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Synthesis and Evaluation of Novel Polymer Modifiers for Biodegradable Polymers

by

James Ashley Burford

A thesis submitted for the Degree

of

Doctor of Philosophy

of

The University of Aston in Birmingham

May 2002

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James Ashley Burford.

PhD 2002

Summary

The effects of ester plasticizers and copolymers on the mechanical properties of the natural biodegradable polymers, poly(3-hydroxybutyrate) [PHB] and poly(lactic acid) [PLA] have been studied after subjecting to melt processing conditions. Ester plasticizers were synthesized from citric, tartaric and maleic acids using various alcohols. A variety of PLA copolymers have also been prepared from poly(ethylene glycol) derivatives using stannous octanoate catalysed ring opening polymerisations of DL-lactide. A novel PLA star copolymer was also prepared from an ethoxylated pentaerythritol. The structures of these copolymers were determined by NMR spectroscopy.

The plasticizing effect of the synthesised additives at various concentrations was determined. While certain additives were capable of improving the mechanical properties of PLA, none were effective in PHB. Moreover, it was found that certain combinations of additives exhibited synergistic effects. Possible mechanisms are discussed.

Biotic and abiotic degradation studies showed that the plasticizers (esters and copolymers) did not inhibit the biodegradability of PHB or PLA in compost at 60°C. Simple toxicity tests carried out on compost extract and its ability to support the growth of cress seeds was established.

PLA was found to be susceptible to limited thermal degradation under melt processing conditions. Conventional phenolic antioxidants showed no significant effect on this process, suggesting that degradation was not predominantly a free radical process. PLA also underwent photo-oxidative degradation with UV light and the process could be accelerated in the presence of a photoactivator such as iron (III) diisononyl dithiocarbamate.

The mechanisms for the above processes are discussed.

Finally, selected compounds were prepared on a pilot plant scale. Extruded and blown films were prepared containing these additives with conventional polymer processing equipment. The mechanical properties were similar to those obtained with laboratory produced compression moulded films.

KEYWORDS: Poly(lactic acid), Poly(3-hydroxybutyrate), lactide, degradation, plasticizers.

To my Mother

Acknowledgements

Firstly, I would like to take this opportunity to thank the European Union, whose significant funding under the Craft programme made this work possible.

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On a personal note, my sincere appreciation goes to my partner, Rebecca, for her patience, encouragement and moral support throughout the duration of this project.

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Abbreviations

ECO	Poly(ethylene-*co*-carbon monoxide)
EHC	Tri(2-ethylhexyl) citrate
EHM	Di(2-ethylhexyl) maleate
EHT	Di(2-ethylhexyl) tartrate
EVA	Poly(ethylene-*co*-vinyl acetate)
FeDNC	Iron (III) diisononyl dithiocarbamate
IBC	Tri(*iso*butyl) citrate
IBM	Di(*iso*butyl) maleate
IBT	Di(*iso*butyl) tartrate
Irganox 1076	Octadecyl-1-3,5-di-*tert*-butyl-4-hydroxyhydrocinnamate
LLDPE	Linear low density polyethylene
MeOPEG	Poly(ethylene glycol)methyl ether
Metone A	2,2'-Methylene bis cyclohexane-1,3-dione
MFI	Melt Flow Index
NOC	Tri(n-octyl) citrate
NOM	Di(n-octyl) maleate
NOT	Di(n-octyl) tartrate
PCL	Poly(ε-caprolactone)
PDLA	Poly(D-lactic acid)
PHB	Poly(3-hydroxybutyrate)
PLA	Poly(lactic acid)
PLLA	Poly(l-lactic acid)
PP150	Pentaerythritol ethoxylate
PTSA	*para*-toluene sulfonic acid
TMHC	Tri(3,5,5-trimethylhexyl) citrate
TMHM	Di(3,5,5-trimethylhexyl) malate
TMHS	Di(3,5,5-trimethylhexyl) succinate
TMHT	Di(3,5,5-trimethylhexyl) tartrate

Chapter 1

Introduction

1.1 Waste disposal

Polymers in general have a range of excellent physical and mechanical properties and for this reason have enjoyed great success as construction materials often replacing glass, wood and even metals in certain applications. Moreover, because of increasing technological improvements to existing polymeric materials, their uses have become increasingly more widespread. Not all of these applications of polymers are replacements for durable goods. Indeed polymeric materials have created their own markets and applications, amongst which are the uses of polymers in packaging systems. Consequently, plastic materials constitute a tremendous proportion of today's waste, the majority are polymers mostly derived from oil based feed stocks. These materials include polymers such as polypropylene (PP), polyethylene (PE), polystyrene (PS) and polyvinyl chloride (PVC). At the end of their useful lives, plastic materials may be incinerated or disposed of in landfill sites, along with other household wastes, where they persist (because of their inherent stability) for many years. Indeed most of these plastic materials have additional extremely effective antioxidants and other additives added to them so resist degradation for long periods of time. In Western Europe, the consumption of plastic materials was approximately 24 million tonnes in 1995 [1]. However, despite the huge demand, plastic waste only accounts for 0.6% of total waste by weight but it has a large environmental impact by virtue of its low density and large volume.

In recent years, there have been attempts to develop recycling strategies in the wake of environmental legislation. More importantly, particularly in Western Europe, suitable areas for landfill sites are diminishing rapidly. Consequently, many waste management schemes to control disposed waste have been developed. The Department of the Environment, Transport and Regions (DETR) has estimated that

27 million tonnes of household waste was sent for landfill in the United Kingdom in 1995 [2], 60% of which was assumed to be biodegradable. By 2015, 30% of household waste is expected to be composted or recycled and 45% of municipal waste should be recovered. The various waste components are shown in Table 1.1. The main concern with biodegradable household waste is that it produces methane as it degrades, which is a significant greenhouse gas [3]

Municipal waste component	**Portion of municipal waste stream %**	**Biodegradable content (1=all, 0.5=half, 0=none)**	**Biodegradable portion of municipal waste stream %**
Paper/card (including newspapers, cartons, card packaging)	32	1	32
Food and garden waste	21	1	21
Textiles	2	0.5	1
Particulates	7	0.5	3.5
Miscellaneous (eg disposable nappies)	8	0.5	4
Miscellaneous non-combustibles	2	0.5	1
Other (ferrous & non-ferrous metal, glass, plastic)	28	0	0
Totals			62.5%

Table 1.1. Waste streams to landfill [2]

There are several alternatives to landfill disposal, such as, recycling, incineration and composting. However, these alternatives may not be as straight forward as they first appear. Boustead [4] has produced a life-cycle-analysis review in which he shows that the benefits of recycling etc. depend strongly on the objectives. For instance, most of the virgin paper in the United Kingdom is derived form pulp and paper mills in Scandinavia where the waste is used to generate their energy requirements. Hence, very little fossil fuel is consumed. If, however recycled paper is collected from around the United Kingdom then diesel is consumed by the trucks, fuel oil is used for steam generation in the de-inking and re-pulping processes and coal and gas is used for re-manufacturing. The result is that the second grade paper uses more fossil fuel in its production than the virgin material. The preference for each product depends on the aim, saving trees or conserving fossil fuels.

In many cases recycling leads to lower grade products. For instance, recycling of used paper and plastics can give second generation products with inferior physical properties. This is particularly true for plastic materials [5]. The systems that are now in place only recover about 10% of the total plastic waste stream for reuse, either in the form of energy or as recovered plastic material. However, in the near future the recovery of packaging waste will need to exceed 50 % by weight to meet legislative constraints.

Plastic materials are sorted on the basis of specific gravity, although this does not separate PVC effectively from PET. Infra red spectroscopy can be used to recognise these polymers but efficient recycling is still somewhat limited because sorting mixtures of different polymers with similar basic characteristics has not yet been refined. Recently, laser-induced plasma spectroscopy [6] has been used for identification of components of waste plastic with good identification success. Only recently have large scale polymer sorting plants been developed.

Incineration (including polymers) is one of the most widely used methods for making use of waste material. This method also has its drawbacks. For instance,

combustion of these materials can produce toxic substances, such as dioxins [7], which, if not properly and carefully removed using suitable scrubbing equipment, can enter the environment.

Finally, composting is slowly developing into a commercial method for disposing of organic waste. The organic material is ultimately broken down by microorganisms into carbon dioxide and water. However, this technique is generally only used for organic household waste items. Common polymeric materials such as polyolefins are not destroyed by composting, and generally considered not to be biodegradable and therefore generally sent to landfill where they remain for long periods. However, recent evidence [8] suggests that some heavily oxidised polymers may undergo biodegradation.

1.2 Biodegradable polymers

Over the past 20 years a variety of new biodegradable polymers, based commonly on esters have been developed that are compatible with biological systems and are broken down in the environment or the body into harmless substances. Examples of such materials are summarised in the Table 1.2 below. The majority of commercial interest is centred on polyesters, mainly poly(3-hydroxybutyrate) [PHB], poly(ε-caprolactone) [PCL] and poly(lactic acid) [PLA].

Polymer class	Comment	Example
Polyesters	Readily degradable	poly(lactic acid), poly(hydroxybutyrate)
Polyamides	Only structurally modified polyamides are biodegradable	Hydroxylated nylon
Polyurethanes	Only structurally modified polyurethanes are biodegradable	Hydrophilic ether urethanes
Polyethers	Short chain polymers are found to dissolve water and also degrade	Poly(ethylene glycols), poly(ethylene oxide)
Polypeptides and proteins	Naturally occurring polyamides containing amino acid units	Natural proteins, collagen and gelatin
Polysaccharides	Basic sugar units joined by ether linkages. Hydrolysed abiotically and by enzymes	Naturally occurring starches and forms of cellulose

Table 1.2. Biodegradable polymers

1.3 Environmental degradation of polymers

The majority of polymeric materials, in common with fats and oils degrade upon environmental exposure. This degradation occurs mainly through exposure to atmospheric oxygen [9, 10] and ultra-violet radiation [11]. However, this process is usually extremely slow because of the presence of very effective additives used to protect the materials during their useful lifetimes.

Conversely, polyesters such as PHB and PLA degrade relatively rapidly in the environment into harmless substances. Although the structures of these materials are fundamentally similar, they degrade by entirely different mechanisms. It is believed that PHB is consumed predominantly biologically[12,13], whereas, PLA degrades by hydrolysis [14] prior to biodegradation [15].

1.4 Biodegradation

1.4.1 Definition

There is a lack of common consensus on a definition of biodegradation. However, a general summary can be considered as:
Biodegradation is the natural process by which organic materials are converted into simpler compounds by the action of enzymes and or by chemical decomposition. The process can be by oxidation, hydrolysis or biological degradation by enzymes. The chemical processes are homogeneous in nature, taking place throughout the material. Attack by enzymes occurs at the surface only.

A number of standards authorities have produced definitions for biodegradable plastics, which are listed below [16].

ISO 472: 1998. A plastic designed to undergo a significant change in its chemical structure under specific environmental conditions resulting in a loss of some properties that may be measured by standard test methods appropriate to the plastics and application in a period of time that determines its classification. The change in chemical structure results from the action of naturally occurring micro-organisms.

ASTM sub committee D20.96 proposal. Degradable plastics are plastic materials that undergo bond scission in the backbone of a polymer through chemical, biological and/or physical forces in the environment at a rate which leads to fragmentation or disintegration of the plastics.

Japanese Biodegradable Plastic Society [17] draft proposal. Biodegradable plastics are polymeric materials, which are changed into lower molecular weight compounds where at least one step in the degradation process is through metabolism in the presence of naturally occurring organisms.

DIN 103.2 working group on biodegradable polymers. Biodegradation of a plastic material is a process leading to naturally occurring metabolic end products.

1.4.2 Factors affecting degradation

1.4.2.1 Polymer morphology

The morphology of a particular polymeric substance has a significant effect on its physical properties and susceptibility to undergo biological degradation. Stereoregular polymers exhibit a high degree of crystallinity because of the easy alignment of the polymer chains. Introducing other groups, side chains, and random structures may inhibit alignment and produce a more amorphous material, which is undesirable for many applications. Amorphous polymers generally have lower softening points and reduced mechanical strength. However, amorphous polymers or blocks can be introduced into crystalline polymers to fine tune flexibility, crystallinity and degradation rate for particular applications

The biological synthesis pathway ensures that PHB is stereoregular and as such has a degree of crystallinity in the region of 80%. These crystalline regions have been shown to be more resistant to attack by micro-organisms than the amorphous parts[18]. However, the morphology of a polymer is influenced by its thermal history. Tsuji and Ikada [19] have shown that different annealing processes gave L-PLA films with a range of morphological structures and physical properties. The morphological differences were suggested to be due to the nucleation density prior to heating.

Such morphological changes affect the rate of hydrolysis [20] of PLA films. It was shown that the main molecular weight peak remained relatively unchanged during hydrolysis, while there was growth of lower molecular weight species (M_n approximately 1×10^4) reported to be "one component of one fold in the crystalline region" [21]. This indicated that the bulk film underwent no noticeable hydrolysis.

Microscopy results appeared to show that hydrolysis occurred preferentially in the amorphous regions connecting the crystalline lamellae in the spherulites (Figure 1.1). In addition, crystallisation occurred in the amorphous regions during hydrolysis. It was concluded that the hydrolysis of film was by a surface erosion mechanism.

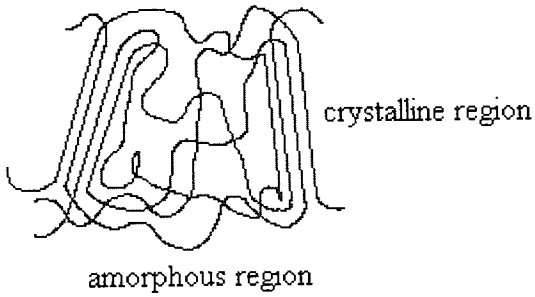


Figure 1.1. Schematic diagram showing the crystalline and amorphous region of a polymer

Chain flexibility can have a significant effect on the rate of hydrolysis and biological degradation. As the polymer chains become more flexible, there is a greater potential for interaction with enzymes and water absorption. Consequently, the glass transition temperature (Tg) is significant with respect to its degradability. However, the presence of hydrophilic segments can offset this dramatically [22]

The molecular weight of polymers also can have a significant effect on their degradability. Pitsner *et* al [23] reported that high molecular weight poly(L-lactide) could lose 70% of its weight compared to 40% for a lower molecular weight sample in 10 weeks when implanted in a rat.

1.5 Applications

Over the past 20 years various biodegradable/ compatible polymers have been developed mainly for medical applications such as medical sutures i.e. Dexon® and Vicryl® bone fixation devices [24, 25] and controlled drug release systems [26, 25]. Holland and Tighe [27] have carried out a comprehensive review of their pharmaceutical uses. These materials traditionally compete with stainless steel and titanium. However, polymers have the advantage in that they resemble the strength of bones much more closely than metal implants. In addition, it is much more difficult to over tighten plastic fixings, which could result in further tissue damage.

In addition to medical devices, degradable polymers find use in agricultural applications. These include, time release pesticides [28], crop protection systems such as mulch films [29], which normally use low-density polyethylenes, poly(vinylchloride), polybutylene or copolymers of ethylene with vinyl acetate. In addition to large scale agricultural uses, niche market applications such as planting containers [30], and time release fertilizers are being developed.

1.5.1 Other uses

Bags: In 1999 starch based carrier bags were introduced into the Mediterranean and Scandinavian markets [31]. The carrier bags have been introduced into areas where organic waste separation is well established. The bags are accepted as biodegradable composting bags.

Food packaging: Applications are mainly related to food service ware applications, such as replacements for expanded polystyrene trays currently used for packaging meat products. The gas barrier properties of this type of packaging are particularly important if the package contains fresh meat [32]. Thermoformed PLA cups and trays are also available.

Foamed Packaging: Loose fill packaging (i.e. ECO-FOAM) represents the main use of starch based materials. Loose fills are made from 85 percent destructured starch which is water soluble [33]. This material competes favourably with expanded polystyrene.

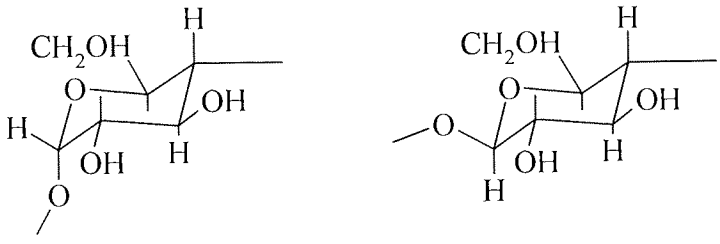
PLA Fabrics [34]: Spun PLA fibres find uses for clothing applications. The fabrics have excellent feel, breathability and compatibility with natural fibres, such as wool and cotton but these properties have yet to be realised in a marketable product.

Toiletries: Disposable razors manufactured from PHB have been marketed in Japan. These sort of items are generally disposed of in private, and therefore tend enter the sewerage system via the lavatory. Degradable products therefore provide a significant advantage over conventional plastics.

1.6 Natural biodegradable polymers

1.6.1 Polysaccharides

The two polysaccharides of greatest biological and economic importance are starch and cellulose (Figure 1.2). These polymers, based on D-glucopyranoside units, are linked by acetyl groups [35].

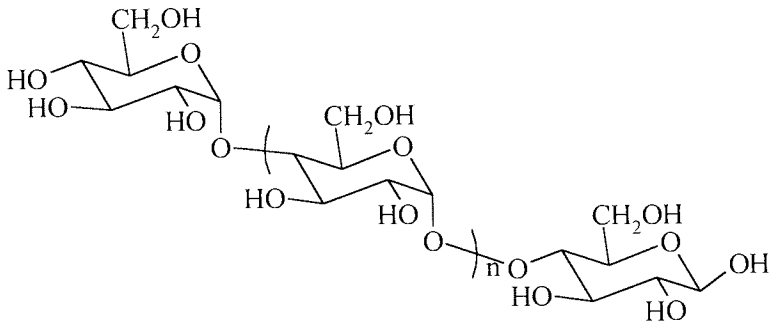


Starch Cellulose

Figure 1.2. Starch and cellulose monomer units

Starch is a polymer of glucose in which monosaccharide units are linked by 1, 4'-α-glycoside bonds. It is used as an energy source in plants, such as potatoes, rice and corn and occurs in two forms.

Amylose (Figure 1.3) accounts for approximately 20% of starch and has an average molecular weight of approximately 10^6. The more complicated branched structure of amylopectin (Figure 1.4) accounts for the remainder and has as many as a million glucose units.



n = 1000-6000

Figure 1.3. Amylose

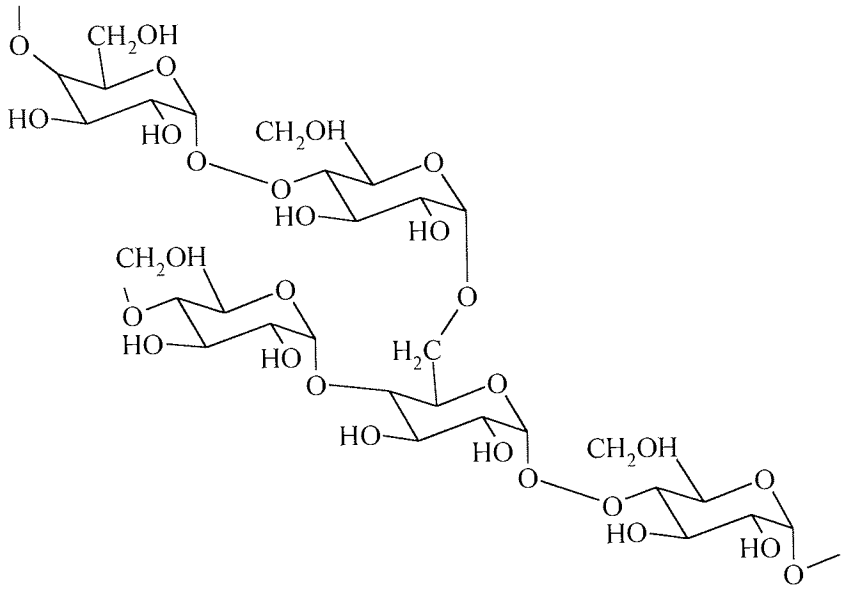


Figure 1.4. Partial structure of amylopectin

Cellulose (Figure 1.5) consists of a repeat unit of D-glucose linked via 1,4'-β-glycoside bonds. The polymer is generally high molecular weight and is used by plants as a structural material to impart rigidity.

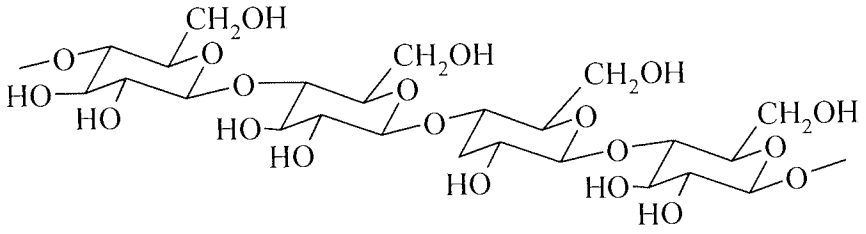


Figure 1.5. Cellulose

Poly(3-hydroxybutyrate) falls within the category of 'natural biodegradable polymer'. It can also be prepared synthetically see section 1.7.2 Synthesis of poly(3-hydroxyalkanoates) (PHAs).

1.7 Synthetic biodegradable polymers

1.7.1 Synthesis

Polymers can either be prepared synthetically or biologically. However, microorganisms do not normally break down synthetic polymers. There are in fact a few examples of synthetic polymers that are consumed in the environment. For example, poly(vinyl alcohol) [PVA] [36, 37], poly(ε-caprolactone) [PCL] and PLA. PLA is discussed in more detail in section 1.8. The only notable biologically produced family of polymers (excluding the common natural polymers such as cellulose etc) are the poly(hydroxyalkanoates) [PHA's]. The most common are Poly(3-hydroxybutyrate) [PHB] and poly(3-hydroxybutyrate-*co*-valerate) [PHBV]. These materials are produced inside living cells and consumed when the food source is limited. Different polymers are prepared by changing the feed materials. For instance, using acetic acid gives PHB, whereas propionic acid yields PHBV. Poly(3-hydroxybutyrate) is discussed below.

1.7.2 Synthesis of poly(3-hydroxyalkanoates) (PHAs)

The simplest example from the family of aliphatic PHA's produced biologically is poly(3-hydroxybutyrate) shown in Figure 1.6.

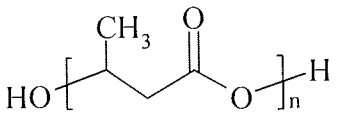


Figure 1.6 PHB

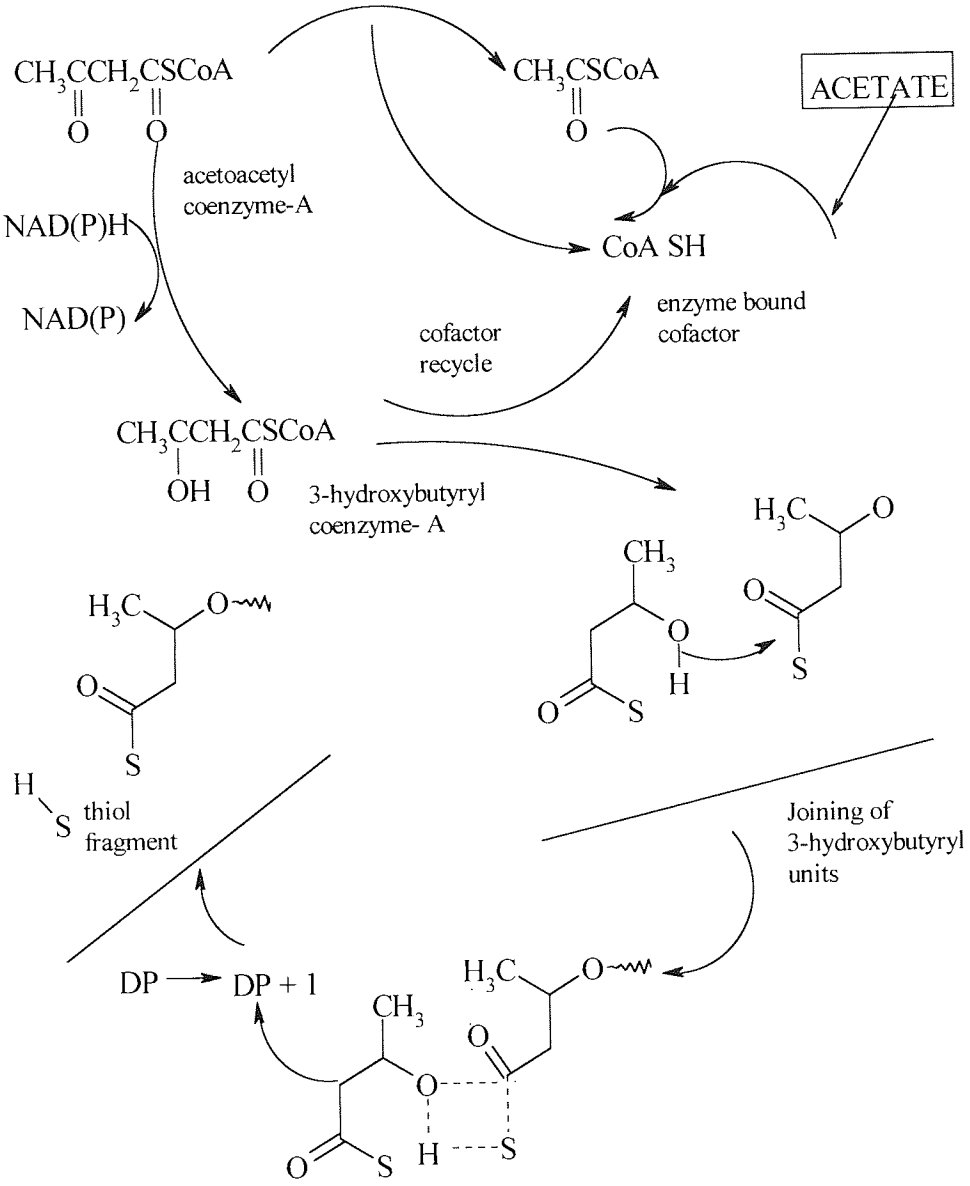
This polymer was first discovered about sixty years ago by Lemoigne [38] but it was only in the late 1950's that it was recognised as a polymeric substance.

In the 1970's, ICI developed a large scale fermentation process to produce PHB. However, various post production treatments were required to improve its properties. Addition of nucleating agents (to increase the rate of crystallisation) and cold rolling (calendering) [39] to reduce the size of the crystallites and to give a product with reasonable physical properties. PHB undergoes a rapid decrease in its molecular weight at temperatures close to its melting point (180°C) [40], these properties as well as its brittleness were major disadvantages. Articles and particularly films prepared from this material have gas barrier properties comparable to poly(vinyl chloride) and poly(ethylene terephthalate) [41].

Until recently, Monsanto produced a PHB copolymer (formerly made by ICI) with better physical properties using a glucose/propionic acid mixture as the carbon source for the cells. This copolymer was poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) marketed under the name Biopol® and formed the basis of a number of consumer products. Perhaps the best known of these was a Wella® shampoo bottle. Production of this material has been abandoned mainly because of its uncompetitive high cost and increased competition from other polymers. Only small scale manufacture is continuing at present.

Most commercial polymers are prepared synthetically and it is possible to prepare poly(hydroxyalkanoates) by polymerisation of the relevant lactones using aluminium or zinc catalysts [42]. This method is not commercially competitive however, as lactone monomers are expensive, very toxic and yields are usually low. Poly(3-hydroxyalkanoates) are prepared commercially by the action of enzymes. This family of polymers is produced within a variety of living cells, such as *Athiorhodaceae, Pseudomonadaceae, Spirillaceae, Rhizodiaceae* and *Bacillaceae* using a fermentation process [43]. The cell stores the polymer to preserve its osmotic balance under certain conditions and the polymer is reconsumed when conditions

dictate. The biosynthetic route to PHB is reasonably well understood and shown in Scheme 1.1 below [44].



Scheme 1.1. The biosynthetic pathway of PHB production.

The process starts with the conversion of an appropriate carbon source (alcohol, acid or sugar etc) to acetate. The bacteria introduce a thioester bound enzyme cofactor into the acetate, which is condensed to give acetoacetyl coenzyme-A. This is followed by reduction to 3-hydroxy butyryl coenzyme-A and subsequent joining of two units gives PHB. The cofactor is recycled. The translucent polymer granules (about 0.5μm in diameter) are formed in the cytoplasmic fluid of cells. The polymeric material can be isolated using a variety of techniques, extraction with a suitable solvent or digestion of the cell with sodium hypochlorite being the most common methods.

1.7.3 Synthesis of poly(lactide)

Poly(lactic acid) (PLA), [Figure 1.7] below can be prepared synthetically by a variety of ring opening polymerisation reactions of lactide using, stannous octoate (tin II 2-ethylhexanoate) [45], lithium alkoxides, metal oxides [46], a [5-Cl-salen]AlOMe complex [47], zinc-β-diketiminate ligand [48] and recently a Sn-N,N- chelate complex [49]. Stannous octoate is by far the most widely investigated catalyst for the polymerisation of lactide.

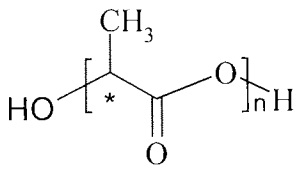
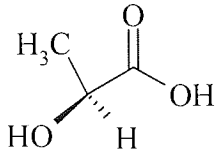


Figure 1.7. PLA

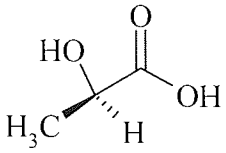
The structure of the PLA polymer produced by ring opening polymerisation is determined by the configuration of the lactic acid and subsequently the lactide used. Lactic acid can be synthesised using petrochemical feedstocks, involving the oxidation of ethylene to acetaldehyde followed by reaction with HCN, which gives lactonitrile. This is then converted to racemic lactic acid (mixture of D (S) and L (R)

isomers) shown in Figure 1.8 and Figure 1.9 by hydrolysis. However, lactic acid is usually manufactured by the fermentation of starch based materials to give the natural L (or R) -isomer.



S-lactic acid

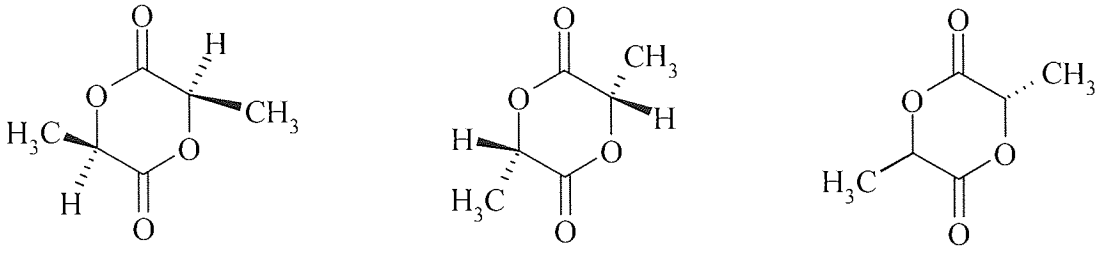
Figure 1.8



R-lactic acid

Figure 1.9

The structural configuration of the cyclic lactide shown in Figure 1.10 is determined by the configuration of the lactic acid units. Racemic lactide, is an equal mixture of (R,R) and (S,S)-lactides.



(R,R)-lactide (S,S)-lactide meso-lactide

Figure 1.10. Structural configuration of lactide

When these materials are polymerised (assuming no side reactions) the following polymers result:

(R,R) or (S,S)-lactides produce polymers with isotactic dyads (Figure 1.11).

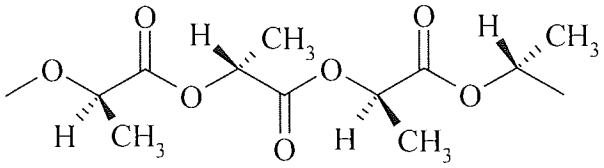


Figure 1.11. Isotactic PLA

Racemic lactide (a equal mixture of R,R and S,S isomers) gives an overall atactic polymer (Figure 1.12).

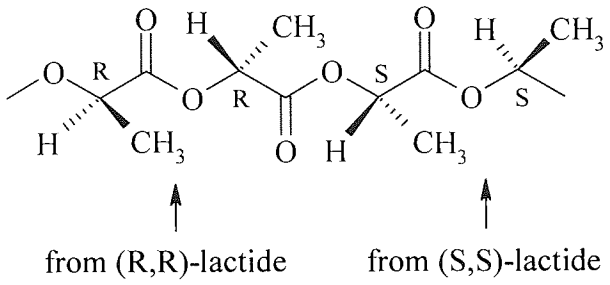


Figure 1.12. Atactic PLA formed from *rac*-lactide

The polymer formed from *meso*-lactide is also predominantly atactic and shown in Figure 1.13

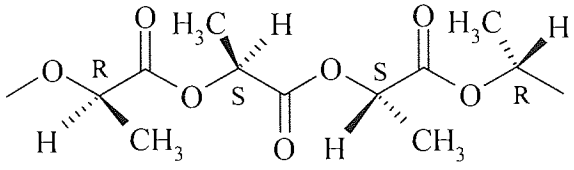


Figure 1.13. Atactic PLA formed from *meso*-lactide

The tacticity of the polymer has a dramatic effect on physical properties. Crystalline polymers are hard and tough because of structurally regular chains. Irregularities in the polymer matrix give rise to amorphous materials. The crystallinity and properties of PLA polymers can be modified by introduction of meso-lactide.

It is the poly(L-lactic acid) polymer [P(LLA)] that is most conveniently and economically manufactured from natural sources and represents one of the most promising biodegradable thermoplastics available. Unfortunately, the homopolymer suffers from similar drawbacks as PHB in that it is stiff, with poor mechanical properties arising from its tacticity. Presently PLA is widely used in the medical

health sector as bio-absorbable sutures and fixation devices [24]. Articles are mainly fashioned from the copolymer poly(lactide-co-glycolide).

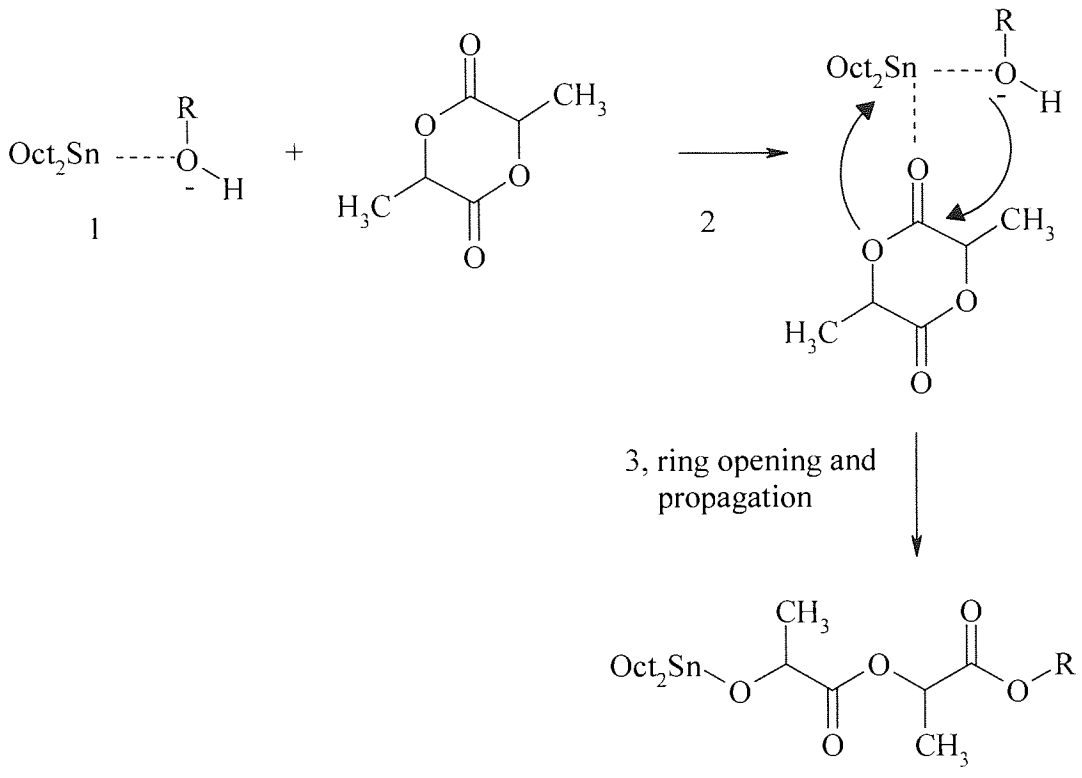
1.7.3.1 Polymerisation mechanism

1.7.3.1.1 Stannous octanoate initiated polymerisations

Although stannous octoate [$Sn(Oct)_2$] initiated polymerisations have been widely studied, it is only in recent times that there has been a greater understanding of the mechanisms involved. Notable contributors to that understanding have been Leenslag and Penning [45] Kricheldorf *et* al [50], Schwach *et* al [51] and particularly Majerska and co workers [52]. Kricheldorf *et* al. showed that increasing the concentration of $Sn(Oct)_2$ gradually lowered the molecular weight of the polymer produced at constant monomer concentration. It was suggested, and supported by ^1H NMR evidence that the polymer contained 2-ethylhexyl end groups. In addition, coinitiation with benzyl alcohol gave benzyl-terminated polymers. Consequently, it was suggested that benzyl alcohol complexed with $Sn(Oct)_2$, which was manifested by a strong downfield shift of the OH group in the proton NMR spectrum. An even stronger effect was observed with ethyl lactate a model of an active chain end. Such complexation reactions are in competition with lactide complexing and the order of complexing activity was suggested to be: lactide < benzyl alcohol<< ethyl lactate. The steps of the reaction were described as (Scheme 1.2).

1. Coordination of catalyst and alcohol followed by
2. Complexation with lactide through free d orbitals and then
3. Ring opening and propagation.

The reaction was suggested to follow a 'complexation mechanism or a second order insertion mechanism'.



Scheme 1.2. Lactide polymerisation

Du *et* al [53] proposed that there was competition between propagation and initiation in which initiation was favoured in the case of primary alcohols. However, propagation was favoured in the presence of tertiary alcohols. Recently, Majerska *et* al [52] provided evidence that the half alkoxide, Oct-Sn-OR was a possible initiating species. Any Oct-Sn-OH formed by the reaction of $Sn(Oct)_2$ with adventitiously present moisture (Scheme 1.3) was trapped by a proton trapping agent (Figure 1.14 and Figure 1.15). This leaves the Oct-Sn-OR formed by the reaction with the ROH initiator as the active species. Moreover, the rate of polymerisation was equal if not faster than a reaction carried out without the proton trap, rationalised by the shift of the equilibrium in favour of Oct-Sn-OR. The use of such trapping agents precludes reactions involving cationic species. In addition, reactions using amines [54] and triphenylphospine [55] as coinitiators gave similar results. The formation of ammonium or phosphonium salts, formed by the reaction with cations, was not observed, reinforcing the above hypothesis.

$Sn(Oct)_2 + H_2O \rightleftharpoons OctSnOH + OctH$

$OctSnOH + Sn(Oct)_2 \rightleftharpoons OctSn\text{-}O\text{-}SnOct + OctH$

$Sn(Oct)_2 + ROH \rightleftharpoons OctSnOR + OctH$

Scheme 1.3: Proposed reaction of $Sn(Oct)_2$ catalyst with ROH

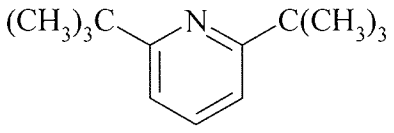


Figure 1.14. 2,6 –Di-*tert*-butyl pryidine

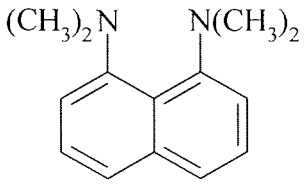


Figure 1.15. 1,8-bis(dimethylamino)naphthalene

1.8 Degradation

1.8.1 Biodegradation of poly(3-hydroxybutyrate)

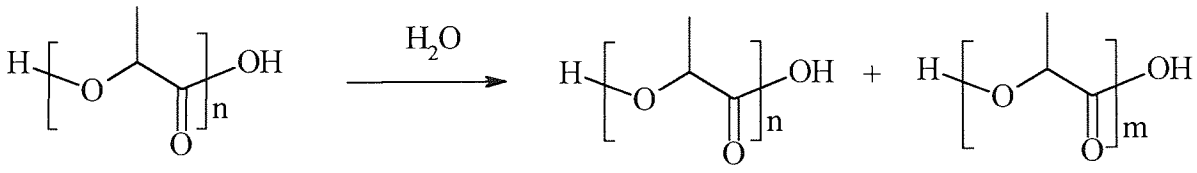
Many different types of micro-organisms produce enzymes capable of depolymerizing aliphatic polyesters [56]. Under optimum conditions the rate of degradation can be extremely fast (hours). However, processed samples have been found to degrade more slowly over days or weeks, rather than minutes or hours [56]. PHB specific enzymes are believed to be located in the lipid membrane surrounding the polymer granules and consist of two distinct enzymes [57]. The first degrades the high molecular weight polymer to its dimer and the second completes the degradation to the monomer. Some micro-organisms possess extracellular depolymerases, which degrade and solublise the polymer so that a nutrient rich solution can be absorbed by the cell. Many factors such as average molecular weight, degree of crystallinity, chemical composition and factors affecting microbial growth can influence the rate of microbial attack on a polymer. In the initial stages however, the surface properties of the sample play an important role [44]. The first step in the biodegradation process is the modification of the polymer surface from hydrophobic to hydrophilic by hydrolysis which can take about a week under normal conditions. Bacterial and fungal colonisation can then begin and the speed of this process depends upon the temperature and pH of the system. As degradation proceeds, the surface becomes pitted, the surface area increases and the rate of degradation commensurately increases.

