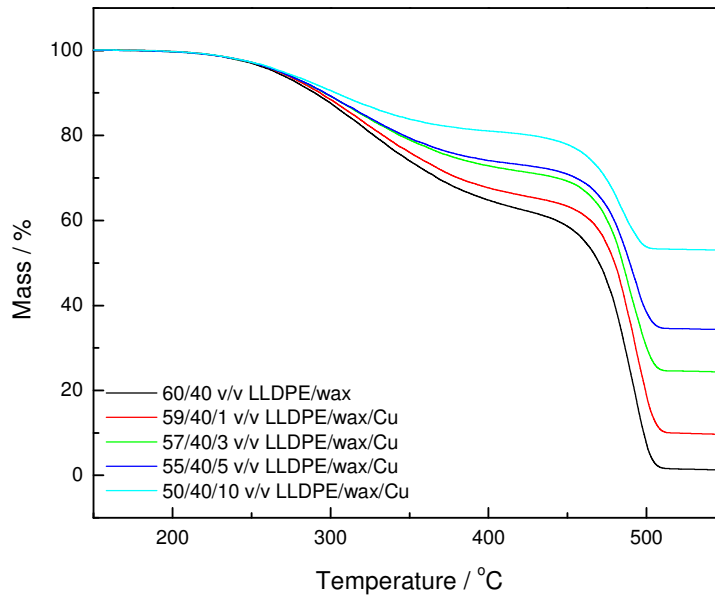


Figure 4.37 TGA curves for LLDPE, wax and different LLDPE/wax/Cu micro-composites

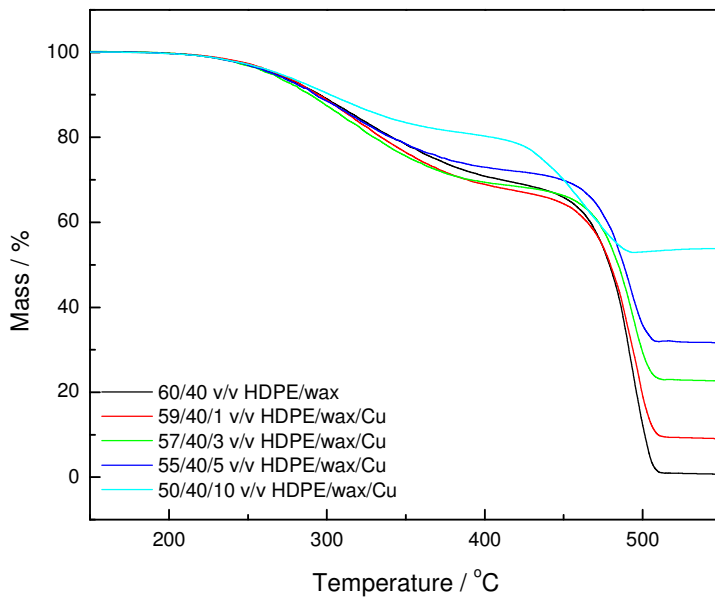


Figure 4.38 TGA curves for HDPE, wax and different HDPE/wax/Cu micro-composites

4.5 Tensile properties

4.5.1 Stress-strain curves

The tensile characteristics (stress and strain at break and Young's modulus) of the pure polymers, blends and composites were determined from stress-strain curves (typical examples in Figs. 4.39 and 4.40). The stress-strain curves of the pure polyethylenes demonstrate the differences between these PE's. HDPE displays a significant yield point followed by cold flow. However, strain (orientation) hardening during stretching is not pronounced and therefore the stress at break is lower than the yield stress. A different situation is in the case of LLDPE where the material undergoes orientation hardening during stretching and has a higher stress at break than yield stress. LDPE does not show a pronounced yield point or strain hardening. These differences are caused by different molecular weights and structures of the investigated polyethylenes.

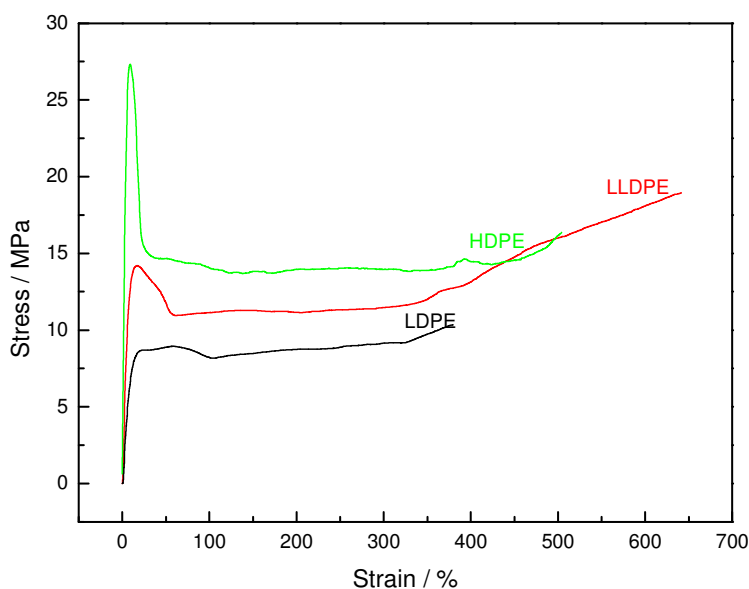


Figure 4.39 Stress-strain curves for pure polyethylenes

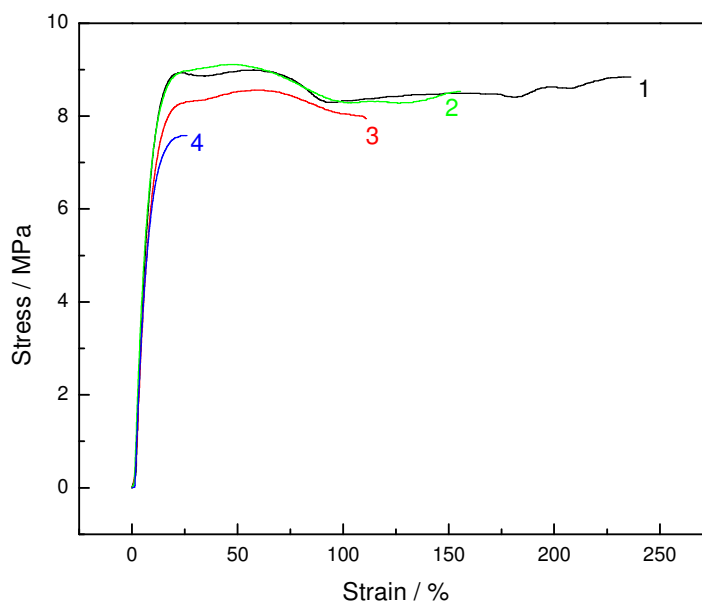


Figure 4.40 Stress-strain curves for LDPE/Cu micro-composites with different concentrations of copper powder: (1) 0 vol.%, (2) 1 vol.%, (3) 5 vol.%, (4) 10 vol.%

From the stress-strain curves of pure LDPE and LDPE/Cu micro-composites (Figure 4.40) it can be seen that an increase in copper content in the composites induces an increase in their stiffness. The presence of the filler reduces both cold flow and orientational hardening, and therefore significantly reduces drawability of the materials. Similar behaviour was observed for the LLDPE/Cu and HDPE/Cu micro-composites and their stress-strain curves are presented in the appendix (Figs. A16-A17).

4.4.2 PE/Cu micro-composites

The mechanical properties of the different PEs and their Cu micro-composites are listed in Table 4.9, and the changes in these properties are illustrated in Figs. 4.41 to 4.43. The stress at break of all three PEs decreases with increasing Cu content (Figure 4.41). The highest decrease is observed for LLDPE, where the suppression of cold flow and orientation hardening is the most pronounced. The smallest decrease is observed for LDPE, where no orientation hardening was observed, even for the pure polymer. In all the cases no reinforcing

effect of the filler was observed. This is due to a weak interfacial adhesion between the filler and the matrix as was shown by the SEM results.

Table 4.9 Mechanical properties of PE/Cu micro-composites

v/v	$\sigma_b \pm S\sigma_b$ / MPa	$\varepsilon_b \pm S\varepsilon_b$ / %	$E \pm sE$ / MPa
LDPE/Cu			
100/0	10.1 ± 0.5	336 ± 0.0	120 ± 8
99/1	9.6 ± 0.4	325 ± 10	135 ± 5
97/3	9.1 ± 0.2	223 ± 5.0	155 ± 7
95/5	8.6 ± 0.5	86.3 ± 10	158 ± 5
90/10	8.6 ± 1.0	19.2 ± 1.3	191 ± 4
85/15	8.6 ± 0.6	20.0 ± 3.2	192 ± 7
80/20	9.3 ± 0.8	19.9 ± 5.1	207 ± 5
75/25	9.4 ± 0.5	10.6 ± 6.4	219 ± 4
LLDPE/Cu			
100/0	25.7 ± 1.4	1054 ± 3.0	123 ± 1.0
99/1	20.9 ± 1.2	911 ± 8.0	171 ± 16
97/3	19.6 ± 1.2	874 ± 4.0	169 ± 15
95/5	18.2 ± 0.4	857 ± 2.0	141 ± 4.0
90/10	14.0 ± 0.4	741 ± 2.0	194 ± 9.0
85/15	12.0 ± 0.5	669 ± 6.0	176 ± 19
80/20	8.7 ± 0.7	454 ± 15.0	222 ± 27
75/25	8.1 ± 1.0	278 ± 13.0	237 ± 34
HDPE/Cu			
100/0	15.6 ± 5.3	792 ± 3.0	566 ± 8
99/1	11.7 ± 5.8	769 ± 4.0	594 ± 3
97/3	9.1 ± 2.2	276 ± 5.0	597 ± 2
95/5	7.1 ± 5.4	158 ± 2.0	594 ± 3
90/10	9.5 ± 3.4	31.5 ± 2.5	670 ± 4
85/15	14.6 ± 1.3	14.5 ± 1.8	670 ± 4
80/20	13.2 ± 2.8	12.8 ± 1.5	780 ± 7
75/25	13.8 ± 8.7	13.8 ± 0.7	552 ± 3

σ_b is the stress at break and $S\sigma_b$ is the standard deviation, ε_b is the elongation at break and $S\varepsilon_b$ is the standard deviation, E is Young's modulus and sE is the standard deviation

Pure LLDPE has the highest value of stress at break. At 10 vol. % of Cu micro-particle content, the initial stress at break of LLDPE (25.7 MPa) decreases to the value of 14.0 MPa, and for LDPE decreases from 10.1 MPa to 8.6 MPa, while that of HDPE decreases from 15.6 MPa to 9.5 MPa. As pointed out above, LLDPE has a very significant orientational hardening, which will always be reduced by the presence of filler particles, and therefore the decrease in stress at break is more pronounced for the LLDPE matrix than for the LDPE or HDPE matrices. The presence of defects in front of the neck has a critical influence on the

drawability. A higher concentration of the defects, caused by higher local concentration of the filler, results in a steeper decrease in stress at break for the HDPE matrix, which is probably due to its higher crystalline content. Since the filler is located only in the amorphous phase, the concentration of the filler related to the amorphous content is higher in LLDPE and HDPE than in LDPE. The consequence of this is that the amorphous part in the more crystalline polymer (HDPE) is more reinforced compared to the relatively low crystalline polymer (LDPE) due to a higher local concentration of the filler in the amorphous phase. The mechanical properties of metal filled polymers are strongly affected by factors such as type, concentration, size, shape and orientation of the filler particle [15-20]. These parameters are affected by the strength of the adhesive bond between the two phases, the type of dispersion and the amount of particle agglomeration. The influence of these factors on the tensile behaviour is often difficult to separate and evaluate in a quantitative manner. Since there is no good general theory about the stress-strain behaviour of metal filled polymers [15,16], it is known from observations that the tensile strength of a material decreases with an increase in filler content [15-22]. However, it is not always the case that the stress at break decreases with an increase in filler content. For example, in the case of the HDPE composites investigated in this thesis, the initial decrease is caused by a reduction in the drawability as well as by the presence of defects. However, if there is good interaction between the polymer and the filler or reinforcement due to immobilization of the polymer chains onto the filler surface, there may be a reinforcing effect and an increase in stress at break is observed [15]. This can result in stress at break values that are higher than that of the pure polymer.

The dependence of the elongation at break on the filler content in the composites is shown in Fig. 4.42 and the elongation at break data of the PE/Cu micro-composites are summarized in Table 4.9. There is a significant drop in the drawability after addition of the copper particles. A decrease in the elongation at break for polymers filled with inorganic fillers is always observed [15-20]. A few models, that describe this behaviour, were reported in the literature [15,17,21]. They assumed homogeneous distribution of the particles, regular shapes and homogeneous drawing. The most well known model, describing the decrease in elongation at break with an increase in filler volume fraction, is the Nielsen model [15,17,20,21] given by Eq. 4.2.

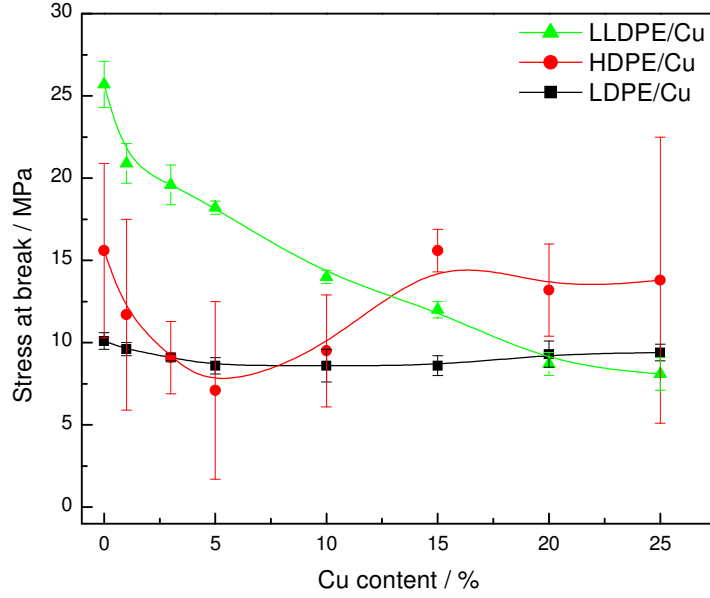


Figure 4.41 Stress at break as function of copper content in the micro-composites

$$\frac{\varepsilon_{b,c}}{\varepsilon_{b,m}} = 1 - \Phi_f^{1/3} \quad (4.2)$$

where $\varepsilon_{b,c}$ and $\varepsilon_{b,m}$ are the elongation at break of the composite and the matrix, respectively, and Φ_f is the volume fraction of the filler. This model is valid for particles having spherical shapes, and assuming perfect adhesion between the phases, which is not applicable in the current study. Our copper powder particles have irregular shapes with many sharp edges, and they are not uniform. These factors are expected to contribute significantly to a dramatic decrease in elongation at break. The use of Nielsen's model is correct only if the deformation is homogeneous. In the case of polyethylene, a neck is created during drawing and therefore stretching is not homogeneous. The presence of defects in front of the neck has a critical influence on the drawability. According to Rusu *et al.* [20] the occurrence of particle agglomeration is responsible for the appearance of metal particle contacts, instead of polymer-metal particle contacts, characterized by a total lack of adhesion. In this case a considerable decrease in the elongation at break of the PE/Cu micro-composites is observed with an increase in Cu.

It can be seen in Table 4.9 that the elongation at break of pure LLDPE and HDPE show higher values than pure LDPE, because when force is applied, the polymer chains have enough space and time to orientate, which is the result of the chemical structure of crystalline polymers. Immediately when the chains are oriented, they start to form orientation crystallinity, which evokes an increase in the strength of a sample. Adding filler to the polymer matrix reduces chain mobility, giving rise to a rapidly decreasing elongation at break (Fig. 4.42). When 10 vol. % of copper micro-particles are incorporated into the respective matrices, the initial elongation at break of pure LLDPE decreases from 1054% to 740%, for pure HDPE it decreases from 791% to 31.5%, and for pure LDPE it decreases from 336% to 19.2%.