1.8.2 Degradation of poly(lactic acid)

1.8.3 Hydrolysis

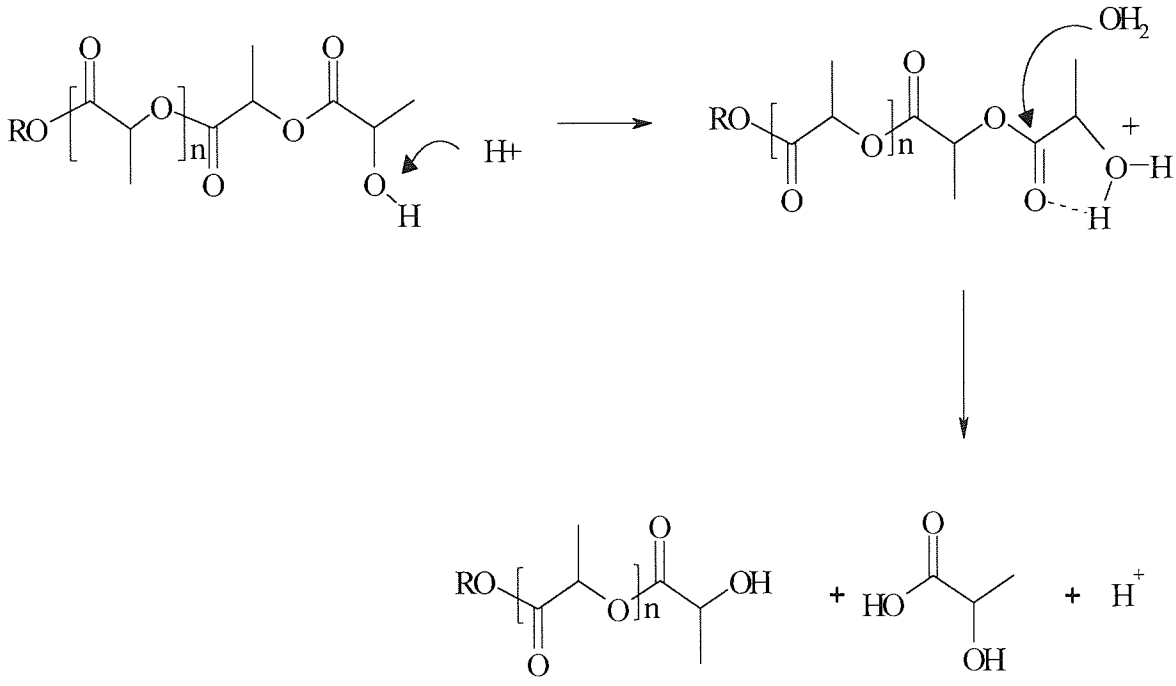
It is known that PLA, in common with esters, degrades by abiotic hydrolysis as shown in Scheme 1.4. Recent work has shown that the mechanism of degradation of articles in thin sections is different to that of thick materials [14, 58]. This phenomenon

is based on the autocatalytic effect of carboxylic chain ends, and their rate of diffusion into the surrounding aqueous solution. When hydrolysis occurs in a thin-sectioned article or film, the lower molecular weight carboxylic acid chains diffuse into the aqueous solvent. However, when hydrolysis occurs in articles of thick section, the carboxylic acid chains tend to be more soluble in the degrading central part of the polymer and become trapped, causing autocatalysis to occur inside the polymer matrix. This difference in concentration of the acid groups leads to a skin containing the central more degraded polymer. Thick-sectioned items eventually become hollow caused by the diffusion of monomers or dimers through the relatively intact skin and into the surrounding aqueous solution in which they are more soluble. In addition, it has been shown that the addition of basic materials such as coral [59] and tricalcium phosphate [60] slow the hydrolytic degradation process by neutralisation of the acid components counteracting the autocatalytic process.



Scheme 1.4. Polyester hydrolysis

It has been suggested by Shih [61], that base catalysed hydrolysis of PLA proceeds by random chain scission, whereas during acid catalysed hydrolysis chain end scission was preferred whilst Belbella *et* al [62] drew the opposite conclusions. Recently de Jong *et* al [63] demonstrated that the OH end group in oligomeric PLA played a crucial role in its degradation in both acidic and basic solutions. In neutral or basic solutions intramolecular tranesterification or back biting reactions occur forming oligomers and lactide. At lower pH the OH end group can be protonated to enable it to form a hydrogen bond with its adjacent carbonyl oxygen leading to a stable cyclic five membered structure which can be split off leaving a polymer with a degree of polymerisation of n-1 (Scheme 1.5).



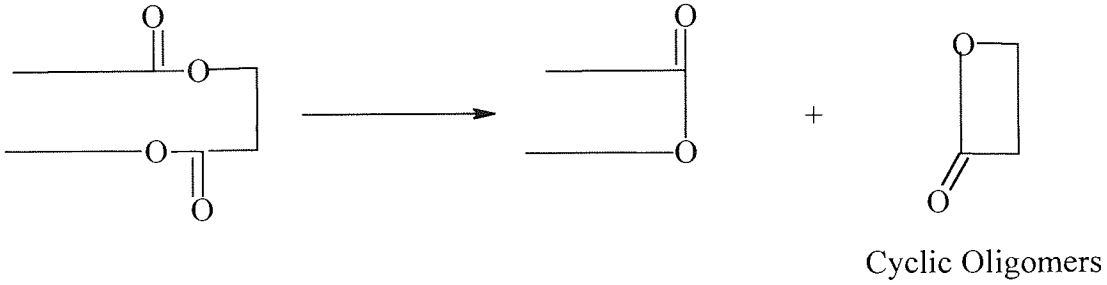
Scheme 1.5. PLA hydrolysis under acid conditions

After hydrolysis, the lactic acid and low molecular weight oligomers are then available for consumption by micro-organisms. However, until recently it was uncertain whether high molecular weight poly(lactic acid) was degraded enymatically in the same way as PHB. Reeve and co-workers [64] suggested that PLA was degraded by protinase K and Hakkarainen *et* al [65] suggested that new degradation products, ethyl ester of lactoyl lactic acid, propionic acid and acetic acid were formed during biotic degradation. These low molecular weight species were suggested to aid the growth of micro-organisms on the film surface. The degradation rate was increased relative to samples without lactoyl lactic acid.

1.8.4 Thermal degradation.

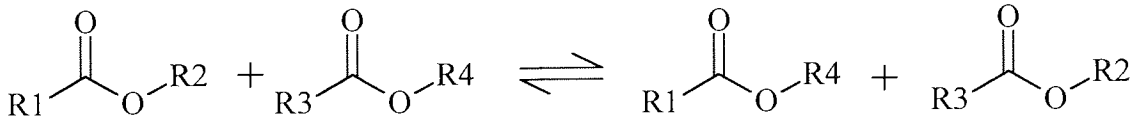
Both poly(hydroxybutyrate) and poly(lactic acid) undergo thermal degradation during melt processing. Reductions in molecular weight of up to 53% have been reported for PHB and 88% for PLA [40]. However, there appeared to be no increase in low molecular weight components as reported by other workers [66, 67,68]. Injection moulding led to a decrease in the melting temperature and the heat of melting in the polylactides. The degradation products associated with the reduction in molecular weight, in particular PLA, have been studied by Kopinke *et* al [66]. They suggested that there were five main reactions involved.

1. Intra and intermolecular ester interchange to give lactide and cyclic oligomers (Scheme 1.6 and Scheme 1.7).



Cyclic Oligomers

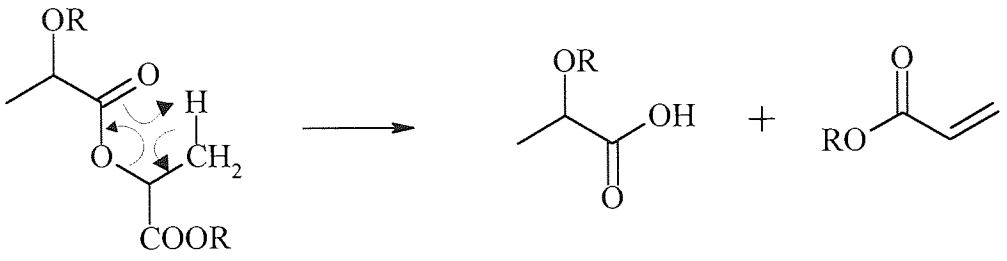
Scheme 1.6. Intramolecular ester interchange



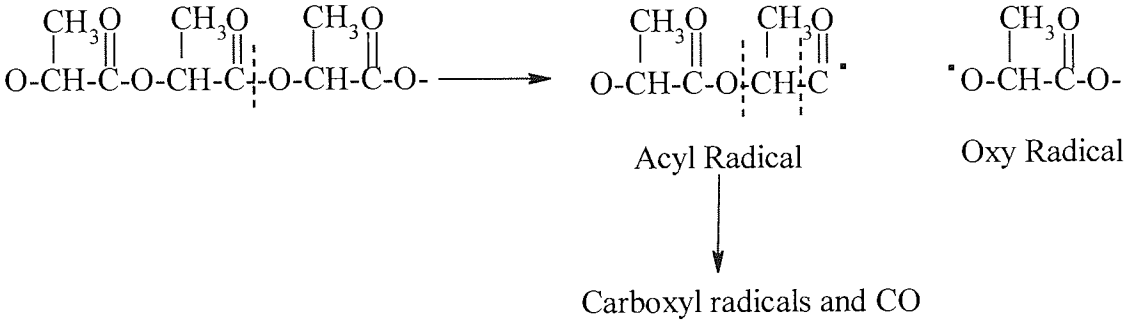
Scheme 1.7. Intermolecular ester interchange

2. Cis elimination, forming acrylic acid and acrylic oligomers (Scheme 1.8).

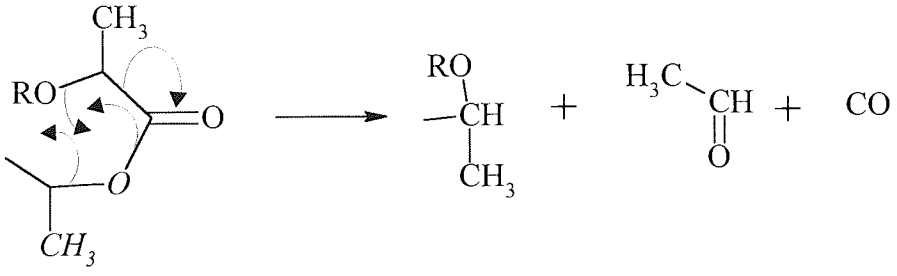
3. Radical and non-radical reactions, producing acetaldehyde and carbon monoxide (Scheme 1.9 and Scheme 1.10).



Scheme 1.8. Cis elimination



Scheme 1.9. Radical formation



Scheme 1.10. Non-radical formation.

4. Further radical reactions and,

5. $Sn(Oct)_2$ catalysed depolymerization to lactide.

It was suggested that PLA is thermally more stable than PHB despite their apparent activation energies. This is in disagreement with the findings of Gogolewski *et* al [40] and McNeill and Leiper [67] who also found that PLA degraded rapidly. In addition they showed that end-group acetylation increased the thermal stability of PLA by limiting back biting reactions of the hydroxyl end group. They also showed that the presence of a radical inhibitor, 1,4-diamino anthraquinone shown in Figure 1.16 significantly reduced the rate of degradation at 230°C, indicating a free radical degradation pathway in such cases.

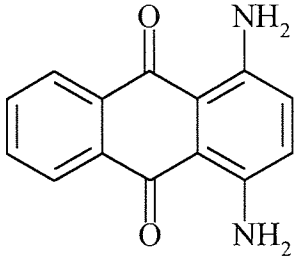


Figure 1.16. 1,4-Diaminoathraquinone

Wachsen *et* al [69] emphasised the importance of residual tin catalyst and the effect of open and closed systems on the molecular weight of thermally treated PLA. It was shown that increasing the catalyst concentration affected the ring-chain equilibrium in favour of smaller, more volatile rings, which was in agreement with Kopinke [66]. In closed systems, volatile rings were unable to leave the melt and recombination was favoured. Effective stabilisation of the melt was observed using tropolone (2-hydroxy-2, 4, 6-cycloheptatrien-1-one) Figure 1.17, which can deactivate the tin catalyst through the formation of stable chelate complexes [70]

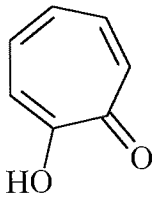


Figure 1.17. Tropolone

1.8.5 Other degradation routes

1.8.5.1 Thermo-mechanical oxidation

During melt processing polymeric materials encounter high shearing forces that are known to be contributory factors in polyolefin degradation [71, 72]. Degradation begins with abstraction of a hydrogen atom from a tertiary carbon to form macro alkyl radicals ($R^{\cdot}$) which then react instantaneously with atmospheric oxygen forming alkyl peroxy radicals ($ROO^{\cdot}$). Alkyl peroxy radicals abstract hydrogen from the polymer forming alkyl hydroperoxides (ROOH), which are thermally and photolytically unstable and undergo homolytic cleavage to give more radicals. The reaction is autocatalytic in nature so that the radicals break the polymer backbone forming ketones, alcohols and other low molecular weight products.

1.8.5.2 Photo-degradation

Relatively little work has been conducted on the photo-stability of biodegradable polymers. However, work done by McNiell and Leiper [67] showed that photolysis of PLA gave a slight broadening of the ultra-violet spectrum at approximately 230nm. They also suggested that a possible breakdown product was acrylic acid. More recently, Ho and Pometto [73] showed that PLA was degraded by ultra violet light. It was found that degradation of L-PLA films was accelerated by UV radiation at 365

nm by up to 97%. In addition, the percentage elongation at break was significantly reduced.

1.9 Polymer modification

Biodegradable polymers are relatively expensive materials compared to common commodity thermoplastics such as polyethylene. This applies particularly in the case of polymers that have been manufactured biologically by fermentation [40], as the output to volume ratio is generally low as high dilutions are found and expensive isolation techniques are involved. The restricted use of these materials is not only due to cost. Biodegradable polymers generally exhibit relatively poor physical and mechanical properties [74] compared with commodity polymers [75]. In an attempt to overcome these problems, a variety of established modification techniques have been applied to biodegradable polymers to improve their physical characteristics. These include.

1. Addition of plasticizers [76, 77, 78,79]
2. Blending with other polymers [80,81,82]
3. Copolymerisation [83] and
4. Polymer chain modification [84].

These techniques are in some cases, expensive because the synthesis methods and chemistry involved increase the cost of the polymer further. The improvements made to the physical properties of the polymer by the addition of plasticizers, particularly with PHB, have been limited even with the large changes in the glass transition temperatures using di-butyl phthalate [85] and polyethylene oxide [91]. However, more success was achieved with PLA using commercial plasticizers [76].

1.9.1 Plasticizers

Plasticizers are materials that soften polymeric materials, making them more ductile. The most common plasticized plastic material available is poly(vinyl chloride) [PVC], which can contain up to seventy parts of plasticizer per hundred of polymer. There are a variety of substances used, the majority of which are esters particularly phthalates, for example, dioctyl, phthalate (DOP) and di 2-ethylhexyl phthalate (DEHP). The addition of these materials turns PVC from a hard glassy material to a rubbery substance at room temperature.

1.9.2 Plasticizer properties

A plasticizer can best be described as a solvent for a polymer, and as such, it is usually a liquid. In order to function effectively the plasticizer and the polymer should have similar solubility coefficients. The following set of general rules can be applied to plasticizers:

1. They should be substances with a low volatility, i.e. of high molecular weight, usually greater than 300 Da.
2. Have a similar solution parameter (δ), to that of the polymer.
3. If a polymer has a tendency to crystallise, the plasticizer should have a specific interaction with the polymer
4. They should not be crystalline solids unless 3 applies.
5. They should be compatible with the polymer and not migrate to the surface of the polymer.

The plasticizing effectiveness of a particular compound depends on a variety of physical interactions and other processing parameters that influence the polymer structure. The following factors are important [86].

1. There should be functional groups present in both polymer and plasticizer that can afford mutual attraction.
2. Such groups should be located in relation to each other so as to permit attractive forces to function.
3. The plasticizing molecule should be of the correct shape.

These general observations can only act as a guide to the effectiveness of a substance on a particular polymer. The plasticizing efficiency of a material can only be accurately determined experimentally.

The way(s) in which a plasticizer acts on polymer substrate to allow it to become more flexible is still not completely understood. An effective plasticizer for one polymer may therefore be ineffective for another. An effective plasticizer can be considered as a moderately high molecular weight substance, (usually a liquid), that in sufficient concentration would act as a solvent for that polymer. Two theories were developed in the1940's in an attempt to explain the plasticizing mechanism.

The "Lubricity" theory [86] suggests a lubricating action of the polymer by the plasticizer, the extent of which is governed mainly by plasticizer-polymer interactions, such as hydrogen bonding. The Lubricity theory was rather simplistic and was later superseded by the "Gel" theory [87]. The resistance to deformation of the polymer chains was not regarded as being due to intermolecular friction, but rather to the elastic resistance of a three-dimensional gel formed by the polymer-polymer contacts at active centres along the chains. Attraction-separation of the polymer chains is called aggregation-deaggregation. Therefore, it was suggested that plasticizers improve the flexibility of polymers not by acting as lubricants between polymer molecules but by opposing and reducing the aggregation of the polymer molecules by a solvation-desolvation process. It may be assumed that the introduction of any material into a polymeric substance could result in increased flexibility, brought about by the deformation of the three dimensional network. This assumption is only partly true however. Any substance introduced into a polymer

will indeed force the chains apart and break the polymer-polymer contacts but unless the added substance has significant solvating power, the deformation of the gel structure will have limited life. Over time, the attractive force between the polymer chains will gradually "squeeze out" the non-solvent plasticizer

1.9.3 Blending

The physical characteristics of a polymer can be sometimes be modified by blending with another suitable polymer. For example, if a hard crystalline material is blended with a soft flexible one, the combined blend could possibly have intermediate physical properties. However, in many cases, the thermodynamics of mixing prevent a completely miscible blend and phase separation occurs. This situation has been reported for PHB and PCL blends [88] and blends with poly(ethylene-*co*-vinyl acetate) [EVA] (low vinyl acetate concentration) [89]. Some polymers are compatible with PHB: these include poly(vinyl acetate) [87], poly(ethylene oxide) [90], poly(epichlorohydrin) [91] and poly(vinyl alcohol) [92]. To encourage polymers to mix efficiently, compatiblizing agents are added [93]. These substances ideally have portions of the molecule that are compatible with both polymers. For example Yoon and co-workers [94] compatiblized PHB and L-PLA using poly(ethylene glycol)-*block*-poly(L-lactide) and Buckman *et* al [95] blended polymers of hydroxybutyric acid and polyolefins using diblock copolymes containing an alkyl block and a hydroxy acid block. However, when two biodegradable polymers are blended the biodegradability of the composite can, in some cases, be compromised. For example, Kumagai and Doi [88] have shown that a mixture PHB and PCL (50-100% PCL) showed relatively little weight loss but a mixture of 80:20 PHB: PCL showed accelerated degradation. Scandola [96] also showed that degradation occurred when PHB was blended with poly(epichlorohydrin) but was suppressed when blended with cellulose esters. However, when PHB was blended with a conventional polyolefin the degradable component was eroded leaving a finely divided powder of non-degradable material

1.10 Scope and objectives of the present work

Biodegradable polymers based on poly(3-hydroxybutyrate) and poly(3-hydroxybutyrate-*co*-valerate) have been available for many years but as discussed above the scope of application of these materials in the market place is restricted by cost and their limited physical and mechanical properties such as, elongation at break that render them unsuitable for the production of packaging films. On the other hand, polymers such as polycaprolactone are much cheaper to produce and are readily biodegradable and whereas these films have a high elongation at break their tensile properties are unsatisfactory. Poly(lactic acid) has emerged as a material with a potential for degradable packaging applications. PLA is again a crystalline polymer and therefore possesses similar physical properties to PHB. Like PHB, PLA has a high tensile strength (>40 Mpa) and a low elongation at break (< 5%). In general when compared to commodity materials such as polyolefins, not only are their physical properties inferior they would in some cases incur a high ecological premium without generating any significant technological advantage.

The current literature has highlighted the enormous potential of PHB/PHBV and PLA for use in packaging and biomedical applications provided that their mechanical properties can be improved. Conventional plasticizers such as citrates, phthalates, polyethylene glycol based derivatives and other high molecular weight substances have been used in PHB and PLA [76, 97] to improve their mechanical properties with varying degrees of success. These existing commercial compounds have a low unit cost and in some cases have been shown to impart good improvements to biodegradable polymers [76]. However, a thorough investigation into the long term physical properties and degradation of plasticized biodegradable polymers has not been carried out. In addition, there are questions over the safety of phthalate esters, which are the most common class of plasticizers. Concerns have developed that these plasticizing substances may be carcinogenic, therefore their use in infant's toys, medical devices [98] and articles associated with food contact is being reduced. Moreover, there is concern over their persistence in the environment.

Cadogan [99] has recently carried out a review of the safety of these materials with respect to their biodegradability and carcinogenic properties.

Poly(3-hydroxybutyrate) and poly(lactic acid) were chosen for the present investigation because of their potential commercial use in variety of areas. One of the prime purposes of this study was to synthesise and characterise a range of potentially biodegradable ester plasticizers based on natural carboxylic acids eg citric and tartaric acid using various linear and branched alcohols. An investigation into their effects on the physical and mechanical properties was carried out. The compatibility of the plasticizers with the base polymer was also established.

Another objective of this work was the preparation of copolymers containing the base polymer in the expectation that they could act as highly compatible modifiers. Subsequently these materials either alone or in combination with a chosen ester plasticizer (from above) were melt processed with PHB or PLA respectively followed by evaluation of their mechanical properties. This allowed an assessment of the their potential for use a packaging additives. When suitable properties were obtained the chosen blends were assessed for their susceptibility towards both hydrolytic and enzymatic degradation. The biodegradation rate was measured by exposure to stable compost, which is believed to simulate as closely as possible conditions existing in municipal composting facilities. Hydrolytic and other abiotic degradation tests were used to establish the useful lifetime of the blends and their suitability for certain applications. In addition, the stability of the polymer blends during processing and subsequent exposure to heat and ultraviolet light was carried out.

In certain applications (like crop protection film) it is essential that when a plastic article has served its useful purpose it quickly degrades into harmless substances [100]. An attempt was made to accelerate the degradation the polymer in a controlled way using commercial photo-prooxidants [101, 102].

Finally an attempt was made to explain the mode of plasticizer action based on technical and model compound studies.

Chapter 2

General Experimental Techniques:

2.1 Instrumental methods

2.1.1 Fourier Transform Infrared Spectroscopy (FTIR)

All infrared spectra were recorded using a Perkin Elmer 1650 Fourier Transform Infrared Spectrometer in the range 4000-600 cm^{-1}. Liquid samples were analysed as thin films on NaCl windows. Solid samples were pressed into KBr pellets. Polymer samples were investigated as thin films cast after evaporation of the solvent.

2.1.2 ^{13}C and ^{1}H magnetic resonance spectroscopy

All prepared additives (plasticizers and copolymers) were analysed using a Bruker 300 MHz NMR instrument using the P.E.N.D.A.N.T. [103,104] technique (Polarization Enhancement Nurtured During Analysis Nuclide Technique). The PENDANT technique allows the detection of any insensitive nuclei, particularly ^{13}C coupled to ^{1}H, in particular it enables the simultaneous detection of C, CH, CH_2 and CH_3 carbon resonances. In ^{13}C spectra, carbon as CH_3 and CH appeared as positive peaks and CH_2 and C as negative. Selected copolymers were also analysed using the S.P.E.E.D [105] technique (Selective Polarization Enhancement and Edited Detection), which enhances weak signals associated with the carbonyl region.
Both proton and carbon chemical shifts were reported as shifts in p.p.m from the reasonance associated with tetramethylsilane (TMS), an internal reference. All samples were dissolved in deuterated chloroform.

Both ^{1}H and ^{13}C spectra were integrated and edited on a personal computer using WinNMR software from Bruker.

2.1.3 Differential Scanning Calorimetry (DSC)

All samples were analysed using a Polymer Laboratories PL STA 625+ differential scanning calorimeter. The instrument was entirely computer controlled. The oven could be cooled manually using liquid nitrogen delivered from a low pressure Dewar flask

Differential scanning calorimetry and scanning thermal analysis (STA) are common techniques used for determining energy changes or mass changes within a sample. They can be used together or independently. The equipment consists of a hang down balance with space for two aluminium pans (sample and reference) capable of weighing to an accuracy of ±0.01mg. Each is connected to a thermocouple in order to monitor the temperature differences between the pans. A vertically movable oven surrounds the whole assembly. During heating, the thermal changes in the sample pan are monitored with respect to the reference so that the heat input can be adjusted so that the temperatures are always identical. In this way endothermic and exothermic changes are measured. The analysis is displayed as a plot of energy change with time and since the temperature is scanned at a constant rate it is possible to measure the heat. Additionally mass changes are also monitored.

2.1.4 Gel Permeation Chromatography (GPC)

Molecular weight analysis of the polymers and copolymers was carried out using a Knauer gel permeation chromatograph fitted with two Plgel 5μ mixed-C columns in series (Figure 2.18) held at 40°C. Molecular weights were calculated using a personal computer running the in built PL Calibre software. The results were automatically printed. Gel permeation chromatography is used to separate a polymer sample into its component fractions according to hydrodynamic volume. The columns are filled with a cross-linked gel that swells in the presence of solvent (THF). The swelled cross-linked gel contains pores of varying sizes that allow the injected polymer molecules to permeate. Low molecular weight (small) components permeate a greater volume of solvent within the pores than do larger molecules and

so take longer to elute. The presence of polymer in the eluent was monitored by a differential refractometer, which compares the refractive index of the eluent with that of the pure solvent in the reference. Any change in the refractive index is proportional to the concentration of the polymer at any time.

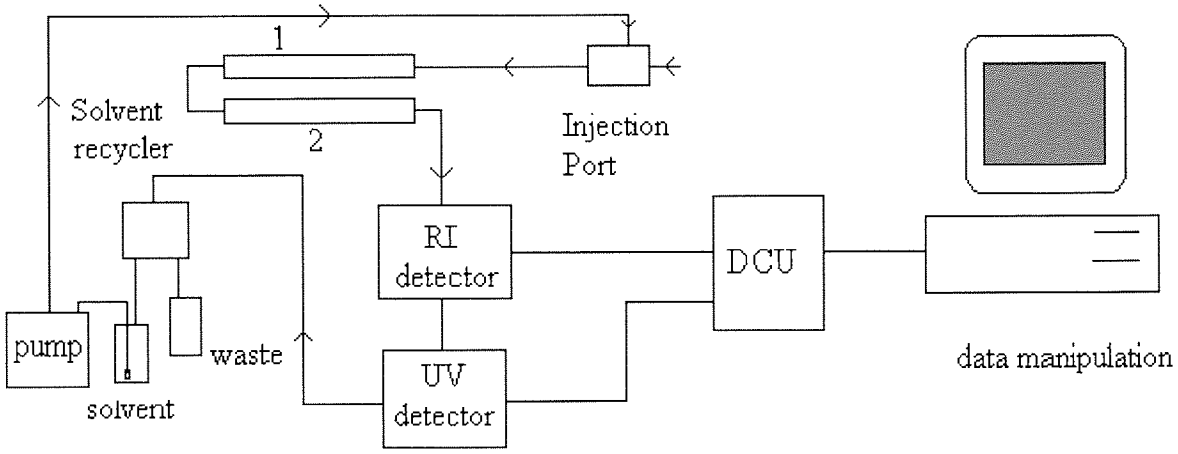


Figure 2.18. Schematic diagram of the GPC equipment

The GPC is not a primary technique and was calibrated using a series of narrow standards of known molecular weight. This homologous series of polymers was dissolved in the eluent and injected. The elution volumes were recorded for each standard and a plot of log (molecular weight) versus elution volume was constructed. Assuming that the standard molecular weights are precise, it is possible to derive a function in the form log(M) = f (V) so that the molecular weight corresponding to any elution volume can be calculated.

The GPC was calibrated using polystyrene standards but because of differences in the properties of different polymers (hydrodynamic volume, chemical attractions) the calculated molecular weights are expressed as polystyrene equivalent molecular weights.

Samples were injected as a 1-2% w/v solution in THF and eluted using THF solvent. Consistent sample sizes were obtained by using a 100µl Rheodyne injector loop system.

2.1.4.1 Molecular weight determination

The curve obtained from the GPC raw data is actually a molecular size distribution curve. Which is converted to a molecular weight distribution using the calibration information.

It is conventional to express the distribution of molar masses as either a number average molar mass (Mn) or a weight average molar mass (Mw). In the definition of these molar masses it is envisaged that the molar mass distribution is split into discrete fractions of molar mass (Mi) that is made up of molecules that contain a discrete number of *i* repeat units.

Mn is defined as the sum of the products of the molar mass of each fraction multiplied by its mole fraction. (Xi)

$$\mathrm{Mn} = \sum Xi\,Mi$$

By definition the mole fraction (Xi) is the ratio of the number of molecules of length *i* (Ni) to the total number of molecules (N). Therefore:

$$\mathrm{Xi} = \frac{Ni}{N}$$

So: $$\mathrm{Mn} = \sum Ni\,Mi/N \quad \text{or} \quad \mathrm{Mn} = \frac{\sum Ni\,Mi}{\sum Ni}$$

It is often more convenient to deal in mass fractions (wi) rather than numbers of molecules. Similarly wi is defined as the mass of molecules of length i divided by the total mass of all molecules.

$$wi = \frac{Ni\,Mi}{\Sigma Ni\,Mi}$$

The weight average molar mass is defined as the sum of the products of the molar mass fraction multiplied by its weight fraction

$$Mw = \sum Ni\,Mi$$

Therefore:

$$Mw = \frac{\sum Ni\,Mi^2}{\sum Ni\,Mi}$$

The value of M_w is always bigger than M_n except for mono disperse samples, in which they are identical. The ratio M_w/M_n is a measure of the polymer molecular weight distribution.

2.2 Experimental techniques used for the processing and evaluation of the polymers and polymer blends

This section contains the general experimental techniques involved in the polymer processing. Other experimental techniques are described in the relevant chapters.

2.2.1 Processing of polymers in the Brabender Torque Rheometer

PLA (30g) was processed using a Brabender Torque Rheometer. The Brabender Torque Rheometer consists of a small chamber containing two contra-rotating screws, turning at slightly different speeds. A standard rotor speed of 60 r.p.m was adopted for all processing and the temperature of the apparatus was controlled by a Churchill oil heat exchanger unit. The mixing chamber may be operated open or closed to the atmosphere via a pneumatically operated ram. For all processing work a 30g charge of polymer was used and the chamber was generally operated closed to the atmosphere at 180°C and for a normal processing time of ten minutes. However, open chamber processing and longer processing times were sometimes used. On completion of the processing, the polymer was quickly removed from the apparatus and quenched into cold water to prevent further reactions.

2.2.1.1 Addition of the additives to the torque rheometer

Access to the processing chamber of the torque rheometer was via a 15-20cm long, 2.5cm^2 heated pneumatic ram guide. To be sure of successful processing, solid additives needed to reach the chamber without making contact with the sides of the addition port. To overcome this, an appropriate amount of additive was weighed into a PLA film parcel made from a triangular shaped pouch (3×3 cm) which was heat sealed at the edges. This small packet could then be dropped easily into the torque rheometer. Liquid plasticizers were either mixed or adsorbed on to the powdered polymer or added directly to the molten polymer in the chamber using a pipette. A photograph of the torque rheometer is shown in Figure 2.19 below.

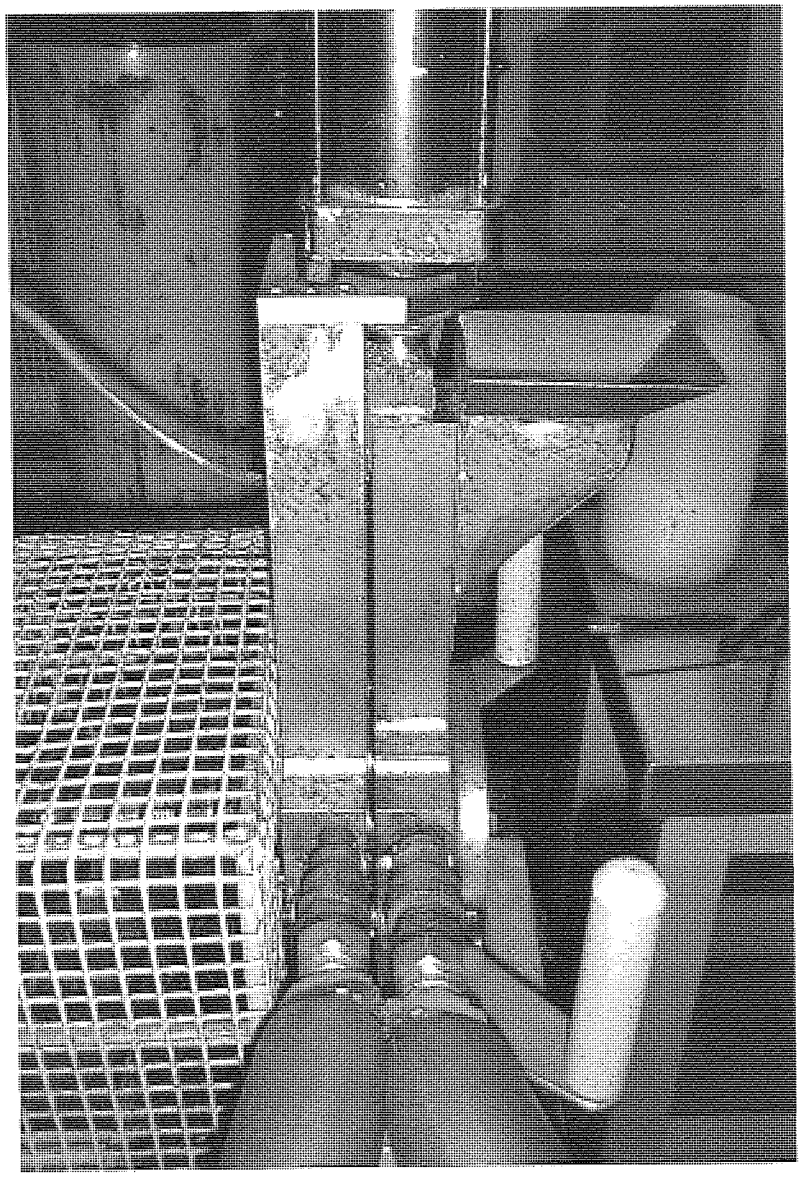


Figure 2.19. The torque rheometer

2.2.2 Preparation of film from processed samples

Polymer films suitable for tensile measurements were prepared by compression moulding at 180°C, using an electrically heated hydraulic press shown in Figure 2.20. An appropriate weight of processed polymer (5-6g) was cut into small pieces using a guillotine and placed between two sheets of a heat resistant polyester

"Melinex" film. This film in turn was sandwiched between two polished stainless steel platens separated by 0.25 mm spacers.

The platens were closed but no pressure was applied for two minutes to allow the polymer to soften fully. The pressure was then held at 1-2 tonnes/in^2 for 30 seconds to allow the polymer to melt and flow, followed by 6 tonnes/in^2 for a further minute. The time to produce a film of approximately 0.25mm thickness was 3.5 minutes. The platens were removed from the press. The Melinex sheets containing the molten polymer film was carefully removed and the sample quenched to 10°C using cold water.

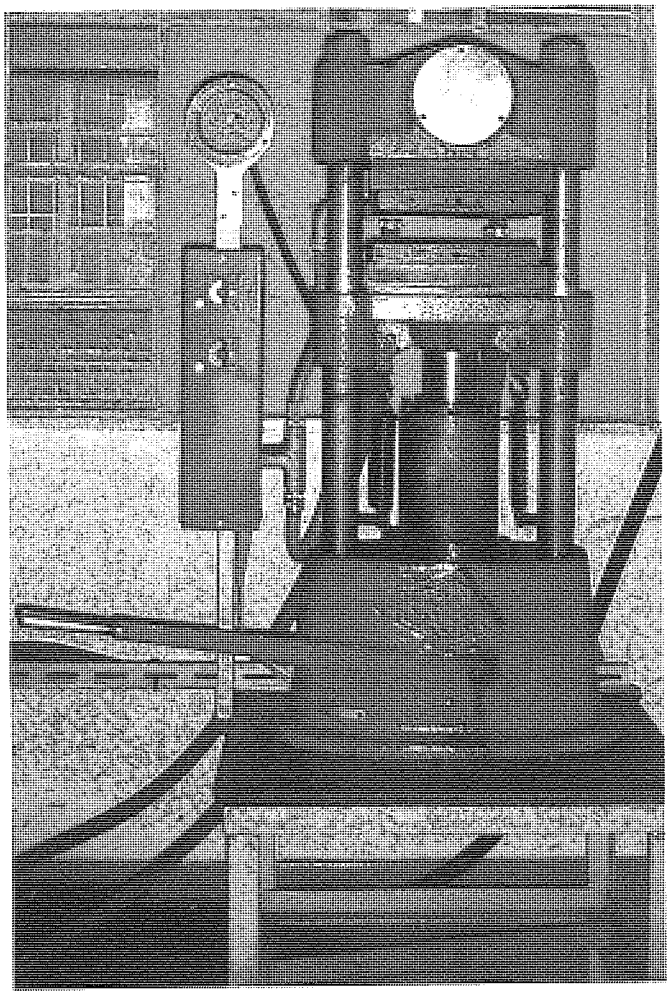


Figure 2.20. The electrically heated hydraulic press

Films for spectroscopic measurement were made using an electrically heated, hand operated Specac accurate film press. The press has a mould or die with interchangeable spacers of exact thickness from 15-50μm. Approximately 0.3-0.7g of the crude film (pressed previously) was cut up and pressed again in the Specac press between two sheets of Melinex at 180°C. A pressure of 4 tonnes/in^2 was sufficient for producing a suitable film.

2.2.3 Processing of polymers using the PRISM Twin Screw Extruder (TSR)

PLA was processed in a Prism Eurolab, 16 inch twin screw extruder shown schematically in Figure 2.21. The temperature of the electrically heated barrel was controlled thermostatically. All parameters such as temperature, screw speed, torque and pressures were monitored and controlled by built-in software and an interface system. The output of processed polymer was approximately 3 kg hr^{-1}. The temperatures of the various zones were adjusted according to the experiment but a die temperature of 160°C was generally found adequate

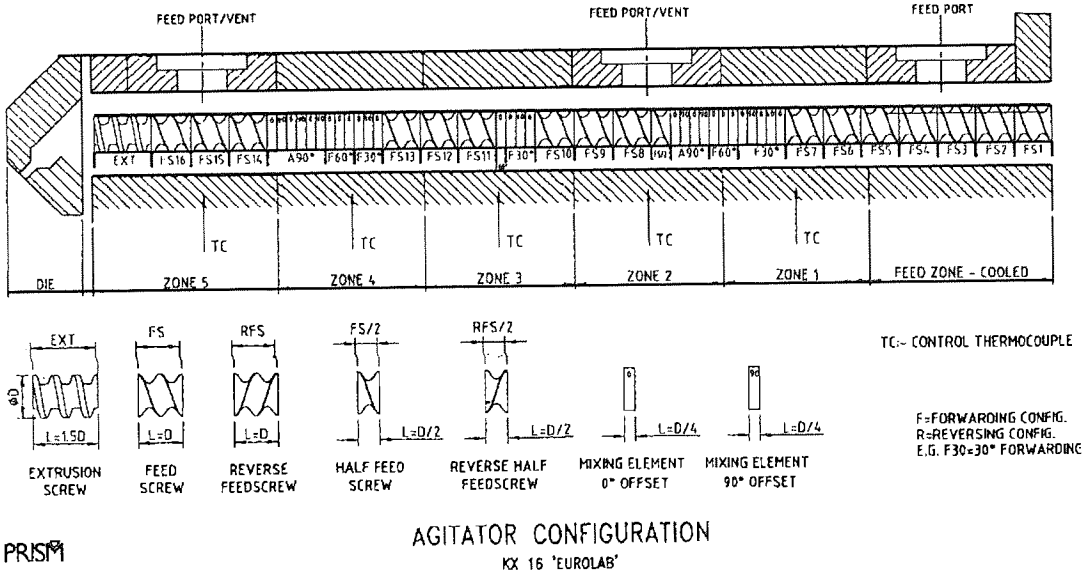


Figure 2.21. Cross-section of the EROLAB twin screw extruder

2.2.4 Preparation of blown film

Blown film containing various additives was formed by fitting a circular film die attached to the end of the extruder barrel. The polymer passed into the film die and was extruded vertically through a ring shaped orifice. The molten polymer was gathered together and inflated by compressed air forced through the centre of the die. The pressure of the trapped air then theoretically controlled the size of the bubble. The thin film cooled sufficiently quickly in the air to prevent significant crystallisation and did not stick together when the film reached the rollers at the top of the apparatus.