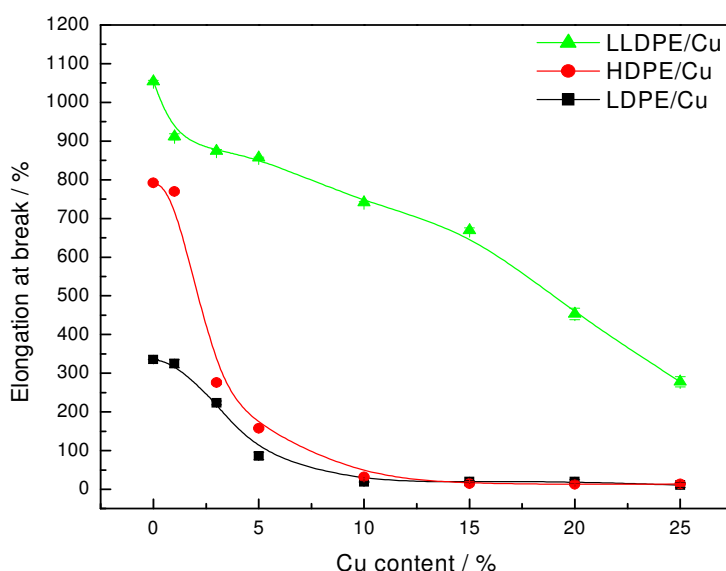


Figure 4.42 Elongation at break as a function of copper content in the micro-composites

The dependence of Young's modulus of the composites on the volume percentage of filler is shown in Fig. 4.43 and the Young's modulus data of pure the PEs and their Cu micro-composites are summarized in Table 4.9. Young's modulus slightly increases with an increase in copper content for all three polyethylenes, except for HDPE at the highest filler content. The size and distribution of the filler plays a significant role, since the filler is much stiffer than the polymer matrix, and the stiffness increases with increasing filler content. The extent depends on the filler surface area. This is common behaviour for polymers filled with inorganic fillers [16-18,20]. The modulus of the HDPE composites increases up to 20 vol. %

of copper, but for the 25 vol. % Cu containing composite the value drops even lower than that of pure HDPE. This is probably caused by insufficient de-wetting of the filler and de-bonding of the matrix, similar to the case of stress at break, since the bonds between the polymer and the Cu particles are weak. Similar behaviour was observed where HDPE was filled with an inorganic filler [19].

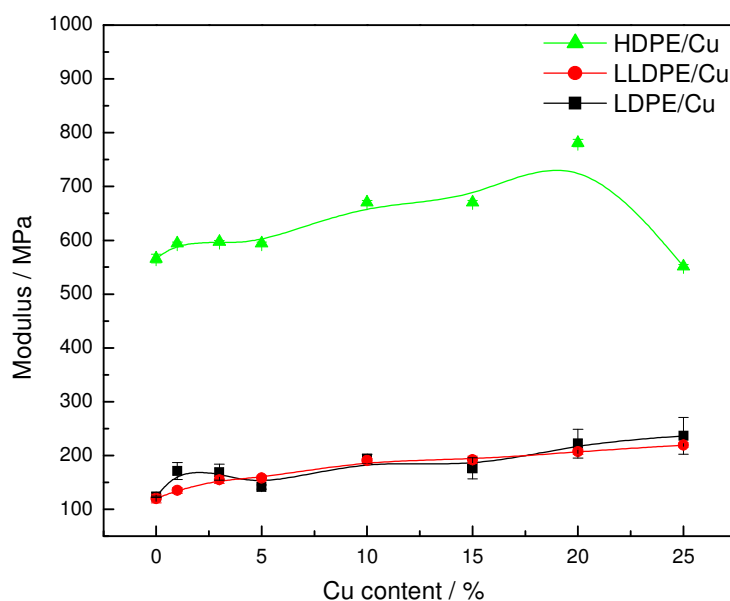


Figure 4.43 Young's modulus as function of copper content in the micro-composites

4.4.3 PE/Cu nano-composites

The stress at break results for the PE/Cu nano-composites are presented in Fig. 4.44 and in Table 4.10. The presence of copper nano-particles in the PE matrices slightly decreases the stress at break of the nano-composites. The lower stress at break values of the nano-composites could be due to a number of reasons such as weak interfacial bonding between the Cu nano-particles and matrix interfaces, aggregates of Cu nano-particles and nano-size processing related defects. There are no obvious differences in stress at break values between the HDPE micro- and nano-composites. The values for the nano-composites are slightly lower for LDPE and slightly higher for LLDPE than those of the micro-composites. It is difficult to

establish a relationship between these observations and the respective morphologies of the polyethylenes.

The dependence of elongation at break on Cu nano-particle content is summarized in Table 4.10. Fig. 4.45 shows a decrease in elongation at break with an increase in Cu nano-particle content for all the investigated nano-composites. The decrease is much more significant for HDPE and LDPE than it is for LLDPE. The decrease is also more significant for the nano-composite samples compared to the micro-composite samples. The reason for the difference in behaviour between LLDPE on the one hand and LDPE and HDPE on the other hand is not obvious. However, the more significant decrease for the nano-composites compared to the micro-composites may be explained in terms of the increase in number of nano-particles in the polymer matrix and the accompanying increase in number of defect points.

Table 4.10 Mechanical properties of the PE/Cu nano-composites

v/v	$\sigma_b \pm S\sigma_b$ / MPa	$\epsilon_b \pm S\epsilon_b$ / %	$E \pm sE$ / MPa
LDPE/Cu			
100/0	10.1 ± 0.5	336 ± 0.0	120 ± 8.0
99/1	8.6 ± 0.4	153 ± 1.0	134 ± 4.0
97/3	8.9 ± 0.2	55.8 ± 1.2	158 ± 4.0
95/5	7.4 ± 0.5	14.4 ± 4.0	159 ± 7.0
LLPE/Cu			
100/0	25.7 ± 1.4	1054 ± 3.0	123 ± 1.0
99/1	22.3 ± 1.1	917 ± 4.0	216 ± 8.0
97/3	23.6 ± 0.6	900 ± 3.0	260 ± 6.0
95/5	18.7 ± 1.4	749 ± 5.0	273 ± 4.0
HDPE/Cu			
100/0	15.6 ± 5.3	792 ± 3.4	566 ± 8.0
99/1	10.3 ± 2.2	402 ± 4.1	621 ± 6.0
97/3	8.6 ± 4.1	33.9 ± 7.7	709 ± 7.0
95/5	7.8 ± 6.3	19.3 ± 7.5	726 ± 5.0

σ_b is stress at break and $S\sigma_b$ is the standard deviation, ϵ_b is elongation at break, $S\epsilon_b$ is the standard deviation, E is Young's modulus and sE is the standard deviation

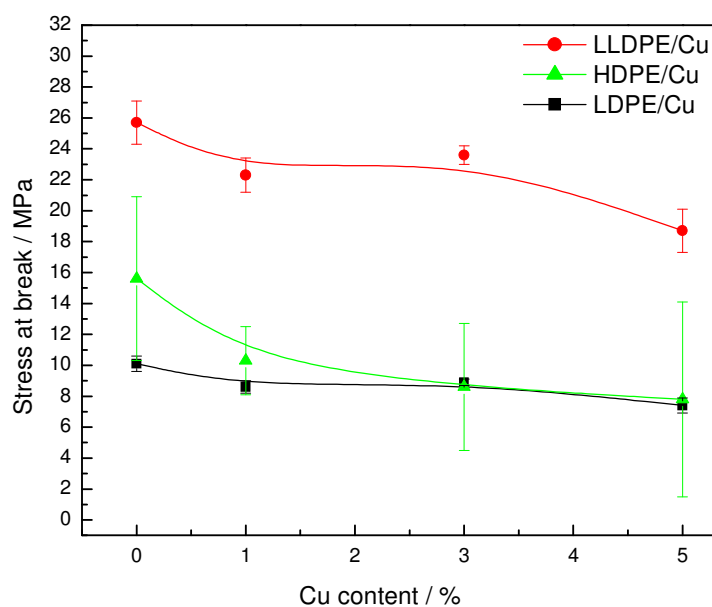


Figure 4.44 Stress at break as function of copper content in the nano-composites

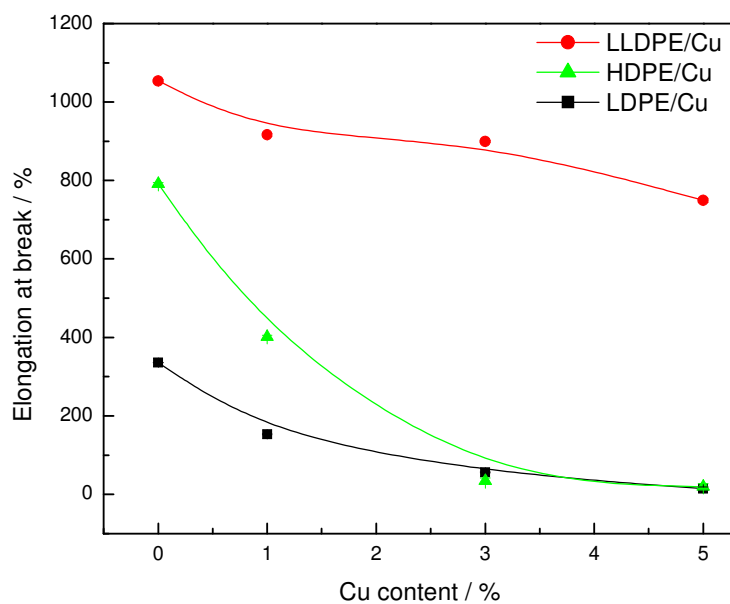


Figure 4.45 Elongation at break as function of copper content in the nano-composites

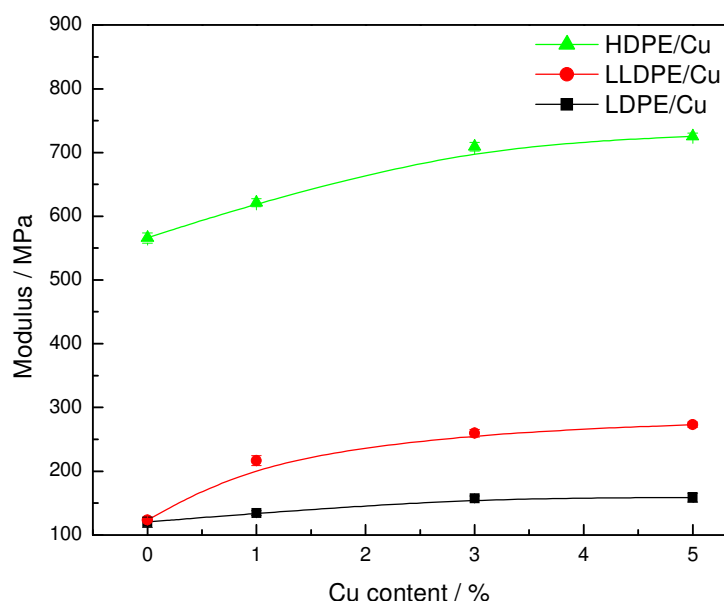


Figure 4.46 Young's modulus as function of copper content in the nano-composites

Young's moduli of the nano-composites as function of the Cu nano-particle content are shown in Fig. 4.46, and the values are summarized in Table 4.10. The values increase with an increase in filler content for all three polymers. If the increase is taken as a percentage of the modulus value of the pure polymer, the increase is much more pronounced for LLDPE, followed by HDPE, while the LDPE moduli did not change appreciably with increasing Cu content. The moduli of the LDPE micro-composites are almost the same as those of the nano-composites, while those of the LLDPE and HDPE micro-composites are lower than the those of the nano-composites. All these observations may be explained in terms of the fact that the Cu particles are most probably located in the amorphous regions of the respective polymers. The higher the amorphous content, the weaker the influence of the Cu particles on the overall chain mobility of the polymer. As a result of their higher total surface area, the nano-particles have a stronger influence, especially in the more crystalline polyethylenes.

4.4.4 PE/wax blends

The data presented in Table 4.11 shows that blending wax with PE significantly influences the mechanical properties of the materials. In all the investigated PE/wax blends, the stress at break decreased with an increase in wax content (Fig. 4.47). The main reason for this decrease is due to the increased amount of low molecular weight wax, which deteriorates the tensile strength of the blend. Wax itself has very poor tensile properties and the wax crystals in the amorphous phase of the respective polymers act as defect points for the initiation and propagation of stress cracking. Increasing wax content had a more significant influence on the tensile strength of LDPE, probably because of the higher amorphous content in this polymer. Lower values of stress at break were also observed by Mtshali *et al.* [14], after blending LDPE with wax. They showed that the changes at lower wax concentrations are within experimental error, but at higher wax concentrations significant deterioration of the basic properties of the materials were observed.

Table 4.11 Mechanical properties of the PE/wax blends

v/v	$\sigma_b \pm S\sigma_b$ / MPa	$\epsilon_b \pm S\epsilon_b$ / %	E $\pm$ sE / MPa
LDPE/wax			
100/0	10.1 $\pm$ 0.5	336 $\pm$ 0.0	121 $\pm$ 8.0
70/30	9.0 $\pm$ 0.2	30.0 $\pm$ 4.7	163 $\pm$ 14.0
60/40	9.1 $\pm$ 0.6	19.0 $\pm$ 9.4	185 $\pm$ 12.0
50/50	5.4 $\pm$ 0.5	4.9 $\pm$ 0.7	192 $\pm$ 4.0
LLDPE/wax			
100/0	25.7 $\pm$ 1.4	1054 $\pm$ 3.0	123 $\pm$ 1.0
70/30	12.6 $\pm$ 1.3	610 $\pm$ 21	175 $\pm$ 4.0
60/40	8.4 $\pm$ 0.9	570 $\pm$ 18	166 $\pm$ 5.0
50/50	7.7 $\pm$ 1.3	542 $\pm$ 47	212 $\pm$ 24
HDPE/Cu			
100/0	15.6 $\pm$ 5.3	792 $\pm$ 3	566 $\pm$ 8
70/30	10.3 $\pm$ 2.2	301 $\pm$ 30	378 $\pm$ 18
60/40	8.6 $\pm$ 4.1	254 $\pm$ 5	325 $\pm$ 42
50/50	7.8 $\pm$ 6.3	101 $\pm$ 34	314 $\pm$ 12

σ_b is stress at break and $S\sigma_b$ is the standard deviation, ϵ_b is elongation at break, $S\epsilon_b$ is the standard deviation, E is Young's modulus and sE is the standard deviation

Figure 4.48 show the elongation at break of PE/wax blends and the data is summarized in Table 4.11. An increase in wax content results in a decrease in elongation at break of all the investigated blends. This can also be explained by the wax crystals acting as defect points for the initiation and propagation of stress cracking. Elongation at break is also influenced by the

immiscibility of the components. Since there is phase separation in all the blends, the materials loses drawability and elongation at break strongly decreases.

Young's moduli of all the blends are summarized in Table 4.11 and presented in Figure 4.49. An increase Young's modulus with an increase in wax content is observed for the LDPE and LLDPE blends, indicating that the modulus of the wax is higher than that of both these polymers. This is probably associated with its higher degree of crystallinity. The degree of crystallinity of wax, LDPE and LLDPE are 58.9, 25.7 and 29.7%. These values were calculated according to Eq. 4.3.

$$X_c = \frac{\Delta H_m}{\Delta H_m^+} \times 100\% \quad (4.3)$$

where X_c is the degree of crystallinity, ΔH_m is the specific melting enthalpy of the sample and ΔH_m^+ is the specific melting enthalpy for 100% crystalline polyethylene. In this study we used $\Delta H_m^+ = 293 \text{ J g}^{-1}$ [24,25] for the polyethylenes, and we assumed that 100% crystalline wax has the same melting enthalpy. There is an interaction between the crystalline and amorphous regions of the polyethylenes, giving rise to the elongation energy being transmitted from the amorphous to the crystalline phase. The presence of the wax may affect this energy transfer, which may be responsible for the increase in stiffness of the polyethylene/wax blends. In contrast with the observations on LDPE/wax and LLDPE/wax blends, the moduli of the HDPE/wax blends decreased with increasing wax content. Since the wax has a lower crystallinity than HDPE, the modulus (which depends on the sample crystallinity) decreases with increasing wax content.

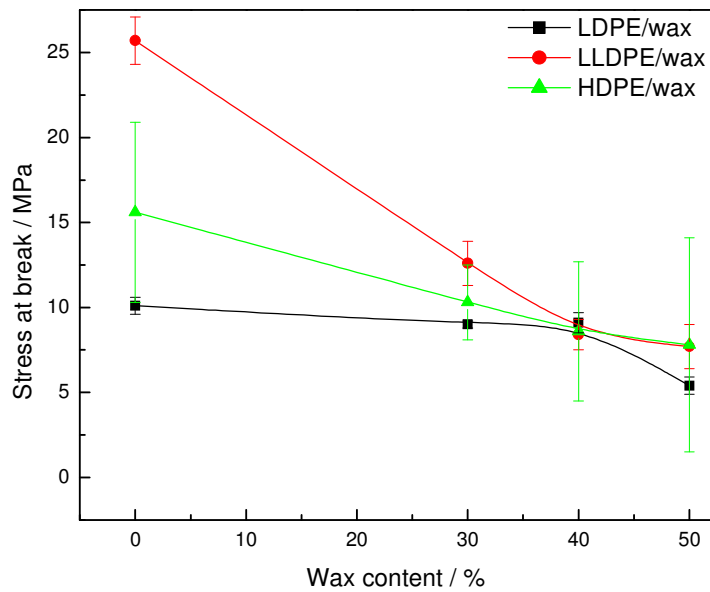


Figure 4.47 Stress at break as function of wax content in the blends

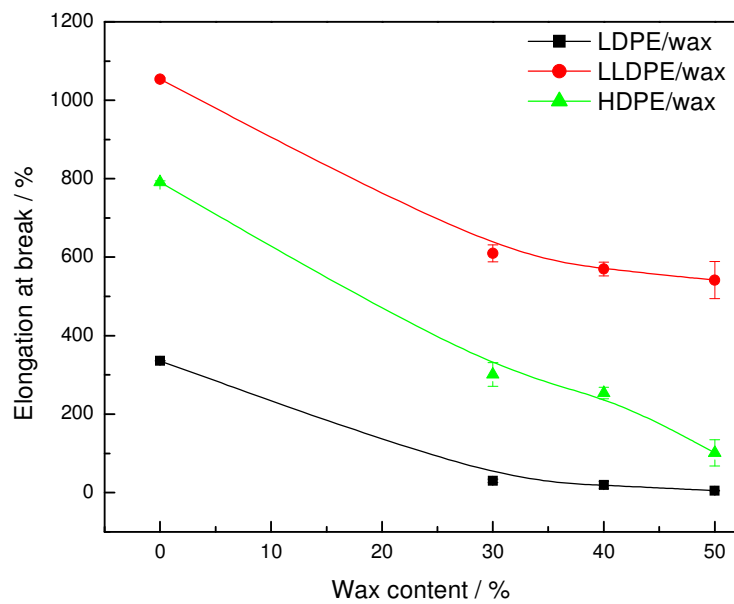


Figure 4.48 Elongation at break as function of wax content in the blends

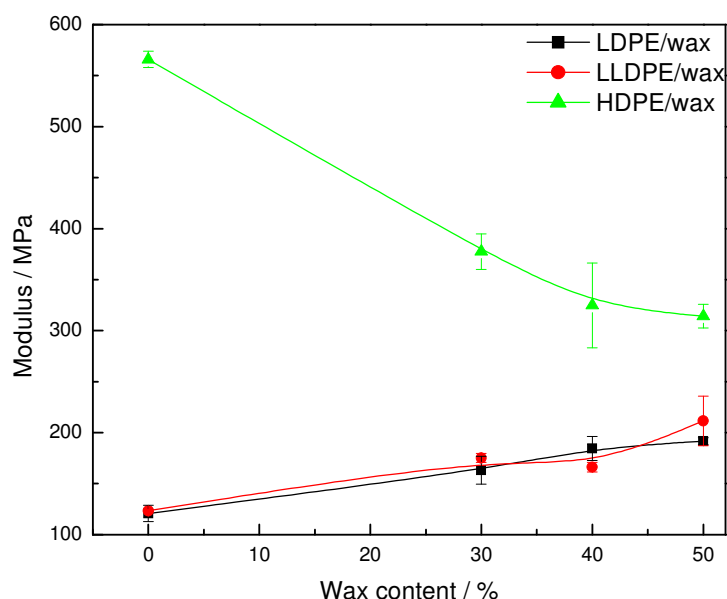


Figure 4.49 Young's modulus as function of wax content in the blends

4.4.5 PE/wax/Cu micro-composites

Figure 4.50 shows the plots of stress at break for the PE/wax/Cu composites as a function of filler content at constant 40 vol. % of wax, and the data are summarized in Table 4.12. The presence of copper powder at constant wax content causes an increase in tensile strength for LDPE and LLDPE at low Cu contents, followed by a decrease as the Cu content in the composites increases. The reason for the initial increase in tensile strength is not clear, but the decrease is probably the result of wax-covered Cu particles that form defect centres in the amorphous phase of the polymer. The poor mechanical properties of the wax, as well as the fact that wax seems to have weaker interaction with the polymer than Cu (the mechanical behaviour of composites depends on the quality of adhesion between matrix and filler, and in this case the filler is wax-covered Cu particles), will also contribute to the observed decrease in tensile strength with increasing Cu content. According to Nielsen [26] and Kunori [27] a strong interfacial adhesion between the dispersed and continuous phases produces a high stress at break in the composite. The HDPE/wax/Cu composites show very little change in tensile strength with increasing Cu content, similar to the HDPE/Cu microcomposites. This trend can therefore also be explained in a similar way (see section 4.4.2). Orientational

hardening of the polymer matrix also contributes to a decrease in the tensile strength of the composite. The smallest decrease in tensile strength is observed for LDPE and HDPE, where no orientational hardening was observed even for pure polymer. In all these cases no reinforcing effect of the filler was observed.

The dependence of elongation at break on the Cu content in the blend composites is shown in Fig 4.51 and the data are summarized in Table 4.12. The observed trends are the same as for the stress at break and may be explained in a similar way.

Table 4.12 Mechanical properties of the PE/wax/Cu micro-composites

v/v	$\sigma_b \pm S\sigma_b$ / MPa	$\epsilon_b \pm S\epsilon_b$ / %	$E \pm sE$ / MPa
LDPE/wax/Cu			
60/40/0	9.1 ± 0.6	19.0 ± 9.4	185 ± 12.0
59/40/1	9.4 ± 0.1	20.6 ± 0.1	183 ± 11
57/40/3	8.9 ± 0.2	16.8 ± 0.4	207 ± 0
55/40/5	8.4 ± 0.2	11.4 ± 2.9	179 ± 3
50/40/10	6.8 ± 0.9	4.3 ± 1.2	271 ± 19
45/40/15	4.7 ± 1.4	3.6 ± 1.1	226 ± 33
LLDPE/wax/Cu			
60/40/0	8.4 ± 0.9	570 ± 18	166 ± 5.0
59/40/1	10.4 ± 2.0	683 ± 84	149 ± 5
57/40/3	9.4 ± 0.2	532 ± 29	169 ± 7
55/40/5	7.7 ± 0.3	524 ± 46	193 ± 6
50/40/10	7.0 ± 0.1	153.5 ± 5.9	199 ± 10
45/40/15	7.1 ± 3.1	13.7 ± 3.1	250 ± 18
HDPE/wax/Cu			
60/40/0	8.6 ± 4.1	247 ± 140	325 ± 42
59/40/1	8.1 ± 5.5	35.7 ± 4.1	353 ± 31
57/40/3	10.0 ± 4.8	27.8 ± 4.1	354 ± 32
55/40/5	10.2 ± 2.7	15.5 ± 8.1	351 ± 1
50/40/10	11.1 ± 0.6	14.8 ± 4.4	304 ± 18
45/40/15	9.0 ± 1.0	10.4 ± 4.7	300 ± 8

σ_b is stress at break and $S\sigma_b$ is the standard deviation, ϵ_b is elongation at break, $S\epsilon_b$ is the standard deviation, E is Young's modulus and sE is the standard deviation

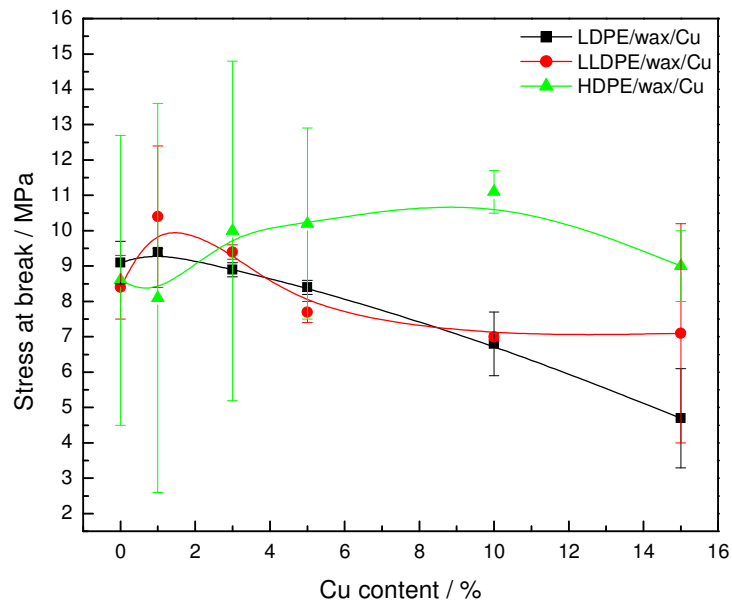


Figure 4.50 Stress at break as function of copper content in the micro-composites

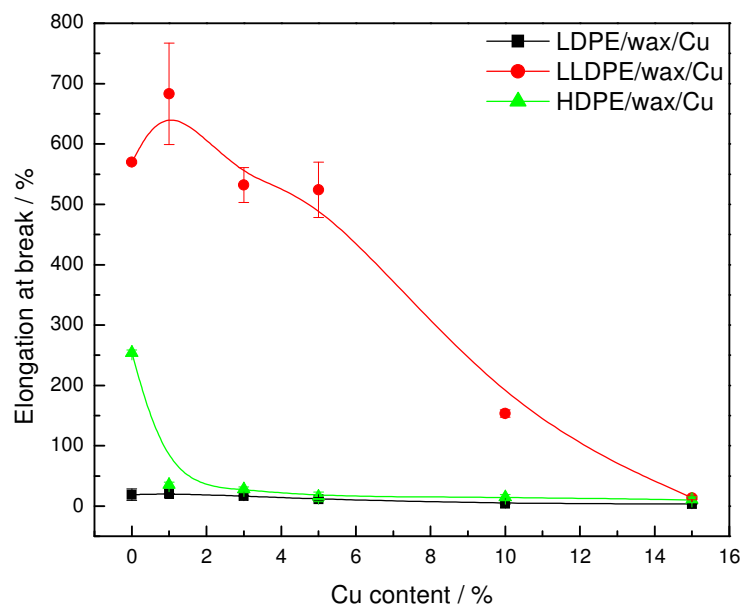


Figure 4.51 Elongation at break as function of copper content in the micro-composites

Young's moduli of the PE/wax/Cu composites as function of Cu content at 40 vol. % of wax are shown in Fig. 4.52, and the data are summarized in Table 4.12. It can be seen that Young's modulus increases with an increase in filler content at constant wax concentration for the LDPE/wax/Cu and LLDPE/wax/Cu composites, but it slightly decreases for the HDPE/wax/Cu composites. The reason for drop in Young's modulus of HDPE/wax/Cu micro-composites is probably caused by insufficient interaction between HDPE and the wax-covered Cu particles, which increases chain mobility in the vicinity of the filler. The values are higher for the LLDPE than for the LDPE matrices (Table 4.12). This is in line with the known crystallinities of the respective polyethylenes. The HDPE composites have higher Young's modulus values than the LDPE and LLDPE composites, because of the higher crystallinity of HDPE.

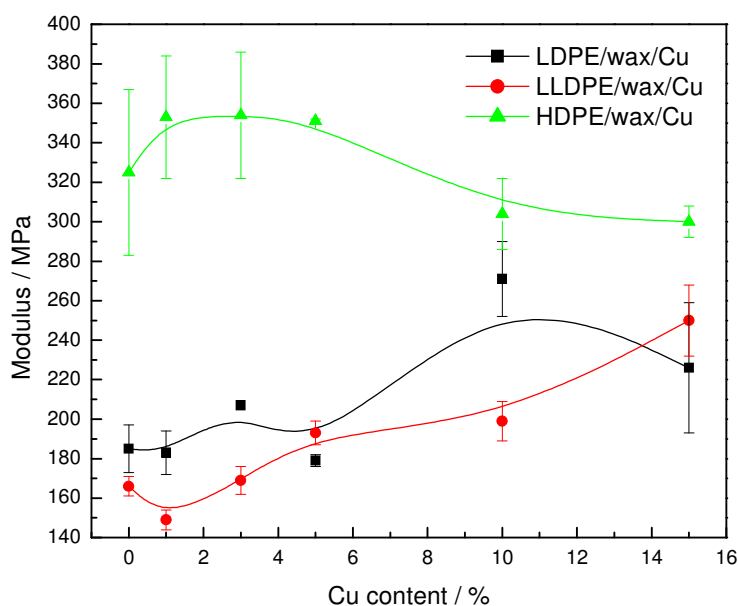


Figure 4.52 Young's modulus as function of copper content in the micro-composites

4.5 Dynamic mechanical analysis

4.5.1 PE/Cu micro-composites

The DMA results are shown in Figs. 4.53 to 4.55. Generally, for all three polyethylenes, the storage modulus increased with an increase in Cu content. This increase is attributed to presence of Cu particles which results in the stiffening of the polyethylene matrices. This is in line with the tensile results, where Young's modulus increased with increasing Cu particle contents. The storage moduli for all the samples show a decrease with increasing temperature, and the slopes of the lines change at transition temperatures, that are different for the different types of polyethylene. These relaxations are due to an increased mobility in the side chains or branches of the polyethylenes. These transitions can be seen at temperatures around -16, -27 and 40 °C for the LDPE/Cu, LLDPE/Cu and HDPE/Cu composites respectively.