2.2.5 Preparation of extruded film

The extruded film was prepared using the same temperatures and conditions described 2.2.4 above but the blown film die was replaced with a sheet film die shown schematically in Figure 2.22. The die aperture was fixed and therefore the thickness of the film was controlled by the die head pressure and the draw rate (haul off speed). Different film thicknesses were prepared between 0.15 and 0.3 mm. This technique was used to prepare a large quantity of film and is further described in chapter 7.5.1

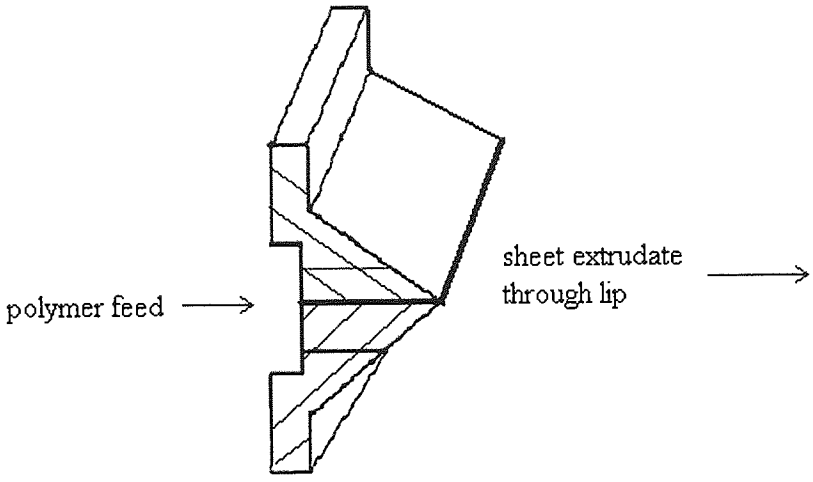


Figure 2.22. Cross-section of a sheet film die

2.2.6 Melt Flow Index (MFI)

Melt flow index measurements were made using a Davenport Melt Flow tester. The ASTM D1238-95 method *'Standard test method for flow rates of thermoplastics by extrusion plastometer'* was followed. This method is used to determine the flow rate of a molten polymer through a standard die with pressure exerted with a standard mass. The apparatus was brought to a steady 190°C ± 0.5°C before beginning the experiment. The barrel was charged with 4.5 grams of polymer (cut in to small pieces) and tamped down with the charging tool to exclude air. The time taken to charge the barrel should not exceed one minute. The polymer was allowed to melt for 2 minutes before the weight (2.1 kg) was applied. Sample collection started at the first mark on the piston and continued at regular intervals until the second mark was reached. The extrudate was cut with a suitable sharp-edged instrument. Samples of the collected polymer extrudate were weighed and any samples containing air bubbles were excluded. From these measurements (usually 4 or 5) the MFI and molecular weight was calculated. The melt flow index is defined as the amount of polymer in grams extruded through a standard die in a given time (e.g. 10 minutes)

2.2.7 Determination of tensile properties

Dumbbell shaped pieces for tensile testes were cut from 0.25mm thick film using the appropriate British Standard (E-type) cutter in a hand operated press.

Tensile properties, i.e. ultimate tensile strength, elongation at break etc, were determined using an Instron Model 4301 Universal Testing Instrument, controlled by a Dell 425si personal computer. The system was driven by software supplied by Instron Corporation Series IX Automated Materials Testing System Version 1.20. The thickness of each sample was measured in three different places and an average taken before the tests were carried out. This average value was used in all subsequent calculations relating to a particular sample.

The test specimen was held in two pneumatically operated clamps; one immovable fixed to the base of the tester, the other to the cross-head via a load cell. A strain gauge was then attached to the sample using two pinch clamps. After ensuring the cross-head and strain gauge were both set to zero, the sample was extended at a constant rate of 50mm minute until it ruptured. The stress and strain recorded by the load cell and strain gauge respectively were monitored. Once the sample had ruptured, the instrument returned automatically to its starting position. At least five samples were tested for each set and an average of the results taken. Any one result could be excluded on the basis of gross random error, the complete set of results were recorded and printed out by the software.

2.2.8 Accelerated thermal ageing using a Wallace cell oven

Samples of polymer blends were aged thermally in a Wallace cell oven. The oven has seven, separate cylindrical cells in which samples could be suspended from removable frames. The temperature of the oven was accurately controlled thermostatically. A constant air flow was maintained, and monitored using a flow meter. The temperature was varied depending on the test. Strips of 0.25mm thick film were used for molecular weight and DSC measurement and dumbbell

specimens were used for tensile measurements. The test pieces were periodically removed for analysis.

2.2.9 U.V. cabinet

Two different types of U.V. cabinet were used for irradiation of the samples. The first was a S/B-type cabinet and consisted of a cubic aluminium cabinet containing 8 sun lamps and 24 actinic blue lamps arranged in a regular symmetrical 1 to 3 sequence designed to simulate natural sunlight shown in Figure 2.23. In the centre of the cabinet was a rotating drum to which the samples were attached. The rotation of the drum ensured that all the samples received identical amounts of radiation. The spectral distribution of the radiation was 290-400nm with peak emission at 317nm for the sun lamps and 367nm for the blue lamps. The average radiation output was 33 W/m^2. The temperature inside the cabinet was maintained at $29° \pm 1°$ C by a driven ventilator under the drum.

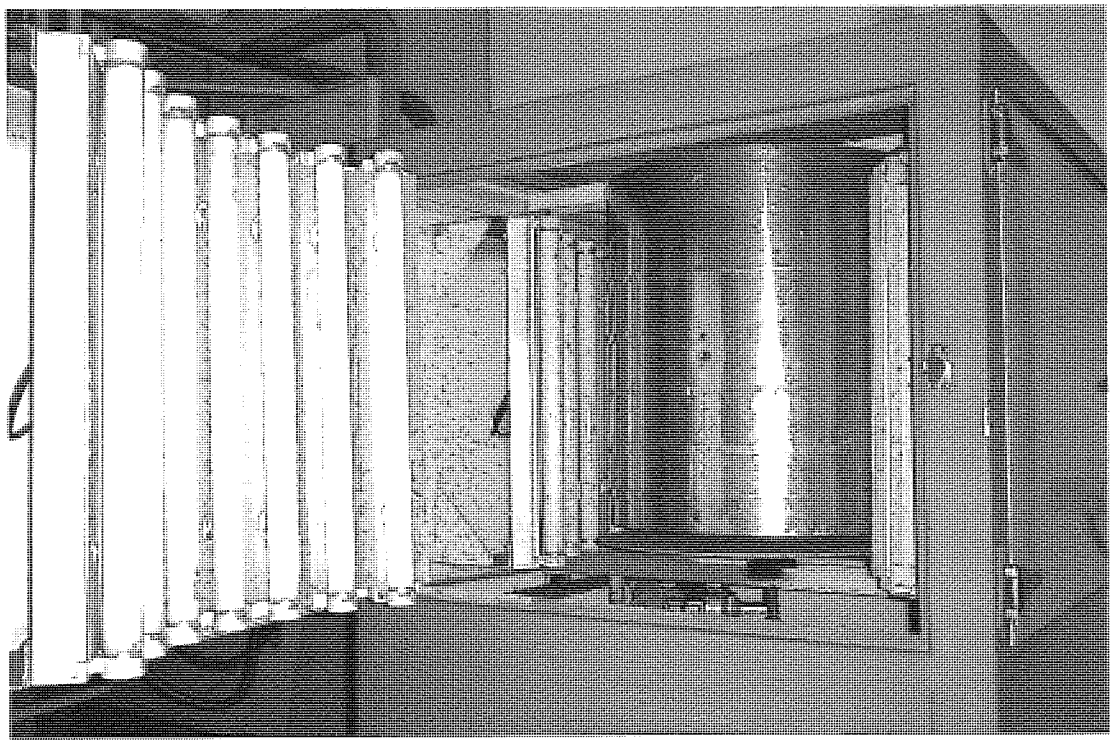


Figure 2.23. S/B UV cabinet

The second UV cabinet was a SEPAP 12-24 photo-ageing unit (Figure 2.24) designed at Les laboratories de Photochemie in Clermont-Ferrand. The samples were irradiated with four medium pressure mercury bulbs each of 400W. These emitted ultraviolet light between 290-350nm with their peak intensity at 310nm. The average radiation output was 55W/m^2 The internal temperature was maintained at 75°C. Samples were mounted on a rotating turret to ensure each sample received identical irradiation.

Figure 2.24. UV 12-24 cabinet

2.3 Biodegradation

2.3.1 The batch screening process

The majority of the tests were carried out using the batch screening process. This technique allowed the screening of a large number of samples relatively quickly. The technique simply involved weighing an appropriate quantity of polymer film cut into approximately 1cm^2 pieces. These pieces were placed in brown jars containing compost, which were then sealed. The samples were then heated to 50 or 60°C depending on the polymer. The jars were opened and aerated at intervals to ensure that the degradation was aerobic rather than anaerobic. Periodically, the plastic pieces were removed, cleaned as well as possible using distilled water, dried and weighed. The weight loss over time was calculated.

2.3.2 The bioreactor

The bioreactor was a device to measure the complete mineralisation, i.e. the conversion into carbon dioxide and water, of a particular polymer sample; the method was based on ISO/DIS 14855. The apparatus, shown in Figure 2.25 below which consisted of a series of 1L jacketed glass vessels with multi-necked lids, inside was a sintered glass bed to support the contents. A reactor was filled with moist compost and water at the appropriate temperature was circulated around the jacket. Carbon dioxide free air was drawn through the base of the flask, through the compost and out via a condenser to a carbon dioxide detector. The background CO_2 from the compost was allowed to stabilise before addition of any samples which took approximately two weeks. Test specimens (50g) were then mixed into the compost (600g). One of the reactor vessels always contained cellulose which degrades at a consistent rate under these conditions. The CO_2 evolution was recorded twice daily for six weeks and the cumulative amount produced by each was calculated as a percentage of the theoretical CO_2. The conversion of polymer into carbon dioxide could therefore be monitored. One of the reactors contained only compost to give a background value.

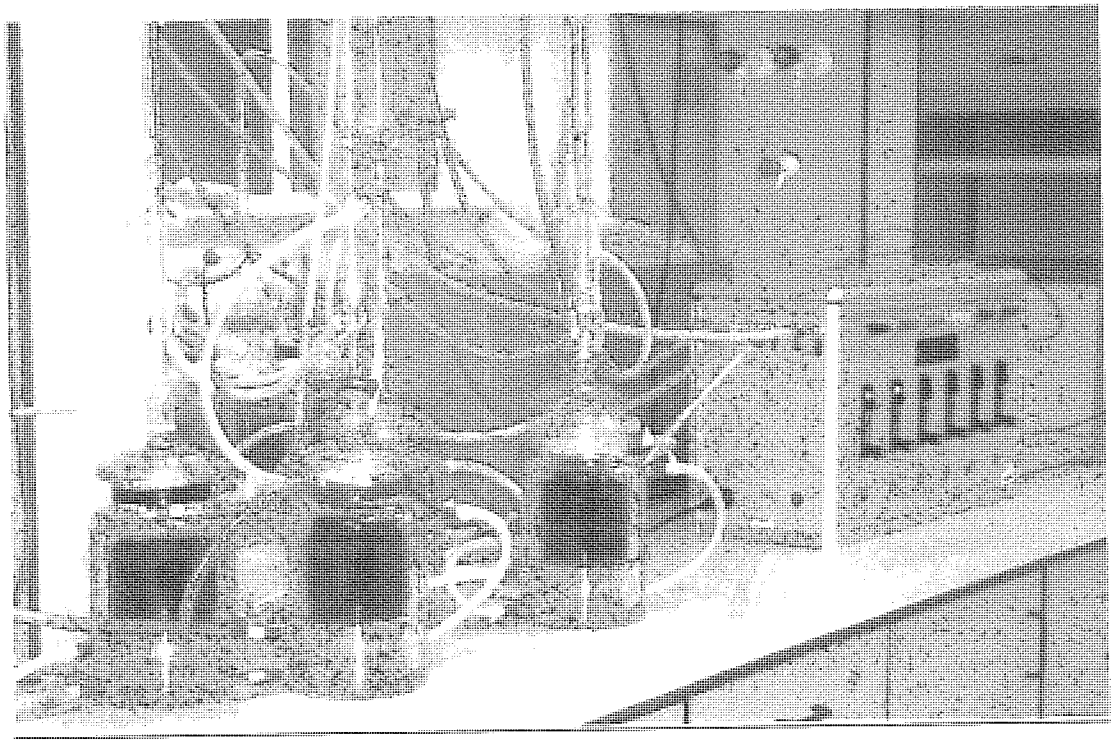


Figure 2.25. The bioreactor

2.3.3 General toxicity determination of decomposition products under composting conditions

A representative sample of compost containing degradation products was dried at 60°C overnight and another at room temperature for several days. 25 g of this compost was soaked in 25 ml of distilled water and held at room temperature for 3 hours. Extracts were filtered through a paper filter and then through a 0.2 μ syringe filter. Germination tests using cress seeds were run in quadruplicate with 20 seeds on a filter paper in a Petri dish containing $4cm^3$ of the above solution. Water was used as a reference. The seeds were left to germinate at 28°C in the dark for 24 hours. The general toxicity of the degradation products formed in the bioreactor could therefore be assessed.

2.4 Estimation of peroxide concentration in processed PLA samples

During processing polymers are exposed to high temperatures and high shear forces and under such conditions, polymers can undergo chain scission forming macroalkyl radicals (R·), which react rapidly with atmospheric oxygen to form alkyl peroxy radicals (ROO·). These species are capable of abstracting hydrogen from other polymer molecules to form hydroperoxides (ROOH).

Iodometry is one of the most widely used techniques for the estimation of the extent of hydroperoxide formation. In this method, the iodide ion is oxidised quantitatively to iodine by hydroperoxide in an acidic medium.

$$ROOH + 2I^- + 2H^+ \rightleftharpoons ROH + H_2O + I_2$$

Dialkyl peroxides can also oxidise iodide to iodine but this reaction is much slower.

An iodometric method based on the oxidation of sodium iodide was used. The use of sodium iodide in place of the potassium salt has the advantage of a greater solubility, the result of which will keep the equilibrium far to the right with the result that:

$$I_2 + I^- \rightleftharpoons I_3^-$$

1. The loss of liberated iodine due to purging or boiling is prevented, as the tri-iodide ion is involatile
2. The tri-iodide ion will not add to any double bonds present in the polymer. Errors due to unsaturation are therefore eliminated.

The method used by Manasek [106] *et* al and Geddes [107] was modified as follows: A sample of polymer film (1g) was weighed accurately and was cut into small pieces.

The polymer was allowed to stand in deaerated chloroform overnight. To this solution was added $3cm^3$ glacial acetic acid and $2cm^3$ of a 5% w/v solution of sodium iodide dissolved in deaerated methanol. The sample bottle was flushed with nitrogen and allowed to stand for 4 hours. An identical solution without polymer was always prepared as a blank. After four hours, water and a few drops of starch indicator were added to the chloroform solution immediately before titration with 0.01 M sodium thiosulfate solution. The volume of sodium thiosulfate required to discharge the blue-black colour was recorded. From the equation below, 1 mole of iodine requires 2 moles of sodium thiosulfate.

$$I_2 + 2\ NaS_2O_3 \longrightarrow 2\ NaI + Na_2S_4O_6$$

The mount of iodine liberated is then calculated by the following equation:

$$Moles\ of\ I_2 = \frac{Volume\ of\ thiosulfate\ (cm^3)}{1000 \times molarity\ of\ thiosulfate\ solution}$$

This value is equal to the moles of hydroperoxide present as 1 mole of iodine is liberated per mole of hydroperoxide

2.5 Saponification

Esters were analysed using the saponification method. In this method, the ester was broken down quantitatively into its component acid and alcohol by hydrolysis by alcoholic potassium hydroxide. The reaction partially consumes the potassium hydroxide and this quantity can be calculated by back titration with standard acid and reference to a standard.

The ester (2g) was weighed accurately into a round bottomed flask and $50cm^3$ of approximately 1M ethanolic KOH was added with 2-3 drops of phenolphthalein solution. An identical mixture was also prepared but without the ester. Both samples were heated to reflux for approximately forty minutes and the solutions were then titrated with standard 1M hydrochloric acid. The amount of hydroxide in the standard was compared to that in the sample and thus the molecular weight the of the ester was calculated according to the formula:

$$\text{Molecular Weight} = F\left(\frac{W \times 1000}{(B-T)\times M}\right)$$

Where:

W = weight of sample.

B = blank titre

T = test titre

M = molarity of HCl

F = functionality of the ester

The molecular weight derived for the ester was compared to the theoretical molecular weight and the purity could be calculated.

$$\text{Purity} = \frac{\textit{theoretical molecular weight}}{\textit{observed molecular weight}} \times 100\%$$

2.6 Determination of extracted ester plasticizer using FTIR spectroscopy

Polymer additives can be extracted into water or organic contact fluids over a long period of time, which is particularly important for food contact applications. It was necessary therefore to determine the stability of the polymer blends containing the

various additives. A method was required to enable the determination of the quantity of the additive extracted from the polymer.

2.6.1 Standard solution preparation

Solutions in the range 0.05-1% by weight were prepared accurately in HPLC grade hexane and the sample was measured using a 0.5mm fixed path KBr cell. The height of the carbonyl absorbance corresponding to that of ester (shown in Figure 2.27) was measured in each sample using the in built peak height facility of the PE 1650 FTIR. A typical spectrum is shown in Figure 2.26.

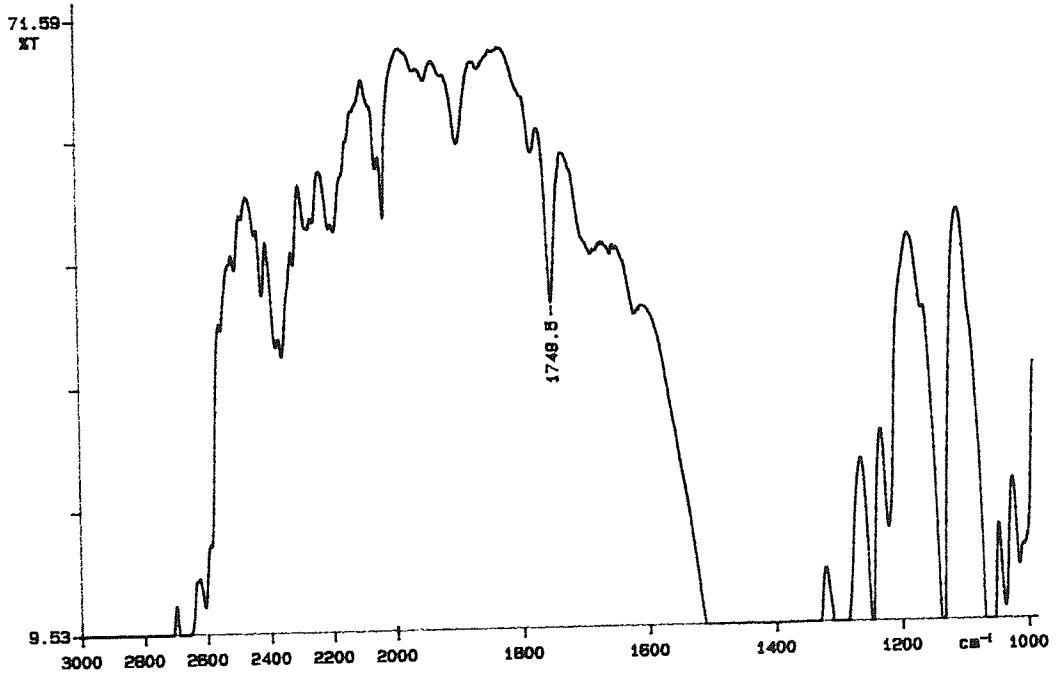


Figure 2.26. Typical FTIR of TMHT in hexane (0.1%w/v)

The peak height was measured from an appropriate consistent baseline. The absorbance was plotted against the concentration of the ester in hexane as shown in Figure 2.27. The background value for hexane was 0.014.

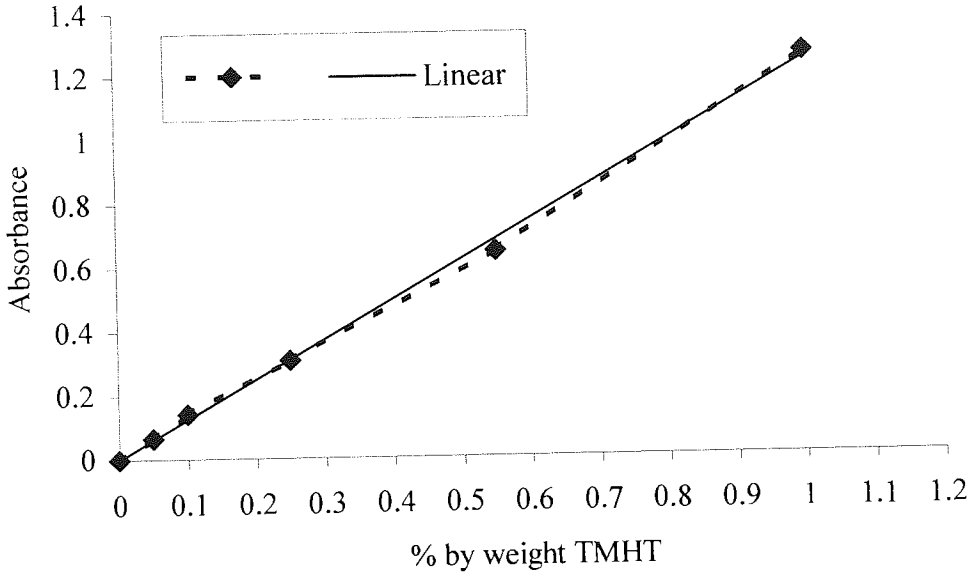


Figure 2.27. Plot of FTIR absorbance againgst concentration of TMHT in hexane

The linear dependence obtained indicated that this was a suitable method for the determination of low concentrations of extracted additive.

2.6.2 Exhaustive extraction of plasticizer

1.00g of blown PLA film approximately 6×5 cm^3 was cut into strips 5-8 mm× 25mm and immersed in exactly 50cm^3 HPLC hexane. The flask was connected to a double face reflux condenser and heated to 50°C in a thermostated bath. Accurate 0.5cm^3 samples of the hexane were removed after 2, 4, 6 and 24 hours, the absorbance of the carbonyl band was measured and the quantity of ester calculated by reference to the calibration graph (Figure 2.27).

2.6.3 Water extraction

Three 1g pieces of blown film were taken from the appropriate sample and cut into strips as described above. The three samples were each immersed in 50 cm^3 of deionised water. The flasks were sealed and heated to 50°C. One of the three samples was removed after 2, 4 and 24 hours and treated as follows:
The contents were cooled to room temperature and the water decanted into a separating funnel. The remaining contents were washed three times with water ($5cm^3$) and combined with the first. The combined extract was then extracted with $2\times10cm^3$ HPLC hexane. The total hexane extract ($20cm^3$) was made upto $25cm^3$ in a $25cm^3$ volumetric flask (Care was taken to minimise water contamination.). The FTIR spectrum was recorded.

2.7 Hydrolytic stability of polymer films

Dumbbell test specimens were immersed in buffer solutions or deionised water, depending on the test. The test pieces were allowed to age at room temperature. Samples were removed periodically and before being tested, the specimens were allowed to dry in an evacuated dessicator at room temperature. The physical properties of the extracted test pieces were then measured. In addition to the dumbbells, approximately 6g of plasticized blown film was allowed to degrade at room temperature and 50°C. The weight loss of the films was monitored periodically.

Chapter 3

Experimental

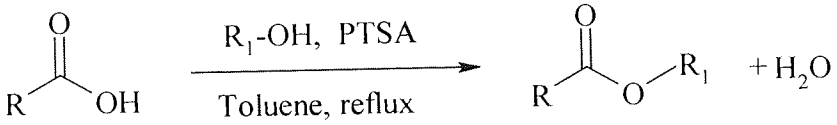
3.1 Synthesis and characterisation of ester and copolymer plasticizers

3.1.1 Materials

All materials in this section were used as received without further purification. The alcohols were obtained from bulk supplies from Robinson Brothers Ltd. The carboxylic acids were obtained from Aldrich.

3.1.2 Synthesis of esters: general method

The general method outlined below (Scheme 3.11) was used for the synthesis of all esters; any significant deviations are described as appropriate.



Scheme 3.11. Ester synthesis

Condensations were carried out in the Sovirel apparatus shown in Figure 3.28. The Sovirel equipment is a multipurpose modular glass reaction vessel that consists of a standard multi-necked glass lid to which can be fitted different sized reaction flasks. The flask was sealed to the lid by means of a gasket and eight clips. The reaction mixture was stirred mechanically using an overhead electric motor connected to a glass stirrer shaft with a screw thread fitting, to which could be attached a suitably shaped PTFE stirrer paddle. A variety of fittings could be attached to the lid to suit reaction requirements. In the case of condensation reactions a Dean and Stark or a standard condenser system was used.

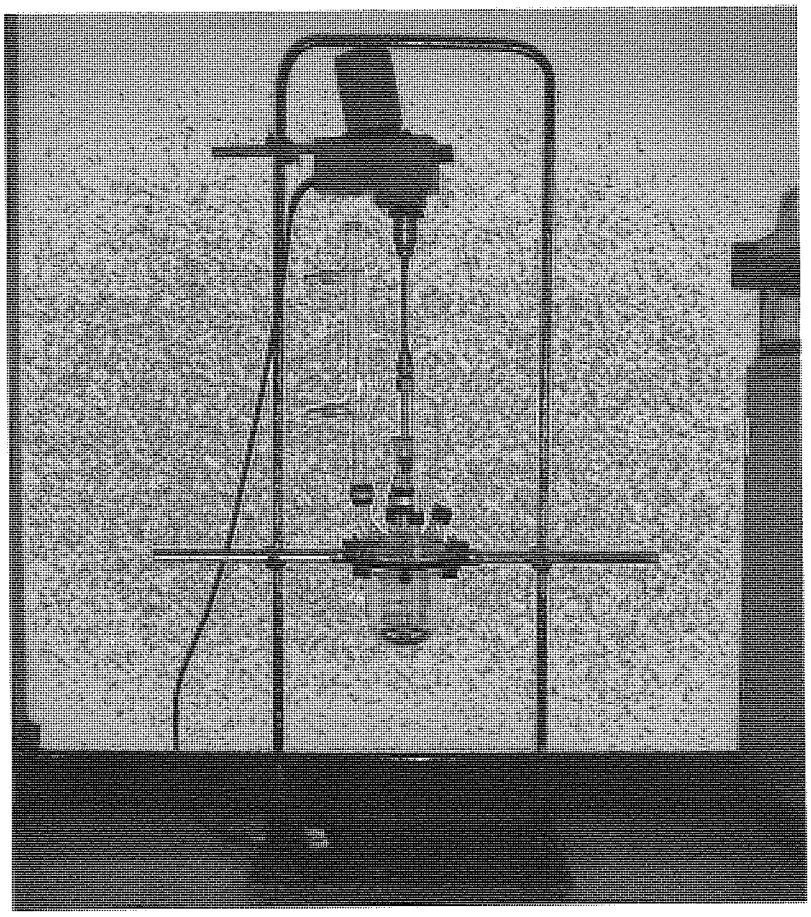


Figure 3.28. The Sovirel equipment

In a typical reaction, tartaric acid (50g, 0.33 mol), 2-ethylhexanol (83.3g, 0.64 mol) and p-toluene sulfonic acid (PTSA) [1.2g, 0.007 mol] were placed in a 500cm^3 Sovirel apparatus. Toluene (300cm^3) was added to the reactants and the contents were heated to reflux. When the mixture was above 60°C water was visible in the vapour space. The reaction was maintained at reflux until the evolution of water had ceased, which generally took 6-8 hours. During this time the carboxylic acid gradually dissolved and the reaction mixture turned hazy. The solution was cooled to approximately 40°C and washed twice with water (2×200cm^3) to remove any unreacted acid and catalyst. The toluene layer was dried over anhydrous sodium

sulfate, filtered and distilled on the rotary evaporator at 90°C under full water pump vacuum (~10mm Hg) and the ester recovered (yield = 167.1g, 94.1%).

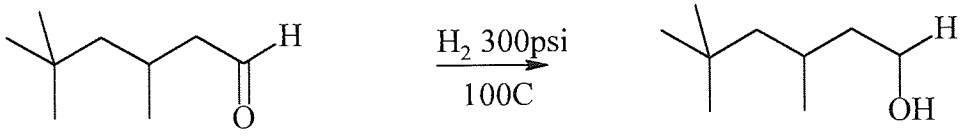
In the preparations of esters using low boiling alcohols, the alcohol was used as both solvent and reactant. When the evolution of water had stopped the excess solvent/reactant was removed under reduced pressure and replaced with fresh solvent. The reaction mixture was then returned to reflux for approximately 1 hour. The distillation process was then repeated. Toluene (~300cm^3) was then added and the product was washed with water and isolated as described above.

The esters prepared by this method are shown in Table 3.3, which also details the purity and the infrared carbonyl frequency. A summary of their structures are given in appendix 1. All the alcohols with the exception of 3,5,5-trimethylhexanol were obtained from commercial sources. The preparation of 3,5,5-trimethylhexanol is described below.

3.1.3 Preparation of 3,5,5-trimethylhexanol

3,5,5-Trimethylhexanol (isononyl alcohol) is only available from the commercial chemical suppliers as a mixture of isomers or as a low purity, technical grade material. However, the aldehyde is available commercially as the single 3,5,5-isomer.

3,5,5-trimethylhexanal (400g, 3.05 mol) was catalytically reduced without solvent at 100°C using Raney nickel catalyst (type J10H) (4.0g) at 300psi (2.07x10^6 Pa) with hydrogen. (Scheme 3.12). The reaction was carried out in a laboratory scale rocking autoclave shown in Figure 3.29 below. The pressure was maintained between 100 and 300psi. The reaction was deemed complete when the pressure remained constant.



Scheme 3.12. Catalytic reduction of trimethylhexanal

The product was analysed by gas liquid chromatography to confirm the absence of the aldehyde. At the end of the reaction the reaction mixture was filtered to remove catalyst residues. Yield = 392g (98%) of a colourless liquid with a characteristic pungent odour. Bp = 88-92°C at 8 mm Hg. Purity = 99.8% (GLC). The infrared spectrum showed a characteristic broad hydroxyl absorbance at 3329.1cm^{-1} and the absence of the aldehyde absorbance at 1727.1cm^{-1}

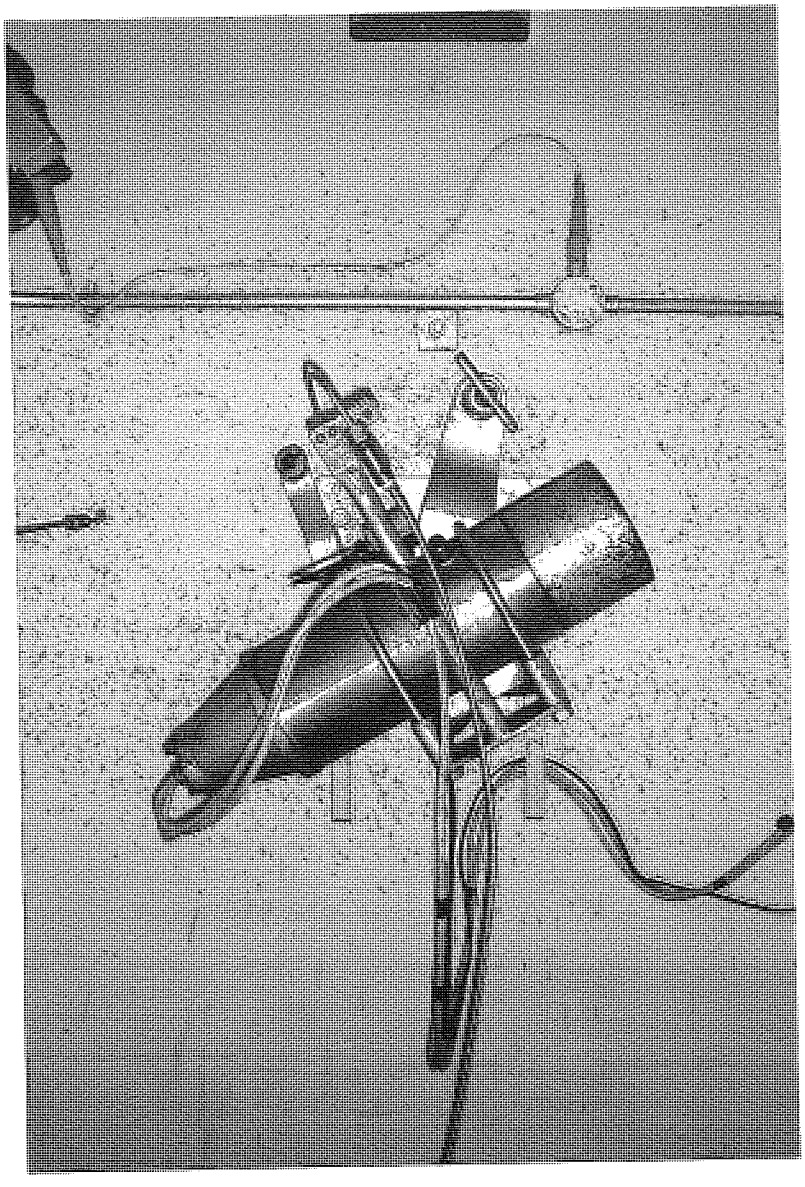


Figure 3.29. Laboratory rocking autoclave

Compound	Yield %	Purity *%	Ester Carbonyl Frequency (cm^{-1})
Tri (n-octyl) citrate (NOC)	97.0	97.8	1741.8
Tri (3,5,5-trimethylhexyl) citrate (TMHC)	87.4	98.2	1740.9
Tri (2-ethylhexyl) citrate, (EHC)	93.6	96.9	1741.6
Tri (2-isobutyl) citrate(IBC)	96.4	96.5	1737.6
di(n-octyl) maleate (NOM)	98.8	97.2	1731.2
di (2-ethylhexyl) maleate (EHM)	85.6	98.5	1734.8
di(isobutyl) maleate (IBM)	97.7	99.0	1731.5
di(n-octyl) tartrate (NOT)	98.8	97.2	1754.9 and 1721.1
di(2-ethylhexyl) tartrate (EHT)	94.1	94.0	1751.1
di(isobutyl) tartrate (IBT)	86.6	95.3	1750.6
di(3,5,5-trimethylhexyl) tartrate (TMHT)	98.5	98.5	1746.4
di(3,5,5-trimethylhexyl) malate (TMHM)	90.6	97.9	1741.2
di(3,5,5-trimethylhexyl) succinate (TMHS)	87	97.9	1738.7

Table 3.3. Yields and infrared characteristics of esters prepared

*By saponification

The purity of the esters were calculated titrimetrically by saponification as described previously in chapter 2 and were found to have the correct degree of substitution. The compounds were also analysed using FTIR spectroscopy. These results are also included in Table 3.3.

3.1.4 Discussion

The esters described in this section were all mobile to moderately viscous liquids, except for isobutyl and n-octyl tartrates which unusually were solids and had melting points of 76-77°C and 46-47°C respectively. All esters gave a clear ester carbonyl absorbance at around 1750 cm^{-1} in the infrared, which is distinct from those of aldehydes (1740-1720 cm^{-1}), ketones (1725-1705 cm^{-1}) and carboxylic acids (1725-1710 cm^{-1}). However, n-octyl tartrate showed two carbonyl absorbances at 1755 and 1721cm^{-1} (Figure 3.30 [A]), which was unexpected. On closer examination it was felt that this type of compound would be expected to exhibit some degree of hydrogen bonding between the OH groups and carbonyl oxygen as depicted in Figure 3.31. In this configuration, certain carbonyl oxygens (circled) are not able to participate in hydrogen bonding because of steric hindrance from the alkyl chain. These carbonyl groups would therefore be expected to display the conventional ester carbonyl absorbance. Branched chain esters like TMHT and EHT cannot form such complexes (and are therefore liquids) giving a single carbonyl absorbance. Therefore, it can be suggested that the straight chain n-octyl groups allow the carbonyl groups to be in close proximity. This hypothesis is supported by solution infrared spectroscopy (Figure 3.30 [B]). The double carbonyl peak is transformed into a single, sharp peak in solution. In addition, the OH band has also become a single sharp peak, indicating a free, rather than hydrogen bonded hydroxyl group.

In further experiments, di n-butyl and di decyl tartrates were prepared to test the effect of the straight alkyl chain. n-Butyl tartrate was a liquid at room temperature and showed only a single carbonyl absorbance. However, decyl tartrate was a solid melting at 52-54°C and had the double carbonyl band. Its Infrared spectrum is shown in Figure 3.32 below. This clearly suggests that branched alkyl chains prevent ester molecules from forming a regular structure to produce crystals, whereas straight alkyl chains, regardless of length, allow solidification to occur. The close proximity of the molecules then gives rise to hydrogen bonds on certain carbonyl groups producing the split carbonyl band in the infrared.

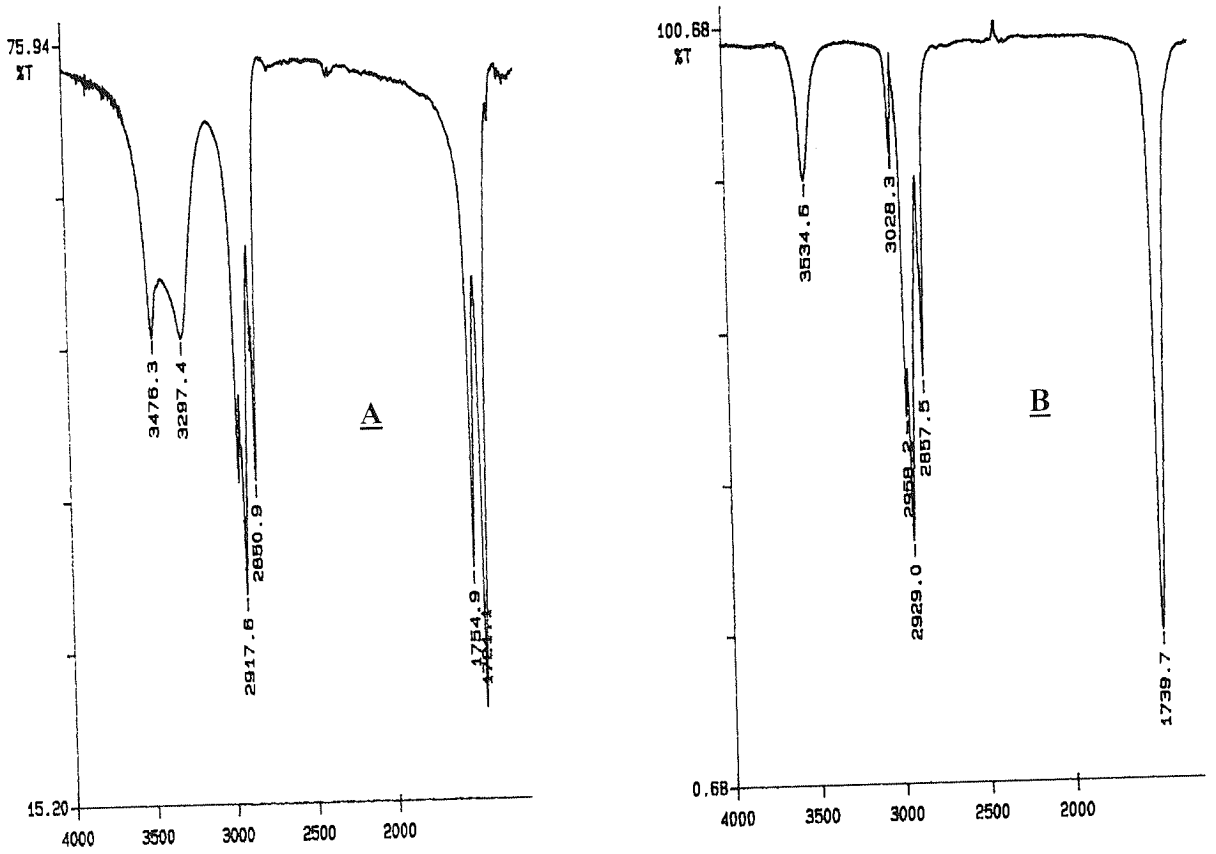


Figure 3.30. FTIR spectra of n-octyl tartrate. (A= KBr and B= $CHCl_3$ Solution)

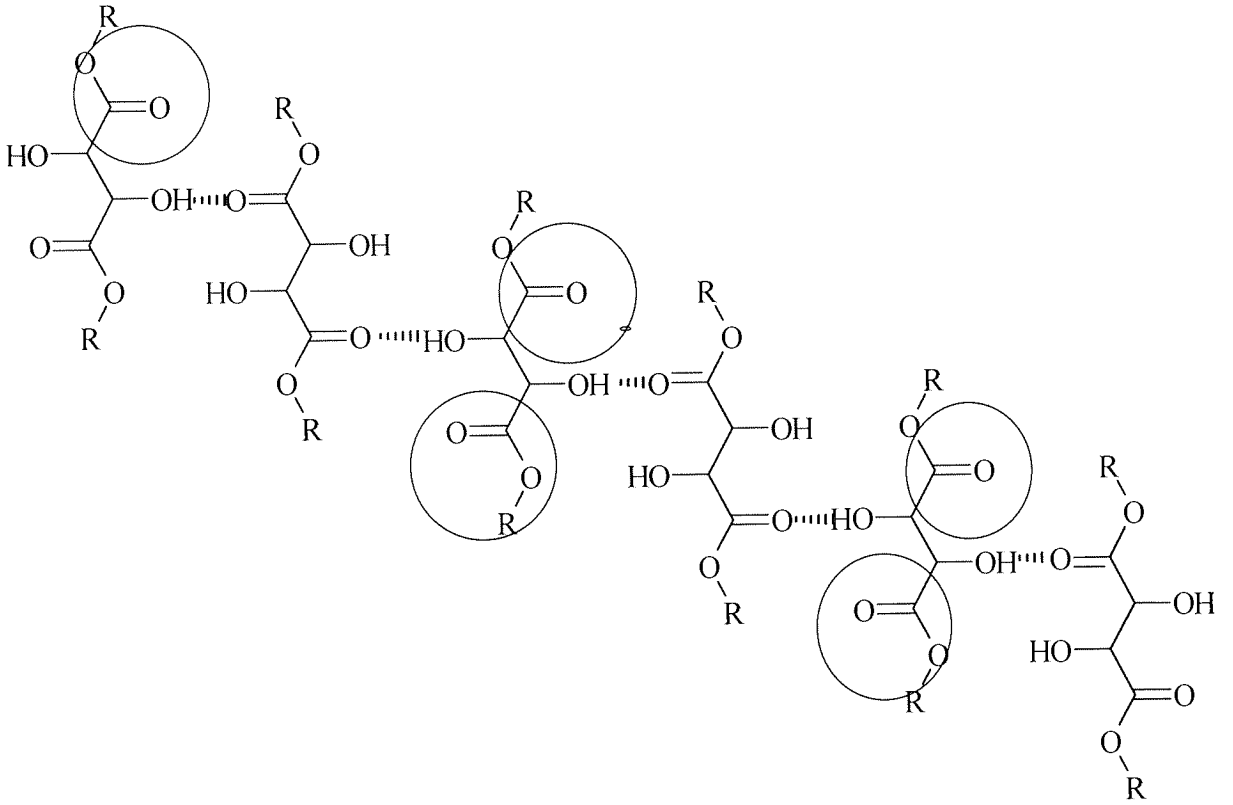


Figure 3.31. Tartrate ester different potential hydrogen bonding sites

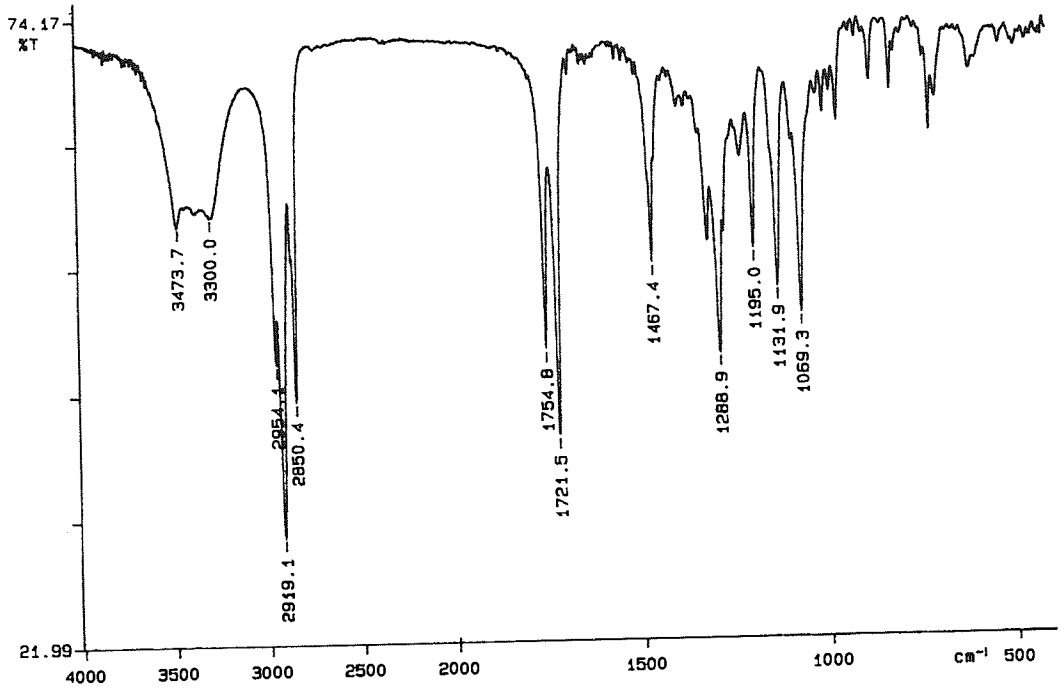


Figure 3.32. FTIR spectra of di-decyl tartrate

3.2 Copolymers

Copolymers are known as internal plasticizers and have significant advantages over externally plasticized polymers. Firstly, there are no extractable components in the polymer which is particularly adventitious when the material is used *invitro*. Secondly, the polymer matrix is stable over time, as generally little morphological change occurs, which can have a detrimental effect on the strength, flexibility or degradation rate of an article.

3.2.1 Materials: copolymer synthesis

DL-lactide was obtained from Aldrich and recrystallised from toluene before use.

Polyethylene glycol methyl ethers (MeOPEG) of number average molecular weight of 2000 and 5000 respectively were also purchased from Aldrich and reprecipitated from tetrahydrofuran solution into hexane before use and were continually dried under vacuum at room temperature.

Stannous octanoate (tin (II) 2-ethylhexanoate) was also obtained from Aldrich and also used as received.

MeOPEG 350 and 750 were obtained from Union Carbide and used as received.

L- lactide was purchased from Purac and used as received.

Ethoxylated pentaerythritol (M_w ~797) was obtained from Perstorp Polyols (PP150™) and used as received.

GPR toluene was used for this work and was dried over calcium hydride before use.

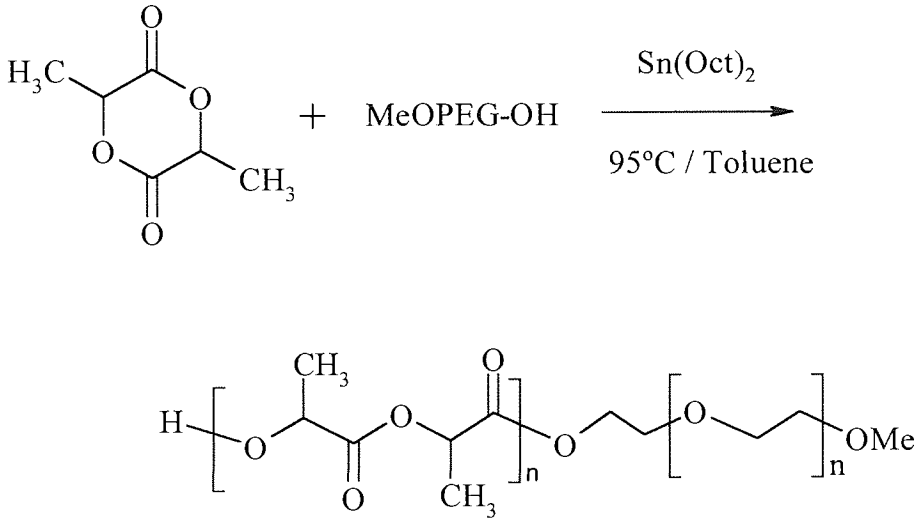
The solvent, calcium hydride dried GPR grade toluene was distilled into the reaction vessel using the high vacuum line.

3.2.2 Preparation of PLA block copolymers

A series of poly(ethylene glycol)methylether-*co*-DL-lactide diblock copolymers were prepared. A novel star type copolymer based on a commercially available pentaerythritol was also synthesised. In addition, several poly(caprolactone)-*co*-poly(lacic acid) polymers were also prepared using similar techniques to those described here. The preliminary results of this work are discussed in appendix 2.

3.2.3 Synthesis of Poly(ethylene glycol) methylether-*block*- PLA copolymers (MeOPEG-PLA)

Lactide polymerization can be carried out using hydroxy terminated initiators, with tin octanoate as catalyst. This approach was extended to the use of poly(ethylene glycol) methyl ether as initiator, which also effectively acted as a chain control agent. The reaction scheme is shown below (Scheme 3.13):



Scheme 3.13. Formation of MeOPEG-PLA block copolymers

In a typical reaction, DL-lactide (1g, 0.0069 mol), MeO-PEG(750)-OH (1.03g, 0.00137 mol) and $Sn(Oct)_2$ (0.01g, 2.5×10^{-5} mol) were weighed into a pre-dried polymerisation vessel. The high vacuum system was generally used for transferring and manipulating moisture sensitive reagents.The equipment briefly consists of a high vacuum pump connected via cold traps and a mercury diffusion pump to a glass manifold system. Each arm of the manifold had an isolating tap. Argon could be introduced when required. Reaction vessels were connected to the manifold by Quickfit joints. A vacuum of 10^{-3} mm of mercury could be obtained. The reaction vessel was connected to the high vacuum line and evacuated to remove any last traces of moisture. After approximately thirty minutes the flask was sealed, removed and weighed. The flask was returned to the vacuum line and cooled using liquid

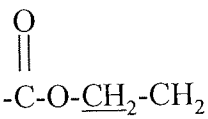
nitrogen. Toluene (6g) was distilled into the vessel using the high vacuum line. When complete, the vacuum was released with argon. The flask and contents were then heated to 95°C and the reaction allowed to take place for approximately 16 hours. It was shown that in some cases the reaction was complete in three to four hours. The first sign of a successful reaction was the absence of any crystallisation of lactide when the solution was cooled. The presence of any amount of crystalline material at this stage indicated an incomplete reaction. However, in most cases this did not occur. The toluene was removed from the polymer under vacuum and replaced with a minimum amount of chloroform (approximately $2cm^3$). The polymer was precipitated into approximately $50cm^3$ of cold diethyl ether. The polymer was recovered either by decanting or filtration and then dried under vacuum. Precipitation was not possible for the low molecular weight polymers. The majority of the syntheses gave copolymers with very narrow poly dispersities with GPC number average molecular weights close to the theoretical values, indicating minimal side reactions and transesterification. The reaction completeness was confirmed by proton NMR of the reaction mixture. The methine hydrogen in the lactide (at 5.03ppm) was shifted to a lower field (5.1ppm) on ring opening. The absence of a detectable lactide signal indicated that the conversion was complete (appendix 3).

Typical block copolymers are shown in Table 3.4 below. A complete list is given in appendix 4

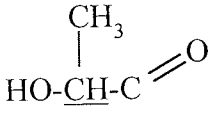
Mn of PEG	Lactide: MeOPEG-OH Mol ratio	% Yield	Theory Mwt	Mn (GPC)	Mw/Mn	Properties
350	28: 1	89	4400	5600	1.1	V .soft solid
750	28: 1	84	4700	5050	1.2	solid
2000	28: 1	80	6030	7500	1.2	Solid
5000	28: 1	96	8960	9500	1.2	Solid

Table 3.4. Control of molecular weight of MeOPEG – PLA copolymers

The NMR evidence for this class of copolymers has been widely reported [46, 108]. The ^{13}C NMR evidence normally presented is only sufficient to determine the presence of poly(lactic acid) and poly(ethylene glycol) chains but is not sufficient to prove the existence of a copolymer. It is necessary to show the junction between the two blocks to ensure the presence of a block copolymer. Proton NMR (Figure 3.33) and particularly ^{13}C NMR (S.P.E.E.D) [Figure 3.35] spectroscopy were able to determine accurately the junction between the MeOPEG and the PLLA or PDLA moiety, however the PLLA copolymers had a much clearer spectrum because their stereo regularity. The proton spectrum shown in Figure 3.33, shows all the required peaks consistent with the copolymer. Particularly important however, is the small complex multiplet centred on 4.3 p.p.m, which contains the protons associated with the following groups [45, 53]



From PLA-MeOPEG junction



From PLA end group

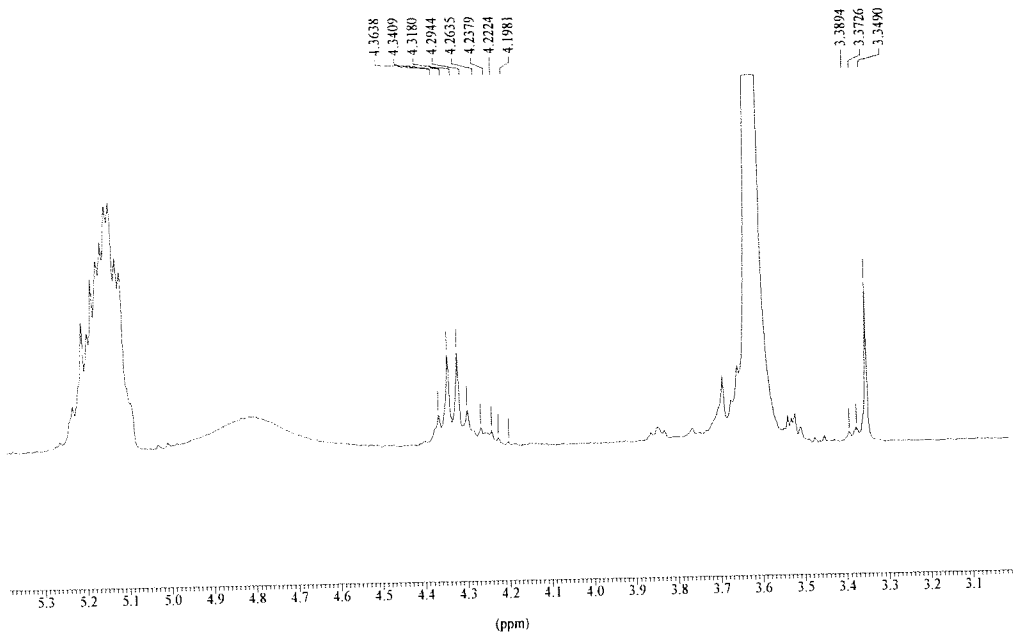


Figure 3.33. Proton NMR spectrum of MeOPEG – PLLA (PLA-PEG junction)

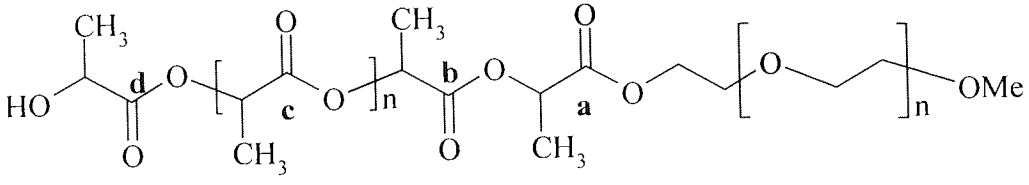


Figure 3.34. Expanded structure of MeOPEG 750-co-PLA (1:10)

The ^{13}C NMR analysis was also found to be invaluable for determining the important junction between the PEG and the PLA blocks (carbon **a** in Figure 3.34). The carbonyl region is particularly sensitive to the chemical environment and the appearance of the small peak at 169.84 p.p.m would suggest a carbonyl carbon joined to a significantly different group to those in the main polymer chain. Figure 3.35 below, shows a typical ^{13}C S.P.E.E.D. NMR spectra (expanded carbonyl region) of a MeOPEG-PLLA copolymer. Table 3.5 gives the carbonyl assignments.

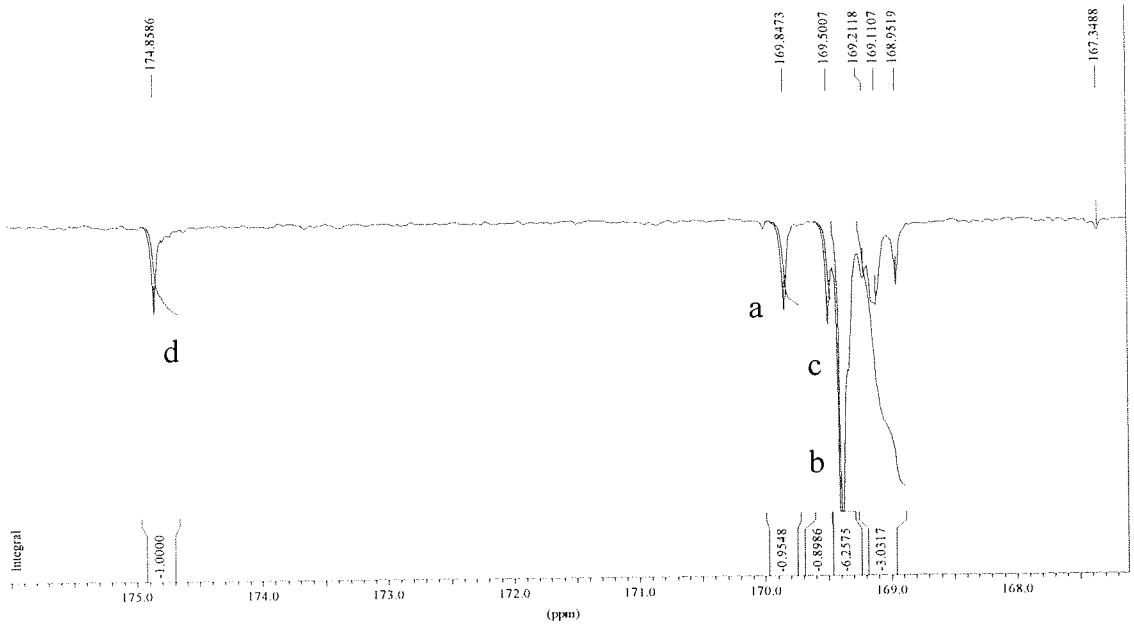


Figure 3.35. ^{13}C Spectra of MeOPEG-*co*-PLLA (1:10) [carbonyl region]

The integration and peak height of **a** and **d** (although not quantitative) are similar and this would indicate a similar number of carbon atoms associated with that resonance. This argument can be extended to the other carbon resonances. It can therefore be tentatively suggested that the S.P.E.E.D NMR technique can resolve the individual carbonyl groups in a low molecular weight PLA copolymer sample, particularly those closest to the junction and near the chain end.

Carbon	Chemical Shift (p.p.m)	Integration	Assignment
a	169.84	1	PLA-PEG junction
b	169.5	0.9	In chain C=O
c	169.4-168.9	9	In chain C=O
d	174.85	1	Terminal PLA C=O

Table 3.5. Proposed carbonyl assignments for –MeOPEG 750-*co*-PLA

3.2.4 Determination of the degree of polymerisation in copolymers using proton NMR spectroscopy

The degree of polymerisation of the PLA chain in the copolymers was calculated using the integration ratio of the OCH_3 end group in poly(ethylene glycol) to that of the CH of the lactyl group. The degree of polymerisation of the PLA chain was therefore:

$$DP_{PLA} = \frac{3}{i_{OCH3}} \times I_{LA}$$

Where i_{OCH3} is the integration of OCH_3 groups in PEG

I_{LA} is the integration of CH in PLA

The degree of polymerisation $(DP)_{PLA}$ of the PLA chains, calculated by proton NMR spectroscopy using the OCH_3 end group, was close to the theoretical value expected from the feed ratio. Table 3.6 shows the results obtained for a range of materials.

Lactide to MeOPEG-OH ratio	Calculated DP	Theoretical DP
70:1 MeOPEG 5000	138	140
55:1 MeOPEG 2000	67	110
28:1 MeOPEG 2000	37	36
10: 1 MeOPEG 2000	20	20
5:1 MeOPEG 750	9	10

Table 3.6. Degree of polymerisation of MeOPEG-PLA copolymers

3.2.5 Effect of catalyst concentration on molecular weight

It has been reported in the literature [51] that the molecular weight of the final polymer is inversely proportional to the concentration of $Sn(Oct)_2$ in a polymerisation. However, its effect during copolymerisations appears not to have been studied. A series of copolymerisations was carried out in which the lactide to initiator [MeO-(PEG 2000)-OH] ratio was kept constant at 10:1 whilst the catalyst concentration was increased. The theoretical molecular weight for this monomer to initiator ratio was 3440. A homo polymerisation was also carried out for comparison

The concentration of catalyst clearly has an effect on the molecular weight of the homo- and copolymers and although the differences were not great, the molecular weights of the products tended to decrease when more than the normal amount of catalyst was used. It was observed that in these reactions all the lactide was consumed. The absence of the lactide CH protons in the ^1H NMR spectrum of a copolymerisation initiated with a low catalyst concentration (appendix 3) and the ^1H NMR spectrum (time= 1.5 hrs) of a copolymerisation in which a high catalyst concentration was used [appendix 5] is apparent. This suggests that the decreased molecular weight was not caused by the incomplete polymerisation of the monomer.

MeO-(PEG2000)-OH: $Sn(Oct)_2$ mol Ratio	Mn by GPC
1: 0.33	3200
1: 0.66	2900
1: 1	2900
1: 2	2600

Table 3.7. Effect of catalyst concentration on the GPC molecular weight of MeOPEG-PDLA copolymer

Unfortunately the differences between the actual and the theoretical molecular weights, although less than the standard MeOPEG-OH to $Sn(Oct)_2$ mol ratio of 1: 0.25, was not enough to draw significant conclusions. Therefore a further reaction was carried out using lactide: MeOPEG-OH: $Sn(Oct)_2$ ratio of 280:4: 8. (Table 3.8) to give a higher theoretical molecular weight of 12080. This reaction gave a greater and more significant difference in the molecular weights of the copolymer.

Lactide: PEG: $Sn(Oct)_2$ mol ratio	Molecular Weight (Mn) by GPC	NMR Calc[d] Molecular weight	Reaction time (hrs)
280: 4: 1 (Standard)	12000	-	2
280: 4: 8	7200 and 7300	7200	2 and 4.5

Table 3.8. Effect of catalyst concentration on the molecular weight of MeOPEG-PDLA copolymer

A similar reaction was also carried out but omitting the MeOPEG to form a homopolymer. A similar result of a lower molecular weight with increasing catalyst concentration was observed (Table 3.9)

Ratio Lactide: $Sn(Oct)_2$	Molecular Weight (Mn)	Reaction time (hrs)
280: 1 (standard)	42900	5
10:1	9500 and 10100	5 and 22

Table 3.9. Effect of catalyst concentration on the molecular weight of PDLA homopolymer

The reduction in molecular weight with increasing catalyst concentration can be most easily rationalised when considering a homo-polymerisation. In this case the reduction in molecular weight is probably due to initiating impurities in the catalyst. However, in the case of copolymerisations the effect is complicated by the presence of added initiator, e.g. MeO-PEG-OH. The present work has demonstrated that ROH is an efficient initiator giving complete reactions within hours (appendix 6). With high concentrations of catalyst (and initiating impurities) it is suspected that there is competition between the impurities and the purposefully added initiator.
In the homopolymerisations carried out with high concentrations of $Sn(Oct)_2$, ^1H NMR indicated the presence of 2-ethylhexyl end groups [54] in the reprecipitated low molecular weight polymers shown in Figure 3.36. This suggests initiation by OctSnOH type species (Scheme 3.14). Unfortunately with conventional (low) catalyst concentrations the molecular weights of the homo polymers is too high for successful end group analysis. However, it may be suggested that theses end groups are also present in polymers initiated with low catalyst concentrations whereas the presence of purposely added initiator allows chain transfer giving an initiator terminated polylactide [54] (Scheme 3.14).

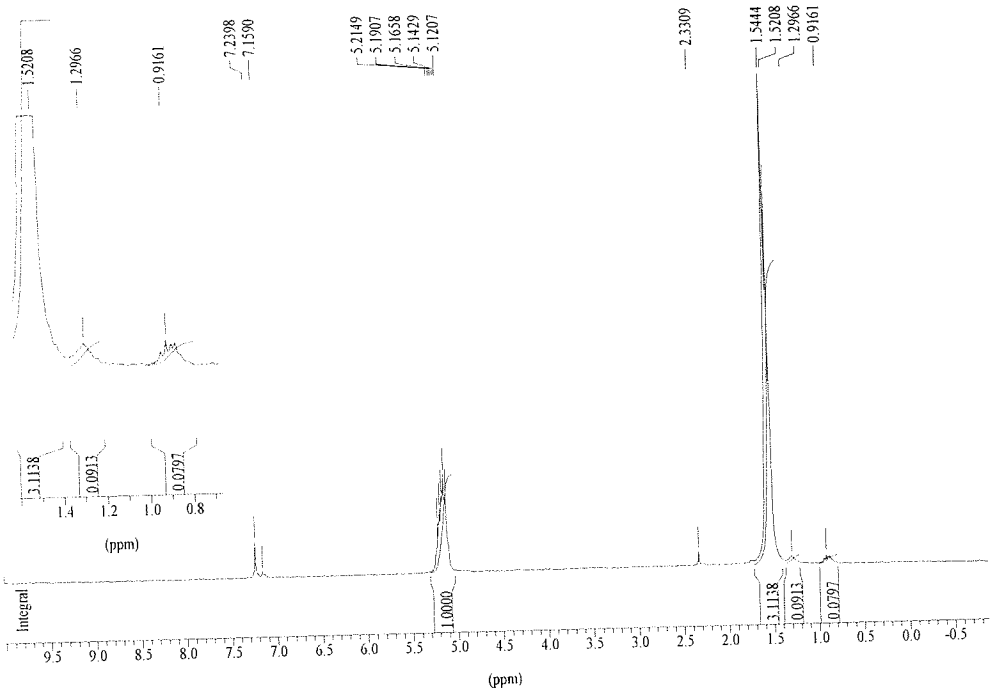


Figure 3.36. PDLA homo polymer (lactide:$Sn(Oct)_2$ ratio = 1:1)

$Sn(Oct)_2$ + ROH $\rightleftharpoons$ OctSnOR + OctH

impurity — low [I], high molecular weight polymers result

$Sn(Oct)_2$ + ROH $\rightleftharpoons$ OctSnOR + OctH

added alcohol — high [I], lower molecular weight polymers result

OctSnOR + LA $\longrightarrow$ OctSnO-(la)n-R

chain growth

Scheme 3.14. Chain growth in alcohol initiated polymerisations

3.2.6 DSC analysis

MeOPEG- DL-lactide copolymers were analysed by DSC as described in section 2.13 and found to be predominantly amorphous. As a consequence only melting endotherms of the MeOPEG chains were detected as shown in Figure 3.37. In a typical analysis, the glass transition temperatures of the constituent blocks could not be detected. However, MeOPEG-PLLA copolymers showed melting point transitions that could be attributed to the low molecular weight PLA segments but the melting point of the MeOPEG was absent. Figure 3.38 shows a typical DSC of a MeOPEG-PLLA copolymer.

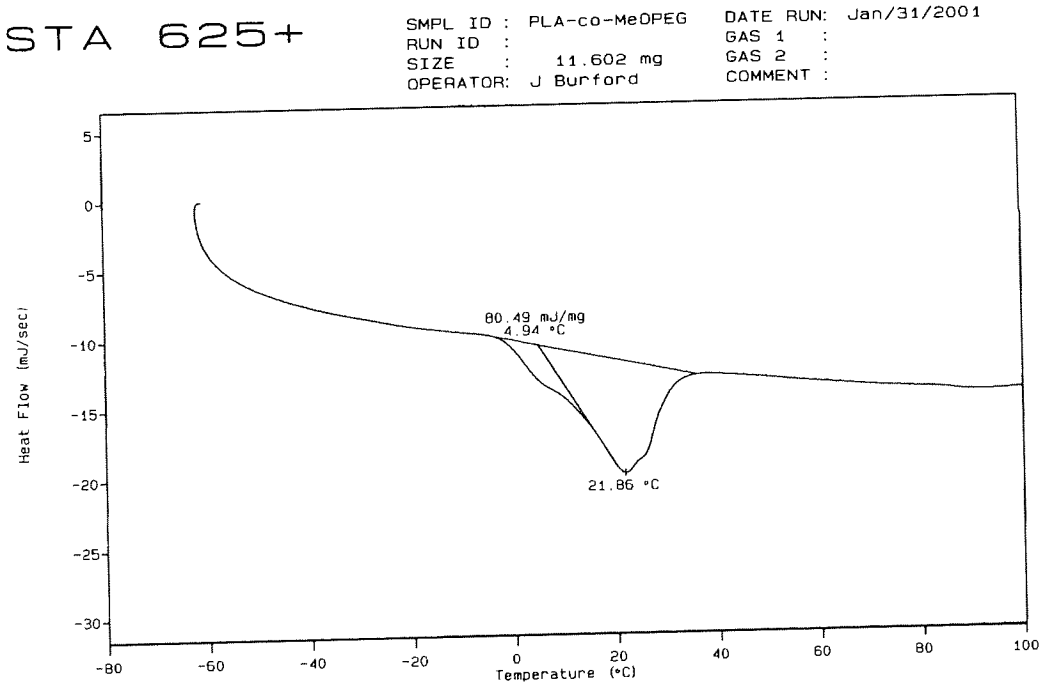


Figure 3.37. DSC of MeOPEG-PDLLA (750) 1:5

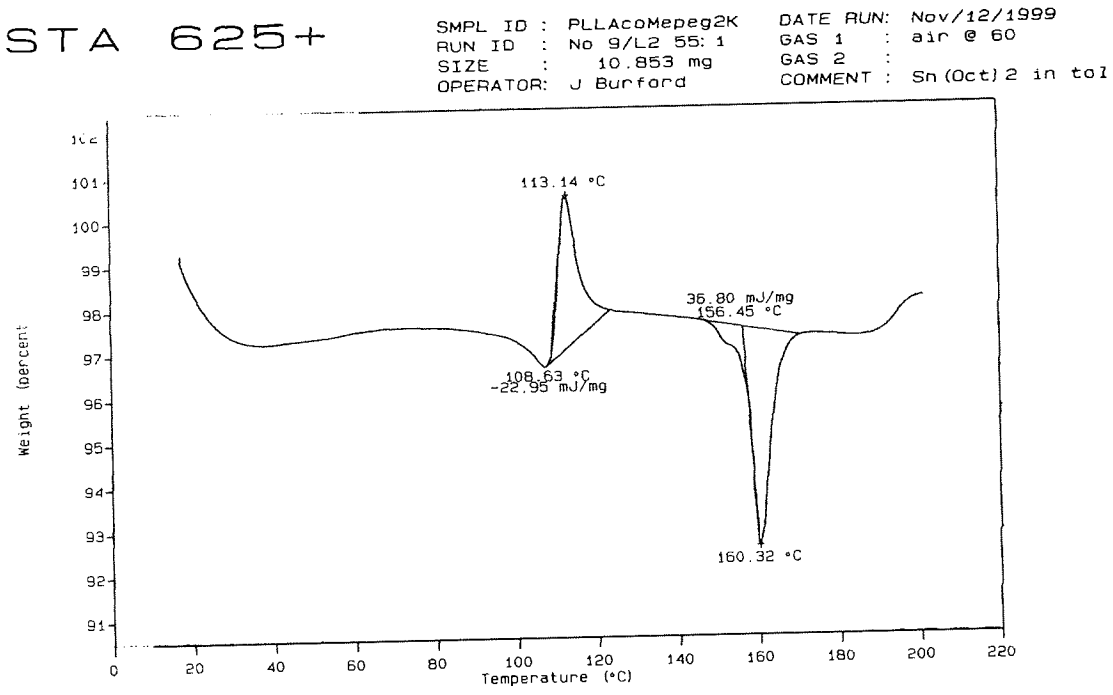
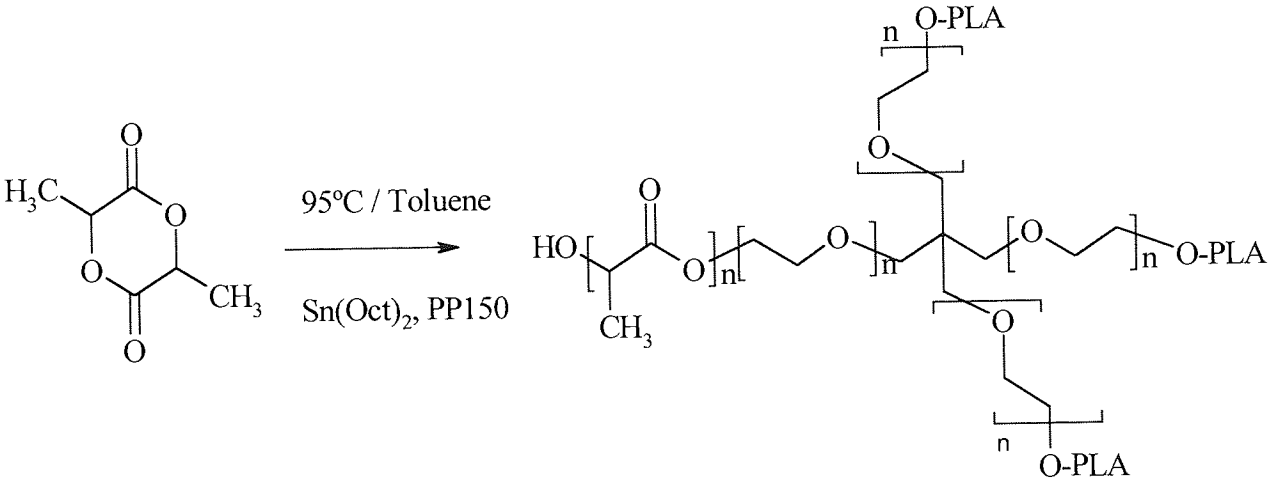


Figure 3.38. DSC of MeOPEG-PLLA (2000) 1:55

3.2.7 Synthesis of pentaerythritol ethoxylate-*co*-PLA star copolymer (pent ethox-PDLA)



Scheme 3.15. Synthesis of pentearythritol ethoxylate - PLA copolymer

The novel pentaerythritol ethoxylate copolymer was prepared and isolated in an identical way to the poly(ethylene glycol) copolymers. The prepared copolymers were water immiscible.

The range of copolymers prepared of this type is summarised in Table 3.10.

Lactide: OH Feed ratio	Molecular Weight Mn (GPC)	Theoretical Molecular Weight	Approx. Molecular weight 'per arm'
70:1	21500	41000	10000
17.5: 1	15000	10800	2500
5: 1	4600	3700	720
3.3: 1	2400	2200	360

Table 3.10. Summary of pentaerythritol-PLA copolymers

3.2.8 Characterisation

The analysis of linear block copolymers has already been described in section 3.2.2. A similar procedure was adopted for the analysis of the star copolymers. However, because of the structure of the polymer (shown in Figure 3.39), the important junction resonances at 4.2 p.p.m are approximately four times larger than an equivalent molecular weight linear copolymer, making identification easier (Figure 3.40). In the case of the star copolymers below in Table 3.11 calculation of the ratio of the CH_2 protons (1) derived from the ethylene oxide unit at 3.36 p.p.m to the PLA CH protons at 5.1 p.p.m indicated that complete incorporation of the lactide monomer took place.

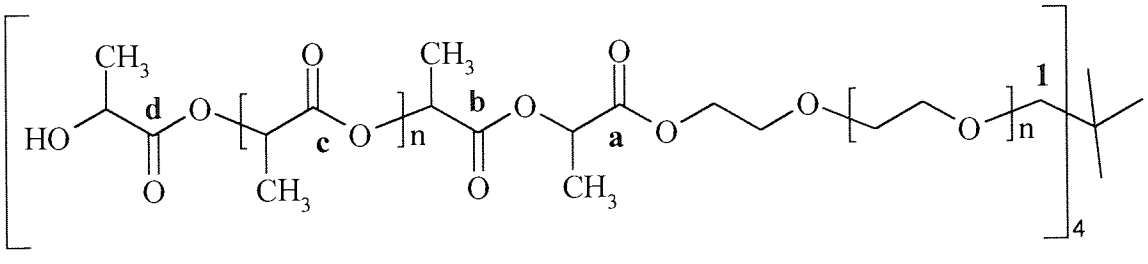


Figure 3.39. Expanded structure of pentaerythritol ethoxylate- PLA copolymer (one arm)

Lactide: Pentaerythritol molar ratio	Incorporated Lactyl units (^{1}H NMR)	Theoretical Lactyl units in copolymer
280:1	-	560
70: 1	152.4	140
20: 1	41.6	40
10: 1	20.3	20

Table 3.11. Dependance of PLA chain length on feed ratio of lactide:pentaerythritol

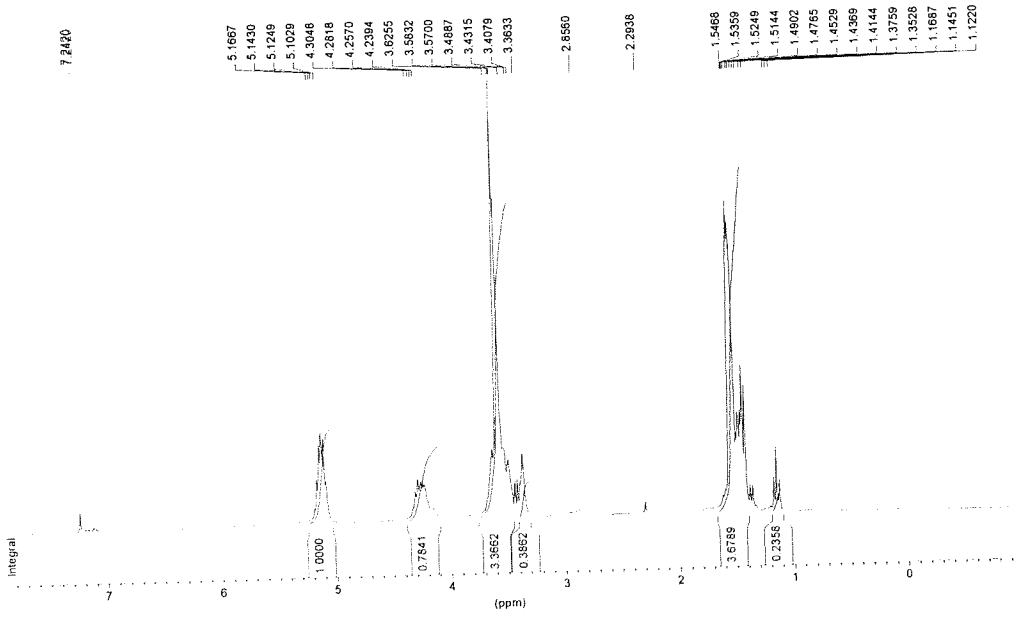


Figure 3.40. Proton NMR spectrum of pentaerythritol ethoxylate-PLLA copolymer 10: 1

The characteristics of the MeOPEG-PLA ^{13}C S.P.E.E.D spectrum are similar to thoses observed in the S.P.E.E.D spectrum of the star copolymer shown in Figure 3.41. The carbonyl assignments are given in Table 3.12. Again, as with the MeOPEG-PLA copolymer, the similarities in the height and number of the individual carbonyl resonances indicate that the individual carbonyl groups have

been separated.. The sum of the integrations of each of the carbonyl signals for this copolymer approximate to five, i.e five lactyl units on each arm.

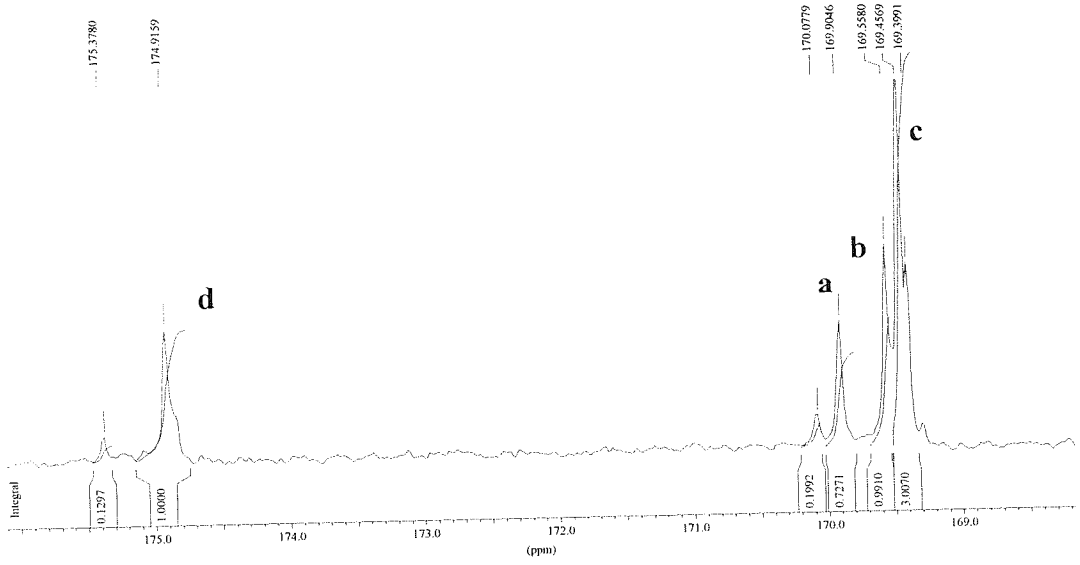


Figure 3.41. ^{13}C S.P.E.E.D. NMR spectrum of pentaerythritol ethoxylate-PLLA copolymer 10: 1 (carbonyl region)

Carbonyl Carbon	Chemical Shift (p.p.m)	Integration	Assignment
a	169.9	0.72	PLA-PEG junction
b	169.5	1	
c	169.45-169.39	3	In chain C=O
d	174.9	1	Terminal PLA C=O

Table 3.12. Proposed carbonyl assignments for pentaerythritol ethoxylate-*co*-PLLA (10:1)

3.2.9 DSC Analysis

DSC analysis of pentaerythritol ethoxylate-PLLA (1:10) star copolymer was carried out at Montpellier University. A glass transition temperature of -16°C was detected. A similar result was found by the author but interestingly a second glass transition was detected at 38.6°C (Figure 3.42). The crystallisation or melting of the PLLA chains was not detected. Similar transitions were also detected for the PDLA copolymers (10-280:1); these are presented in appendix 7

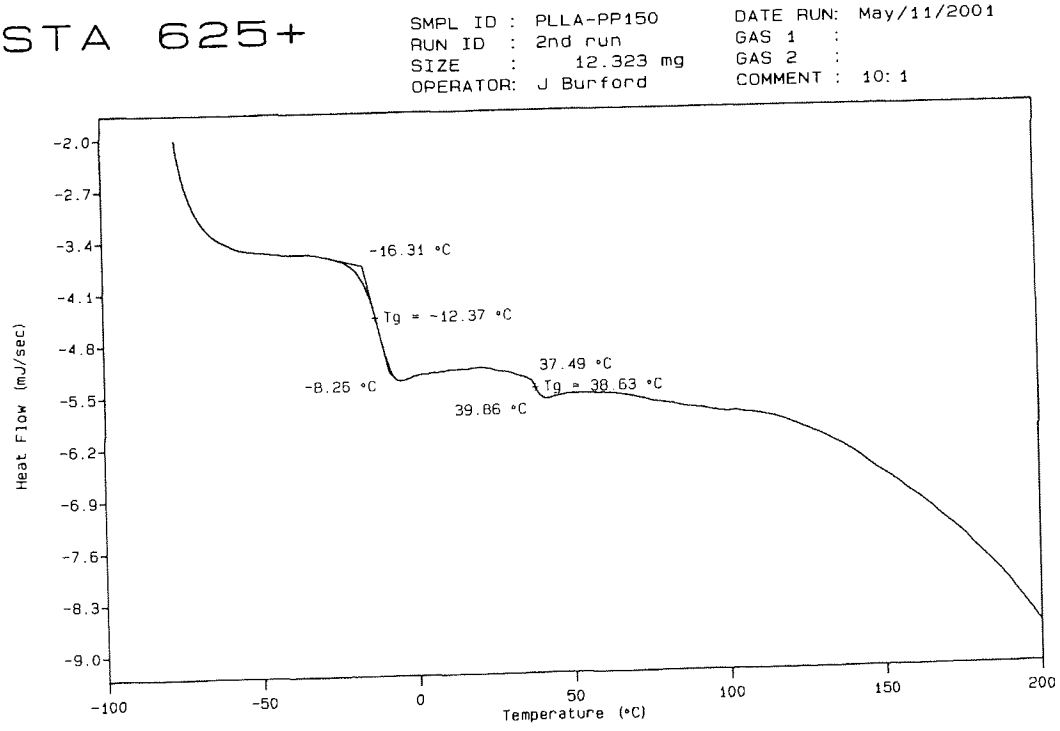
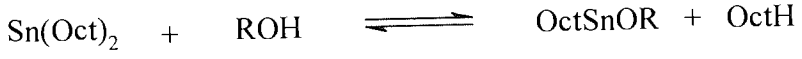


Figure 3.42. DSC of pentaerythritol ethoxylate- PLLA 1:10

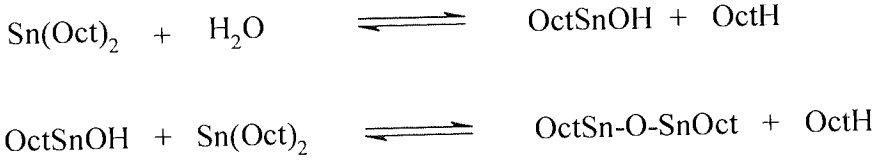
3.2.10 Discussion

The results presented in the S.P.E.E.D NMR spectra above clearly show evidence for the chemical bond between the PLA and poly(ethylene oxide) chains, which is supported by the appropriate signals in the proton NMR and also the GPC molecular weight data. In this way MeOPEG-OH must be able to act as an initiator for the polymerisation of lactide.