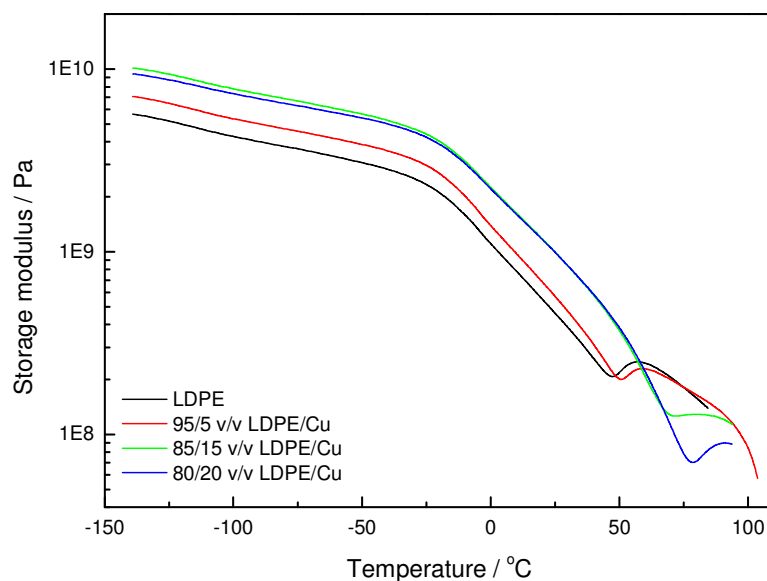


Figure 4.53 DMA storage modulus curves of pure LDPE and LDPE/Cu micro-composites

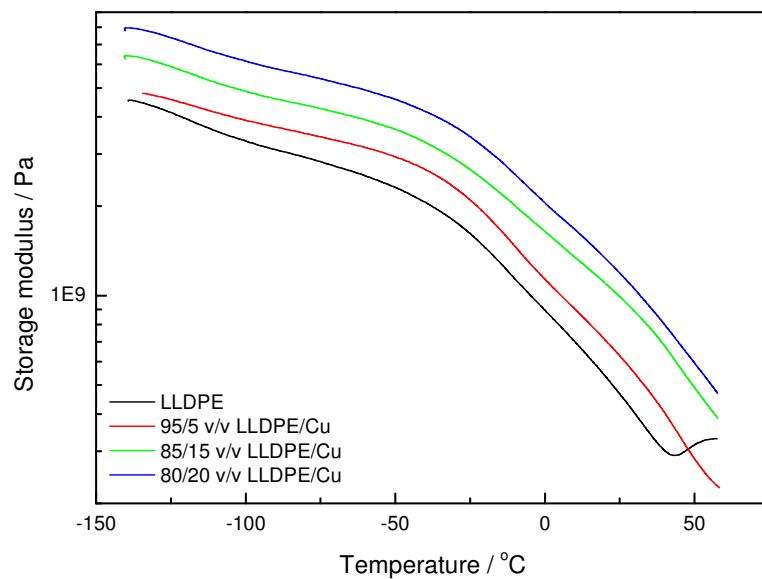


Figure 4.54 DMA storage modulus curves of pure LLDPE and LLDPE/Cu micro-composites

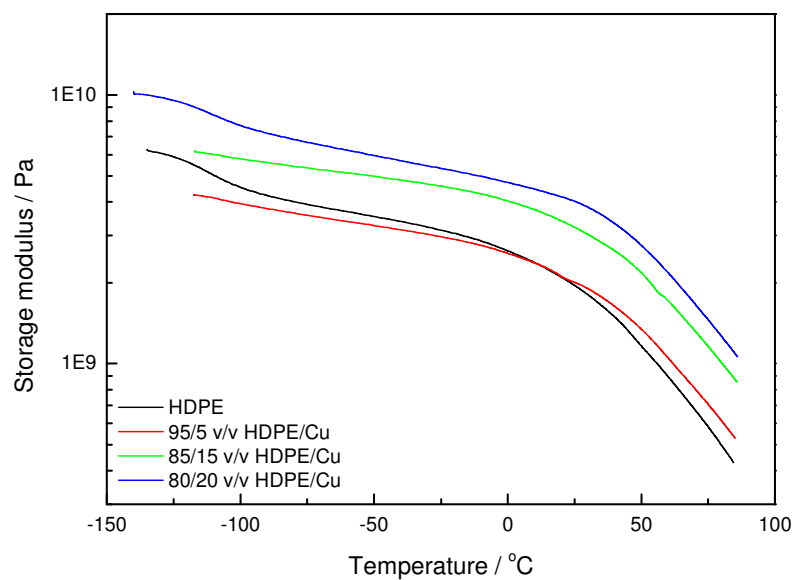


Figure 4.55 DMA storage modulus curves of pure HDPE and HDPE/Cu micro-composites

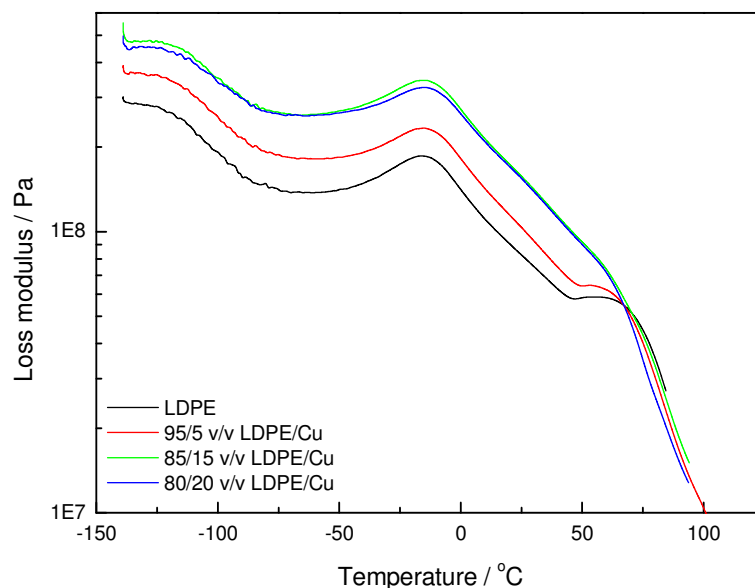


Figure 4.56 DMA loss modulus curves of pure LDPE and LDPE/Cu micro-composites

The loss modulus vs. temperature curves of LDPE and LLDPE show three transitions, namely the α , β and γ transitions, before melting. The α -transition is observed between 20 and 70 °C and is attributed to chain movements in the crystalline region. The position and intensity of this transition depends on many factors like the heating rate, density and branching [28]. An increase in density (which normally is the result of increased crystallinity) increases the intensity of this peak, and therefore the α -transition is more prominent in the case of HDPE. The β -transition occurs between -40 and 20 °C and is due to movement of the side chain segments in the crystalline-amorphous interfacial region. It is therefore prominent in LDPE and LLDPE.

The loss modulus curves for the different polyethylenes and their Cu micro-composites are presented in Figs. 4.55–4.57. Three loss maxima are found at about 66, -16 and -121 °C for LDPE, and at about 25, -27 and -125 °C for LLDPE. For HDPE two loss maxima are found at about 48 and -112 °C. For the purpose of this study, the transitions at -16 °C for LDPE and -27 °C for LLDPE can be seen as their glass transition temperatures. The glass transition is where the chains in the amorphous regions start with coordinated large-scale motion, and it is therefore not observable in the highly crystalline HDPE. The glass transition in highly

crystalline polymers (HDPE) is difficult to identify [29], and this is in line with the current observations. Although there is a controversy concerning the glass transition of polyethylenes [29], it is generally agreed that the beta transition is associated with the transition of branch points. For LDPE, which is a branched polymer, a clear beta transition peak was also detected by other researchers [30]. Sirotkin *et al.* [31] reported that for HDPE the beta transition is usually absent. This relaxation is, therefore, generally attributed to segmental motions in the non-crystalline phase. In this study both LDPE and LLDPE showed clear beta transition peaks. An increase in the loss modulus with an increase in copper particle contents is observed for most of the samples. The higher loss modulus implies lower elastic recovering, which can probably be attributed to the higher polymer rigidity.

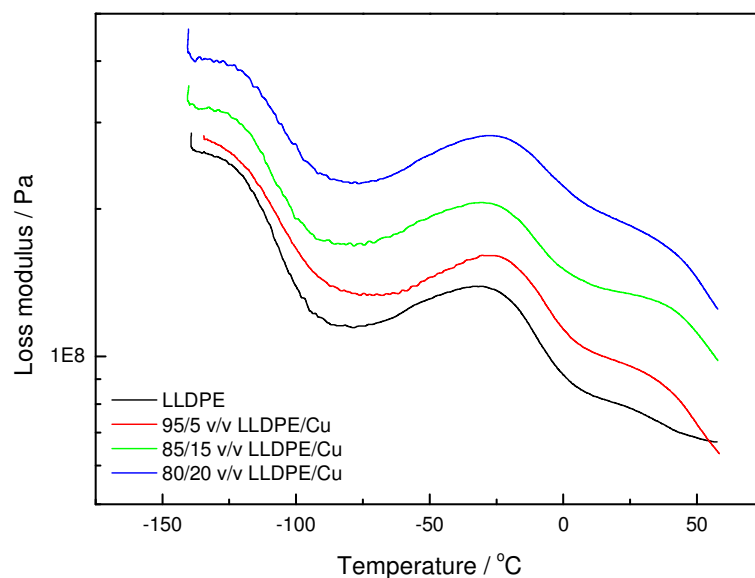


Figure 4.57 DMA loss modulus curves of pure LLDPE and LLDPE/Cu micro-composites

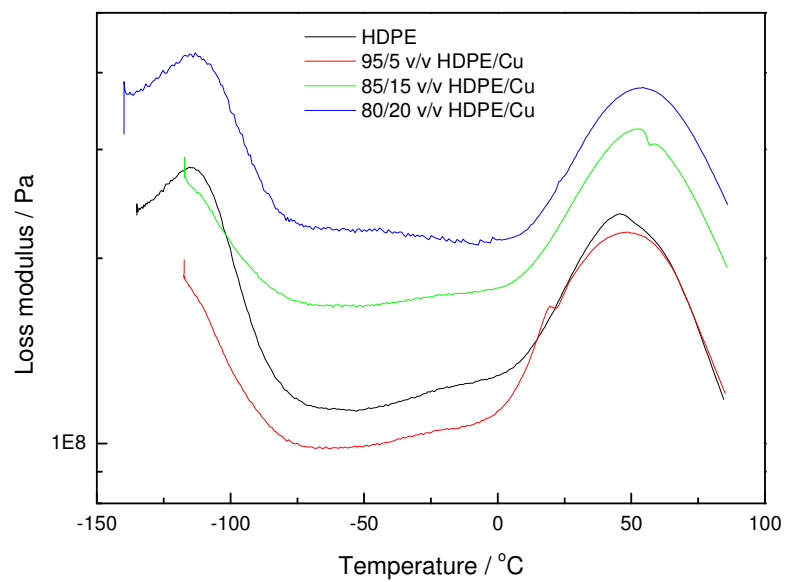


Figure 4.58 DMA loss modulus curves of pure HDPE and HDPE/Cu micro-composites

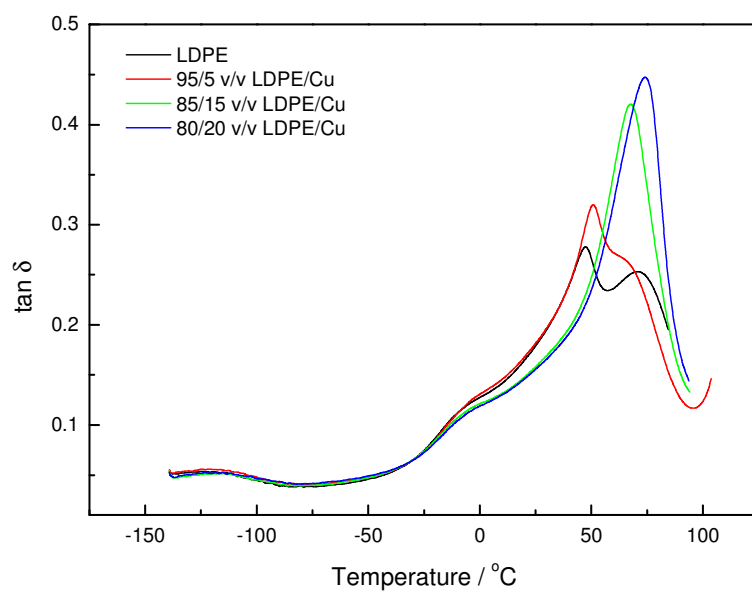


Figure 4.59 DMA damping factor curves of pure LDPE and LDPE/Cu micro-composites

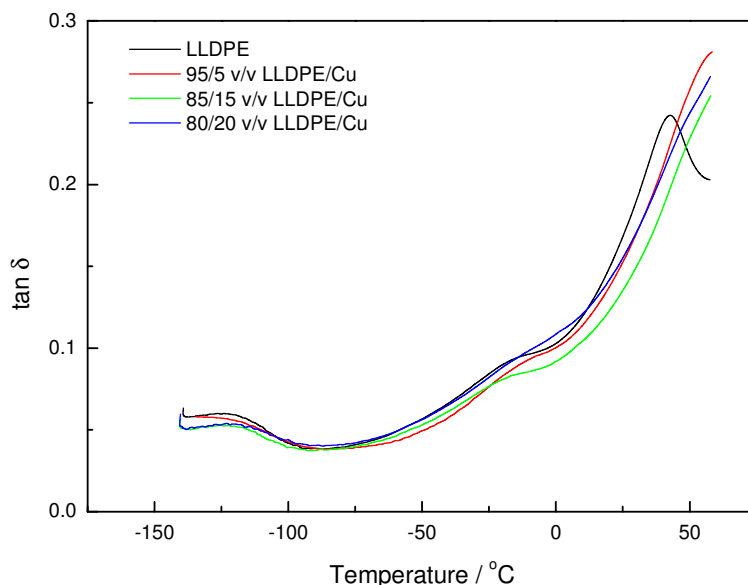


Figure 4.60 DMA damping factor curves of pure LLDPE and LLDPE/Cu micro-composites

The damping factor, $\tan \delta$, is the ratio of the loss modulus to the storage modulus and gives information on the relative contributions of the viscous and elastic components of viscoelastic materials. Figs. 4.59 to 4.61 present the $\tan \delta$ curves of the pure polyethylenes and their composites. In addition to the γ - and β -transitions, pure LDPE shows two transitions – probably the α - and α^* -transitions. The α -transition is related to larger chain segments in the amorphous phase that start to move, while the α^* -transition is associated with the slippage between crystallites [28]. As the Cu particle content increases, the composites show only one transition in this temperature region, indicating that the Cu particles suppress large-scale chain movement in LDPE through chain immobilization. As a result the α - and α^* -transitions merge into a single, more intense transition during which both large-scale chain movement and slippage of crystallites occur.

The damping factor curves of LLDPE and its composites show γ -, β - and α -transitions. In this case there is, however, only one peak in the high temperature region. This is probably due to the higher crystallinity of LLDPE. The α -transition also appears at a higher temperature for the composites compared to the pure polymer, which is the result of the immobilization of the polymer chains in the presence of the Cu particles. In the highly crystalline HDPE and its Cu

micro-composites there is no β -transition, while the α -transition is strong. In this case the α -transition is probably more related to the α^* -transition in LDPE, which is the result of slippage between crystallites. Since the Cu particles are probably located in the small amorphous areas between the crystallites, they should have an influence on the slippage between crystallites. This is, however, not clear from the presented curves in Fig. 4.61.

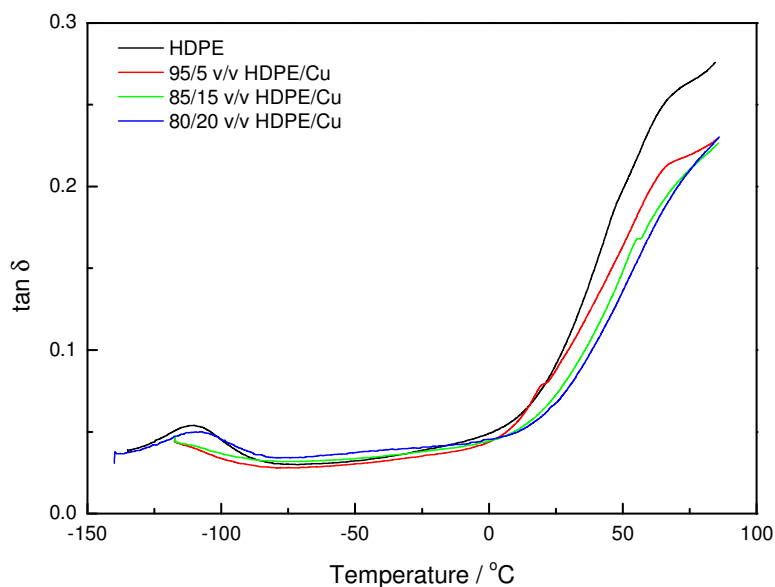


Figure 4.61 DMA damping factor curves of pure HDPE and HDPE/Cu micro-composites

4.6 Thermal conductivity of PCM

4.6.1 PE/Cu micro-composites

Polymers, paraffin waxes as well as their blends are materials with very low thermal conductivity values, that roughly varying from $0.15 \text{ W m}^{-1} \text{ K}^{-1}$ for amorphous polymers to $0.5 \text{ W m}^{-1} \text{ K}^{-1}$ for highly crystalline polymers such as HDPE [32]. There are many reasons, for various industrial applications, to increase the thermal conductivity of polymer-based materials. The applications are associated with requirements for appreciable levels of thermal conductance in circuit boards, heat exchangers, appliances and machinery [33]. A very important issue is the improvement of the thermal conductivity of phase change materials

[34]. Information on the thermal conductivity of materials is necessary for determining the optimum conditions during the processing of materials, as well as for analyzing the heat transport in materials for practical applications [35]. High performance thermally conductive materials are designed by combining polymeric matrices and dispersed conductive fillers. Several inorganic materials, graphite or metallic powders, are frequently used as thermally conductive fillers [36,37]. Silver, copper and alumina particles are the most commonly used fillers due to their high inherent thermal conductivity [17,36-38].