From recent work [52], it appears clear that neither $Sn(Oct)_2$ or R-OH is the true initiating species. Majerska et al [52] has suggested that tin(II) octanoate and ROH take part in an equilibrium reaction in which the half alkoxide is generated as shown in Scheme 3.16.



Scheme 3.16. Half alkoxide formation



Scheme 3.17. Reaction of water with $Sn(Oct)_2$ catalyst

Stannous octanoate exists in equilibrium also with the corresponding acid by reaction with atmospheric moisture (Scheme 3.17). It is suspected that these compounds, particularly that derived from ROH could initiate the polymerisation. It has been shown that carboxylic acids (OctH) can retard the polymerisation by reaction with the growing chains forming dormant species [54, 109]. Therefore it would be expected that the molecular weight of a homopolymer would decrease as the

concentration of $Sn(Oct)_2$ is increasing by the initiation of more chains caused by an increased the amount of initiating impurities. This was found by Majerska et al [52] but they focused on the increased reaction rate rather than the reduced molecular weight. If it is assumed that these impurities initiate the homo-polymerisations (Table 3.9) then a number average molecular weight of 43000 would be equivalent to a degree of polymerisation of 299 which suggests a lactide to propagating centre ratio of 299:1. This would be equivalent to 2.3×10^{-5} mol of initiator in the original 10mg $Sn(Oct)_2$ catalyst charge. A molecular weight of 10000 suggests a degree of polymerisation of 70 which is equivalent to 9.85×10^{-5} mol of propagating centres in the original 0.293g $Sn(Oct)_2$ catalyst charge. These values equate to 2.3×10^{-3} and 3.34×10^{-4} mol respectively per gram of $Sn(Oct)_2$. These results would suggest that there is not a direct linear relationship between the catalyst concentration and molecular weight but to some extent the obtainable molecular weight of a PLA homo-polymer is related to the concentration of impurities present in the particular sample of $Sn(Oct)_2$.[51, 54]

The introduction of R-OH (where R = alkyl or ethylene oxide) significantly complicates the above reaction (Scheme 3.17). It would be expected that the equilibrium in Scheme 3.16 would be pushed further towards the right.

In order to achieve complete and even incorporation of lactide monomer into all of the initiator molecules in reactions where [LA]> [ROH] >> $[Sn(Oct)_2]$ the catalyst must initiate chain growth from ROH by moving from one molecule to another. It is suggested that this process can occur more rapidly in solution than in bulk (neat) polymerisations, as the poly dispersities in the majority of reactions, including homo-polymerisations were narrower (1.1-1.3) than those expressed in the literature [110]. Also, ability to use milder conditions reduces transesterification reactions [111]. Lucke and coworkers [112] using similar techniques as those described herein reported similar narrow Mw/Mn.

Kricheldorf and coworkers [46] and [108] have suggested that the energy of activation of initiation is less when alcohols are used as the initiator than when $Sn(Oct)_2$ is used alone. This would explain the increased rate of reaction during copolymerisation compared to homo-polymerisation. The reduced molecular weight would suggest initiation of more chains, but if more chains were initiated than there are alcohol molecules some degree of homo-polymerisation would be expected. No evidence for materials other than copolymers could be detected however; it is accepted that it is difficult to distinguish between a mixture of homo-polymer and copolymer by NMR spectroscopy but the GPC data only shows one unimodal peak in all cases. It is considered unlikely that the peaks of a homo-polymer and a copolymer would coincide exactly. Increasing the concentration of catalyst may result in "excess catalyst" containing initiating species with potential to initiate homo-polymerisation (hence the much lower molecular weight). However, the rate of homo-polymerisation is much slower than polymerisations initiated by ROH, therefore the any homo-polymer would probably be oligomeric in nature and not be detected by GPC, as most of the monomer would have been incorporated into the copolymer in a short period. However, the observed degree of polymerisation by NMR would be increased.

Chapter 4

Effect of synthesised plasticizers on thermal processing and mechanical properties of poly(3-hydroxybutyrate) [PHB]

4.0 Introduction

In this chapter the results of the evaluation of various novel plasticizers including their effects on the mechanical properties of poly(3-hydroxybutyrate) are presented.

4.1 Poly(3-hydroxybutyrate) [PHB]

As described in chapter 1, poly(3-hydroxybutyrate), shown in Figure 4.43 is a fully biodegradable thermoplastic with a melting point of 180°C. Its melting point and crystallinity are similar to those of polypropylene. However, polypropylene possesses the required processing characteristics and mechanical properties (tensile strength and elongation at break) for many uses. PHB on the other hand cannot be processed easily, crystallises readily from the melt and does not perform well (mechanically) in its pure form. It is also currently much more expensive (£8 Kg^{-1}) than polyolefines (£0.5 Kg^{-1})

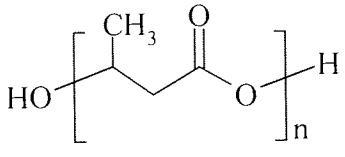


Figure 4.43. Poly(3-hydroxybutyrate) [PHB]

The PHB for this work was supplied by Biomer and used as received. The number average molecular weight (Mn) was determined by GPC to be 34000.

In order to determine the physical and mechanical properties of PHB, PHB was processed in a torque rheometer for 10 minutes at 180°C, compression moulded into 0.25mm films as described previously and cut into dumbbells using the appropriate cutter for tensile measurements. The samples were also analysed by differential scanning calorimetry.

The physical and mechanical properties of PHB processed for ten minutes are shown below.

Glass Transition (T_g)/°C	**Crystallisation (T_{rec})/ °C**	**Melting Point (T_m)/ °C**	**Elongation at Break /%**	**Tensile Strength /Mpa**
--	--	181.4	4	33.2
-12.6 *	37.3 *	147 *		

* Second heating run

On standing, the compression moulded PHB films quickly became opaque and brittle due to reoccurrence of the crystallites in the polymer.

4.2 Effectiveness of the prepared plasticizers on the mechanical and thermal properties of PHB

It is seen from the above section that pure PHB does not possess the required properties during processing and/or in use. However, plasticizers are usually used to modify the properties of a polymer. In this section, the effect of plasticizers on the properties of PHB is studied.

PHB was processed in the torque rheometer at 180°C for 10 minutes with the prepared plasticizers at a concentration of 17% by weight. The processed samples were compression moulded into films for tensile measurements as described in chapter 2. Some of the plasticized films were unsuitable for mechanical testing because of what appeared to be plasticizer-polymer phase separation, producing a soft tacky area in the film. The plasticizers that produced this effect to a significant degree were isobutyl maleate, n-octyl maleate and isobutyl citrate. Table 4.13 below shows the tensile properties of PHB in the presence of platicizers.

Plasticizer	Elongation at Break %	Tensile Strength /Mpa
PHB (unplasticized)	4	33
Isobutyl maleate (IBM)	-	--
n-Octyl maleate (NOM)	-	-
n-Octyl citrate (NOC)	4	24.2
Isobutyl citrate (IBC)	10	24.2
Isobutyl tartrate (IBT)	-	-
Ethylhexyl tartrate (EHT)	12	26.1
Trimethylhexyl tartrate (TMHT)	12	26.5

Table 4.13. Physical properties of plasticized PHB

The effects of all the plasticizers on the thermal characteristics of the PHB films are shown in Table 4.14 below. As expected, the plasticizers have reduced the glass transition and crystallisation temperatures of PHB significantly but with only moderate reductions in the melting point.

Added Plasticizer	Run N°	Glass Transition (T_g)/°C	Crystallisation (T_{rec})/°C	Melting Point (T_m)/°C
PHB	1	-	-	181.4
	2	-12.6	37.3	147.0
NOC	1	--	52.9	174.1
	2	--	51.4	156.2
EHT	1	--	--	169.6
	2	18.5	28.2	154.6
IBC	1	--	--	173.8
	2	-15.2	39.4	155.7
NOT	1	--	--	170.9
	2	-27.6	29.5	142.7
EHC	1	--	--	168.2
	2	-14.1	37.5	157.7
IBT	1	--	--	167.9
	2	-24.7	34.6	129.4

Table 4.14. Glass transition temperature of plasticized PHB films*

*Montpellier University: France

To form a useful article such as a bottle, thread, bag or any item currently fashioned from a thermoplastic, the polymer must normally be strong, flexible and resistant to tearing. It was found that although the glass transition temperature was reduced

significantly by blending with all the plasicizers, the mechanical properties of PHB were not improved.

PHB has a relatively low glass transition temperature shown in Figure 4.44 because of its flexible (C4) monomer unit and is readily crystallised from the melt and at room temperature because of its stereoregular structure, inherent from its biological synthesis pathway. It would seem feasible that its low strength emanates from faults within and between these crystallites and the amorphous regions. Therefore, it is suggested that a reduction in the crystallinity would benefit the tensile properties, as is the case with poly(3-hydroxybutyrate-*co*-valerate) shown in Figure 4.45. However, with its low glass transition temperature, PHB will always tend to crystallise at room temperature. The addition of plasticizers may in fact aid this process by further lowering the glass transition temperature and allowing greater chain mobility, resulting in no improvements in the physical properties of PHB in the presence of plasticizers.

Aston University

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Figure 4.44. Typical DSC of PHB*

*Montpellier University: France

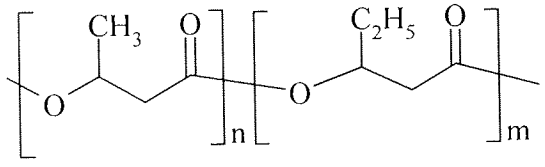


Figure 4.45. Poly(3-hydroxybutyrate-*co*-valerate)

4.3 Polymer blends

In certain cases it is known that blending one polymer with another polymer can modify the properties of the original polymers with the new blend having some intermediate property between the two original polymers. It was thought that a similar effect could be produced when PHB was blended with common non-biodegradable polymers: linear low-density polyethylene (LLDPE), polyethylene-*co*-vinyl acetate (EVA) and a polyethylene-carbon monoxide copolymer (ECO). In addition, PHB was also blended with the biodegradable polymer polycaprolactone (PCL).

LLDPE - copolymer of ethylene with a small amount of linear α-olefines (butene, hexene).
EVA - copolymer of ethylene with vinyl acetate (2-40%)
ECO - copolymer of ethylene with carbon monoxide (8-12%)
PCL – homopolymer of ε-caprolactone (described later)

EVA (Evathane 28-420), ECO and LLDPE were separately blended at 180°C with PHB at 40 and 50% by weight. Similar blends were prepared at 180°C using 5% plasticizer as a compatibilizing agent. The additives used for this work were n-octyl tartrate (NOT), n-octyl maleate (NOM), 2-ethylhexyl maleate (EHM), n-octyl cirate (NOC) and isobutyl citrate (IBC). The samples were pressed into thin films as described in section 2.2.2 but none of the films possessed enough physical strength for meaningful measurement.

Visually it was observed that all prepared films appeared to phase separate during film formation into what appeared to be distinct regions of each polymer. The films appeared to have greater flexibility than pure PHB but their mechanical properties were extremely poor and inconsistent, exhibiting probably less strength than PHB alone.

The DSC results for the LLDPE and ECO blends strongly suggested that the plasticized and unplasticized blends were immiscible at these concentrations. The DSC trace below (Figure 4.46) shows the typical separate distinct melting transitions of incompatible polymers. Similar results were obtained with the ECO blend. The DSC results for the EVA blends (Figure 4.47) did not show any melting transitions for EVA as the polymer is amorphous. However, the melting transition associated with PHB has separated into distinct peaks, which is generally associated with the melting and reorganisation of the lamellae of different thicknesses.

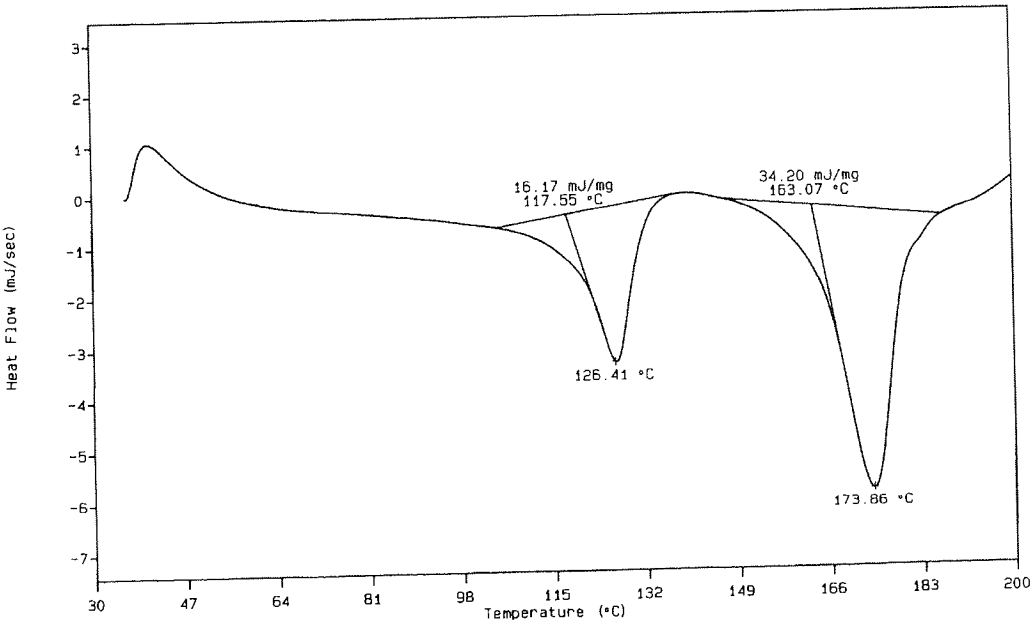


Figure 4.46. Typical DSC of PHB/ LLDPE blends

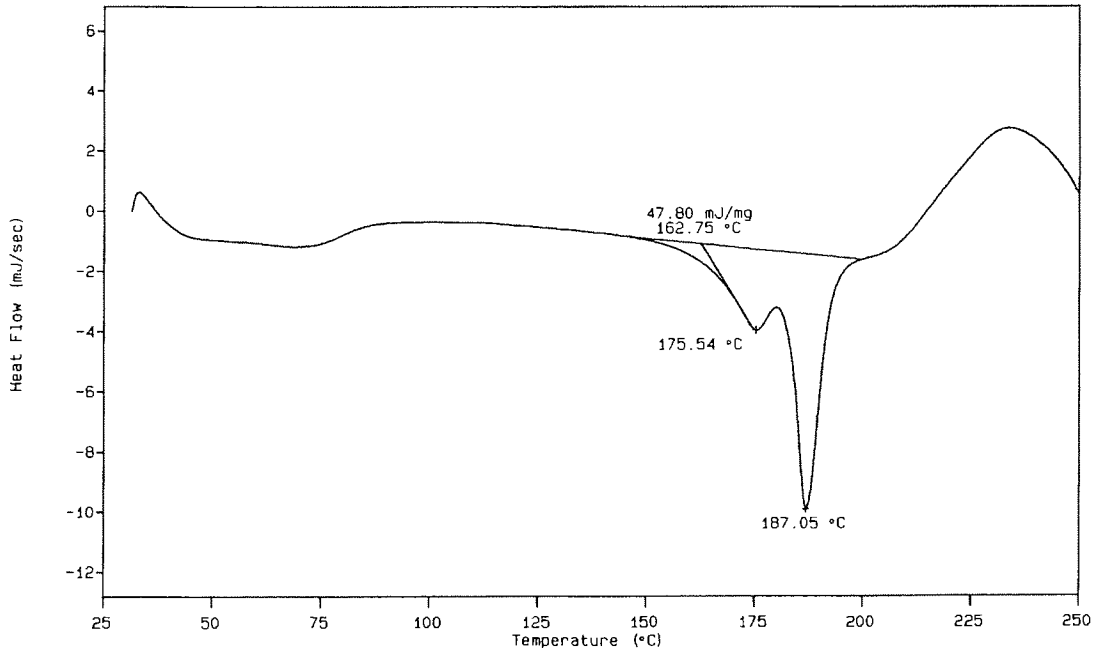


Figure 4.47. DSC of PHB/EVA

The production of a compatible blend would produce a general convergence of the melting points to a single intermediate value or give a significant lowering of the PHB melting point.

4.4 PHB and PCL blends

In this series of experiments, PHB was blended with the biodegradable polymer polycaprolactone (PCL) shown in Figure 4.48 below over a range of compositions. This was used to assess the effect of the PCL ratio on the mechanical properties of the blend and also determine if a plasticizer would have any compatibilising effects on the otherwise incompatible polymers [113].

PCL 'Tone' was supplied by Union Carbide with a number average molecular weight of 48000.

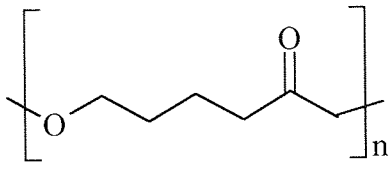


Figure 4.48. Poly(ε-caprolactone)

The blends were produced using the torque rheometer as described in chapter 2, section 2.2.1.The blended material was then compression moulded into films at 180°C for tensile strength and elongation at break measurements. In another series of experiments, similar blends to those above were produced but with the addition of 17% by weight of 2-ethylhexyl tartrate (EHT). Table 4.15 shows the tensile strength and the elongation at break results for the plasticized and unplasticized PHB-PCL blends. The elongation at break (%) of the blends (both plasticized and unplasticized) are plotted against the amount of polycaprolactone present (Figure 4.49).

Composition		Unplasticized Blend		Plasticized Blend	
PHB	PCL	Tensile strength/ MPa	Elongation at break %	Tensile strength/ MPa	Elongation at break %
100	0	33.0	4	10.5	27.0
90	10	33.7	4	19.4	6
80	20	27.3	5	18.3	6
70	30	22.0	5	13.7	4
60	40	8.5	4	13.0	5
50	50	4.3	18	11.5	6
40	60	19.0	2	9.0	354
30	70	19.7	596	18.8	613
20	80	33.2	650	25.0	666
10	90	39.1	712	37.1	854
0	100	65	1071	43.5	887

Table 4.15. Effect of (EHT 17% w/w) on the physical properties of PHB/PCL blends

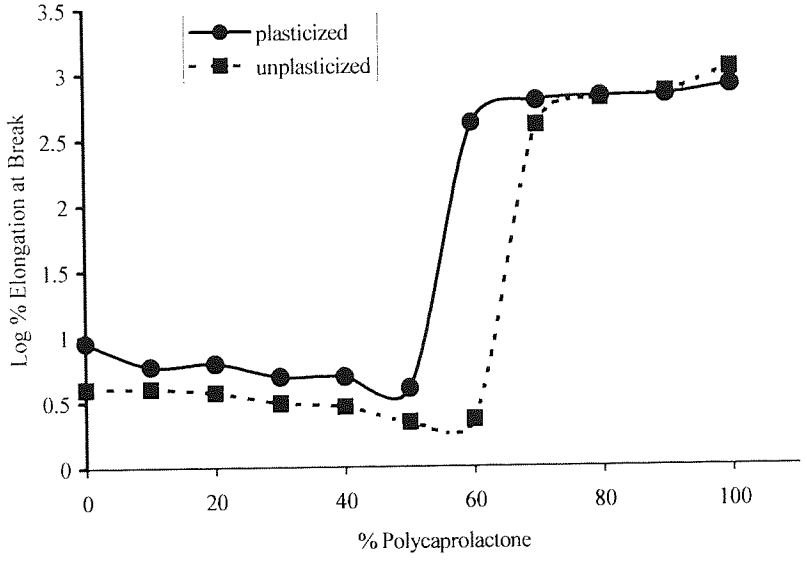


Figure 4.49. Comparison of the elongation at break in plasticized and unplasticized blends of PHB and PCL

It can be clearly seen from Figure 4.49 above that the blends of PHB and PCL (plasticized and unplasticized) did not show any change in their elongation at break at least upto 50% PCL. Above this, the elongation at break increased significantly and remained reasonably constant upto 100% PCL. In addition it can be seen from Table 4.15 that the tensile strength of the blend follows the composition. The tensile strength of the blend containing EHT is reduced slightly compared to the unplasticized blend indicating plasticization of the individual phases and possibly some compatibilising effects of EHT.

The general incompatibility of the two polymers is seen in the DSC (Figure 4.50 below). The individual melting points of the polymers are clearly visible at both ends of the concentration range

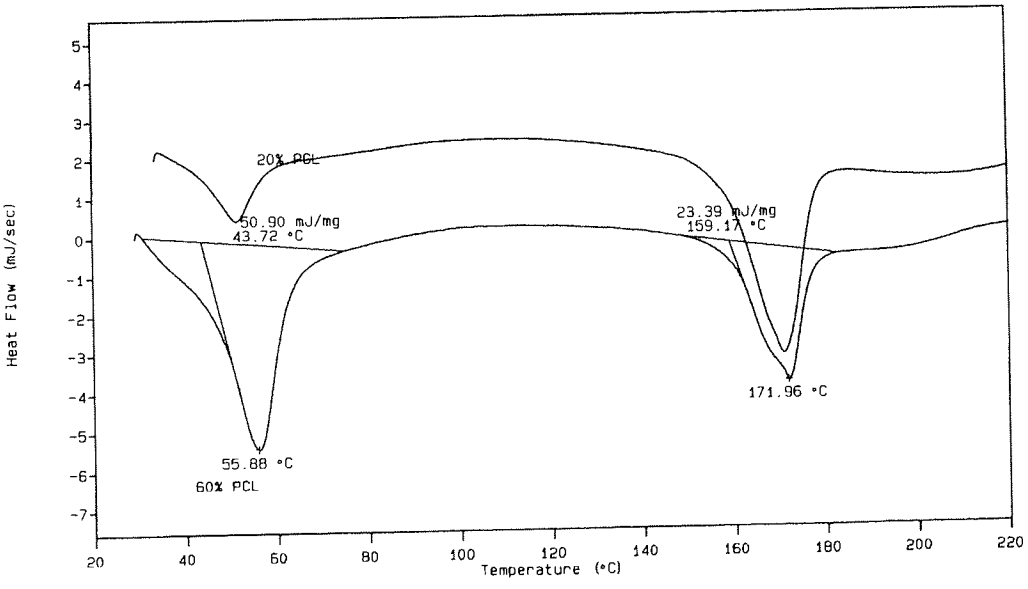


Figure 4.50. DSC of 60:40 and 20:80 PCL-PHB Blends

4.5 Conclusions

The attempts at improving the properties of PHB by blending with LLDPE, EVA, ECO and PCL were unsuccessful. As expected, PHB was found to be incompatible with these polymers. Addition of EHT as plasticizer to these blends had little effect.

It appears that addition of simple plasticizers to PHB does not change the mechanical properties significantly even though the glass transition and crystallisation temperatures were lowered.

4.6 The future of PHB

Recently (1999) Monsanto stopped producing PHB polymers particularly the PHB copolymer Biopol® [poly(3-hydroxybutyrate-co-valerate)] this somewhat reduced the likely commercial interest in these materials, as significant quantities could not be obtained. This coupled with its unforgiving properties has unfortunately made this an unrealistic polymer. The continuing large-scale growth and development PLA manufactured by the Cargill-Dow NatureWorks™ process appeared to offer greater potential.

The PHB work was therefore abandoned.

Chapter 5

Poly(lactic acid) – effect of novel plasticizers on its physical and chemical properties

5.1 Introduction

As discussed in chapter 1, section 1.7.2, poly lactide or poly(lactic acid) [PLA] is a commercial biocompatible thermoplastic with a melting point of approximately 175°C. It can be made in two stereo forms, atactic or isotactic, depending on the structure of the lactide monomer. The monomer is made commercially, from the natural L-lactic acid precursor and this forms a predominantly isotactic polymer. The regular structure permits it to form a polymer with a potentially high degree of crystallinity. Therefore articles made from PLA generally have high tensile strengths, around 60 Mpa, and low elongations at break, 3%, i.e. the polymer is strong but stiff. Its structure is represented in Figure 5.51 below. To make useful articles, such as bags or film, the physical and mechanical properties need to be modified. Ideally the polymer has to be modified to form a material with a higher elongation at break and a lower tensile strength. For example the percentage elongation at break of polyethylene for bag production is 500-600% and tensile strength of 30-40 MPa.

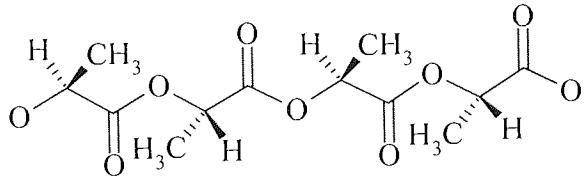


Figure 5.51. L-PLA

5.2 Materials and experimental

In the present study, two types of PLA polymer were used- the first was supplied by Nesté Oy, a subsidiary of Fortum Oil and Gas (Finland). The second sample of PLA was supplied by Cargill Dow Polymers. The latter was a sample of their commercial NatureWorks 2000D product.

The physical properties of both polymers are shown in Table 5.16 below.

Scource	Neste	Dow
Appearance	Brown clear chips	Opaque pearls
Melting point (DSC)	175.0 (+54.2 mJ/mg)	153.1 (+3.1 mJ/mg)
Glass transition °C (Tg)	53.5	60.3
Crystallisation Temperature °C (Tc)	95.3 (-26.5mJ/mg)	No crystallisation detected
Molecular weight (Mn GPC)	49000	83000
Melt Flow Index (MFI)	13 (measured)	4-8 (Dow value)
Tensile strength (Mpa)	58.8	63.0
Elongation at Break (%Eb)	3	3

Table 5.16. Properties of Neste and Dow PLA polymers

5.3 Effect of ester plasticizers on the mechanical properties of PLA

The polymer supplied by Nesté was used in this study. In all cases, 17% by weight of the plasticizers were processed in a torque rheometer at 180°C for 10 minutes. The polymer samples were compression moulded into 0.25mm thick films and tensile specimens were cut immediately from the freshly prepared film.

The following materials were evaluated to determine their effectiveness as plasticizers for PLA.

Di isobutyl tartrate (IBT)
Tri isobutyl citrate (IBC)
Di n-octyl tartrate (NOT)
Tri n-octyl citrate (NOC)
Di n-octyl maleate (NOM)
Di (2-ethylhexyl) tartrate (EHT)
Tri (2-ethylhexyl) citrate (EHC)
Di (3,5,5-trimethylhexyl) tartrate (TMHT)
Tri (3,5,5-trimethylhexyl) citrate (TMHC)
Di (3,5,5-trimethylhexyl) malate (TMHM)
Di (3,5,5-trimethylhexyl) succinate (TMHS)

The physical properties of the plasticized PLA films are compared in Table 5.17 below. The table also includes the physical properties of unplasticised PLA.

Plasticizer	Percentage Elongation at Break ($\%_{EB}$)	Tensile Strength (Mpa)
No plasticizer	3	58.8
NOM (maleate)	271	29.6
IBC	216	16
NOC	274	35.5
EHC	337	33.4
TMHC	300	35.5
IBT	320	33.8
NOT	313	36.5
EHT	297	36.3
TMHT	310	33.3
TMHM	282	32.2
TMHS	8	49.1

Table 5.17. Effect of plasticizers (17% w/w) on the percentage elongation at break and tensile strength of PLA

All plasticizers, with the exception of TMHS, caused a significant modification in both the tensile strength and percentage elongation at break compared to the control sample containing no plasticizer. Although all films were transparent, the sample containing EHC showed significant stress whitening when the samples were cut. DSC measurements of the films containing plasticizers (Table 5.18) clearly show that the thermal characteristics of the polymer were significantly changed by plasticization.

Plasticizer at 17% by weight		Tg °C	Tc °C	ΔHmJ/ mg	Tm °C	ΔH mJ/mg
General increase in OH mol ratio ↑	Control	53.4	95.3	(-26.5)	175.0	(54.2)
	IBC	27.0	78.3	(-24.2)	153.5	(54.0)
	EHC	44.5	74.4	(-19.1)	171.7	(49.9)
	TMHC	37.4	73.8	(-22.0)	169.3	(50.3)
	NOC	--	67.4	(-17.6)	165.6	(41.8)
General increase in branching ↓	IBT	32.5	72.9	(-27.3)	164.8	(54.4)
	EHT	28.3	74.9	(-26.9)	162.3	(54.0)
	TMHT	32.3	68.1	(-22.4)	169.4	(56.3)
	NOT	39.7	74.1	(-29.3)	170.3	(61.3)
	TMHM	35.9	69.5	(-23.4)	168.4	(61.2)
	TMHS	42.1	82.1	(-29.2)	170.8	(61.4)
	NOM	44.7	86.4	(-12.6)	163.9	(42.6)

Table 5.18. Effect of ester plasticizers on the thermal properties of PLA correlated to hydroxyl content and alkyl chain branching

In general, the addition of ester plasticizers lowered the glass transition (Tg), crystallisation temperature (Tc) and the melting point (Tm) of the polymer. A typical DSC thermogram comparing the effects of esters to an unplasticized sample is shown in Figure 5.52. The energy of crystallisation during heating was not changed significantly by the addition of additive.

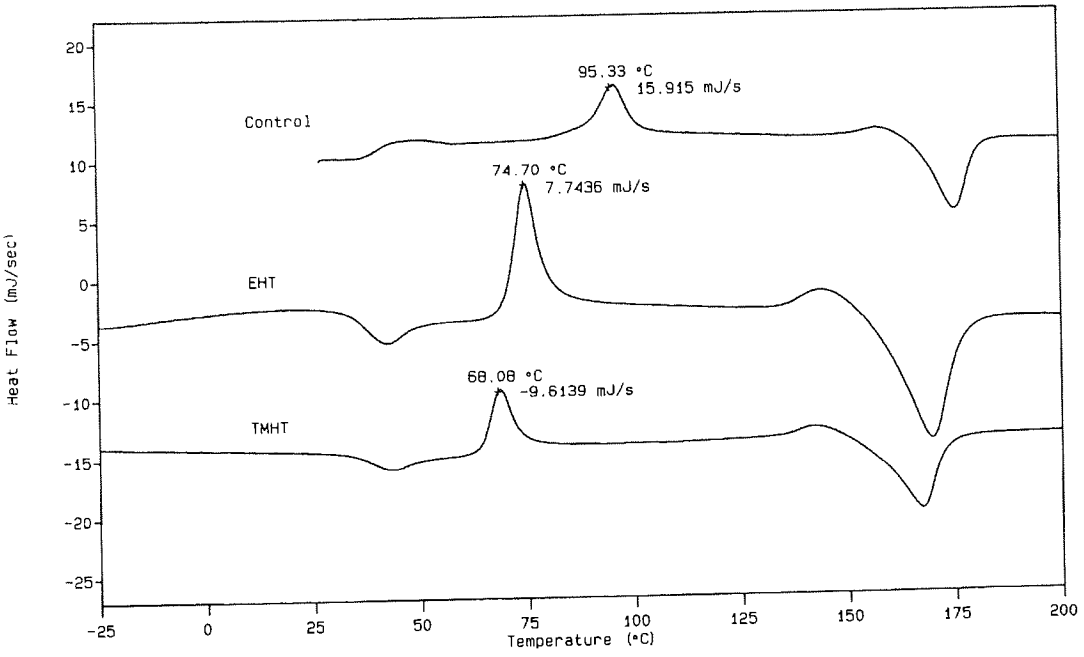


Figure 5.52. Effect of plasticizer on the thermal properties of PLA

5.4 Effect of plasticizer concentration on the physical properties of PLA

Since most of the plasticized samples showed an increase in their elongation at break and a reduction of their tensile strengths, TMHT was studied to evaluate the effect of plasticizer concentration on the elongation at break and tensile strength. It was felt at this stage, that TMHT, with its higher molecular weight, would result in lower volatilisation during high temperature processing and loss by contact with extractant fluids (discussed later).

PLA was blended with TMHT as described previously in various concentrations. The effect of composition on the elongation at break is plotted in Figure 5.53 below

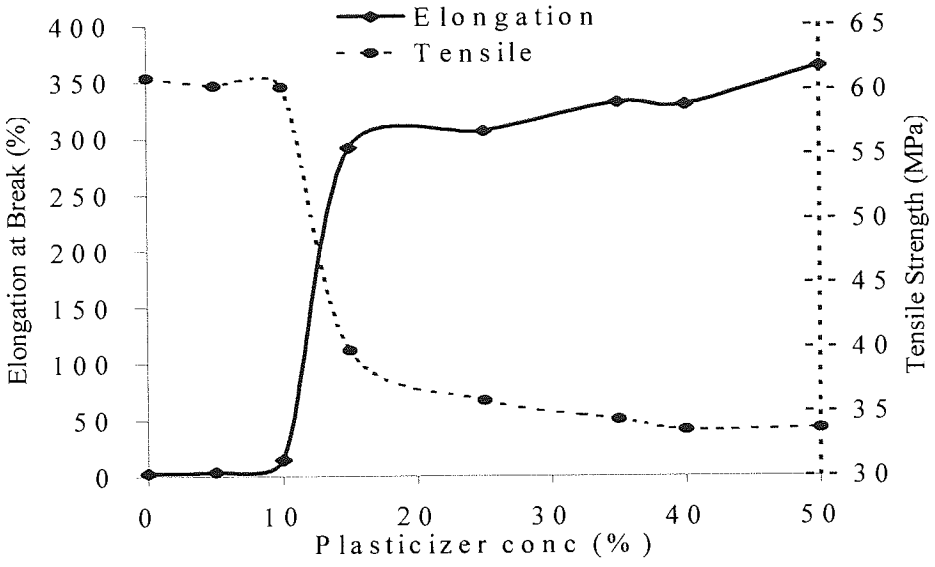


Figure 5.53. Variation of the mechanical properties of a PLA film with TMHT concentration.

Figure 5.53 shows that TMHT was not effective to any significant extent up to 10% (w/w) concentration, however, above this concentration the elongation increase was dramatic and remained fairly constant up to 50% w/w. The DSC traces of the plasticized PLA containing TMHT at different concentrations is shown in Figure 5.54. It can be seen from Figure 5.54 that as the concentration of plasticizer is increased, the crystallisation temperature (Tc) is shifted towards a lower temperature and at the same time the energy involved in the crystallisation is also gradually reduced. It may therefore be inferred that the crystallisation of PLA is gradually inhibited with increased TMHT concentrations.

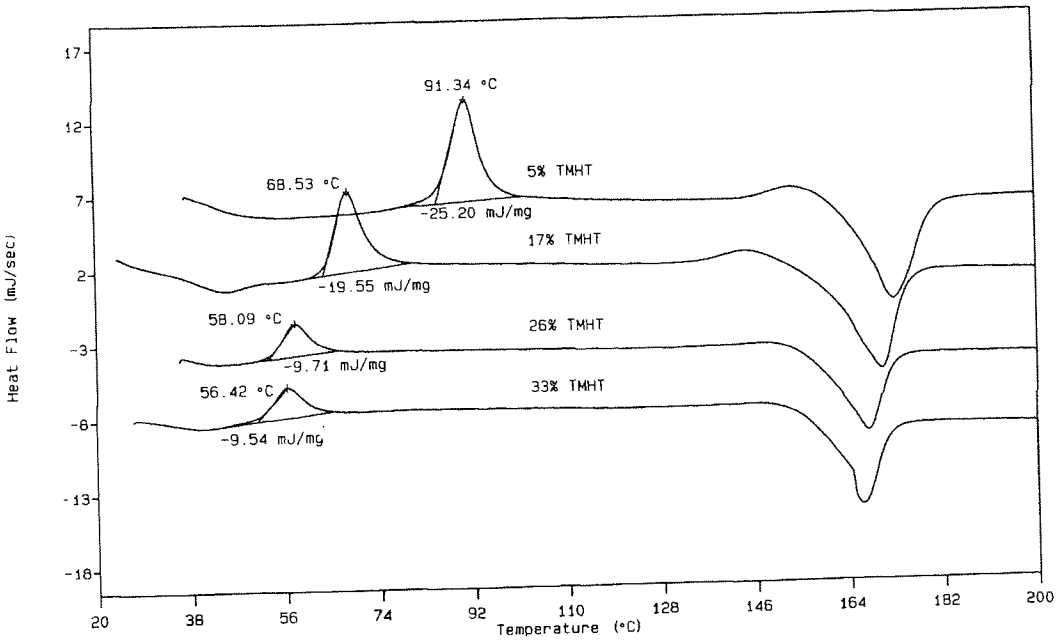


Figure 5.54. Effect of increasing the plasticizer (TMHT) on the thermal properties of PLA films

5.5 Ageing tests

In order to determine the compatibility and volatility of the plasticizers, the plasticized PLA film samples were stored at room temperature and periodically tested for retention of their physical properties. The change in the physical properties of plasticized PLA samples with time is shown in Figure 5.55. DSC measurements on the film containing TMHT was also carried out at suitable intervals in order to determine the changes in the thermal characteristics (Figure 5.56). The PLA samples plasticized with IBC and NOC lost most of their physical properties within a short period of time and are not included in Figure 5.55. Only the PLA samples containing EHC, NOT, EHT and TMHT retained measurable physical properties over an extended period or time.