The thermal conductivities of the PEs (LDPE, LLDPE and HDPE) filled with copper micro-particles are summarized in Table 4.13 and presented in Fig. 4.62.

Table 4.13 Thermal conductivity of PE/Cu micro-composites

v/v	Thermal conductivity / $\text{W m}^{-1} \text{K}^{-1}$
LDPE/Cu	
100/0	0.39
99/1	0.40
97/3	0.43
95/5	0.49
90/10	0.52
85/15	0.73
80/20	0.91
75/25	1.52
LLDPE/Cu	
100/0	0.41
99/1	0.42
97/3	0.45
95/5	0.51
90/10	0.56
85/15	0.78
80/20	1.08
75/25	1.59
HDPE/Cu	
100/0	0.45
99/1	0.46
97/3	0.49
95/5	0.55
90/10	0.70
85/15	0.89
80/20	1.23
75/25	1.70

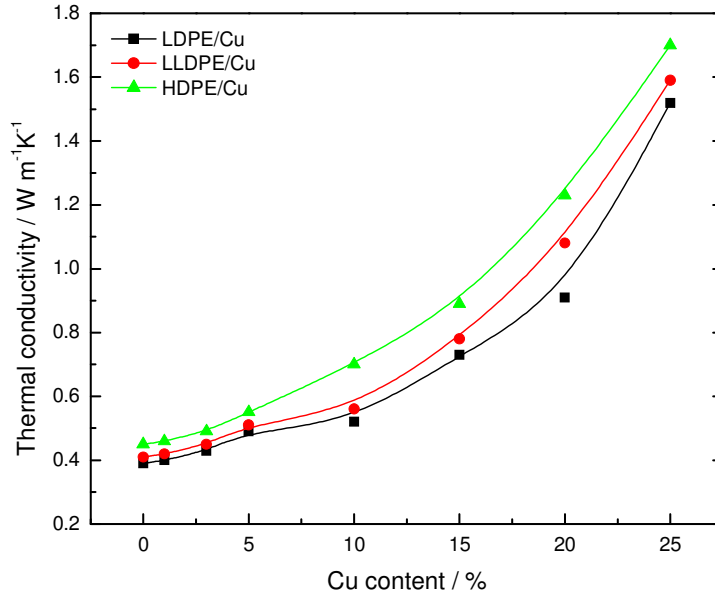


Figure 4.62 Thermal conductivity of the polyethylene composites as function of Cu micro-particle content

A non-linear increase in thermal conductivities is observed with an increase in copper content. This is foreseeable, because the filler has a significantly higher thermal conductivity than the polymeric matrices. It can be seen that thermal conductivities of the HDPE/Cu micro-composites are higher than those of both the LLDPE/Cu and LDPE/Cu micro-composites. This is due to the higher degree of crystallinity of the HDPE matrix. In the case of semi-crystalline polymers, an increase in thermal conductivity with an increase in crystalline content was observed as a consequence of the better transport of heat in the crystalline phase [39]. The simple relation between thermal conductivity of semi-crystalline polymers and the weight fraction of the crystalline phase is expressed in terms of the additive rule [8], given by Equation 4.4.

$$\lambda_m = \lambda_c w_c + \lambda_a w_a \quad (4.4)$$

where λ_m , λ_c , λ_a are the thermal conductivities of the polymer and its crystalline and amorphous phases, respectively, and w_c , w_a are the weight fractions of the crystalline and amorphous phases of the polymer.

Generally, most inorganic fillers have much higher thermal conductivity than polymers, and therefore their incorporation into the polymers leads to an increase in thermal conductivity of the composites [17,20]. Unfortunately, the prediction of thermal conductivity of filled polymers is very difficult and depends on the geometry and orientation of the filler particles in the matrix, the concentration of the filler, and the ratio between the thermal conductivity of the filler and the thermal conductivity of the matrix. Based on these factors, many different models have already been developed, but none of them has general validity [17,20], since most of the model are derived for regularly shaped particles, flakes or fibres that have a uniform size distribution. In this study, the copper particles are not regular.

4.6.2 PE/Cu nano-composites

The addition of the copper nano-particles to the polymer matrices also increases the thermal conductivity of the nano-composites over that of the pure polymers (Fig 4.63). The copper nano-particles also improve the thermal conductivity of the composites. HDPE filled with nano-particles shows the highest thermal conductivity, similar to those of the micro-composites. It can be seen from Table 4.14 that the thermal conductivities of the nano-composites are almost the same as that of the micro-composites.

Table 4.14 Thermal conductivities of the PE/Cu nano-composites

v/v	Thermal conductivity, W.m ⁻¹ K ⁻¹
LDPE/Cu	
100/0	0.39
99/1	0.40
97/3	0.42
95/5	0.52
LLDPE/Cu	
100/0	0.41
99/1	0.42
97/3	0.46
95/5	0.53
HDPE/Cu	
100/0	0.45
99/1	0.46
97/3	0.52
95/5	0.56

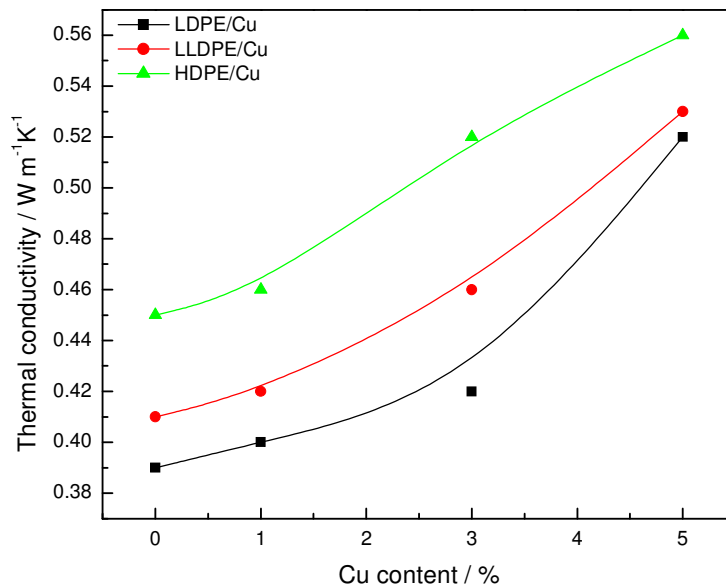


Figure 4.63 Thermal conductivity of the polyethylene composites as function of Cu nano-particle content

The thermal conductivity of all the investigated blend composites initially decreases at 1 vol. % of Cu micro-particles at a constant 40 vol. % of wax (Fig. 4.64). A further increase in Cu micro-particle content shows a non-linear increase in thermal conductivities of the PE/wax/Cu micro-composites. The initial decrease in thermal conductivity can be caused by voids formed at the interface between the polymer and the wax, as was demonstrated by SEM. These voids are filled by air which decreases the thermal conductivity. The thermal conductivities of the PE/wax/Cu micro-composites are lower than those of the PE/Cu micro-composites. Since the wax is probably concentrated around the Cu particles, as discussed earlier, it will isolate the conductive particles from the polyethylene. It is known that the wax ($0.24 \text{ W m}^{-1} \text{ K}^{-1}$) has a lower conductivity than the ($0.39 \text{ W m}^{-1} \text{ K}^{-1}$), which explains the lower thermal conductivities of the blend composites.

Table 4.15 Thermal conductivities of PE/wax/Cu micro-composites

v/v	Thermal conductivity, $\text{W}\cdot\text{m}^{-1}\text{K}^{-1}$
LDPE/wax/Cu	
100/0/0	0.39
59/40/1	0.39
57/40/3	0.36
55/40/5	0.42
50/40/10	0.47
45/40/15	0.68
LLDPE/wax/Cu	
100/0/0	0.41
59/40/1	0.38
57/40/3	0.41
55/40/5	0.46
50/40/10	0.52
45/40/15	0.71
HDPE/wax/Cu	
100/0/0	0.45
59/40/1	0.32
57/40/3	0.36
55/40/5	0.42
50/40/10	0.47
45/40/15	0.68

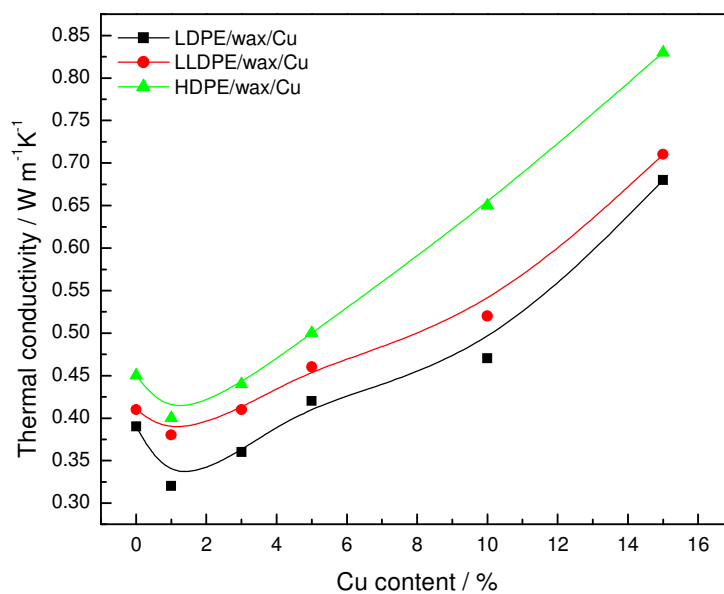


Figure 4.64 Thermal conductivity of PE/wax/Cu micro-composites

Finally we can conclude that both micro and nano particles improved the thermal conductivity of the composites and PCMs with about 50 – 70 %, dependent on the types of PE. No significant difference between the thermal conductivities of the micro- and nano-composites were observed at comparable filler content. One could expect further increases in thermal conductivity of the materials with an increase in the filler content. However, there must be a compromise between the concentrations of all the components, namely polymer, wax and copper particles. A further increase in filler content will happen only at the expense of the polymer or wax contents. However, a decrease in polymer content results in a loss of material compactness (the polymer binds all the components together), whereas a decrease in wax content leads to a decrease in heat absorption effectivity. This fact must always be taken into account when PCM materials are designed.

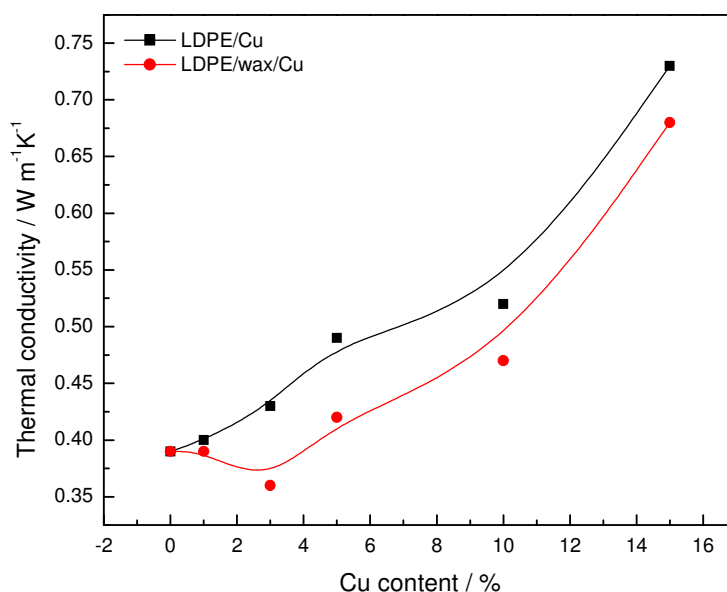


Figure 4.65 Comparison between thermal conductivities of LDPE/Cu and LDPE/wax/Cu micro-composites

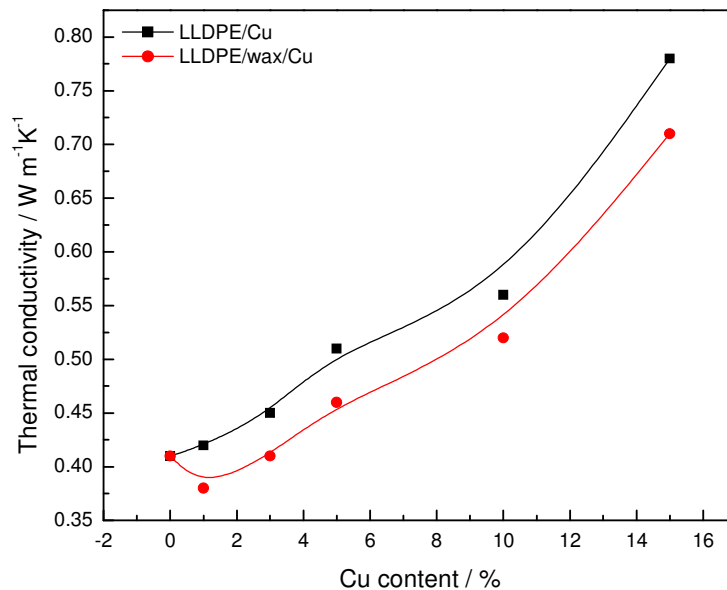


Figure 4.66 Comparison between thermal conductivities of LLDPE/Cu and LLDPE/wax/Cu micro-composites

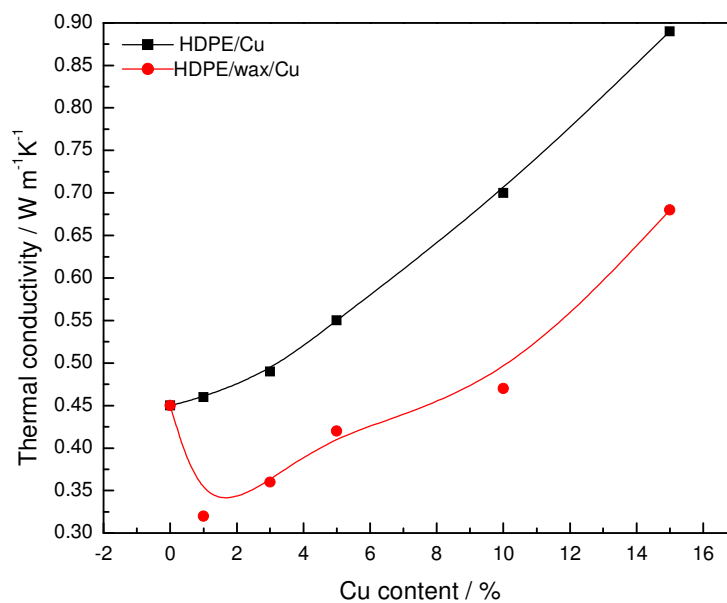


Figure 4.67 Comparison between thermal conductivities of HDPE/Cu and HDPE/wax/Cu micro-composites

4.7 Heat absorption and transport in PCMs

The heat absorption of PCM materials is most commonly characterized by DSC, where the existence of two endothermic peaks (one for the wax and one for the polymer) in the case of heating or two exothermic peaks in the case of cooling are considered as sufficient proof of PCM functionality. This was also observed in this study, as discussed in section 4.2. In this study we also tried to establish a new approach for PCM characterization based on the direct measurement of temperature in the centre of the sample, when the sample was immersed into hot water having constant temperature (90 °C). The initially expected output of this measurement is shown in Fig. 4.68.