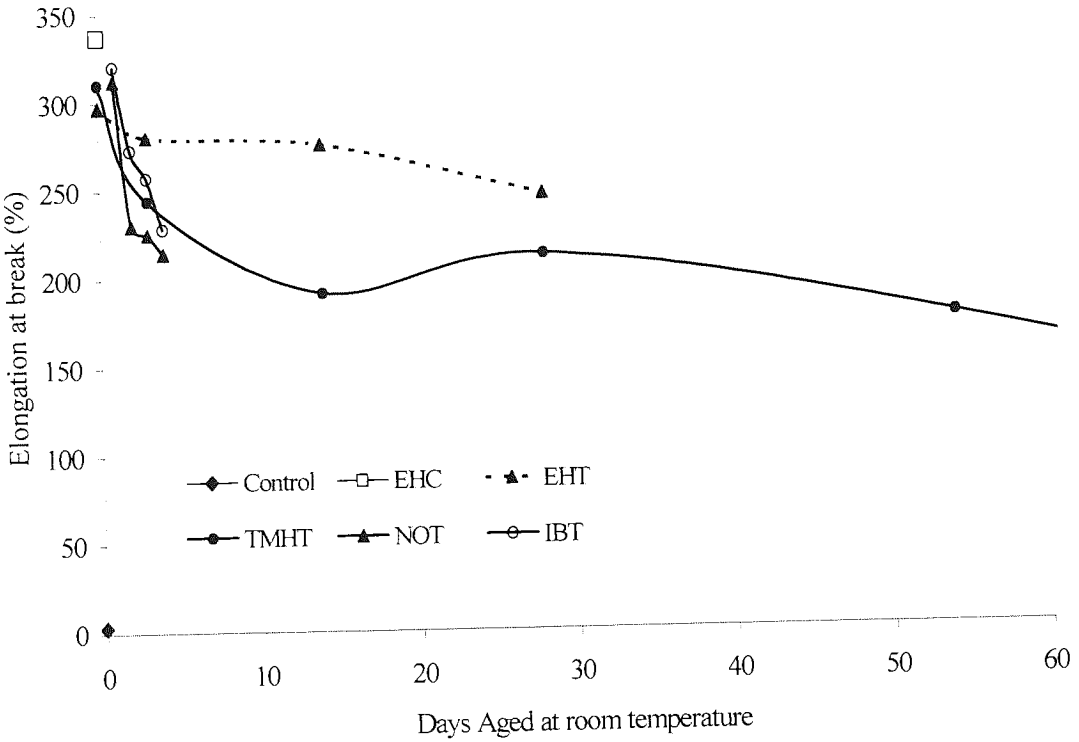


Figure 5.55. Effect of aging of on the elongation at break of various plasticized PLA blends

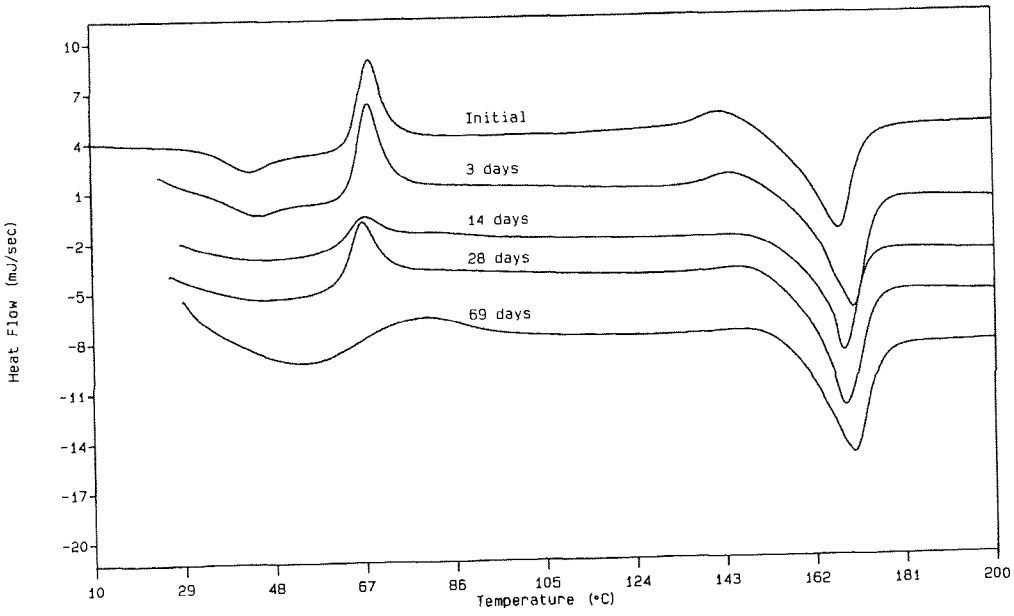


Figure 5.56. The change of the thermal characteristics of PLA film plasticized with TMHT with storage time at 21°C.

Figure 5.55 clearly shows that PLA plasticzied with TMHT (and EHT) retains a significant percentage of it original elongation at break (60%) after 100 days (not plotted). The other plasticized films also appeared stable during the initial ageing period but the films lost much of their elongation at break after this period. It also appears that the polymer tends to crystallise over time (Figure 5.56) which would account for the gradual reduction of its elongation. It was also observed that during this ageing period the crystallisation temperature moved towards a higher temperature and the energy involved was reduced. This effect was more pronounced in the less effective plasticizers. A typical example is shown in Figure 5.57 and compared to Figure 5.56

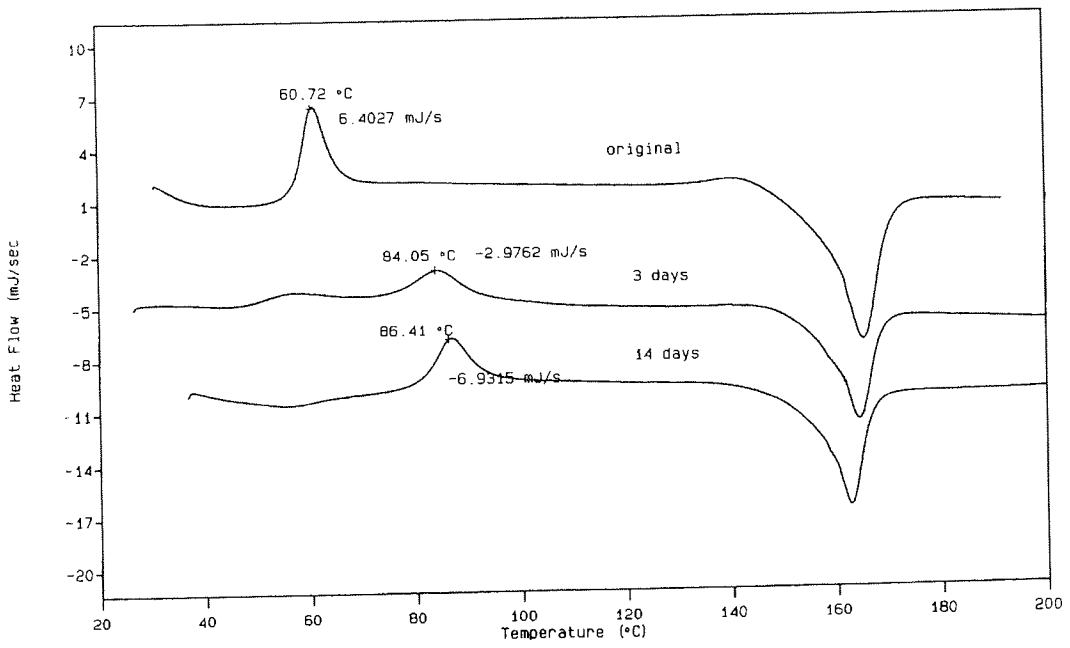


Figure 5.57. The change of the thermal characteristics of PLA film plasticized with EHT over time at 21°C.

5.6 Discussion

The mechanism of plasticization is somewhat difficult to determine. However, it is believed to be a combination of a solvation-desolvation process related to the solubility parameters of the plasticizer and the polymer and flexibility of the polymer chains. The plasticizer-polymer interactions are specific for a particular system and anything more than general rules are difficult to establish.

The plasticizers could be divided into two groups, those that were effective and those that were not. None of them had an intermediate effect. These two extremes suggest that particular structural characteristics were involved in which certain thermodynamic constraints between the additive and polymer were overcome. The sample containing TMHT was considered superior, in light of its novelty, film softness, clarity and retention of it's physical properties over an extended period.

On critical examination of the above results it appears that chain length and the presence of free hydroxyl groups in the plasticizers have a strong influence on the thermal characteristics as well as the mechanical properties of PLA. It appears that the effectiveness of the plasticizers is a combination of two parameters:

1. Solvation-desolvation processes related to the solubility parameters which in turn depend on the chain length and the physical/chemical interaction between the polymer and plasticizer molecules.
2. Chain flexibility or lubrication effect depending on the compatibility of the plasticizers with the polymer.

In this work, it was noticed that the esters containing free hydroxyl groups showed better plasticizing effect than esters containing fewer or no hydroxyl groups (Table 5.17). On critical examination of Table 5.17, it may be inferred that:

1. Tartrate esters (containing two free hydroxyl groups) are in general more effective than the citrate esters that contain one hydroxyl group.
2. Citrate esters were found to be superior to the succinate esters containing no hydroxyl groups, which showed no plasticizing activity.

Comparison between the compounds containing the same number of hydroxyl groups (Table 5.17, di *iso*butyl tartrate versus di n-octyl tartrate) it can be seen that the plasticizing activity might also be dependent to some extent on the molar concentration of the hydroxyl groups. Higher molar concentrations of hydroxyl groups give improvments the plasticizing effect. PLA polymers are to some extent polar in nature, therefore it can be said that plasticizers containing polar groups, i.e. hydroxyl groups would be more compatible. It is possible that the polar hydroxyl groups provide favourable polar interactions and potential for hydrogen bonding or affinity with the lactyl repeat unit. This would also help explain why n-octyl maleate (with no OH but a carbon-carbon double bond) acts as a good plasticizer. The long alkyl chain provides the necessary low volatility, low extractability and high

viscosity characteristics suitable for such materials. It is also important in creating a larger free volume.

5.7 Effect of copolymers on the mechanical properties of PLA

Copolymerisation is a technique commonly used to change and modify the mechanical properties of polymers. The chemically bound blocks introduced during the synthesis of copolymers allow control over the mechanical and chemical properties. The pure copolymer has advantages over conventionally plasticized polymers for instance, the copolymer is not greatly affected by extraction and the absence of extractable compounds is beneficial for use inside the body. However, copolymers are generally expensive to produce and therefore normally only used in specialised areas. It was thought that separately synthesised, low molecular weight copolymers of PLA could be used as plasticizers in the same way as the esters (to reduce cost) and it was hoped that they would offer improved performance through increased compatibility.

Novel blends using selected prepared copolymers of poly(ethylene glycol) methyl ether-*co*-poly(DL-lactide) [MeOPEG-PDLA] were made. These were prepared in a similar manner to those of the previous blends. The copolymers chosen for this study were, MeOPEG (750)-*co*- PDLA (1:5) M_n~1500, MeOPEG (750)-*co*-PDLA (1:55) M_n~8700, MeOPEG (2000)-*co*- PDLA (1:10) M_n~4900 and pentaerythritol ethoxylate-*co*-PDLA (1:10) M_n~2000. As discussed in chapter 2, the water solubility of the copolymers varied with composition but was related generally to the molecular weight ratio of the PLA: MeOPEG block. The water insoluble copolymers were MeOPEG (750)-PDLA 1:55 and pentaerythritol ethoxylate-*co*-PDLA (1:10) and the water soluble copolymers were MeOPEG (750)-PDLA 1:5 and MeOPEG (2000)-*co*- PDLA (1:10). These materials were blended with PLA for 10 minutes at 180°C in the torque rheometer at concentrations of 9 % and 17% by

weight. The effectiveness of the copolymers on the mechanical properties is summarised in Table 5.19.

Copolymer	Concentration (%w/w)	Elongation at Break (%)	Tensile Strength (Mpa)
MeOPEG (750)-PDLA 1:5	9	293	54.5
	17	265	41.0
MeOPEG (2000)-PDLA 1:10	9	3	66.0
	17	261	44.5
MeOPEG (750)-PDLA 1:55	9	3	69.5
	17	5	70.4
Pent ethox-PDLA 1:10	9	4	66.9
	17	3	62.0

Table 5.19. Plasticization effect of PDLA copolymers on PLA films.

The lower molecular weight copolymers MeOPEG (750)-PDLA 1:5 and MeOPEG (2000)-PDLA 1:10 appeared to impart increased elongation at break and a moderately reduced tensile strength to the films than those with a higher molecular weight PDLA block i.e. MeOPEG (750)-PDLA 1:55 and Pent ethox-PDLA 1:10. The thermal characteristics of the films did not appear to change as much as was seen when the films were plasticized with the esters (Table 5.18 and Table 5.20). However, the glass and crystallisation temperatures were lowered to some extent.

Copolymer (17% by weight)	Tg °C	Tc /°C	mJ/mg	Tm/ °C	mJ/mg
MeOPEG 750-PDLA 1:5	47.1	82.5	-24.9	174.4	54.2
MeOPEG 2000 PDLA 1:10	-	77.4	-19.3	173.8	50.2
Pent ethox-PDLA 1:10	46.5	82.3	-28.4	173.4	60.0

Table 5.20. Thermal transitions of PLA films plasticized with PDLA copolymers

Table 5.19 clearly indicates that PDLA copolymers of poly(ethylene glycol) methyl ether significantly increase elongation at break and a moderately reduced the tensile strength of PLA. However, the copolymer based on pentaerythritol ethoxylate did not improve the inherent properties of PLA to any extent, although the glass transition and recrystallisation temperatures are similar to the poly(ethylene glycol) methyl ether copolymers. These results seem to suggest that a PLA film with improved physical characteristics (tensile strength and elongation at break) may have similar thermal characteristics to a film that shows little or no improvement. This implies that lowering the glass transition and crystallisation temperatures is not a prerequisite for improvement in of the physical properties. The reason for this above phenomenon is not yet clear but it could be due to the shape of the copolymer. All the copolymers containing poly(ethylene glycol) methyl ether are linear, whereas the copolymer of pentaerythritol ethoxylate is star shaped (Figure 5.58) with each arm structurally very similar to the prepared MeOPEG-PDLA 750 copolymer. They are both liquids and have more or less the same molecular weight.

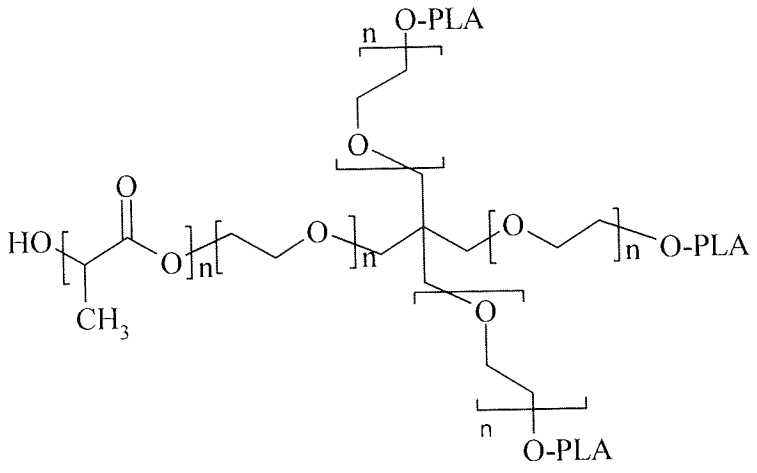


Figure 5.58. Structure of pentaerythritol ethoxylate-PDLA copolymer

In an attempt to understand the processes involved, PLA samples containing 17% by weight of the following materials were prepared in the torque rheometer 180°C for 10 minutes.

1. PLA oligomer with a molecular weight of approximately 700. This was prepared using the previously described techniques using n-butanol as the molecular weight control agent.
2. Poly(ethylene glycol) methyl ether (750).
3. Pentaerythritol ethoxylate (PP150™)

Compression moulded films were then prepared from the processed samples and the tensile properties were measured after twenty-four hours. The results are shown in Table 5.21 below.

Additive	Elongation at Break (%)	Tensile Strength (Mpa)	Comments
PLA Oligomer	3	57	
PP150	3	59	
MeOPEG 750	393	36	Greasy film surface

Table 5.21. Effect of individual copolymer blocks on the mechanical properties of PLA

These results in conjunction with the DSC thermograms (Figure 5.59 below) allow the plasticizers to be arranged in order of plasticizing activity and this is shown in Figure 5.60 below.

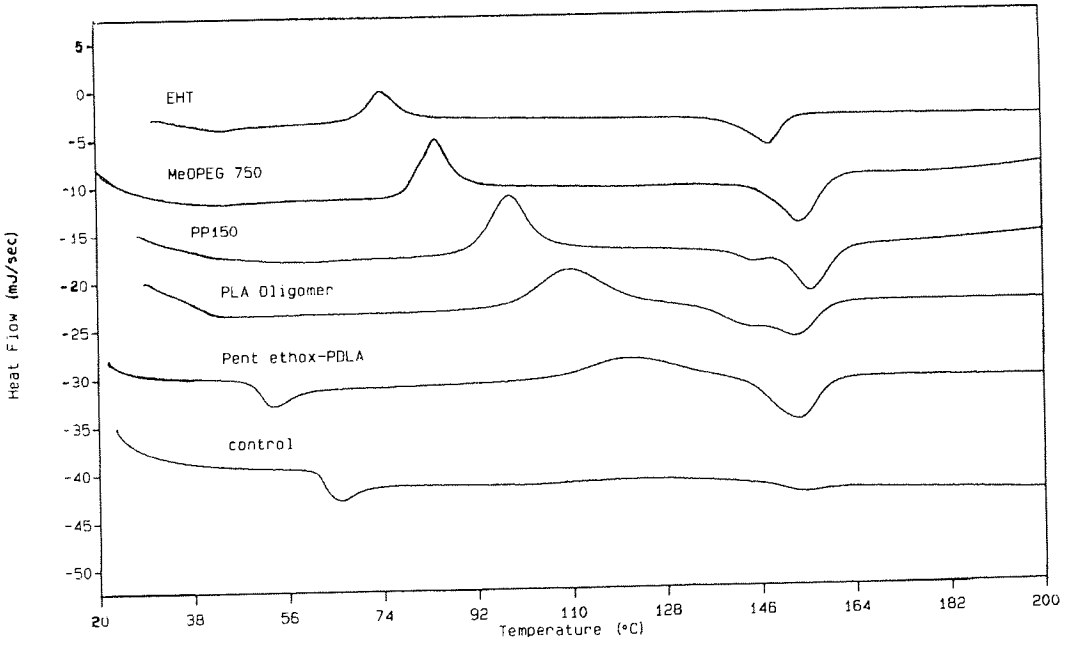


Figure 5.59. Effect of individual copolymer blocks on the thermal properties of Dow PLA

Decreasing plasticizing activity

EHT> MeOPEG-PDLA>MeOPEG 750>> PP150>PLA oligomer>Pent ethox-PDLA

Figure 5.60. Proposed activity of plasticizers

Figure 5.59 clearly shows that the pent ethox-PDLA copolymer has less effect on the thermal properties of PLA than either the oligomeric PLA or the PP150. It is therefore suggested that the PLA chains radiating out from the pentaerythritol core "hide" it from the bulk polymer and reduce any plasticizing effects from the pentaerythritol ethoxylate. Nevertheless, this clearly is not the whole picture as it was expected that because of similar chemical groups and molecular weight, pentaerythritol ethoxylate would act as a good plasticizer in a similar manner to MeOPEG 750. This therefore re-emphasises an apparent importance of the molecular shape.

It is suggested that MeOPEG 750 copolymerised with PDLA behaves as a good plasticizer with a similar effectiveness as MeOPEG 750 alone because the copolymer is linear and therefore the bulk PLA polymer still "sees" the plasticizing poly(ethylene oxide) block.

It appears that oligomeric PDLA (and presumably the PDLA part of the copolymer) plays little or no part in plasticization. However, the presence of the PLA block is extremely important for the compatibility of the plasticizer. It was found that MeOPEG 750 quickly exuded from the PLA film indicating low compatibility. The non-plasticizing PLA block theory explains why the copolymers with a high proportion of PDLA were less or ineffective (Table 5.20).

5.8 Combination of PLA-copolymers with esters (TMHT)

A series of experiments were carried out to determine if there were any synergistic or antagonistic effects between the copolymers and the prepared esters. PLA was blended in the torque rheometer at 180°C for 10 minutes with the above copolymers and ester plasticizers (TMHT or EHT) in equal proportions. The total additive concentration was 17% by weight i.e., 8.5% of each additive.

The PLA films produced with copolymer and ester combinations were smoother and more uniform. The tensile properties of the blends are given in Table 5.22 and Table 5.23. It can be seen from these results that the blend containing the pentaerythritol ethoxylate- PDLA copolymer gave a significant improvement in elongation when used in conjunction with EHT or TMHT. It may be mentioned that TMHT and pent ethox-PDLA at approximately 10% by weight did not give any improvement at all when used alone (Figure 5.53). These results seem to suggest that in order to achieve effective tensile properties, a combination of copolymer and organic ester plasticizer is required. Both internal and external plasticizing effects are useful for the improvements in the properties of PLA. However, MeOPEG(750)-PDLA (1:55) did not produce the same improvements in conjunction with TMHT. It was believed that this was due to the large PLA block in the copolymer, acting more or less like a PLA oligomer (cf. Table 5.21), which had no effect on the polymer. Even when combined with 8.5% TMHT (which has no effect alone) was not sufficient to improve the elongation at break.

Additive TMHT:copolymer (1:1)	% Elongation at Break	Tensile Strength (Mpa)
MeOPEG 750-PDLA 1:5	309	34.2
MeOPEG 2000 PDLA 1:10	305	39.8
MeOPEG 750-PDLA 1:55	6	57.0
Pent ethox-PDLA 1:10	329	41.0

Table 5.22. Effect of a 1:1 mixture of TMHT: copolymer on the mechanical properties of PLA

Additive	Concentration (%)	% Elongation at Break	Tensile Strength (Mpa)
Pent ethox-PDLA 1:10	9	4	66.9
	17	3	62.0
Pent ethox-PDLA 1:10 / TMHT	8.5% each	329	41.0
Pent ethox-PDLA 1:10 / EHT	8.5% each	330	39.0
Pent ethox-PDLA 1:10 / EHT	14% and 3% respectively	320	50.0

Table 5.23. Effect of combining an ester plasticizer with pent ethox-PDLA copolymer on the mechanical properties of PLA

5.9 Effect of storage temperature on the mechanical properties of plasticized PLA

In order to determine the migration and volatility of the plasticizer systems, PLA films containing TMHT at 17%, MeOPEG 750-PDLA 17% and Pent ethox-PDLA 1:10 8.5% / TMHT 8.5% were aged at 50°C (Figure 5.61). A greater retention of physical properties indicates less migration and volatility of the plasticizers.

It appeared that exposure to the elevated temperature had relatively little effect on the flexibility and clarity of the films. After an initial rapid drop in elongation shown in Figure 5.61, which was also observed on storage at room temperature (cf.shape of TMHT curve in Figure 5.55) only a small steady decrease occurred over the remaining period. Plasticizer in excess of a critical concentration was probably exuded during the early stages but followed by a more stable period in terms of exudation.

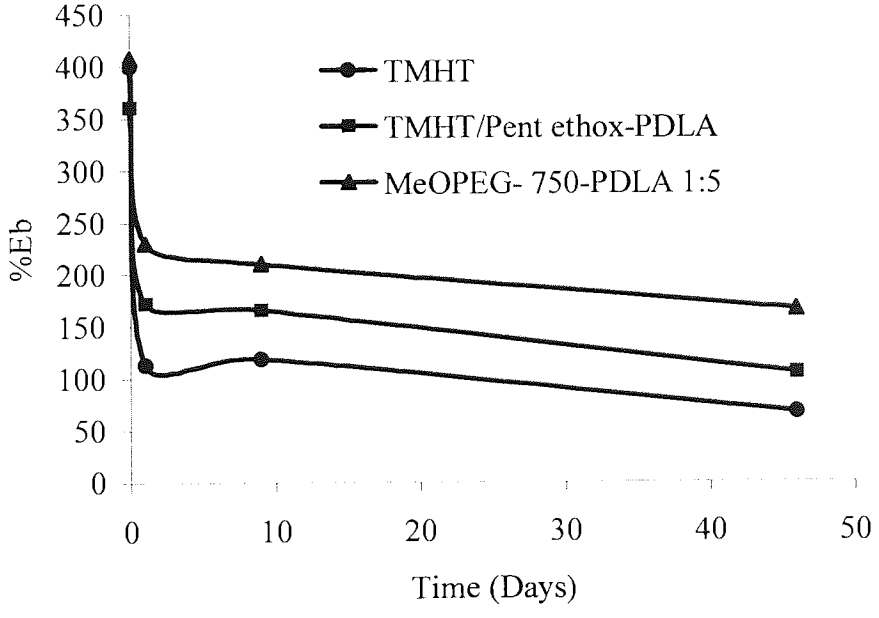


Figure 5.61. Change in the elongation at break of PLA film plasticized with TMHT aged at 50°C

In addition to the measurements of the physical properties of the film, changes in the thermal properties were also examined using DSC. It was observed that all the samples crystallised to a varying degree when held at 50°C as observed by the more or less absent or reduced crystallisation endotherm. However, the area under the melting point exotherm remained reasonably constant and similar to the unaged samples (Table 5.18 and Table 5.24), indicating that the total achievable crystallinity was unchanged.

Additive	Time Aged	Tc/ °C	mJ/mg	Tm /°C	mJ/mg
Control	48 hrs	96.5	-25.9	176.0	+33.1
TMHT	24 hrs	not obsreved	--	169.6	+36.9
TMHT/ pent ethox – PDLA 1:10	24 hrs	81.4	-2.4	172.0	+34.4
	9 days	87.6	-1.37	173.0	+33.4
MeOPEG (750)-PDLA 1:5	24 hrs	84.5	-16.4	172.3	+18.1
	9 days	86.8	-17.2	172.2	+18.6
	46 days	88.7	-8.13	172.0	+27.8

Table 5.24. Thermal properties of plasticized PLA film aged at 50°C

5.10 Plasticization ratio between EHT and pent ethox-PDLA

It was observed in section 5.8 that pent ethox-PDLA alone did not improve the properties of PLA, however when in combination with the organic ester TMHT (or EHT) a significant improvement was observed. The aim of this work was to establish a critical concentration ratio between the copolymer and organic ester plasticizer in order to produce an effective synergism.

A series of blends of PLA were prepared in the torque rheometer at 180°C for 10 minutes (Table 5.25) whereby the ratio of pent ethox-PDLA to EHT was varied keeping the total concentration at 17 %. The polymer used for this series of experiments was supplied by Dow Polymers. Figure 5.62 shows the variation of the elongation at break and tensile strength of PLA with the composition of the plasticizer. The effect on the thermal characteristics is shown in Figure 5.63.

EHT	Pent ethox-PDLA
100	0
88	17
66	33
50	50
33	66
17	88
0	100

Table 5.25. EHT/Pent ethox-PDLA blend composition

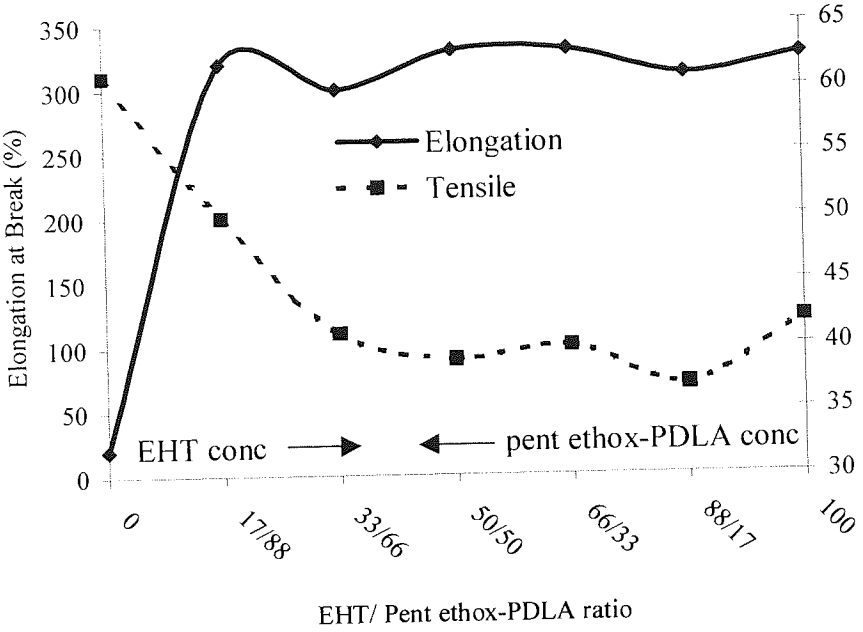


Figure 5.62. Effect of EHT/ pent ethox-PDLA ratio on the mechanical properties of PLA (plasticizer concentration=17%w/w)

It is clear from Figure 5.62 that only a small quantity of ester plasticizer is required to produce a significant increase in the elongation at break of PLA containing pent ethox-PDLA. In addition to the improved mechanical properties, a smooth change in the thermal characteristics of the film was observed (Figure 5.63).

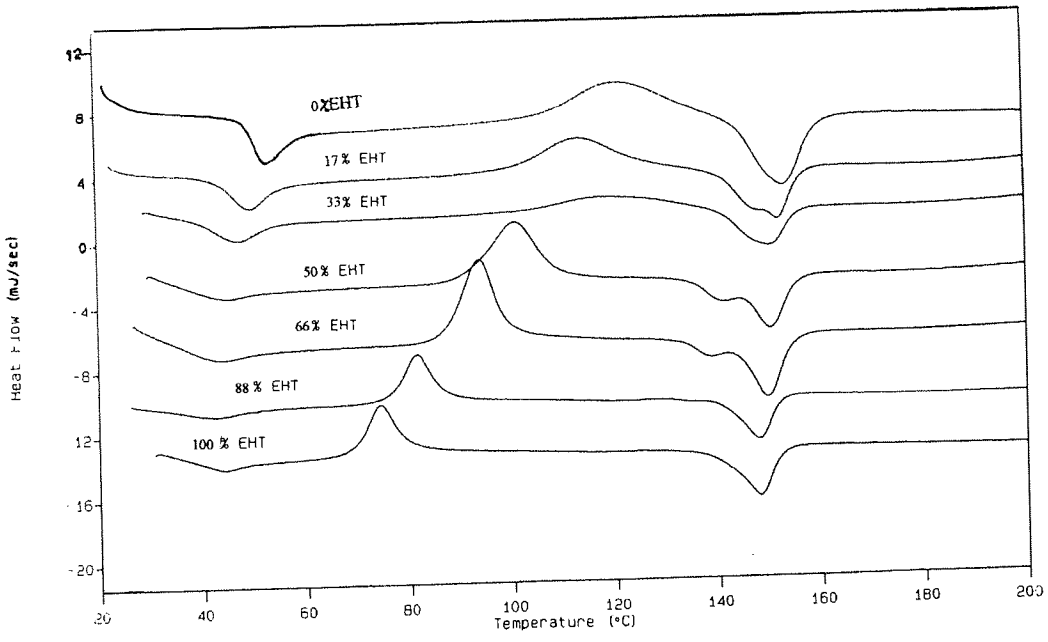


Figure 5.63. Effect of EHT/pent ethox-PDLA ratio on the thermal properties of Dow PLA (plasticizer concentration =17%w/w)

As the ester (EHT) concentration was increased, there was a general lowering and sharpening of the crystallisation exotherm as well as a slight reduction of the melting temperature. In addition, it was observed that a lower melting transition separates from the main peak and then disappears. The glass transition also becomes less well defined. The above results seem to suggest a high degree of synergism takes place between the free volume created by pent ethox-PDLA and chain flexibility produced by the organic ester.

5.11 General discussion

The copolymers, when used alone as plasticizers (MeOPEG (750)-PDLA 1:5 and to a lesser extent MeOPEG (2000)-PDLA 1:10) were initially found to significantly

improve the mechanical properties of PLA. The pentaerythritol ethoxylate copolymer (a star copolymer) on its own did not show any improvement. However when combined with TMHT (at 8.5% each) showed significant improvement Table 5.22) even though the copolymer or TMHT at that concentration were ineffective when used alone indicating synergistic effects between the ester and the pentaerythritol ethoxylate copolymer.

The low molecular weight MeOPEG-PDLA copolymers showed similar improvements in the elongation at break as the ester plasticizers. However, these physical "improvements" were not observed as changes in the DSC analysis (Table 5.20). These films were much more resistant to heat induced thermal changes than the ester plasticized films because of their higher crystallisation temperatures (Table 5.20 and Table 5.24). As a result, thermal crystallisation was retarded at 50°C and consequently, they appeared to retain more of their initial elongation at break.

The lowering of the glass transition temperature is typical of a plasticized polymer (Table 5.18) whether the plasticizer is a discreet compound or a copolymer. In general, the drop in the crystallisation temperature mirrored the lowering of the glass transition temperature which was seen in the ester (but not copolymer) plasticized PLA and these effects are commensurate with a softened polymer. The crystallisation temperature is lowered because the molecules require less energy to rearrange into a crystalline configuration. Therefore, it is suggested that the ester and copolymer plasticizers modify the polymer by subtly different mechanisms. From the DSC and tensile measurements, it can be imagined that the esters solubilise the PLA chains and decrease the thermal transitions and increase the elongation at break in this way. Whereas the copolymers, particularly MeOPEG (750)-PDLA 1:5 may increase the elongation at break by lubrication of the polymer chains (or increase the free volume) allowing the molecules to slip past one another. This would account for the increased elongation with relatively unchanged crystallisation and melting temperatures because the PLA chains are not solublised but only slide on the copolymer additive.

None of the plasticizing systems appeared to change the overall crystallinity of the PLA films. From the DSC data, it is suggested that the prepared films are predominantly amorphous when quenched from the melt and under normal circumstances crystallisation is prevented because of the high glass transition temperature (ca 60°C). Heating in the DSC instrument induces thermal crystallisation between 60-90°C. The observed crystallisation exotherm appears to account for approximately half of the crystallisable material within the bulk polymer. This can be seen if the energy of crystallisation is compared to the energy of melting for various "as prepared" PLA films shown in Table 5.26 and compared to a similar unplasticized PLA sample aged at 100°C for 38 days (Figure 5.64).

Additive	**Energy of Crystallisation (mJ/mg)**	**Energy of Melting (mJ/mg)**
Control	-26.5	43.5
TMHT	-22.8	56.3
EHT	-29.4	54.0
TMHM	-26.3	54.5
TMHS	-30.4	61.8

Table 5.26. Thermal characteristics of PLA films

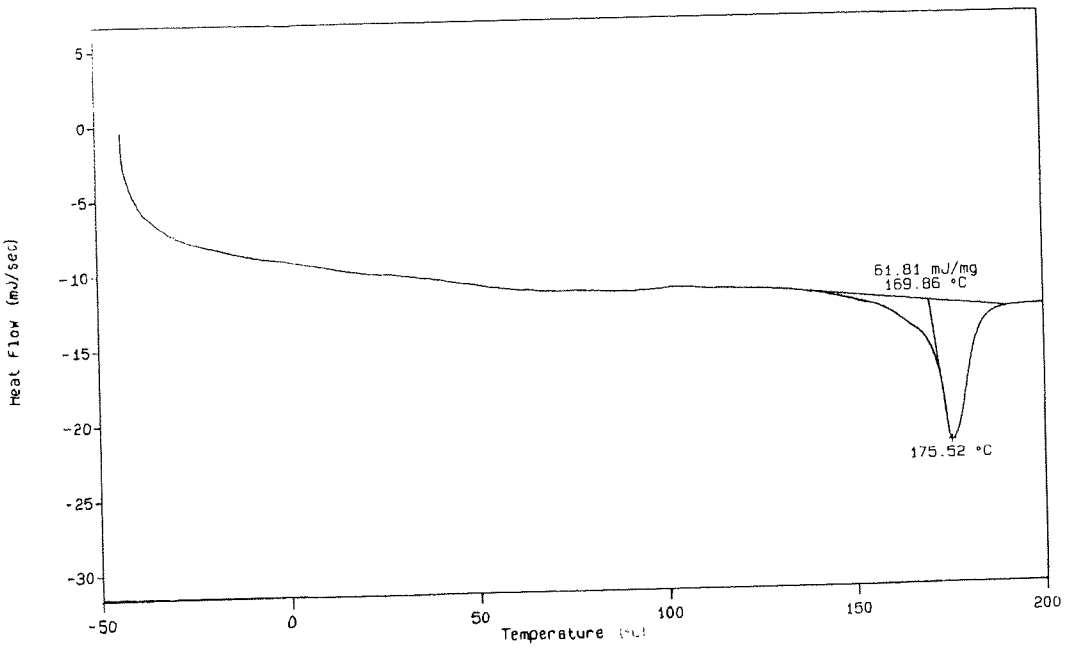


Figure 5.64. DSC of Neste PLA annealed at 100°C for 38 days

It must be assumed that the sample in Figure 5.64 has crystallised to its fullest possible extent in this time. It has been suggested that ΔH_{melt} of a PLLA crystal having an infinite crystal thickness is 93 J/g of polymer [114]. Therefore, the crystallinity of the "as made" quenched control film from Table 5.26 can be calculated: -

$$\frac{(43.5-26.5)}{93}\times 100 = 18.2\%$$

After thermal crystallisation in the DSC during the heating run, it becomes: -

$$\frac{43.5}{93}\times 100 = 46.7\%$$

Moreover, the maximum crystallisation after annealing (Figure 5.64) is

$$\frac{61.8}{93} \times 100 = 66.5\%$$

It is therefore concluded that there is a significant amount of non-crystallisable chains in this PLA sample.

The overall amount of crystallisation obtained in the quenched plasticized films is of course different and ranged between 26 and 36%. It is thought that this is due to the increased chain mobility created by the plasticizers.

As with PHB, PLA was blended with LLDPE, ECO and PCL polymers and properties briefly examined. The results are presented in appendix 8.

Chapter 6

Polymer degradation: poly(3-hydroxybutyrate) and poly(L-lactic acid)

6.1 Introduction

Poly(3-hydroxybutyrate) is a material that is fully consumed by microorganisms [12, 13, 15] and is therefore considered biodegradable. Poly(lactic acid) is fully biocompatible and is believed to be broken down hydrolytically [12] in the environment and is therefore ultimately biodegradable. Additionally, these polymers undergo thermal and photolytic [73] degradation. The above degradation pathways will be discussed in this chapter.

6.2 Experimental

As discussed in chapter 4, a detailed investigation into PHB was abandoned when the availability of the polymer was discontinued. However, the rate of biodegradation of pure PHB was compared to those of plasticized samples and cellulose, which was used as a standard. The extent of degradation was expressed as a percentage weight loss from the film or as a percentage of the total theoretical carbon dioxide evolved.

6.3 Degradation

6.3.1 Poly(3-hydroxybutyrate) [PHB]

The thermally pressed PHB polymer films containing plasticizers (Table 6.27) were assessed for their biodegradation using two methods.

1. Batch composting and
2. Complete mineralisation.

The compost used for these tests was six month old green waste compost obtained from EcoSci (ESI). The typical analysis of this material was as follows: water content 55-60%, volatile solids 35-38% and the percentage carbon 19-22%. The pH was measured as 7-7.5.

6.3.1.1 Batch composting

This method, described previously in chapter 2.3.1 was used to assess the degradation properties of a large number of specimens quickly and simultaneously. All plasticized PHB samples were composted at 55°C and the weight losses that occurred during degradation were recorded. The results are summarised in Table 6.27 and represented graphically in Figure 6.65

PHB + 17% by Weight Plasticizer	**Weight Loss (%)**			
Time / Weeks	After 1 week	After 2 weeks	After 3 weeks	After 4 weeks
PHB	2	24	48	72
NOC	2	9	14	35
EHC	3	2	15	17
IBC	6	25	67	68
NOM	3	5	6	12
EHM	4	9	8	31
IBM	11	15	39	76
NOT	4	8	15	21
EHT	3	8	22	32
IBT	**5 days** 13	**7 days** 18	**14 days** 50	**17 days** 94

Table 6.27. Percentage weight loss from PHB/ plasticizer blends during batch composting

Table 6.27 and Figure 6.65 clearly show that the films containing the *i*-butyl esters appeared to be more susceptible to degradation than PHB alone. The films containing n-octyl or 2-ethylhexyl esters appeared to degrade more slowly than PHB. Figure 6.65 shows data plotted for films containing the long chain esters (dashed lines) and the dotted lines the data for the shorter chain *i*-butyl esters. The separation of these two groups is clear.

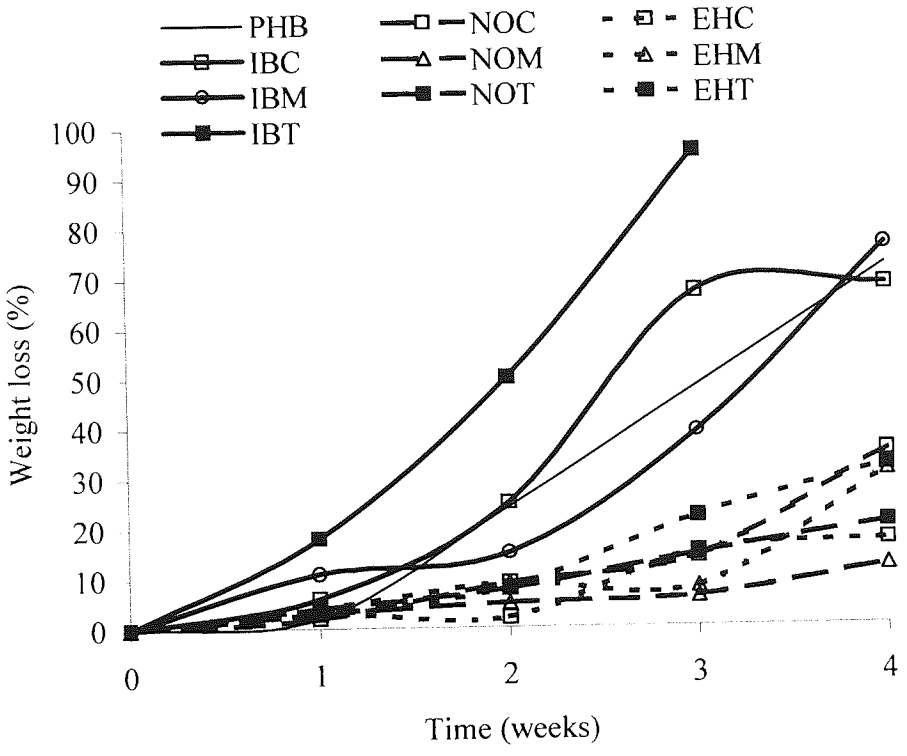


Figure 6.65. Weight loss from batch composted plasticized PHB films

All the ester plasticized PHB films appear to undergo biodegradation under composting conditions at different rates depending on the plasticizer structure. Short chain esters (isobutyl) degrade much faster than the long chain esters. This effect could be attributed to the hydrophilicity/ hydrophobicity of the ester molecules. It may be mentioned that weight loss is only a rough indication of degradation. The observed weight loss could be due to several factors including the loss of the plasticizers into the compost. It would be expected that the shorter chain esters would be lost at a faster rate then the long chain esters.

6.3.1.2 Complete mineralisation

Because of the quantity of material required and the problems associated with composting a large amount of film, only one plasticizer (EHT) was evaluated in PHB. The rates of degradation of the plasticized and unplasticized PHB films were compared with that of cellulose, which was used as a standard. The cumulative carbon dioxide evolved as a percentage of the theoretical is plotted in Figure 6.66 and the percentage degradation after 42 days is shown in Table 6.28.

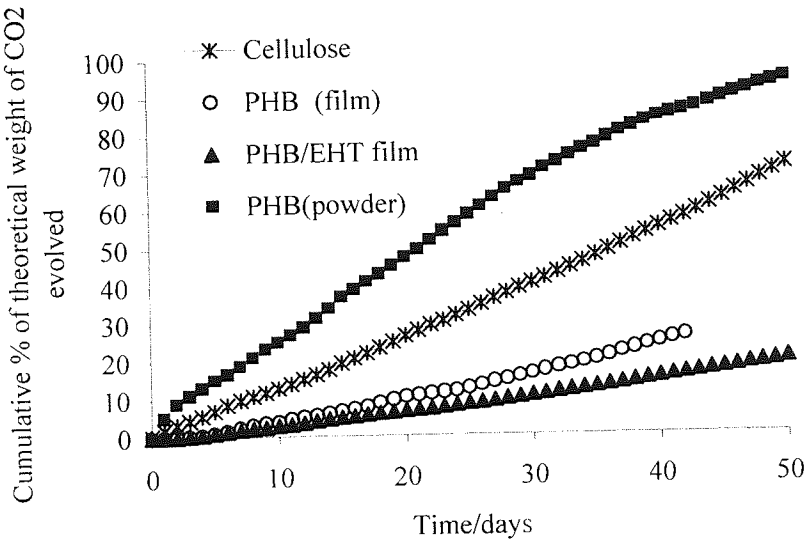


Figure 6.66. Biodegradation of plasticized PHB

Blend	Temperature (°C)	Time/ Days	weight of theoretical CO_2 (%)
Cellulose (powder)	55	42	60.0
PHB (powder)	55	42	86.0
PHB (film)	55	42	26.1
PHB/ EHT (17%w/w)	55	42	16.2

Table 6.28. Complete mineralisation of PHB/ plasticizer blends

Figure 6.66 and Table 6.28 clearly indicate that PHB powder degrades under biotic conditions more rapidly than the cellulose powder standard. However, when PHB is converted to a film it has a slower rate of degradation. It is expected that this mainly due to the difference in surface area of the sample exposed to the compost. Again as observed in Figure 6.65 the presence of EHT retards the rate of complete mineralisation compared to the unplasticized PHB film.

The batch composting tests revealed significant differences in the degradation rate of PHB depending on the additive. The degradation profiles for the polymer-plasticizer blends were encouraging in so far as they did not prevent biological consumption. It appears from Table 6.27 that the isobutyl esters accelerated the degradation with respect to the other esters and PHB alone. In addition, the degradation rate of PHB containing the branched chain 2-ethylhexyl ester and its straight chain analogue appears to be retarded. This could be due to the hydrophobicity of the additive as the longer chain esters would be expected to have more hydrophobic character and be less polar than the shorter chain esters. Indeed, the *i*-butyl esters may increase the degradation rate of PHB by allowing more effective modification of the polymer surface and allowing microbial growth.

6.4 Poly(lactic acid)

In this study various PLA/ plasticizer blends were used for the hydrolytic, biological and photolytic degradation studies. Thermal degradation during processing was investigated using PLA without plasticizers but containing the commercial antioxidant Irganox 1076 (Figure 6.67). Photo-degraded pure PLA films were compared to similar samples containing the pro-oxidant FeDNC (Figure 6.68) or the photo-activator Metone A (Figure 6.69).

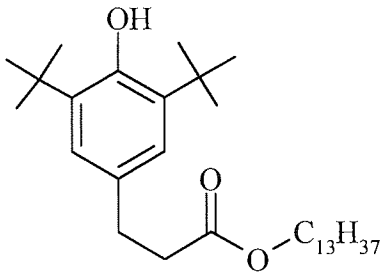


Figure 6.67. Irganox 1076

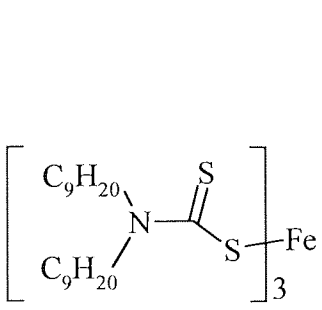


Figure 6.68. Iron (III) di*iso*nonyl dithiocarbamate

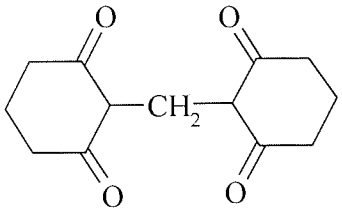


Figure 6.69. 2,2'-Methylene bis cyclohexane-1,3-dione (Metone A)

The degradation of PLA has been studied under the following conditions.

1. Hydrolytic degradation- distilled water at 21 and 50°C and at pH 4.5 and 8.2
2. Biodegradation- batch composting and complete mineralisation.
3. Degradation during processing.
4. Photo-degradation at 30 and 70°C- degradation on exposure to ultraviolet light.

6.4.1 Hydrolytic degradation

Approximately 6g of blown film (50μ thick) containing either TMHT, pent ethox-PDLA / TMHT mixture or MeOPEG 750-PDLA (1:5) respectively at a concentration of 17% by weight were immersed in distilled water at 21 and 50°C. The higher temperature was used to simulate the temperature used in the bioreactor so that a comparison could be made between the effects of hydrolytic degradation and the compost/ microorganisms. The films were removed periodically and the weight loss recorded and compared to the changes in the control sample without plasticizer. At the end of the test, the remaining polymer was recovered by filtration and the molecular weight was determined by GPC. Any degradation products or

organic material dissolved in the water was recovered by removal of the water by distillation on the rotary evaporator at 50°C.
The percentage weight loss from the plasticized PLA films degraded in distilled water are shown below in Table 6.29.

Dumbbell specimens were cut from the blown film and were subjected to the same hydrolysis conditions as the samples described above. These specimens were examined for changes in physical properties over the period of hydrolysis.

Similar tensile specimens of PLA film plasticized with THMT were prepared and degraded in buffer solutions of pH 4.5 and 8.2 to assess the effect of pH on the degradation rate by monitoring the change in the elongation at break. The molecular weights of these samples were also monitored using GPC.

	Weight loss (%)							
Time Days	**Control**		**TMHT**		**TMHT/pent ethox-PDLA**		**MeOPEG 750 –PDLA (1:5)**	
	21°C	**50°C**	**21°C**	**50°C**	**21°C**	**50°C**	**21°C**	**50°C**
6	-	-	0.27	9	0	9.1	4.5	13.3
12	0	brittle	0.72	11	0.89	12	4.9	15.6
32	0	brittle	1.38	12	2.35	14	5	brittle
56	-	brittle	2.3	12.9	3.5	16.5	5.15	brittle
108	0	brittle	3.7	17.4	5.2	22.3	8	35.8*

* mass loss calculated by filtration of polymer pieces

Table 6.29. Percentage weight loss from hydrolytically degraded plasticized (17%) PLA film in distilled water

The control sample did not appear to show any measurable mass loss over a period of 108 days at 21°C but became brittle within 10 days at 50°C. Embrittlement meant that the weight loss could not be measured for samples under these conditions. An oily residue accounting for 6% of the weight of film was recovered from the aqueous extractant at the end of the test. A similar oily residue was also recovered from the samples containing plasticizer. The weight recovered from the samples containing plasticizer matched reasonably with the measured weight loss in Table 6.29. The material recovered in this way was insoluble in toluene but soluble in water, suggesting high polarity. The residue was analysed by NMR (Figure 6.70) and FTIR (Figure 6.71) spectroscopy and found to consist mainly of lactic acid and/or lactic acid oligomers with some contamination from the plasticizers used. A ^{1}H NMR spectrum of the extract of the film containing MeOPEG-PLA copolymer is shown in appendix 9. Figure 6.72 shows the FTIR spectrum of the residue of a DL-lactic acid solution after the removal of the excess water by rotary evaporation. Close examination of Figure 6.71 and Figure 6.72 clearly shows that the carbonyl absorbance of the stripped lactic acid is ester-like, indicating some degree of polymerisation, whereas the carbonyl in the degradation residue is somewhat characteristic of an acid. This suggests that the degradation products of PLA are possibly lactic acid monomers or even lower molecular weight oligomers than the product obtained by careful removal of the excess water from a commercial 85% lactic acid solution.

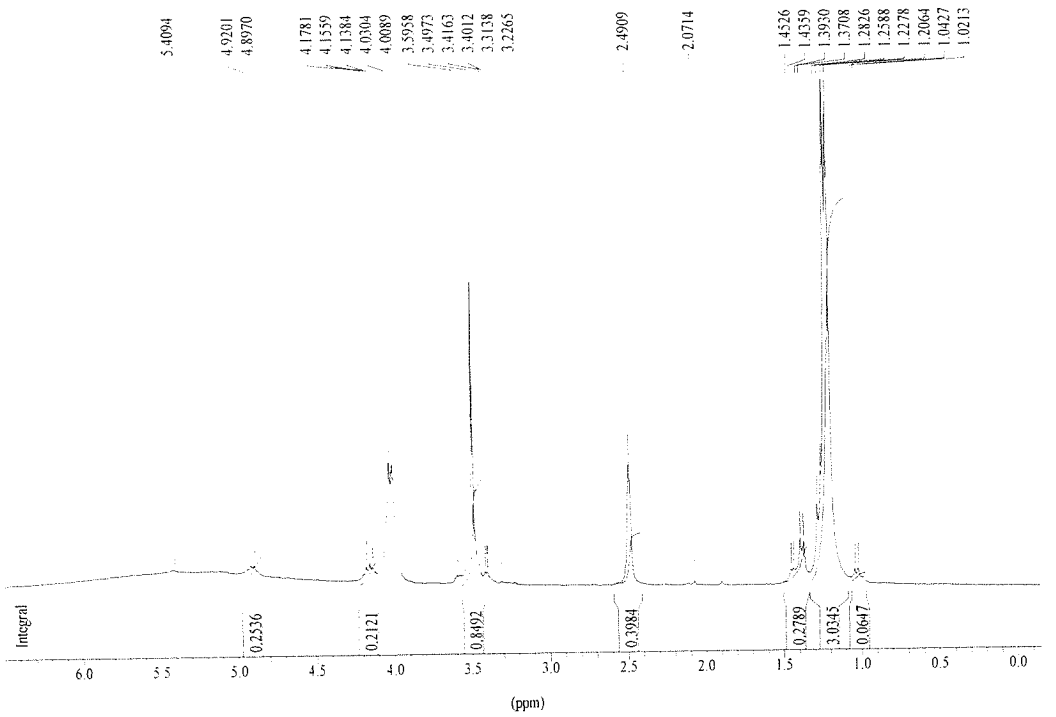


Figure 6.70. Proton NMR of residue recovered from hydrolytic degradation of PLA

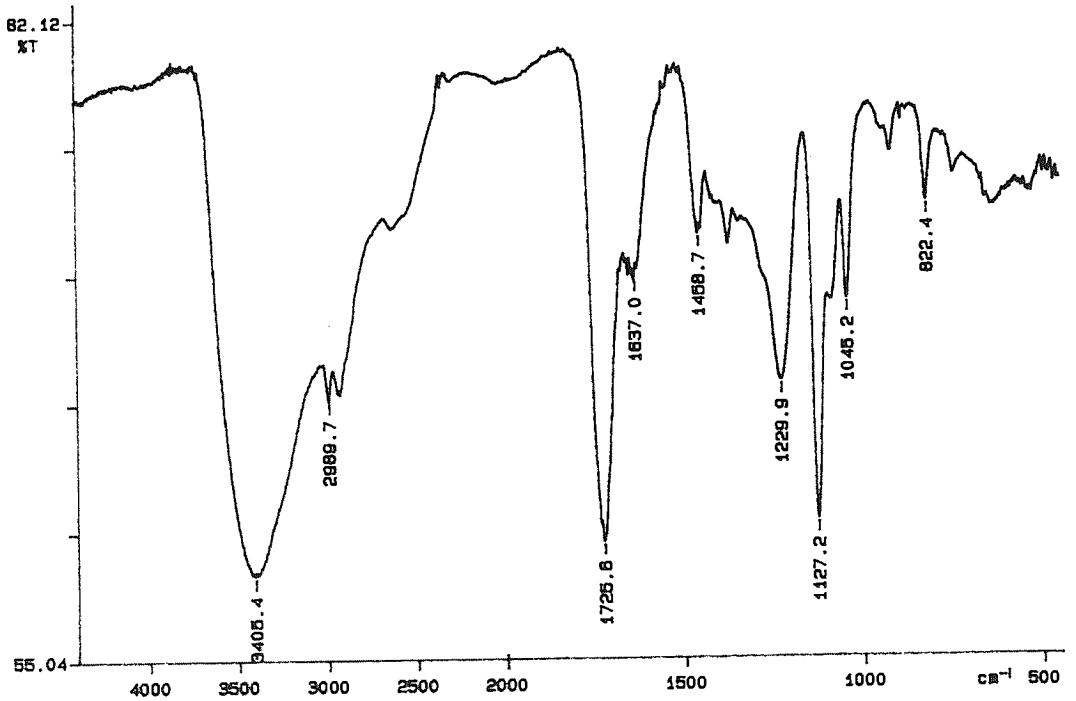


Figure 6.71. FTIR of aqueous extract from degraded PLA

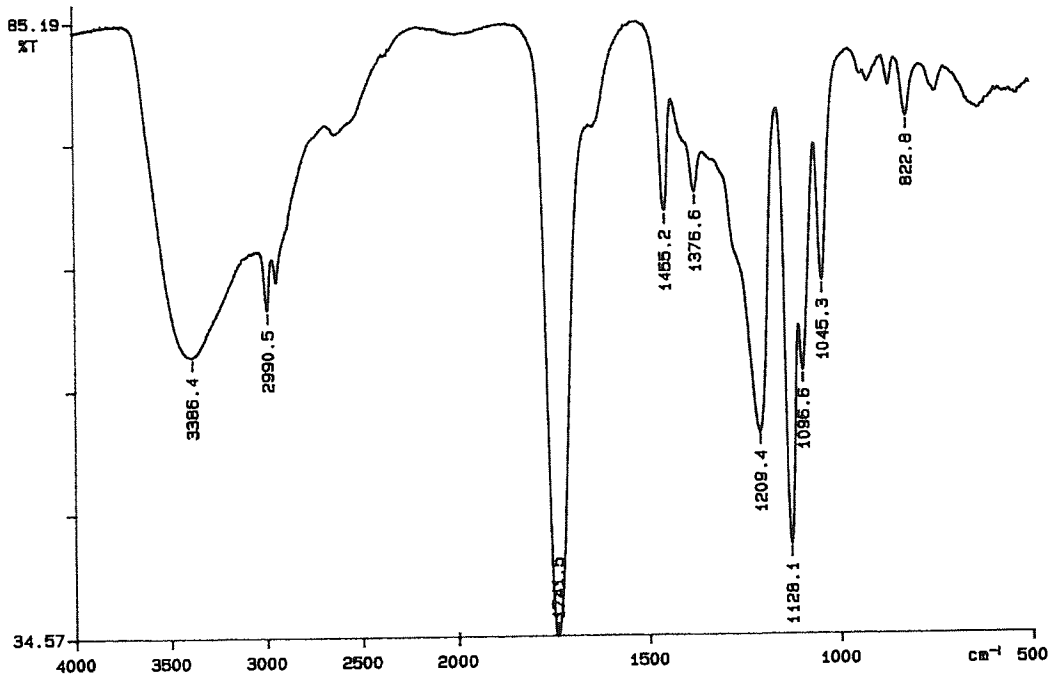


Figure 6.72. FTIR spectrum of DL-lactic acid

The plasticized films remained flexible throughout the tests at room temperature. In addition, both films containing TMHT remained reasonably flexible at 50°C throughout most of the test period indicating that some degree of plasticizer remained. The film containing MeOPEG-PDLA soon became brittle at 50°C.

On critical examination of Table 6.29 it is suggested that:

1. The combination of film flexibility, spectroscopic analysis of the degradation products in the extract and the TMHT extraction tests (discussed later in section 6.6) suggest that only a small quantity of TMHT was extracted at 50°C. This

suggests that the observed 17.4% weight loss is due mainly to the loss of lactic acid fragments by hydrolytic degradation.

2. The weight loss from the TMHT/pent ethox-PDLA film can be similarly explained. A lower concentration of the hydrophobic TMHT allows a higher degradation rate by water. Likewise, it is also expected that most of this weight loss from the films is due to fragmentation of the polymer chain and not additive extraction.

3. The weight lost from the MeOPEG-PDLA plasticized film was double that of the TMHT. It must be assumed that this water soluble additive has been completely extracted by water in this time. This accounts for the first 17.5% of the weight loss. The hydrophilic nature of this additive results in rapid polymer disintegration thereby accounting for the remaining 17.5 percent.

Samples extracted during hydrolysis at 50°C of the unplasticized PLA samples were monitored by GPC to establish molecular weight changes during hydrolysis. At the end of the test, the molecular weight of all the samples were measured and compared to the unplasticized PLA sample. The results of this study are shown in Figure 6.73 below.

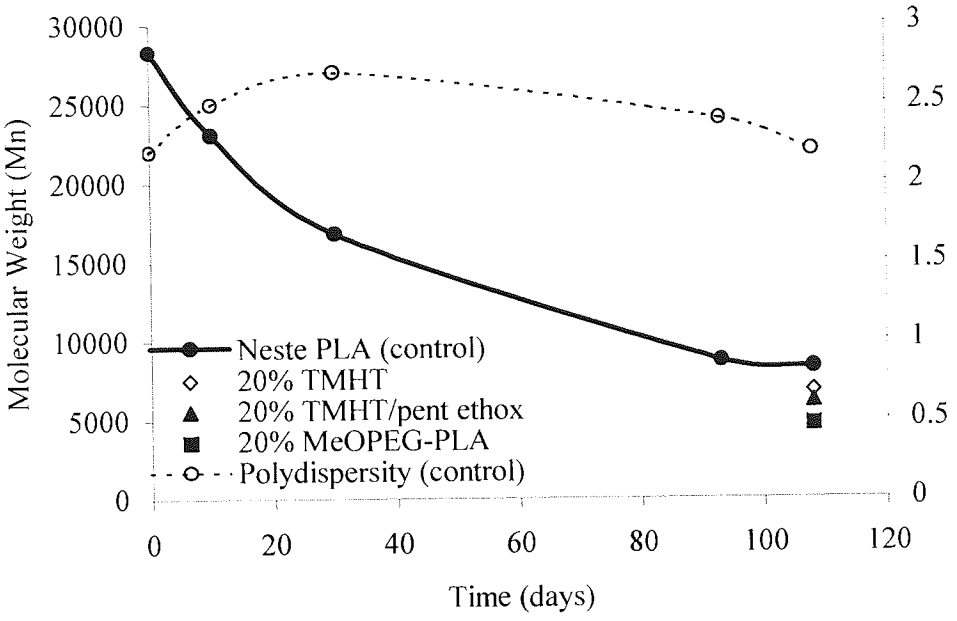


Figure 6.73. Molecular weight change of degraded PLA samples at 50°C in water

Pure PLA shows a steady decrease in its number average molecular weight with time in water at 50°C from around 28000 to approximately 8000 in 109 days. The PLA films plasticized with TMHT, TMHT/pent ethox-PDLA and MeOPEG-PDLA had molecular weights of 5000-7000 at the end of the test. These results show that the plasticizers did not inhibit the hydrolytic degradation of PLA. Moreover, if these results are compared to the mass loss data in Table 6.29 it can be seen that the reduction of the molecular weights matched the embrittlement time and mass loss.

The thermal characteristics, particularly the crystallisation and melting temperatures were monitored, as well as the molecular weight

During the degradation period (particularly at 50°C), there was a general lowering of the melting transition (Figure 6.74). The crystallisation exotherms also disappeared in all the plasticized samples as expected due to the annealing process. A typical example is shown in (Figure 6.75).

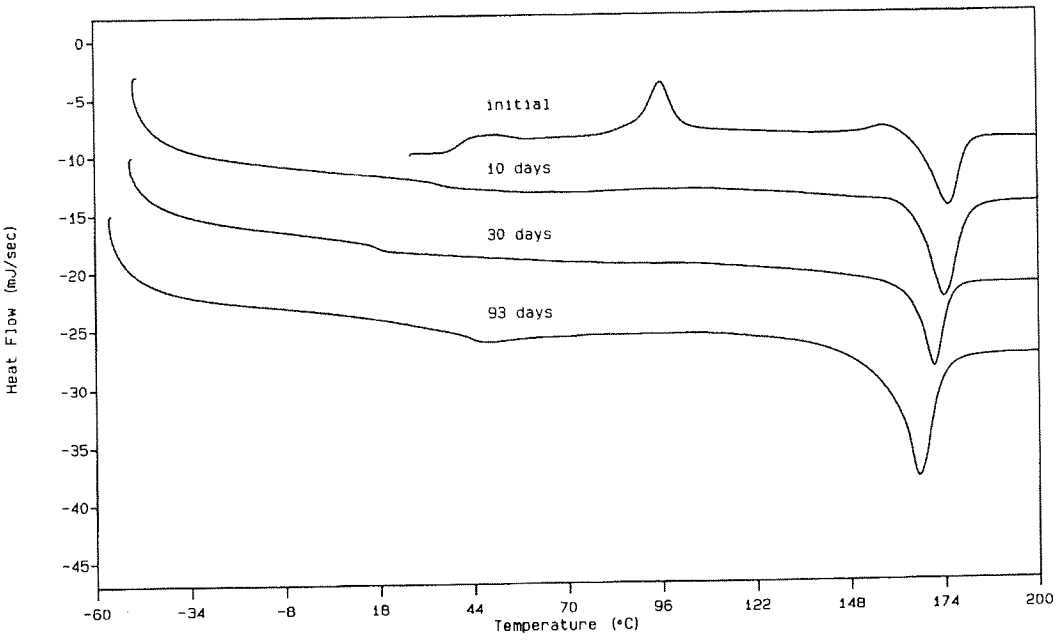


Figure 6.74. Effect of hydrolysis on the melting point of pure PLA (50°C)

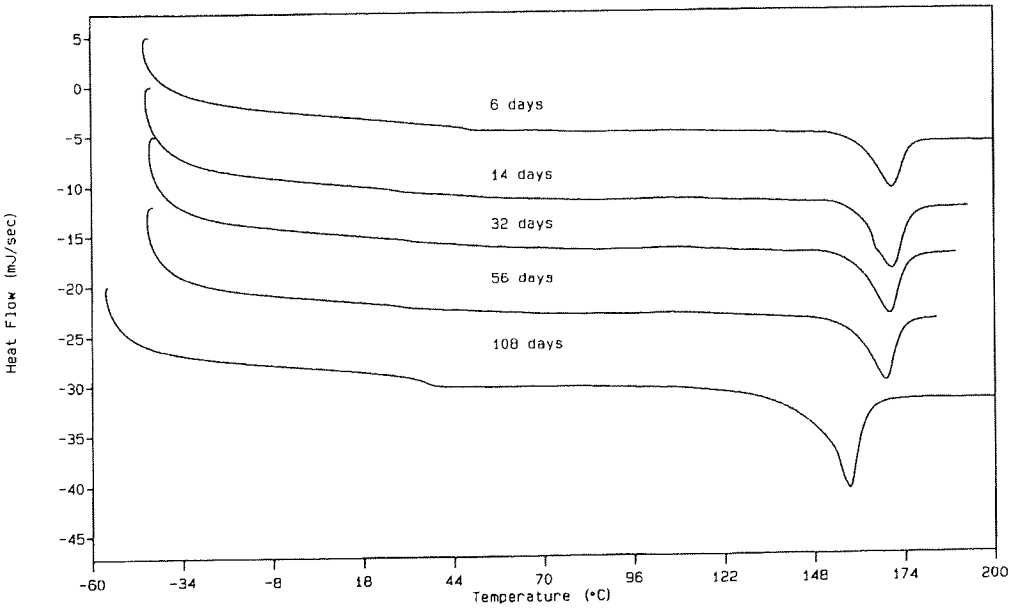


Figure 6.75. Typical changes in the thermal properties of plasticized (TMHT) PLA film during hydrolysis at 50°C

In addition to hydrolysis in pure water described above, the effect of pH on the hydrolysis of PLA (Neste) films plasticized with TMHT was carried out. The tests were carried out at 21°C in buffer solutions of pH 4.5 and 8.2. The elongation at break was used as a measure of the resistance of a film to hydrolysis (Figure 6.76). In addition to the elongation measurements the molecular weights were monitored using GPC (Figure 6.77).

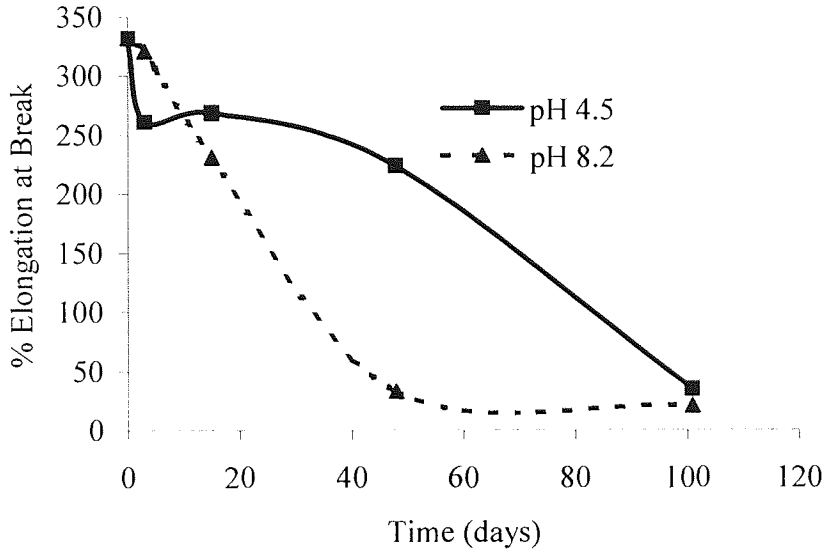


Figure 6.76. Effect of pH on the mechanical properties of PLA film plasticized with TMHT

The results from the tensile measurements were too inconsistent for any real inferences to be drawn from these experiments. However, molecular weight measurements on these films (Figure 6.77) showed that the molecular weight reductions were more or less identical for the acid and base buffers and both had decreased much more that the films exposed to pure water.

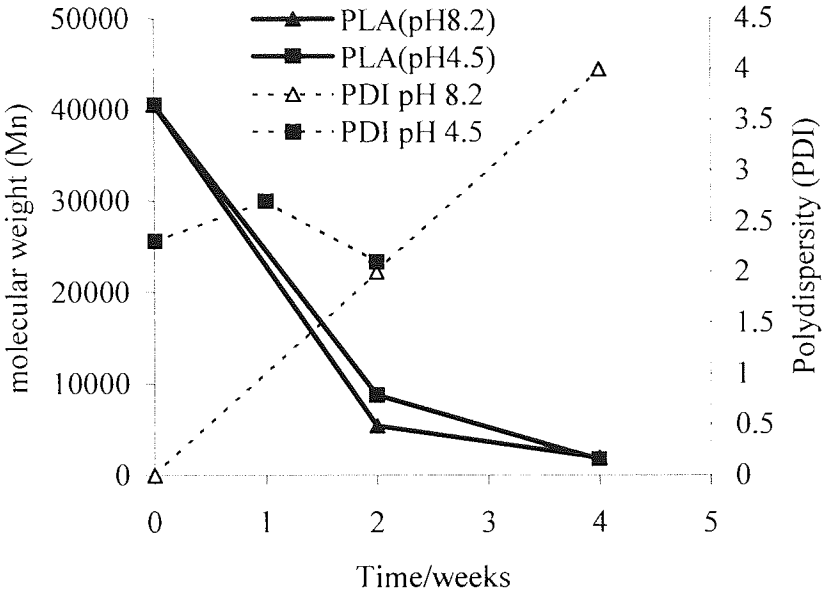


Figure 6.77. Effect of pH on the number average molecular weight of PLA plasticized with TMHT

The reduction of the physical properties for the hydrolysed sample was not an accurate measure of degradation but the reduction in the molecular weight was similar in both the acidic and basic solutions and both were much greater than that observed in pure water at 50°C. Therefore, it can be said that the hydrolysis of PLA is catalysed under acidic and basic conditions.

6.4.2 Biodegradation

PLA films plasticized with TMHT, EHT, TMHT/pent ethox-PDLA and MeOPEG 750-PDLA 1:5 were subjected to the batch biodegradation test (Table 6.30). The films plasticized with TMHT and TMHT/pent ethox-PDLA were also subjected to the complete mineralisation biodegradation test (Figure 6.79). These experiments assessed the effects of the additives on the rate of degradation in terms of molecular weight reduction, mass loss, embrittlement time and carbon dioxide evolution.

Unfortunately, only a few additive combinations could be investigated because of the large quantity of film required and apparatus availability. The toxicity of the compost was tested following the degradation period by monitoring the germination of cress seeds.

In addition to the degradation tests of the plasticized films, the rate of biodegradation of the selected plasticizers was also measured.

	% Weight Loss Over Time (days)				
	7	**14**	**28**	**35**	**42**
PLA control	-	3.2	3.8	7.6	70.4
PLA/ TMHT 17% wt.	6.4	11.1	22.4	45.3	-
PLA/ EHC 17% wt.	4.9	8.5	15.8	78.1	-
TMHT/pent ethox-PDLA	8.7	37.4	>90		
MeOPEG 750-PDLA 1:5	Film was to brittle for meaningful measurement				

Table 6.30. Weight loss of PLA films in compost at 60°C

During the batch biodegradation tests, all the PLA samples became brittle within seven days, which made weight loss measurements difficult. After 14 days, they had become extremely fragile and as time progressed, the pieces became increasingly more fragile and more difficult to separate from the compost. After 4 weeks the pieces of film were virtually impossible to separate from the compost and therefore the percentage weight loss was only a rough indicator of degradation. The films containing plasticizer showed generally accelerated degradation compared to that of the control. The molecular weight of the control film and the film plasticized with TMHT were monitored using GPC (Figure 6.78).

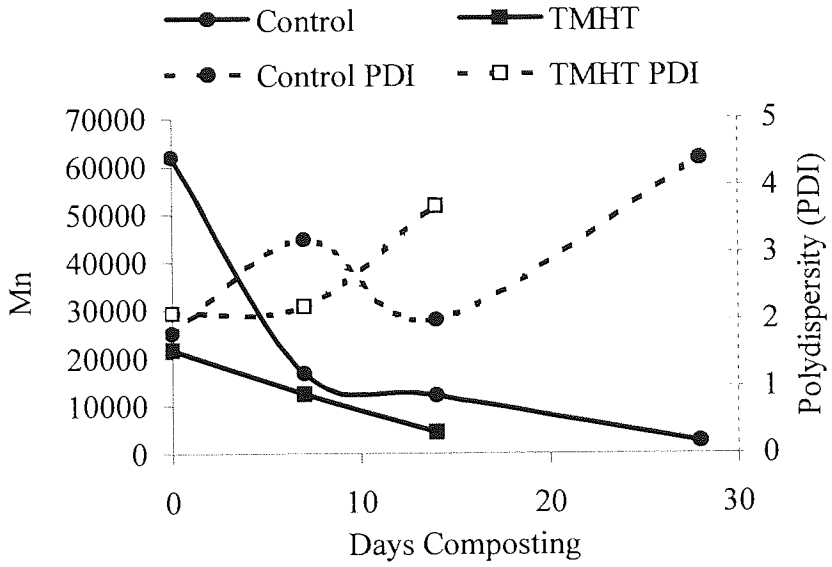


Figure 6.78. Effect of composting on the molecular weight of plasticized and unplasticized PLA

The observed embrittlement time of the plasticized and unplasticized films and molecular weight change (Figure 6.78) suggest that the composting environment increases the breakdown of the films integrity at an faster rate than in the purely aqueous system. In addition, the molecular weight decrease of the film is much greater in wet compost (c.f. Figure 6.78 and Figure 6.73) than in water at similar temperatures. These results seem to suggest that the degradation of PLA is faster under composting conditions.

During the complete mineralisation experiments (Figure 6.79), it was found that pure PLA films degraded steadily after a short induction period of approximately 15 days, producing an increase in the carbon dioxide compared to that produced by the blank compost. The addition of TMHT appeared to retard the carbon dioxide evolution, however, the combination of pent ethox-PDLA and TMHT did not appear to have a significant detrimental effect on the cumulative carbon dioxide evolution.

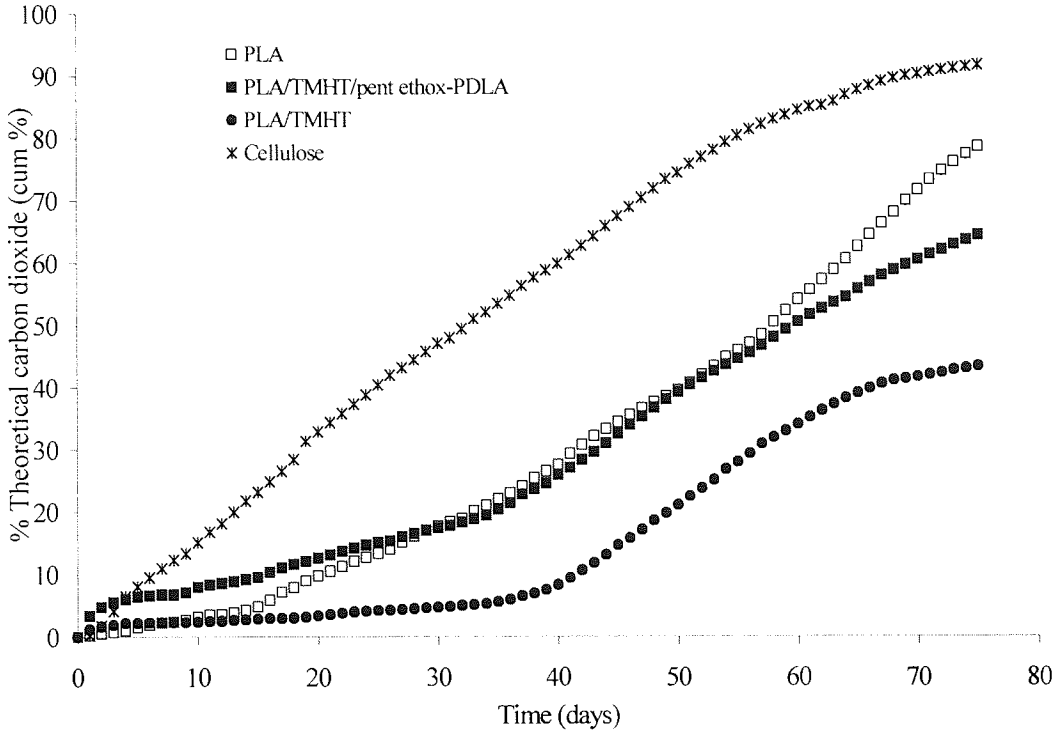


Figure 6.79. Complete mineralisation of plasticized PLA

It may be observed from Figure 6.79 that in contrast to cellulose, PLA shows an initial well defined induction period before the onset of biodegradation. At the end of the induction period however, the rate of carbon dioxide evolution approaches that of cellulose. Complete mineralisation as measured by carbon dioxide evolution, occurs in around 80 days.

As was observed with PHB plasticized with EHT, the addition of TMHT as a plasticizer in PLA increased the initial induction period and the subsequent rate of biodegradation was retarded. It also took a longer time to achieve complete mineralisation. However, the film plasticized with the combination of pent ethox-PDLA and TMHT shows a similar degradation profile to the pure PLA film. It is suggested that the initial induction period before the onset of degradation is

associated with the diffusion of water into the polymer [63] with subsequent modification of the hydrophobicity/ hydrophilicity of the surface of the film. The microorganisms can then begin to assimilate the low molecular weight products at the surface [15]. However, these products may or may not be there before hydrolysis occurs and therefore hydrolysis may not be a prerequisite for biodegradation.

6.4.2.1 Biodegradation of selected plasticizers and copolymers

The pure esters (Figure 6.80), PDLA copolymers (MeOPEG 750-PDLA 1:5) and Pent ethox-PDLA) [Figure 6.81] were individually assessed for their biodegradation characteristics as follows.

Liquid additives (50g) were absorbed onto 45g of silica to form a dry powder. Solid additives were used without silica. The solid was then mixed with the compost (600g) and allowed to degrade in the same way as the films. The carbon dioxide evolution was recorded.

The results of these studies are shown in Figure 6.80 below.

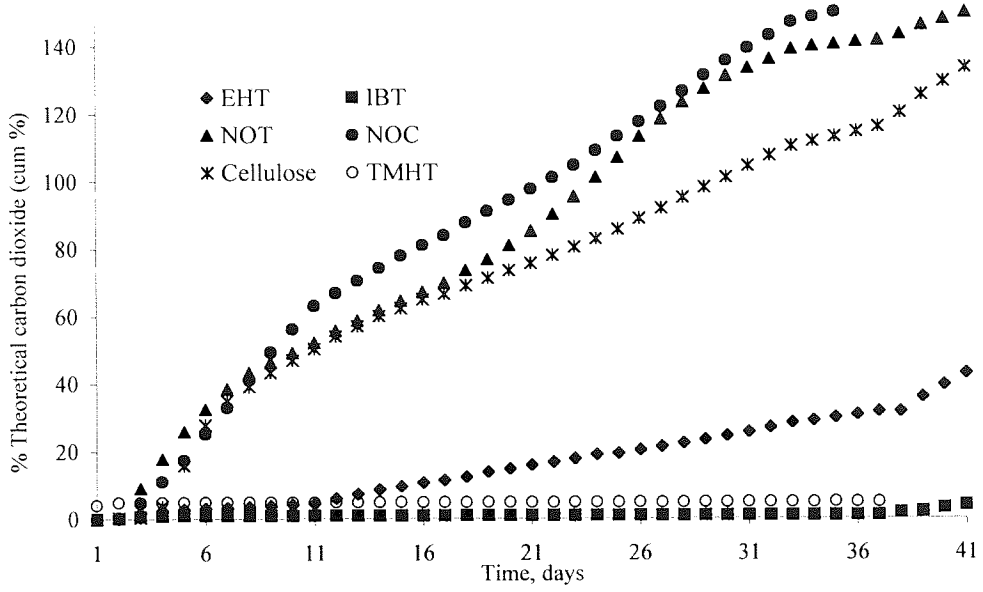


Figure 6.80. Complete mineralisation of ester plasticizers

It was found that the esters of straight chain alcohols (n-octyl citrate and tartrate) degraded at a much faster rate than the esters prepared from branched chain alcohols. This effect could be due to the steric hindrance associated with the branched chain esters possibly preventing biological modification or compatibility of the plasticizer. However, care should be exercised when interpreting these results as the cumulative carbon dioxide was in excess of 100% in some cases and therefore these particular results should only be considered with respect to rate of degradation compared to the cellulose control sample. The high carbon dioxide readings followed after a shut down period of the bioreactor at around 35 days, perhaps initiating other biological processes within the compost.

The degradation of the PLA copolymers was more successful than the ester plasticizers described above. The continuity of the test was preserved and therefore more accurate results were observed throughout the entire test period. The results are shown in Figure 6.81 below.

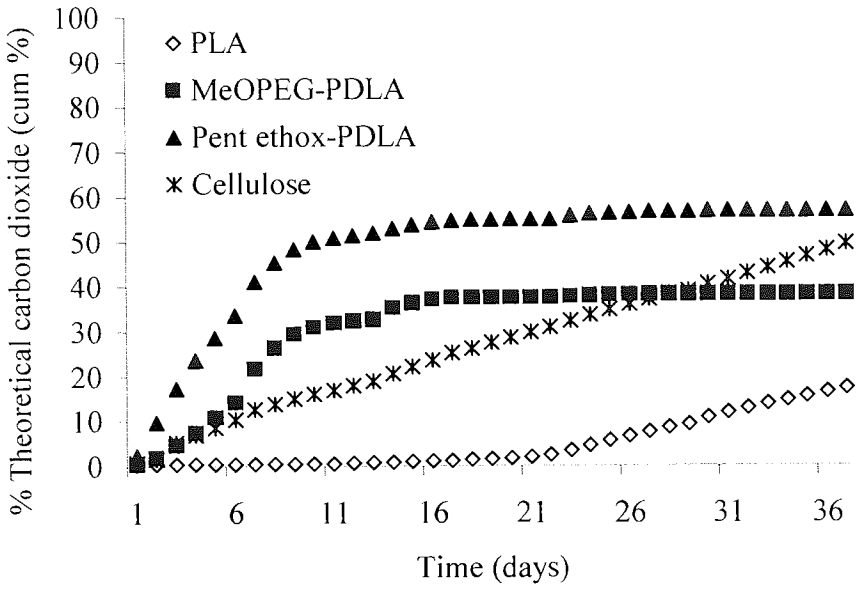


Figure 6.81. Complete mineralisation of PDLA copolymers

This test clearly demonstrates that the PLA copolymers degrade much more rapidly than PLA or even cellulose. The degradation of both copolymers was quite rapid and appeared complete between 11-16 days. The rapid degradation rate of these compounds is almost certainly due to the hydrophilic parts of the copolymers

6.4.3 Thermal degradation

As discussed previously in chapter 1, PLA is thermally unstable and depolymerises into lactide and oligomers. During melt processing, the polymer is exposed to high temperature and high shear conditions so at this time the molten polymer is potentially susceptible to thermal oxidation particularly in the presence of air. This process is common to other polymers like polyolefins and PVC etc [9] and it is conceivable that similar reactions could occur to a greater or lesser extent in linear polyesters.

To protect the polymer during processing and in use, thermal stabilisers are normally added to act as chain breaking antioxidants. These antioxidants function by removing chain initiating free radicals from the system. The antioxidant used in this study was Irganox 1076 (Figure 6.67), a widely used antioxidant for polyolefins and was obtained from Ciba Geigy.