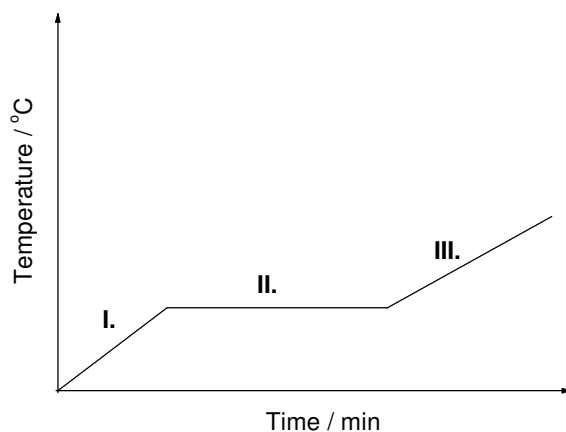


Figure 4.68 The heat absorption stages during the melting

In the first stage (region I) the temperature of the sample should increase due to the heating of the sample. Then, if the wax starts to melt, the temperature of the sample should stay constant due to the heat absorption during melting. Finally, if all the wax is molten, the temperature should start to increase again. Unfortunately, the experimental results did not prove this concept, neither for the heating step nor for the cooling step, as can be seen in Figures 4.69-4.74.

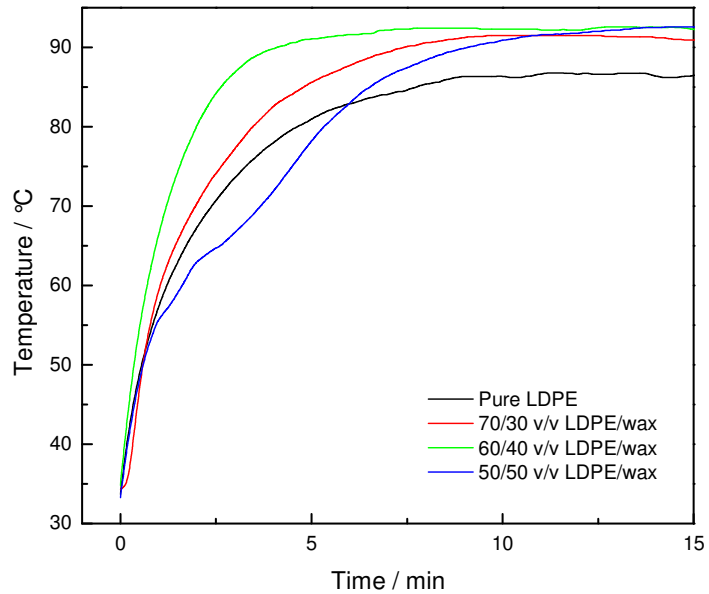


Figure 4.69 Heating curves of pure LDPE and LDPE/wax blends

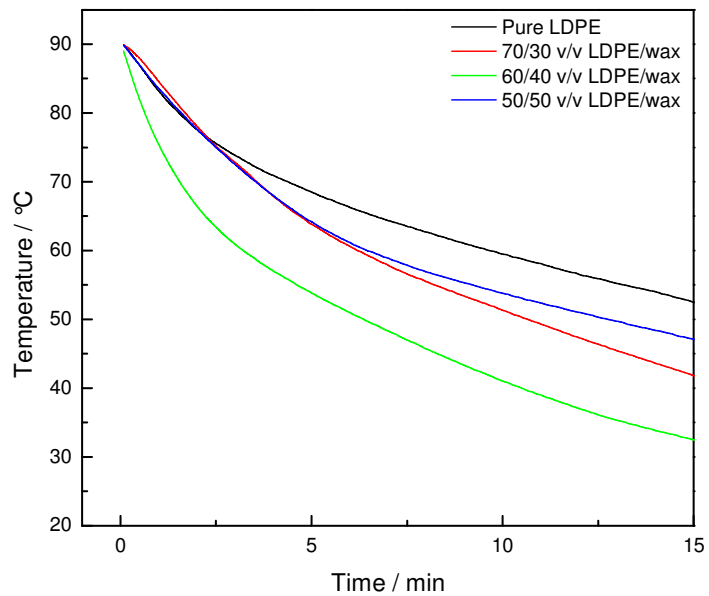


Figure 4.70 Cooling curves of pure LDPE and LDPE/wax blends

As can be seen in Fig. 4.69, the temperature monotonously increases with time. No plateau was observed in the heating curve. Only a small shoulder was observed in the heating curve of the 50/50 v/v LDPE/wax sample that could indicate wax melting. This discrepancy between expectation and reality can be explained as follows: One can suppose that there is not enough time during the heating process to reach thermal equilibrium between the polymeric and wax phases. It means that even during melting of the wax the polymeric phase is heated and therefore the temperature of sample increases. This indicates that the size and internal morphology of the PCM is crucial in designing PCM materials and has to be optimized for any practical application.

It can be seen in Fig. 4.71 that the heat transport is faster in the case of the blend composites compared to the polymer/wax blends. The heat transport in the polymer/wax blends is also faster than in the neat polymer. It is seen that 15 minutes of heating (time of the experimental run) is not long enough to reach thermal equilibrium between the hot water (at 90 °C) and the polyethylene. The same is true for the cooling step.

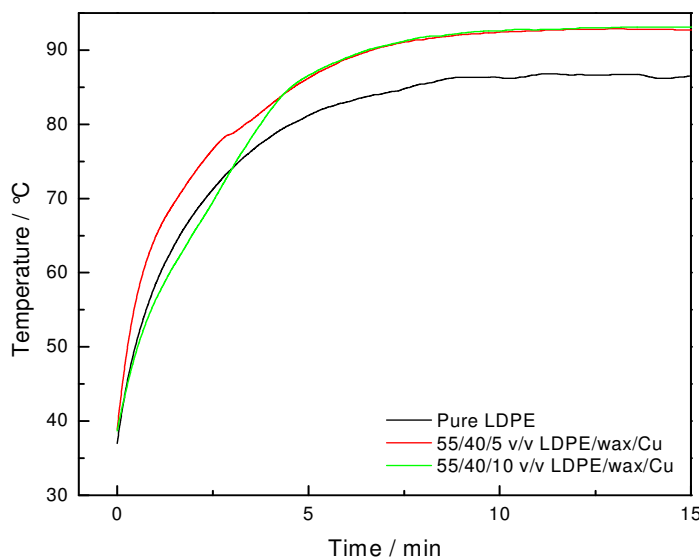


Figure 4.71 Heating curves of pure LDPE and LDPE/wax/Cu micro-composites

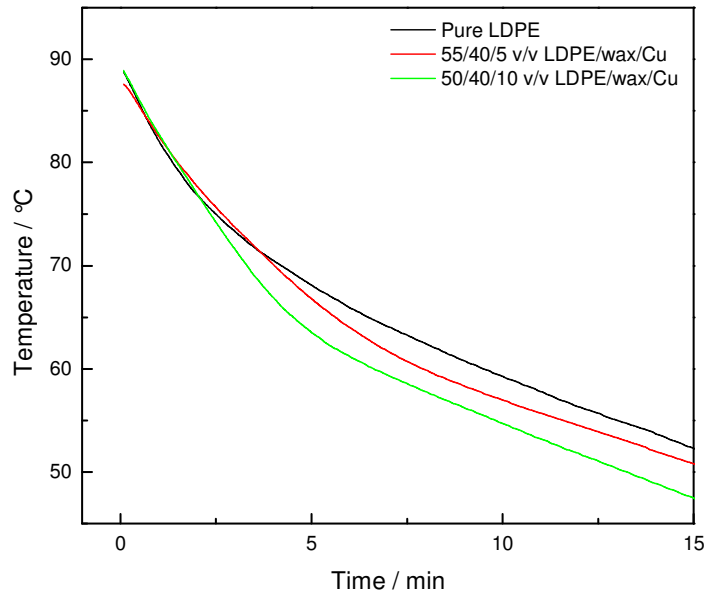


Figure 4.72 Cooling curves of pure LDPE and LDPE/wax/Cu micro-composites

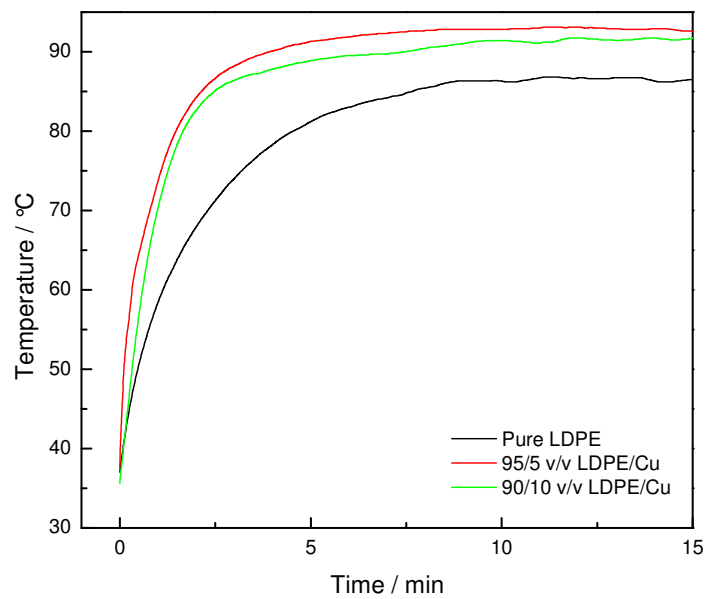


Figure 4.73 Heating curves of pure LDPE and LDPE/Cu micro-composites

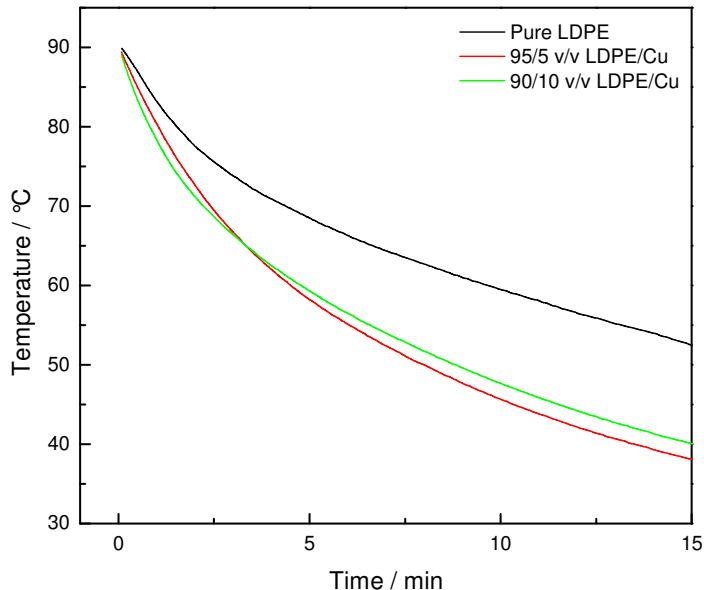


Figure 4.74 Cooling curves of pure LDPE and LDPE/Cu micro-composites

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CHAPTER 5

CONCLUSIONS

The purpose of the study was to form phase change materials (PCMs) that can store and conduct heat. The influence of wax and copper contents on the morphology as well as thermal, mechanical and conductivity properties was investigated through four systems namely, PE/Cu micro- and nano-composites, PE/wax blends and PE/wax/Cu micro-composites.

For PE/Cu micro-composites, the Cu particles were fairly well dispersed in the polymer matrix, but as the filler content increased, voids around the Cu particles were observed indicating poor interaction between the polymer and the Cu micro-particles. The lack of adhesion between the polymer and filler indicates poor interfacial interaction. The Cu nano-particles were well dispersed in the polymer matrix, except that they tended to form agglomerates. This could also account for the deterioration in physical properties, since the transfer of stress from the matrix is less effective. For the blended micro-composites, the results showed that the Cu micro-particles had a greater affinity for the wax than for the polyethylenes, giving rise to preferable crystallization of the wax around the Cu particles.

When wax was introduced in the polyethylenes (LDPE, LLDPE and HDPE), a two-phase morphology was observed, implying the immiscibility of PE and wax at wax contents of 30, 40 and 50%. This showed that PCMs were successfully formed, and that there was no leakage of the wax from the polyethylene matrix. The presence of wax in PE/wax blends reduced the melting temperatures of all three polyethylenes, indicating the plasticizing effect of the molten wax in the PE matrix.

Incorporation of both Cu micro- and nano-particles into the different polyethylenes reduced the crystallinities of the different polyethylenes. Generally the nano-composites had a more significant influence because of the larger total surface area of these particles. Even though the nano-particle tended to form agglomerates, their influence were still more significant than that of the micro-particles. The micro-particles generally had a nucleating effect and facilitated the crystallization process, while the well dispersed nano-particles hindered the crystallization of polyethylene.

With Cu micro-particles present in the PE/wax blends, the polyethylene and wax phases were still phase separated, and all results indicated that there was no wax leakage from the polyethylene matrices. The presence of Cu did not change the melting and crystallization behaviour of the blends, despite the fact that the wax seems to have a higher affinity for the Cu and preferably crystallizes on the Cu surface. The thermal conductivities of the blended composites were higher than those of the wax and the polymer, but lower than those of the PE/Cu composites, probably because of the preferable crystallization of the wax around the Cu particles.

Since linear chain polyethylenes are more difficult to decompose than the branched ones, the pure LDPE degraded at much lower temperatures compared to LLDPE and HDPE. Generally the presence of Cu particles in the polyethylenes showed an increase in thermal stability with increasing Cu content, indicating that the Cu particles either immobilized the free radical chains or inhibited the diffusion of the volatile degradation products. The Cu nano-particles had a more significant influence than the micro-particles, and the influence of both types of particles became less significant with increasing polymer crystallinity. The thermal stabilities of the blends and composites decreased with increasing wax content.

Cu micro- and nano-particles had variable influence on the tensile stress at break, elongation at break and modulus of the different composites, but the presence of high contents of wax generally reduced these properties. Only the modulus values increased in the presence of copper, wax or both. However, HDPE was an exception because of its high crystallinity, which was even higher than that of the highly crystalline wax. It was found that the higher the amorphous content, the weaker was the influence of the Cu particles on the overall chain mobility of the polymer. As a result of their higher total surface area, the nano-particles had a stronger influence, especially in the more crystalline polyethylenes.

LDPE showed four (γ , β , α and α^*), LLDPE three (γ , β and α), and HDPE two (γ and α) transitions. The presence of copper had an influence on some of these transitions because of its chain immobilization effect. This influence became less significant for the polyethylenes with higher crystallinities.

It seems as if the presence of copper improved the rate of absorption of heat during the melting process of the wax in the phase change materials. The other results also indicated the effectiveness of heat absorption and storage by the wax which crystallizes separately in all

three the investigated polyethylenes. Based on this, it will be worth carrying on with investigations into these systems as possible phase change materials in which thermal energy storage and the rate of energy absorption can be controlled.

The Cu nano-filler had almost the same influence on all the investigated properties of the different polyethylenes at about half the filler content compared to the micro-filler. The final conclusions from this research are therefore:

- Generally the presence of copper filler, whether nano- or micro-sized, does not significantly change the thermal properties of the different polyethylenes and polyethylene/wax blends, but the tensile properties were quite significantly influenced.
- The presence of these fillers significantly improved the thermal conductivity and heat absorption of the phase change materials.
- The differences between the influence of Cu nano- and micro-particles on the different material properties were not so significant so as to justify the use of (very expensive) nano-particles for these applications.

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A great Thanks To all

Appendix

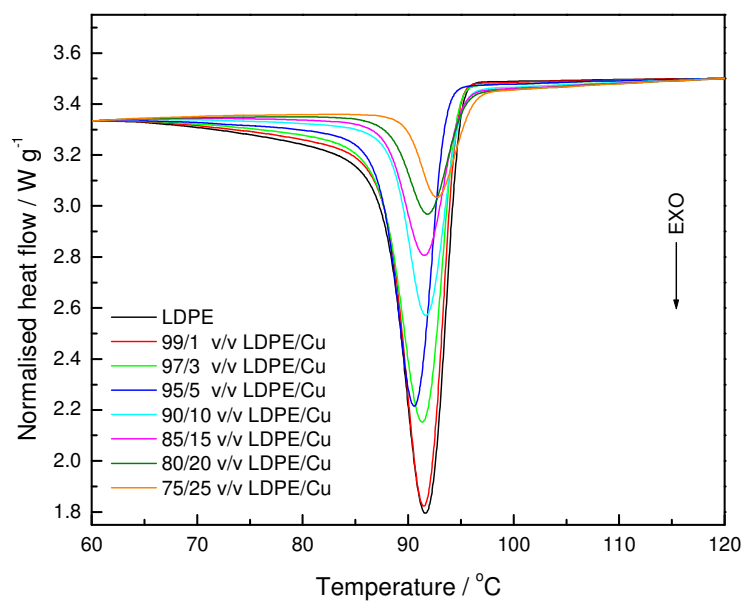


Figure A.1 DSC cooling curves of LDPE and LDPE/Cu micro-composites

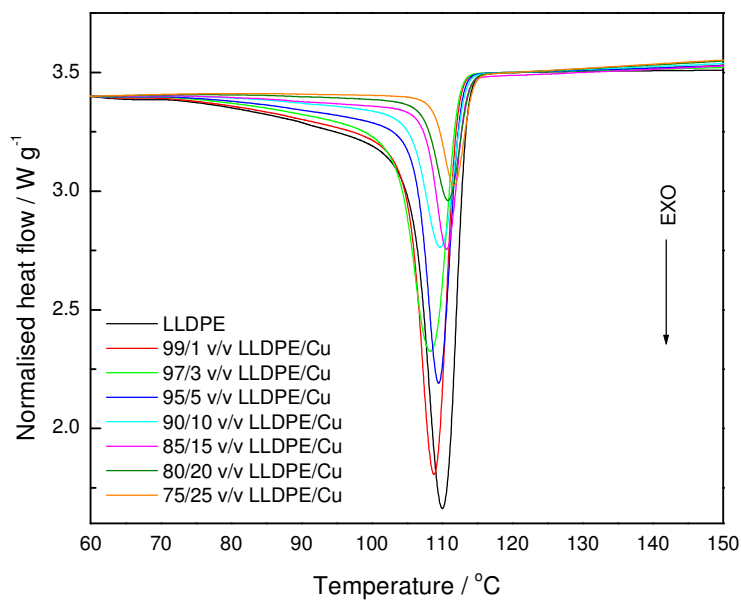


Figure A.2 DSC cooling curves of LLDPE and LLDPE/Cu micro-composites

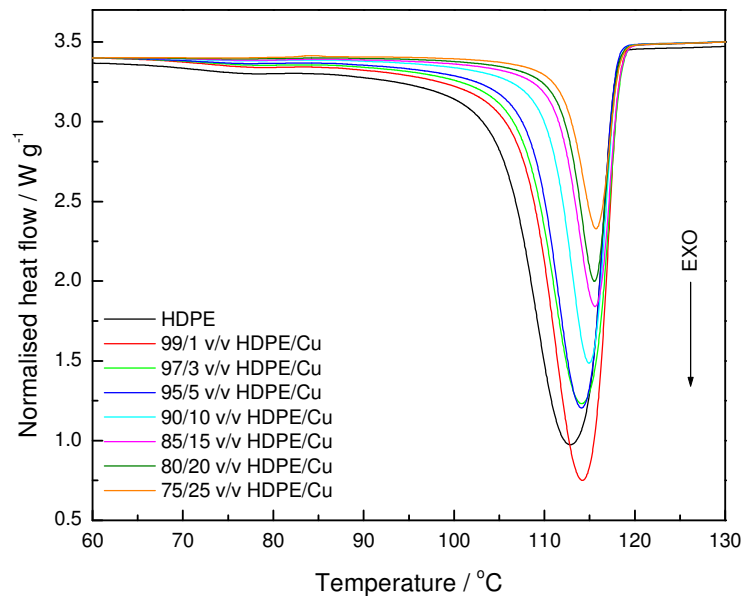


Figure A.3 DSC cooling curves of HDPE and HDPE/Cu micro-composites

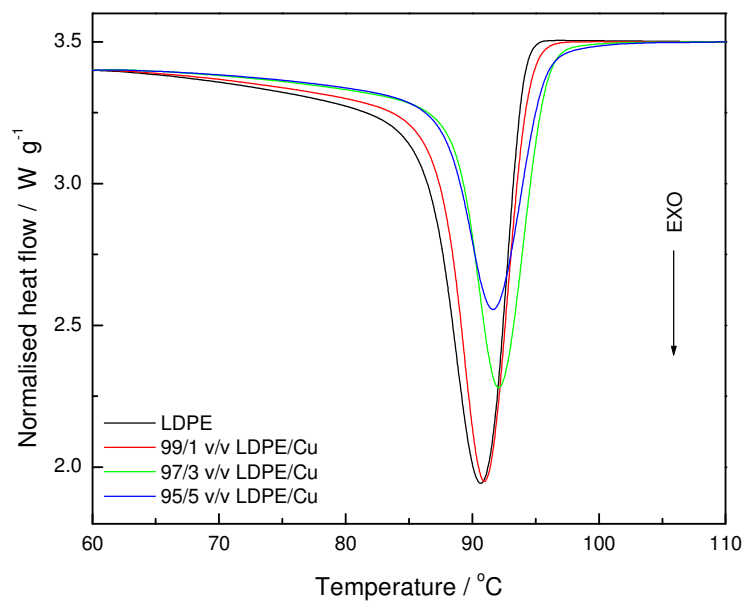


Figure A.4 DSC cooling curves of LDPE and LDPE/Cu nano-composites

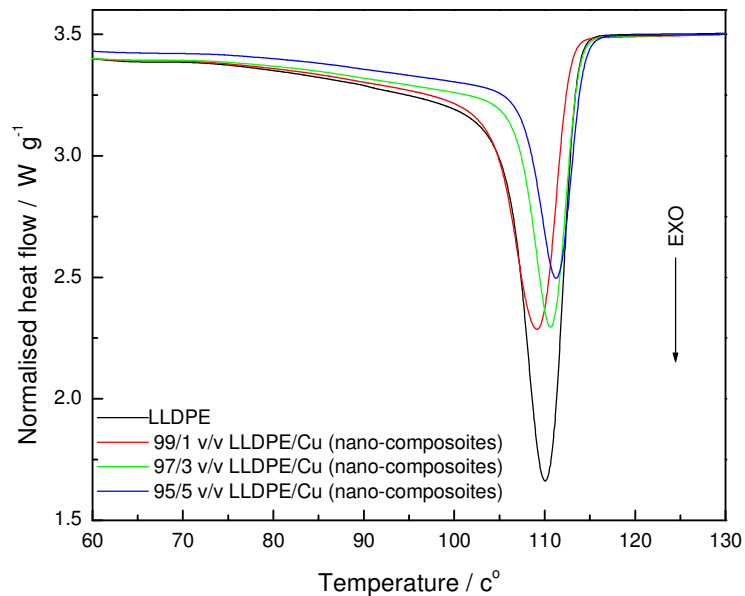


Figure A.5 DSC cooling curves of LLDPE and LLDPE/Cu nano-composites

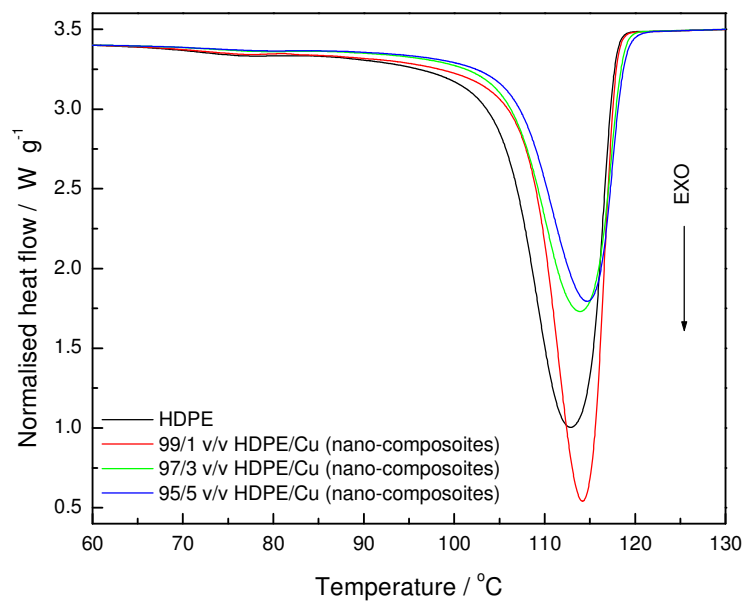


Figure A.6 DSC cooling curves of HDPE and HDPE/Cu nano-composites

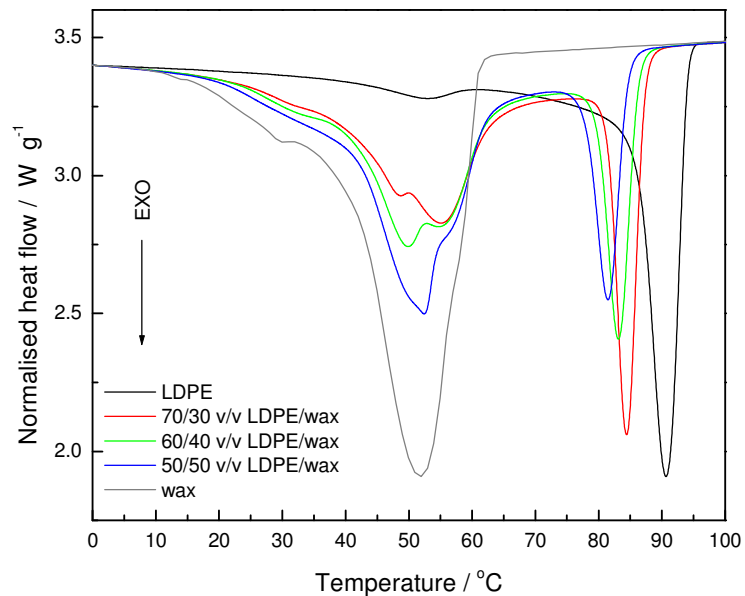


Figure A.7 DSC cooling curves of LDPE and LDPE/wax blends

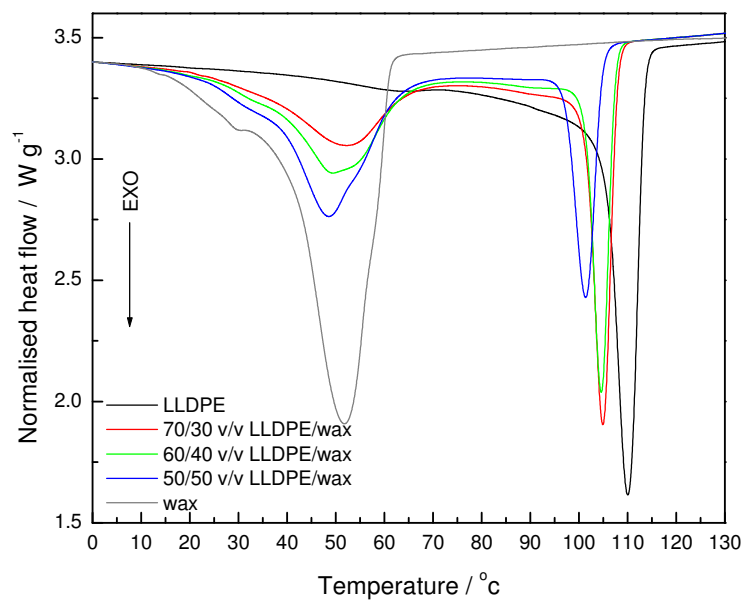


Figure A.8 DSC cooling curves of LLDPE and LLDPE/wax blends

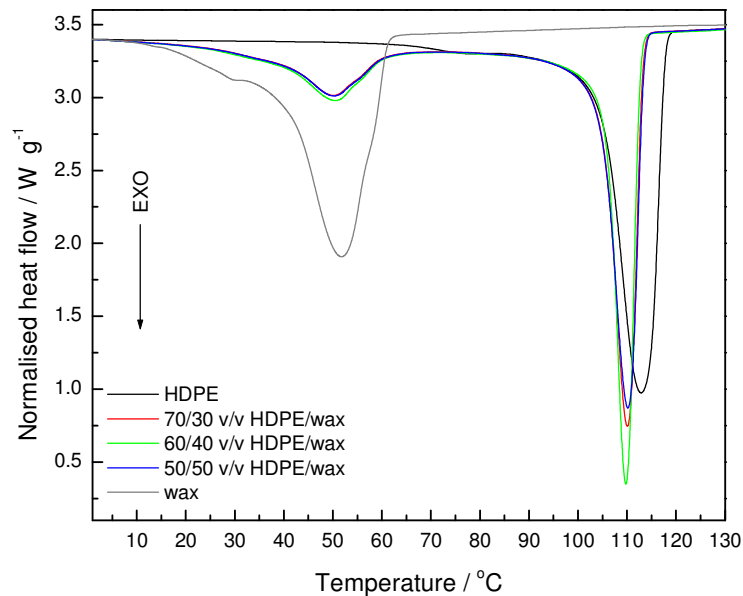


Figure A.9 DSC cooling curves of HDPE and HDPE/wax blends

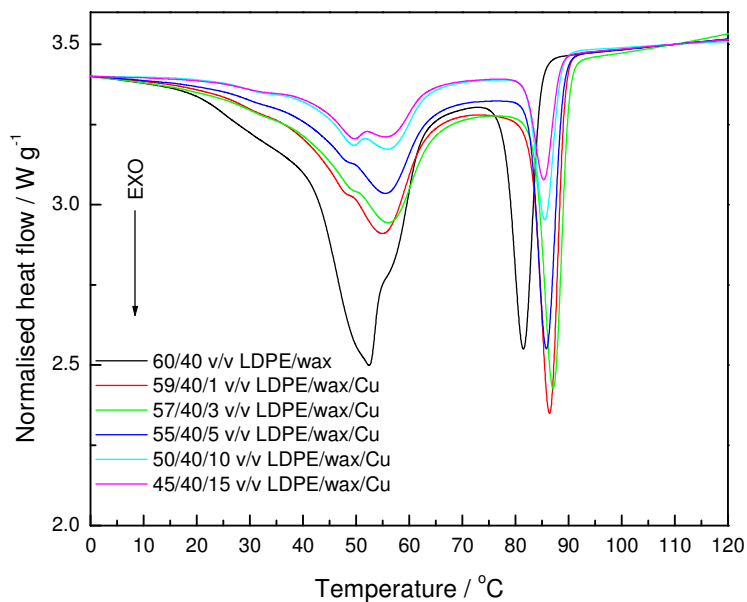


Figure A.10 DSC cooling curves of LDPE and LDPE/wax/Cu composites

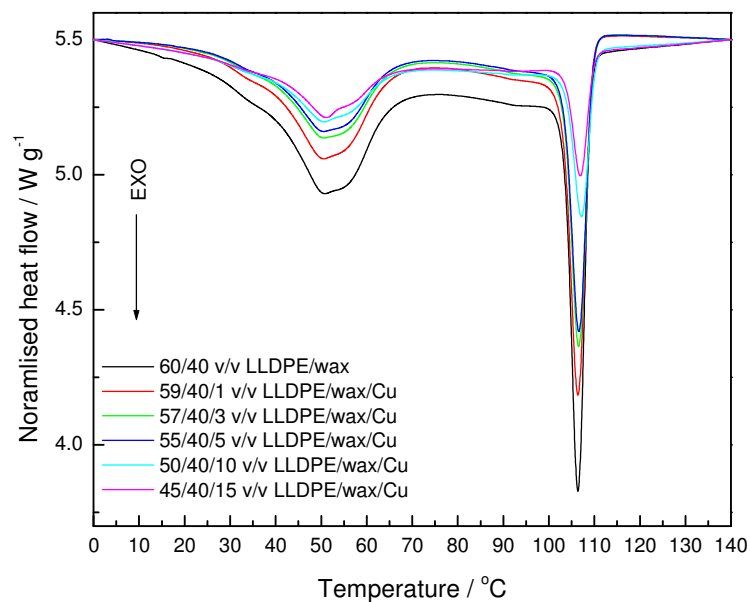


Figure A.11 DSC cooling curves of LLDPE and LLDPE/wax/Cu composites

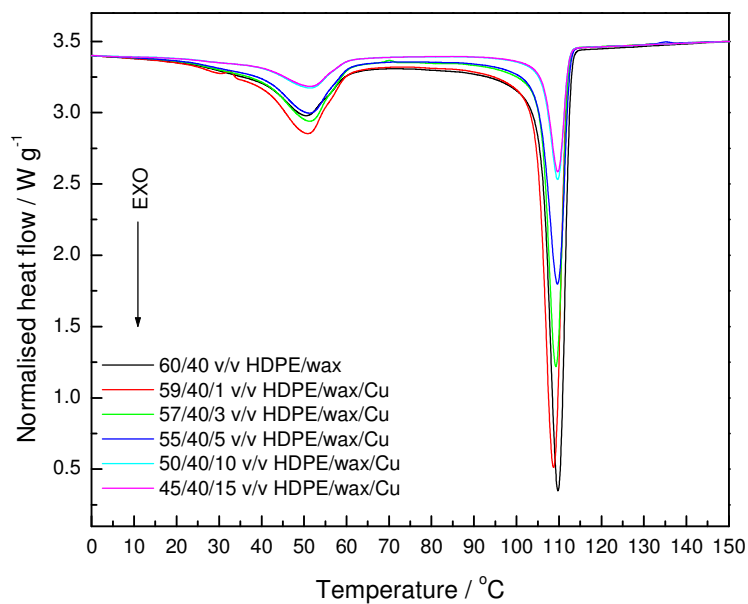


Figure A.12 DSC cooling curves of HDPE and HDPE/wax/Cu composites

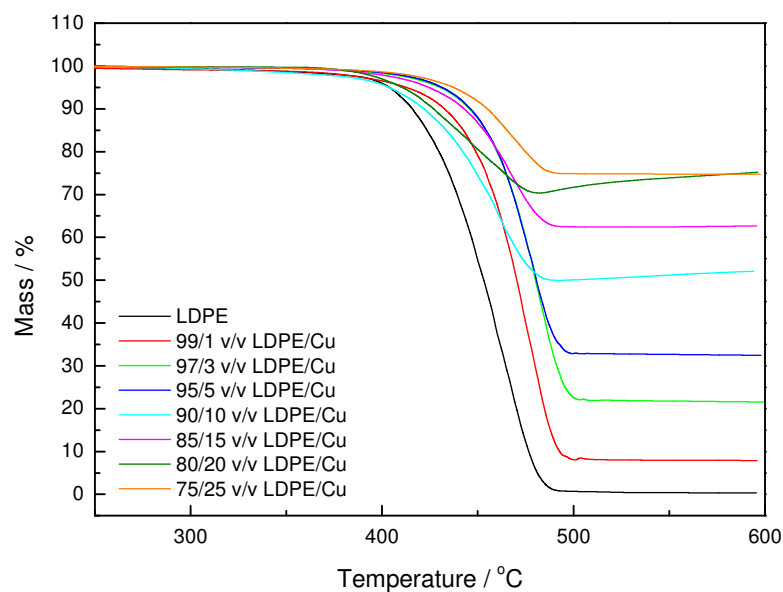


Figure A.13 TGA curves of LDPE and LDPE/Cu micro-composites

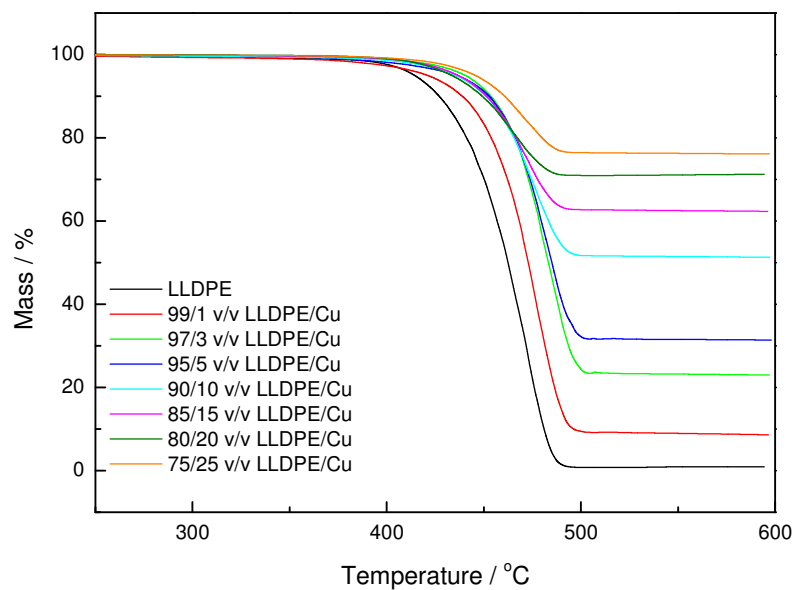


Figure A.14 TGA curves of LLDPE and LLDPE/Cu micro-composites

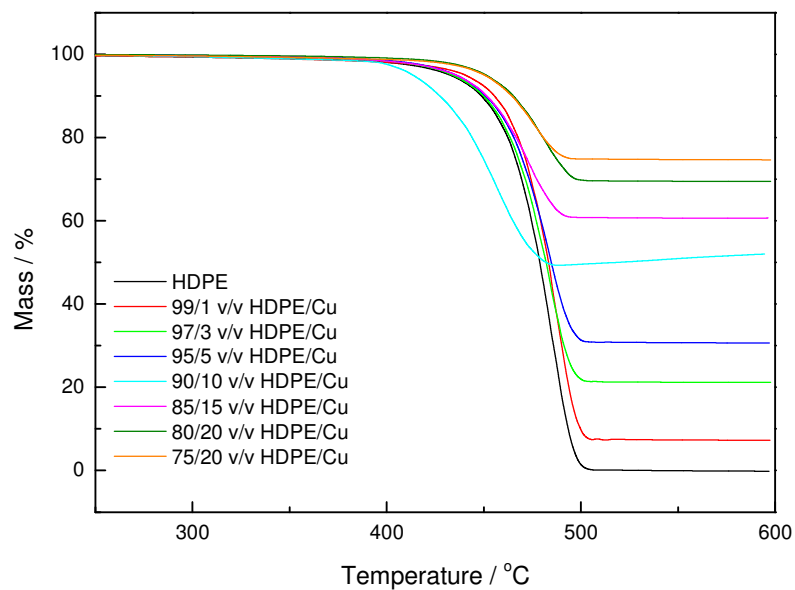


Figure A.15 TGA curves of HDPE and HDPE/Cu micro-composites

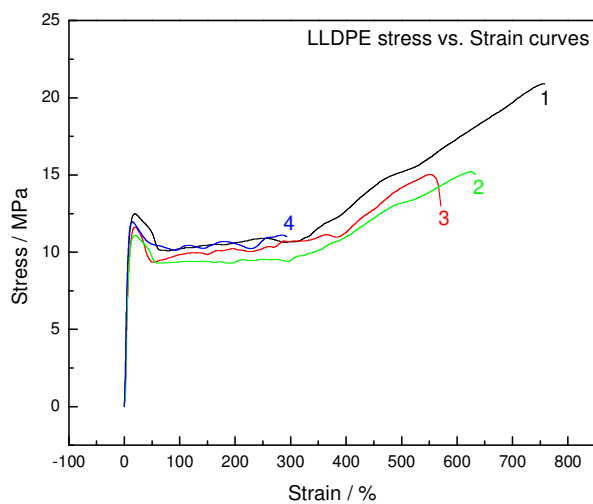


Figure A.16 Stress-strain curves for LLDPE/Cu composites with different concentrations of copper powder: (1) 0 vol.%, (2) 1 vol.%, (3) 5 vol.%, (4) 10 vol.%

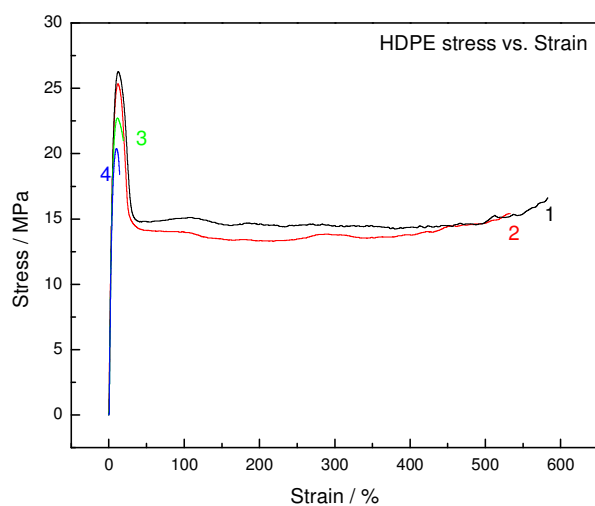


Figure A.17 Stress-strain curves for HDPE/Cu composites with different concentrations of copper powder: (1) 0 vol.%, (2) 1 vol.%, (3) 5 vol.%, (4) 10 vol.%

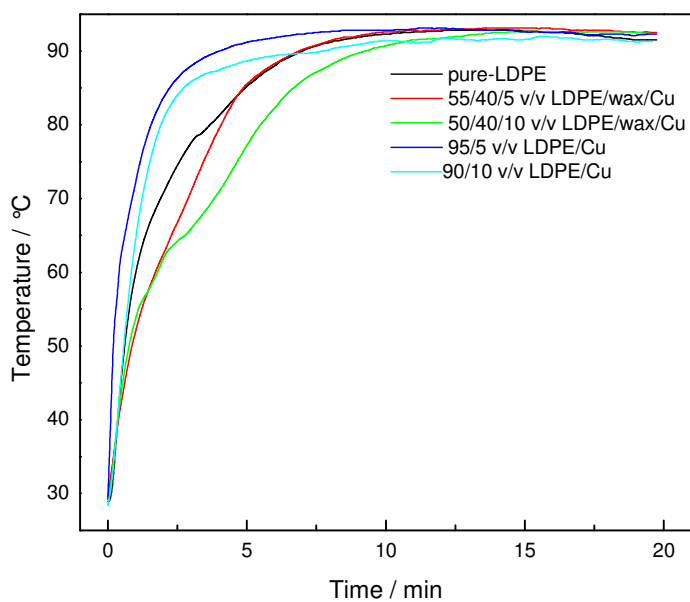


Figure A18 Heating curves of pure LDPE, LDPE/Cu and LDPE/wax/Cu blend composites

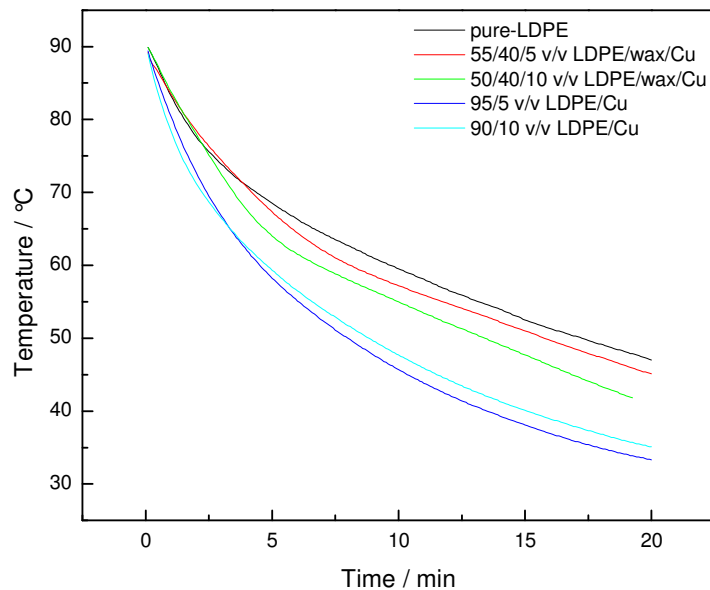


Figure A.19 Cooling curves of pure LDPE, LDPE/Cu and LDPE/wax/Cu blend composites

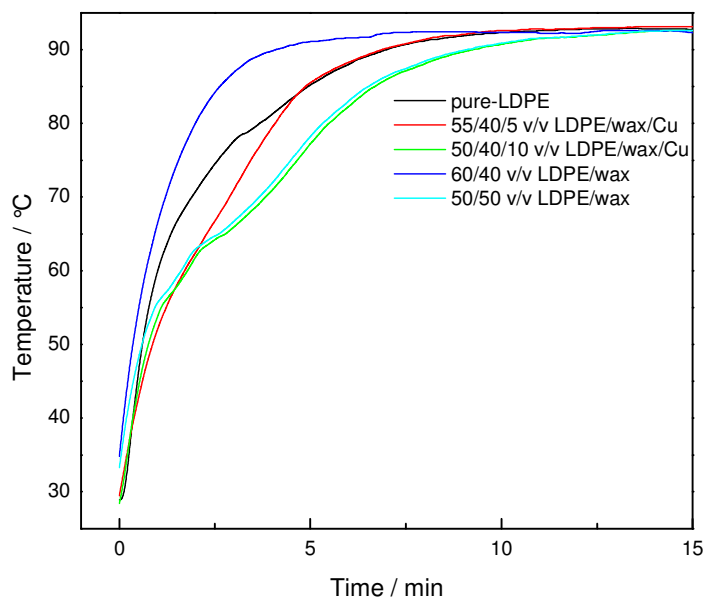


Figure A.20 Heating curves of pure LDPE and LDPE/wax/Cu blend composites

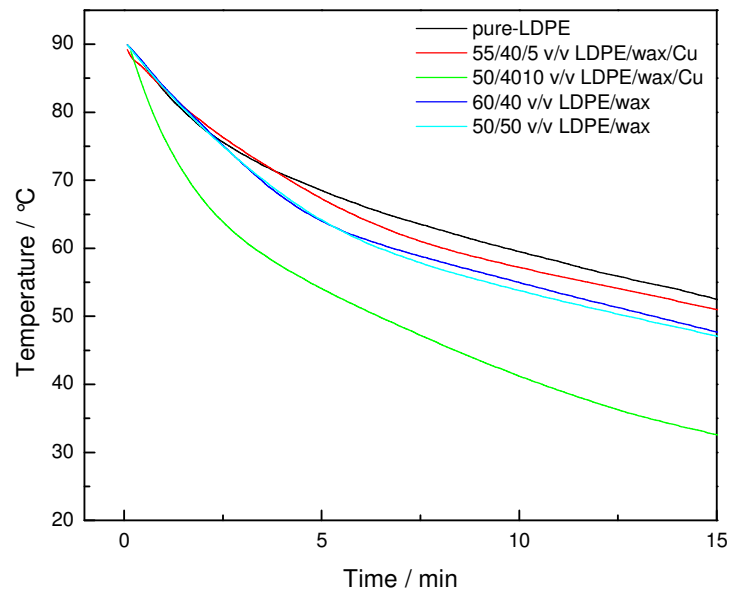


Figure A.21 Cooling curves of pure LDPE and LDPE/wax/Cu blend composites