PLA, alone and in combination with Irganox 1076, was processed in the torque rheometer at 180°C for various lengths of time. The effect of processing time on the oxidative degradation of the polymer was assessed by using number average molecular weight changes (GPC), peroxide formation, melt flow index measurements and onset of weight loss using the DSC/TGA.

Figure 6.82 below shows the change in number average molecular weight of PLA with processing time at 180°C with and without added thermal stabiliser (Irganox 1076) as determined by GPC. All samples showed a rapid initial drop in the number average molecular weight, followed by a reasonably constant molecular weight profile up to 40 minutes processing.

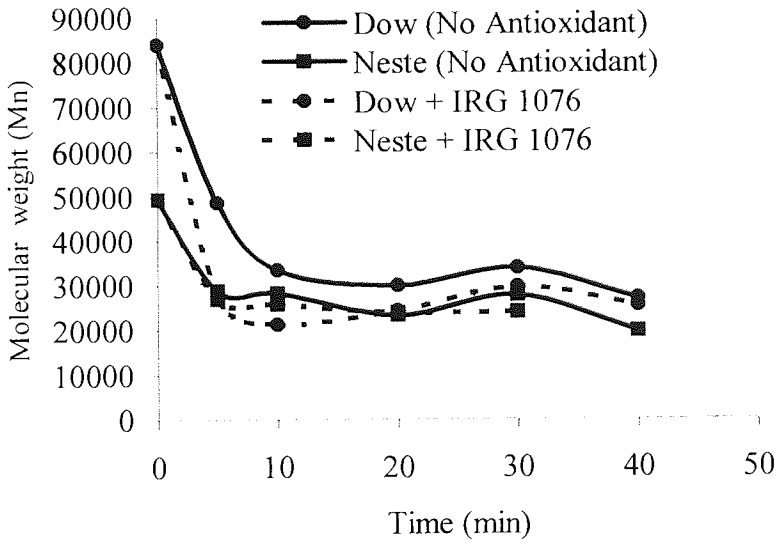


Figure 6.82. Effect of processing time on the molecular weight of PLA

This finding implies that PLA does not undergo oxidative degradation during processing because the thermal processing stabiliser Irganox 1076 had virtually no effect on the molecular weight change. Moreover, the overall molecular weight and similarity of behaviour of both samples strongly suggests that depolymerisation rather than oxidative degradation takes place during processing.

Melt flow index measurements (MFI) [Figure 6.83] show the initial rapid increase of the MFI followed by a more moderate increase on further processing. Again, the addition of thermal stabiliser does not seem to have any significant effect on the MFI of the polymer.

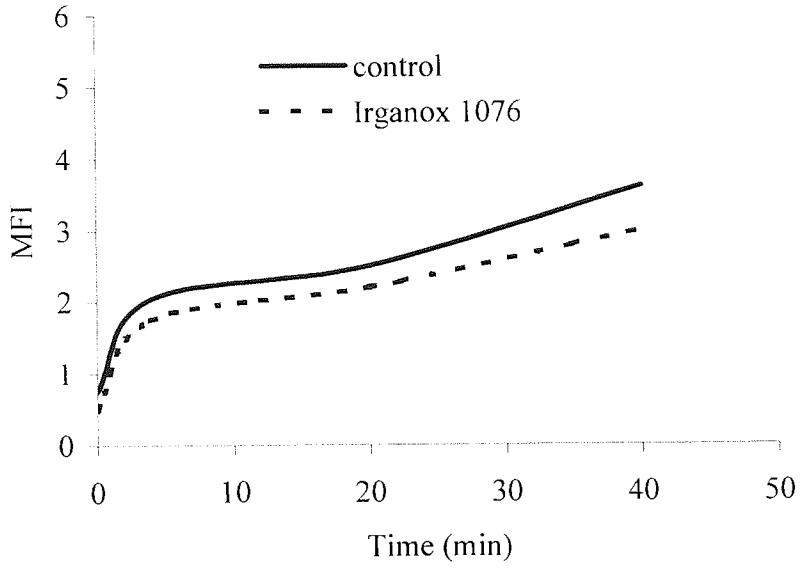


Figure 6.83. Melt flow index of processed PLA

Peroxide formation is a common phenomenon during thermo-oxidative degradation of polyolefins [115]. The concentration of peroxide in the PLA samples processed for various lengths of time was determined iodometrically. The method for the determination of peroxides was described in chapter 2.4. The results of these studies are shown in Figure 6.84. The control sample without stabiliser showed an initial drop in the peroxide concentration (5 minutes processed) followed by an increase in concentration (10 minutes) and finally levelling of to a reasonably steady concentration. This result suggests that thermal oxidation may be present to some extent but probably not causing any significant degradation. In the presence of Irganox 1076, the peroxide concentration appeared to be reasonably constant at the longer processing times which is expected from the mechanism of action for peroxide antioxidants. However, the concentration of oxidising species is so small that the results obtained could be due in some part to experimental error and natural decomposition of peroxides within the polymer over time.

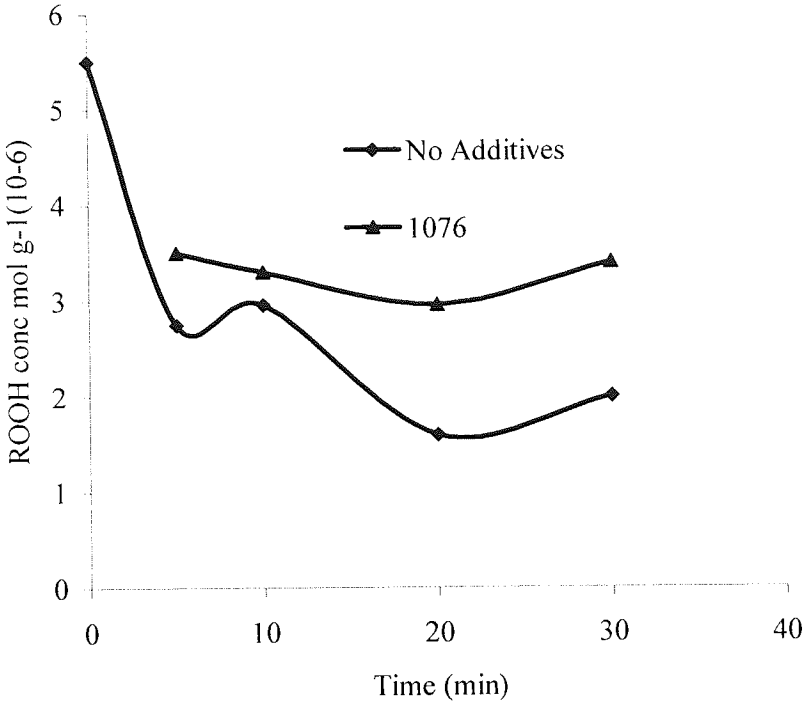


Figure 6.84. Effect of processing time on the peroxide concentration of Neste PLA

6.4.3.1 Thermo-gravimetric analysis (TGA) studies of PLA degradation

The weight loss profile of a processed PLA sample containing Irganox 1076 was compared to a similarly processed pure PLA sample. Figure 6.85 represents the weight loss from the polymers with increasing temperature as determined by thermo-gravimetric analysis (TGA) measurements. The result shows that the onset of weight loss form the control sample (no stabiliser) is very similar to the sample containing Irganox 1076. The weight loss is due to thermal depolymerisation reactions producing small volatile fragments. The similarity in the weight loss curves for the samples containing antioxidant and no antioxidant imply that the therm-oxidative degradation is not a dominant factor in PLA degradation

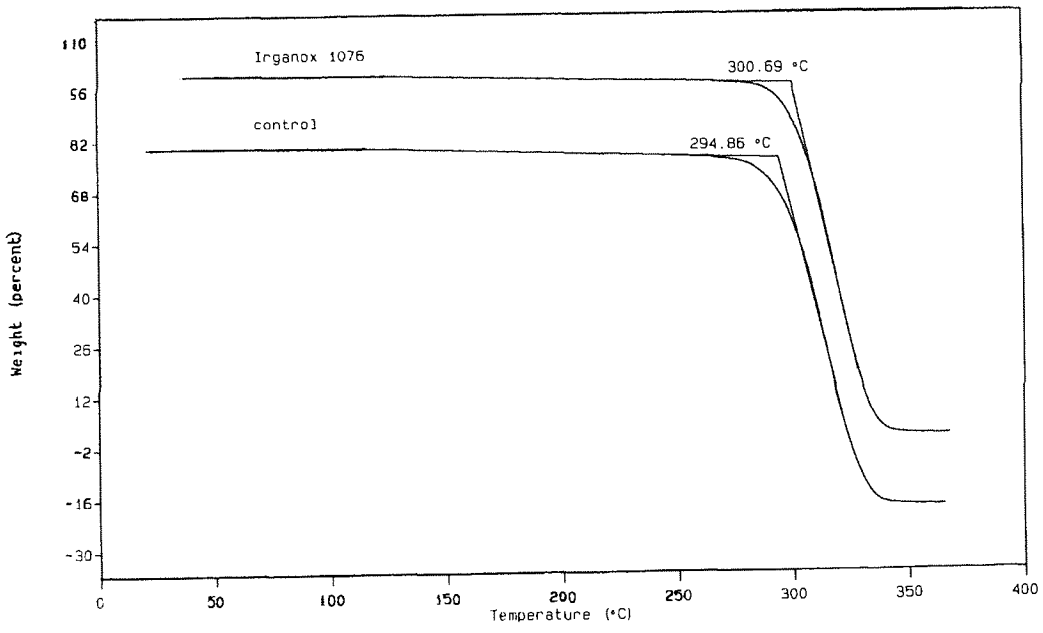


Figure 6.85. Effect of Irganox 1076 on the onset of DSC weight loss from Neste PLA

It is well known that PLA degrades to lactide and oligomers at temperatures close to its melting point [40, 66] by a depolymerisation process. Indeed this process is how lactide itself is prepared. The depolymerisation process is seen when PLA is heated in a DSC instrument and the weight of the sample monitored using TGA (Figure 6.85). Degradation and volatilisation also appear to occur when PLA is degraded isothermally (Figure 6.86). As expected, the weight loss is accelerated as the temperature is increased.

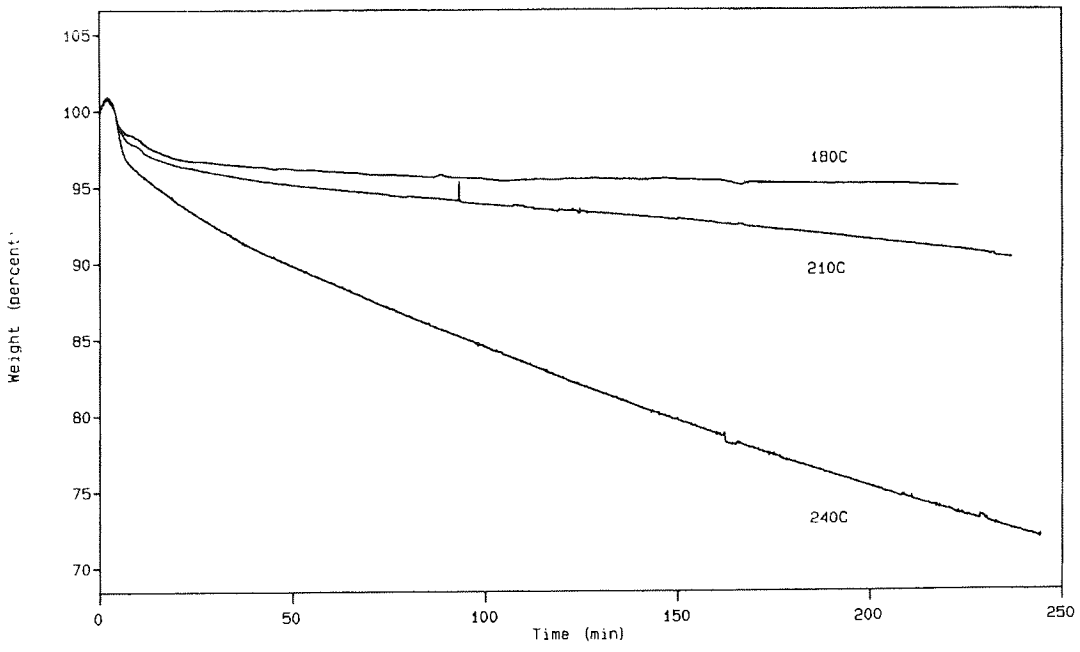


Figure 6.86. Weight loss from Neste PLA over time

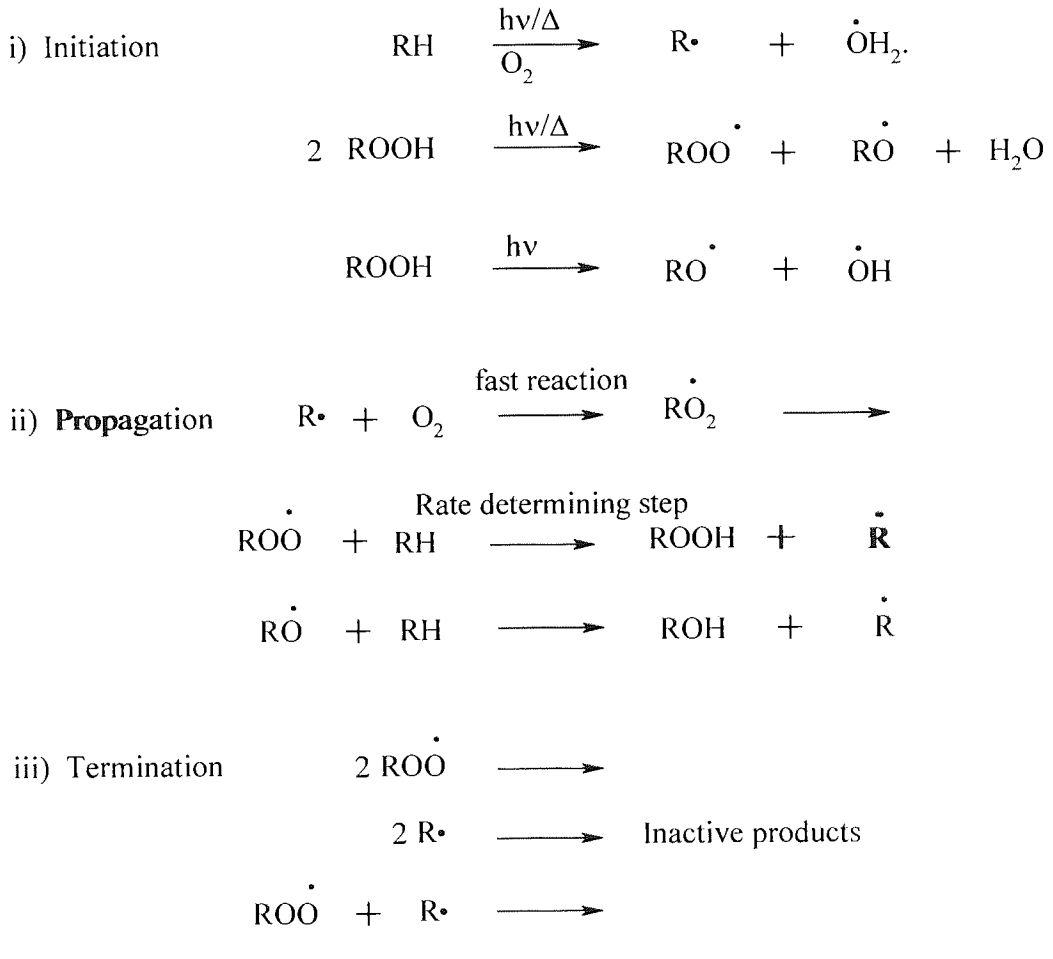
All the findings clearly show that the thermal depolymerisation is very rapid during the initial stages of processing and appears independent of antioxidant. However, at longer processing times, the depolymerisation reactions appear to be reduced and the molecular weight becomes more stable. This stabilisation is not seen in the samples heated in the DSC instrument and this would suggest that different reactions are taking place in these open systems.

6.4.4 Photolytic degradation

All organic compounds and polymeric materials are affected by the ultra-violet radiation present in sunlight (290-400nm) particularly in the presence of oxygen. This process is known as photo-oxidation. Photo-degradation of polymers involves a similar type of free radical mechanism to thermo-oxidative degradation [116,117]. The basic reaction scheme consists of three steps.

1. Initiation,
2. Propagation and
3. Termination.

The general reactions involved are shown in Scheme 6.18 below.



Scheme 6.18. General scheme for photo-oxidation of polymers

In order to determine the photo-oxidative stability of PLA, PLA was processed in the torque rheometer as before with no additive and the pro-oxidant iron di*iso*nonyl dithiocarbamate (FeDNC) shown in Figure 6.68 above. It has been shown that iron complexes act as photo-prooxidants in a variety of polymers [118, 119]. Robinson Brothers Ltd manufactures novel photo-activators [120] such as Metone A (Figure 6.69) and it is hoped that this technology can also be applied to biodegradable polymers.

As described previously in chapter 2.2.9, the PLA samples were exposed two different intensities of ultra-violet light depending on the test. All samples used for tensile measurements were irradiated with simulated sunlight (290-400nm) at 30°C in the S/B cabinet and the samples monitored purely for molecular weight changes were irradiated at 70°C using the SEPAP cabinet (290-350nm). As described previously in chapter 2.2.9 the intensity of the ultra violet light in the SEPAP cabinet is higher compared to the S/B cabinet.

The results of these studies are shown in Figure 6.87 which compares the change in molecular weight with UV irradiation time of PLA samples containing no additive and samples containing pro-oxidant FeDNC at two different concentrations. The samples containing FeDNC appear to have an accelerated rate of molecular weight decrease from the very beginning of UV exposure. The rate appears dependent on the amount of FeDNC used- higher concentrations of FeDNC give a faster rate. Similar samples protected fom the UV light retained their original molecular weight after 168 hours of exposure. This finding is entirely consistent with that observed with olefinic polymers [121], indicating that PLA undergoes photolysis under the conditions of UV exposure. A similar molecular weight reduction was observed when PLA containing Metone A was irradiated. However, it appears that Metone A does not have a significant pro-oxidant effect on PLA (Figure 6.88)

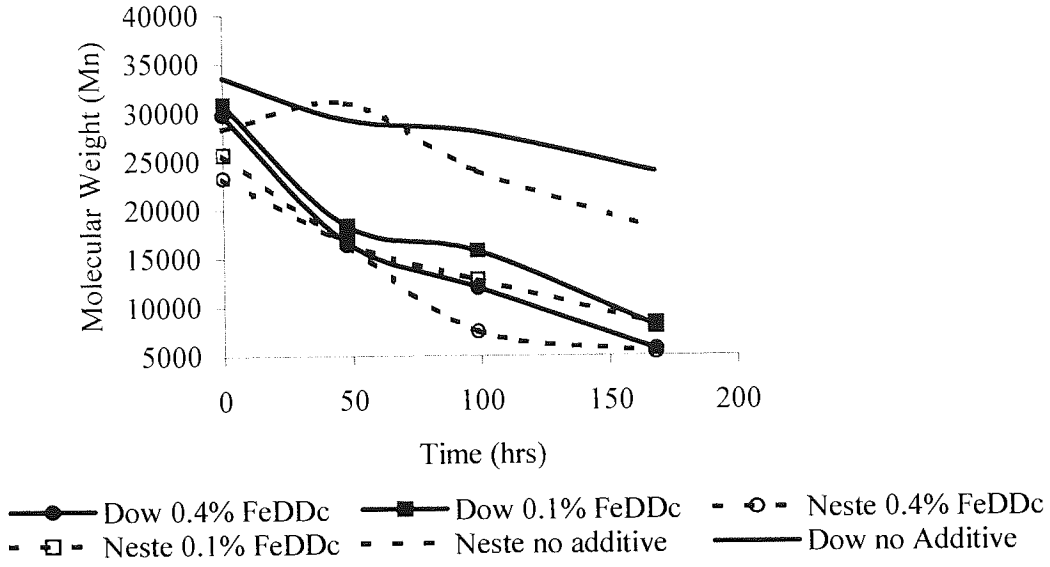


Figure 6.87. Effect of FeDNC on the molecular weight of UV irradiated PLA samples (310nm)

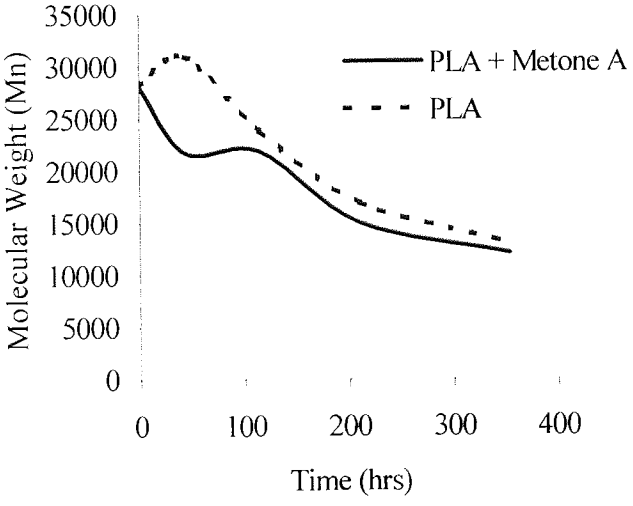


Figure 6.88. Effect of Metone A on the molecular weight of UV irradiated Neste PLA samples (310nm)

The above result was confirmed by irradiating plasticized PLA samples (17% EHT/Pent ethox-PDLA combination) containing Metone A with simulated sun light. In this case, one set of samples were exposed to the light while another similar set were covered in aluminium foil so the sample did not receive any UV light. The elongation at break was measured at regular intervals of time and the results plotted in Figure 6.89 below.

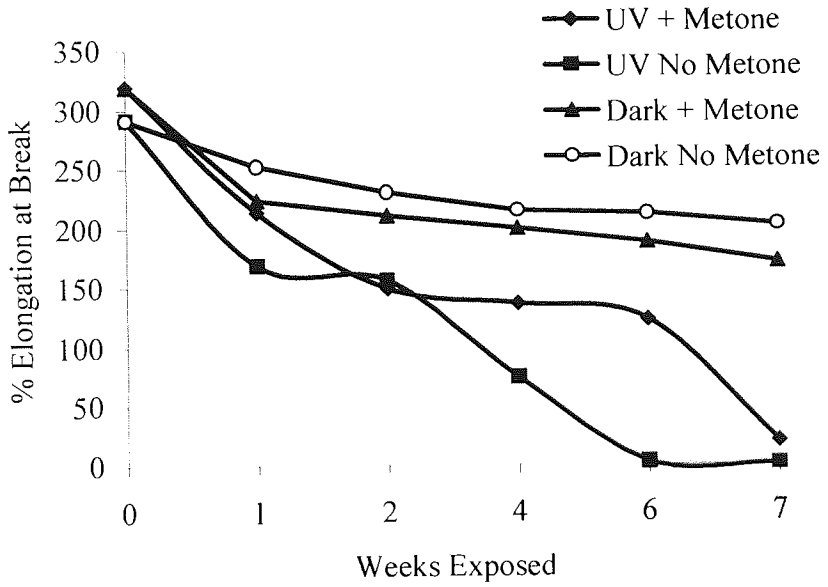


Figure 6.89. Effect of simulated sunlight on the physical properties of PLA plasticized with TMHT/pent ethox-PDLA

As expected the plasticized PLA samples (with or without Metone A) protected from UV light did not show any significant accelerated decrease in their elongation at break. However, the samples that were irradiated showed an apparent decrease in their elongation at break and an increase in their brittleness with increased exposure time to UV. Metone A did not have any significant effect on the plasticized PLA

degradation. The molecular weights of these samples were measured throughout the test and are shown in Table 6.31 below.

	Metone A		No Metone A	
Time (weeks)	**UV exposed**	**Dark**	**UV exposed**	**Dark**
0	28100	28100	28300	28300
1	29000	24600	24100	21700
2	34500	--	23000	--
4	26800	28400	19600	24000
6	26000	--	21700	--
9	21500	24000	17100	25100

Table 6.31. Number average molecular weight changes during simulated sun light exposure

Both PLA samples that were protected from the light did not show any significant reduction in their molecular weights, which is consistent with the elongation results. However, the irradiated films (with or without Metone A) did not show the kind of molecular weight reduction expected from the observed change in physical properties. It is therefore suggested that ultra-violet radiation (sunlight) may induce crystallisation, reducing the flexibility of the films but without significant chain scission observed with higher energy radiation above.

6.5 Conclusions

It appears that the degradation of PLA in an aqueous environment can be modified by the addition of plasticizers, the extent to which this occurs is related to the nature of the additive. Increasing the hydrophilic properties of the additive tends to increase

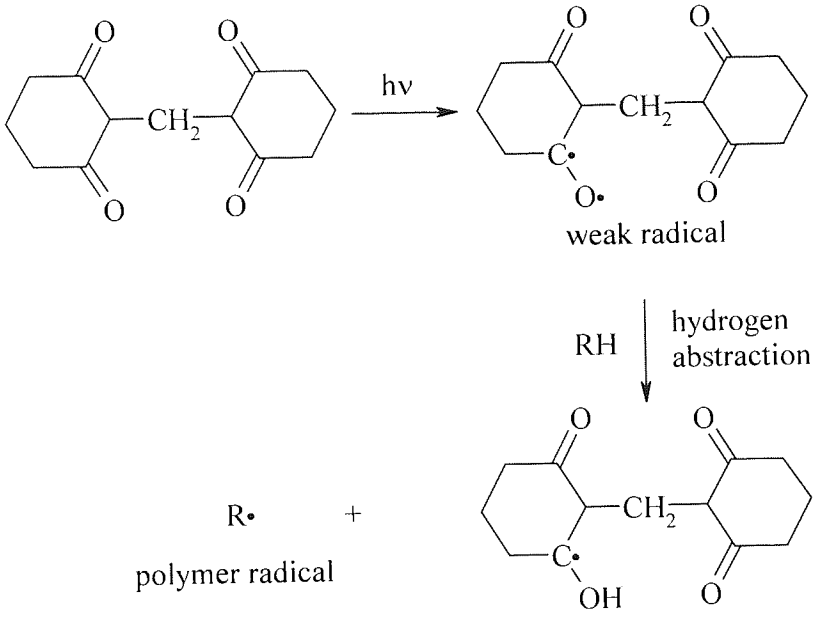
the degradation rate. In addition to the modification of the rate of hydrolysis, the rate of biodegradation could also be accelerated or retarded by judicious plasticizer choice. It is suspected that the hydrophobic/ hydrophilic nature of the additive hinders or promotes hydrolysis at the surface and subsequently it either hinders or promotes bacterial growth. The biodegradation of the PLA and PHB films appears to be related to the structure of the ester plasticizer. The straight chain esters (n-octyl) allow steady bio-assimilation whereas the branched chain esters (2-ethylhexyl and trimethylhexyl) almost completely suppress the degradation of the film. This fact strongly suggests that the microorganisms present in the compost are able to assimilate films containing the straight chain esters or the pure compound alone much more effectively than the branched analogues. As explained before it could be due to steric hindrance associated with the additive, producing a surface that is unfavourable to microorganisms.

Moderate heating of the plasticized films in air does not greatly change their physical properties. In addition, immersion in water at similar temperatures also does not reduce the properties of a film as much as when it is exposed to compost. It is therefore suggested that the PLA films are more resistant to water than wet compost, indicating either true biodegradation or hydrolysis followed by biodegradation promoted by the composting environment takes place.

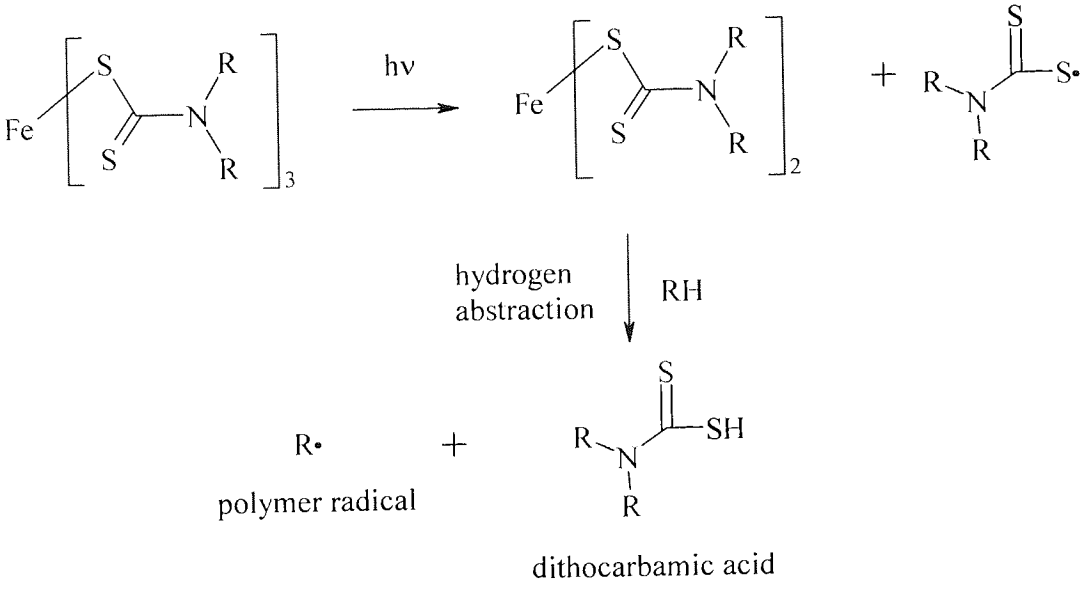
It is known that PLA is degraded thermally and this is easily shown by the DSC results. Many workers [40, 66, 69, 122] have carried out studies on the thermal degradation of PLA and PHB and it is agreed that both these materials degrade rapidly when processed at temperatures above their melting points. The generally accepted degradation pathway is chain scission and backbiting reactions forming low molecular weight volatile products. However, Gogolewski et al [40] found that after melt processing there appeared to be no increase in low molecular weight products, although the molecular weight of the PLA and PHB samples had decreased by 50-88%. In another paper Wachsen et al [69] state that, *"the degradation of PLA is*

mainly caused by an intramolecular transesterification reaction forming macrocycles of lactic acid. This reaction is reversible because recombination is also possible with the insertion of macrocycles into linear polyesters", and *"In a closed system with no evaporation of volatile degradation products (cyclic molecules) transesterification reactions take place constantly. In contrast, in an open system evaporation is possible and the rate of recombination is slow"*. The present work, in addition confirming the above general continual degradation and weight loss observed in the DSC (open system) a phenomenon of stable molecular weight with processing time was seen. Similar findings were reported by Grassie *et* al [68] using PHB. Therefore, it is suggested that during initial heating and melting in the processing equipment (closed system), chain scission occurs, leading to lead to a reduction in the molecular weight by approximately half. As the concentration of macrocycles and carboxylic and hydroxyl chain ends increases, recombination of the low molecular weight species begins and a steady state system with respect to molecular weight is attained. This effect is also seen in the MFI measurements of the processed samples (Figure 6.83) with the rapid rise in the MFI at short processing times followed by a more gradual increase.

In addition to thermolysis, PLA also appears to be significantly degraded by ultra-violet radiation. The samples exposed to UV light become brittle a long time before similar samples kept in the dark. In addition to accelerated embrittlement times, the molecular weight was also significantly reduced. This would suggest chain cleavage initiated by free radicals produced by ultraviolet radiation rather than thermal degradation as the samples protected from the light exhibited virtually no decrease in their molecular weights. The differences in the pro-oxidant potency between Metone A and FeDNC can be explained with reference to their normal mechanisms of action (Scheme 6.19and Scheme 6.20).



Scheme 6.19. Mechanism for polymer degradation initiated by Metone A



Scheme 6.20. General mechanism for polymer degradation initiated by Iron dithiocarbamates.

It is suspected that the radical formed in the photolysis of Metone A is too weak to abstract protons from the PLA polymer. Robinson Brothers Ltd [123] found that Metone A did not accelerate the degradation of polyolefins but was found to have a stabilising effect. The dithiocarbamoyl radical formed by the photo-oxidation of Fe^{III} to Fe^{II} is a much stronger radical and is capable of effectively extracting hydrogen from polyolefins [118].

It is proposed from this work that low concentrations of peroxide or oxidising species are present to some extent in the (Neste) PLA polymer but have an insignificant effect on the thermo-oxidative degradation compared to the effects caused by ultraviolet radiation and thermal depolymerisation.

6.6 Extraction of plasticizers from PLA films

PLA was blended with 17% TMHT (3,5,5-trimethylhexyl tartrate) in the torque rheometer at 180°C and the processed polymer was compression moulded into films. These films were used for the extraction studies. Two different extraction media were chosen- hexane and water. In all cases, a film (1g) containing plasticizer (0.17g) was extracted with 50 cm^3 of solvent at 50°C for 24 hours.

The infra red spectrum of TMHT shows a well defined ester absorbance at 1746.4cm^{-1} in hexane and has relatively little interference from other bands (Figure 6.90). This absorption peak was used to construct the standard calibration graph shown in chapter 2.6.1.

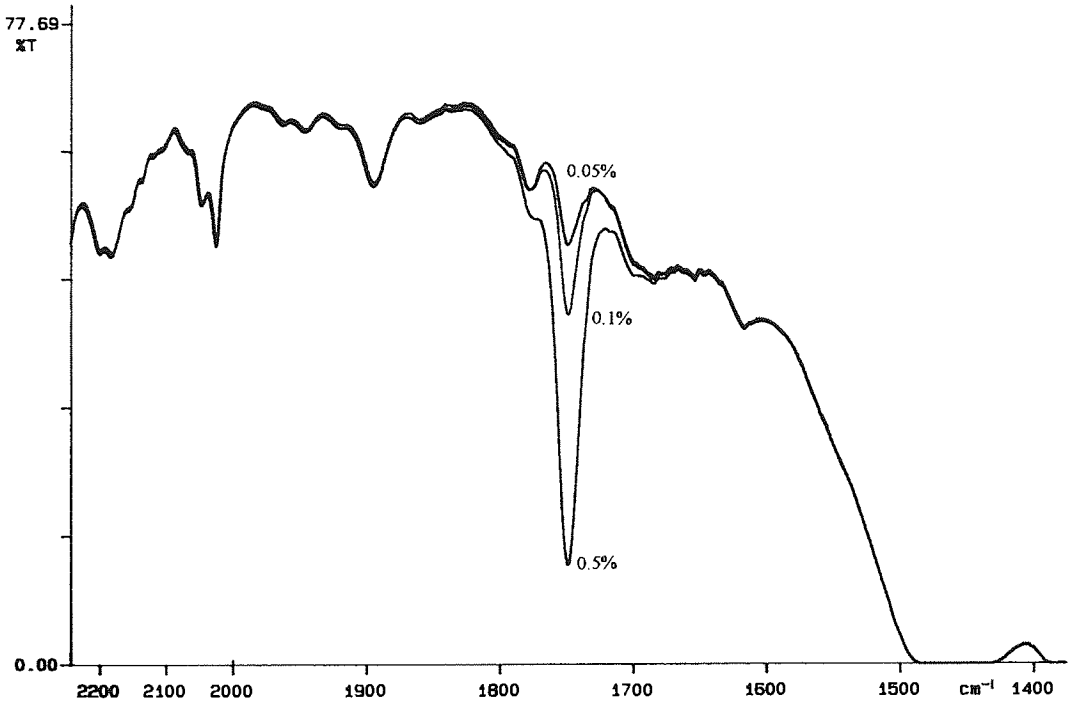


Figure 6.90. FTIR spectra of standard TMHT solutions

With the films that were extracted with water as described in chapter 2.6.3, any extracted TMHT was extracted out of the water with hexane and made upto 25 cm^3. The FTIR of this solution was taken and the concentration calculated from the calibration curve.

Figure 6.91 shows the change in the FTIR spectrum of TMHT extracted from the film using hexane at different time intervals. The height of the ester absorption peak at 1746.4cm^{-1} was measured and the results are tabulated below in Table 6.32

Figure 6.91. FTIR of hexane extract containing TMHT

Time (Hrs)	Peak Height	% TMHT	Weight/g
0	0.014	0	0
2	0.247	0.2	0.1
4	0.272	0.21	0.105
6	0.290	0.23	0.115
24	0.324	0.26	0.135

Theoretical amount of plasticizer in 1g of this film = 0.17g

Table 6.32. Exhaustive extraction of TMHT with hexane

It can be seen from Table 6.32 that, as expected, approximately 80% of the theoretical TMHT was extracted using hexane at 50°C.

When the experiment was repeated using water as the extracting solvent no ester absorbance bands greater than the background could be detected in the $25cm^3$ of hexane extract using the FTIR (Figure 6.92). Even after 24 hours of extraction, only 0.2 percent of TMHT could be detected. This was only possible after concentrating the hexane extract to $1/25^{th}$ of its original volume.

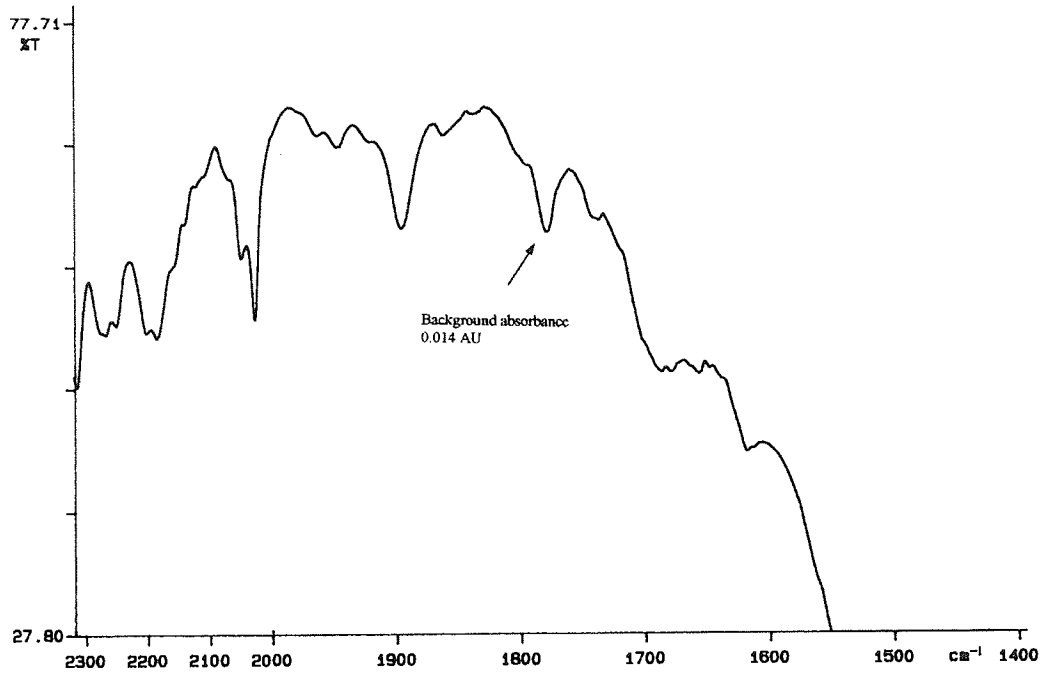


Figure 6.92. FTIR spectra of the original hexane solution from the aqueous extract (24 Hours)

6.7 Toxicological properties of the prepared plasticizers and copolymers assessed using cress seed germination

The method used to determine the toxicological effects of the additives are described in chapter 2.3.3. Polymer films containing plasticizers or plasticizers alone were composted using the bioreactor. At the end of the composting period, the compost was extracted with water. The compost was filtered from the water, and the filtrate (water and water soluble degradation products), was used as the nutrient medium for the growth of cress seeds. The number of seeds that germinated were counted and their mean root length was measured. These factors were then used as an indicator of the toxicity of the extracted products.

Table 6.33 lists the percentage germination and mean root length from the different compost samples. The table also includes the compost from the cellulose control reactor. It can clearly be seen from the table that the water soluble degradation products from the PLA and cellulose control reactors did not inhibit the growth of the seeds as the values are similar to the pure water medium. In contrast, the water sample containing the degradation products from the TMHT/pent ethox-PDLA plasticized film was found to completely inhibit the cress seed germination.

Water Extract from Compost sample	**Germination (%)**	**mean root length (mm)**
Pure water	97	25
original compost	88	15
blank compost (from bioreactor)	87	12
PLA control (no additive)	92	10
Cellulose	91	10
PLA containing TMHT (17%)	3	-
PLA containing TMHT / pent ethox-PDLA (8.5% each)	5	-

Table 6.33. Percentage germination of cress seeds from PLA compost samples

In another experiment, the pure plasticizers (esters and copolymers) were degraded in the bioreactor and the evolved carbon dioxide was monitored as described previously. At the end of the degradation period, the compost samples were treated as described above and the germination of the cress seeds was monitored. Table 6.34 represents the behaviour of the plasticizers.

Sample	Germination (%)	Mean root length (mm)
Pure water	94	16
cellulose	96	11
blank compost	98	10
PLA (no additive)	93	12
MeOPEG-co- PDLA	96	13
Pent ethox-co-PDLA	98	15
TMHT	-	-
EHT	-	-
IBT	90	5
NOT	92	8
NOC	85	7

Table 6.34. Percentage germination of cress seeds from additive compost samples

The above results are consistent with the results obtained in the bioreactor in terms of carbon dioxide evolution. The copolymers, NOT and NOC all produced carbon dioxide at a reasonable rate compared to cellulose, indicating smooth biodegradation. The degradation products from these materials did not inhibit the growth of the seeds. Although the IBT ester appeared not to biodegrade, the germination success of the seeds from its compost sample was adequate. This indicates that non-degraded IBT does not act as a germination inhibitor. Therefore, it is suggested that the n-octyl esters degrade to non-toxic products including carbon dioxide and water, whereas the 2-ethylhexyl and trimethylhexyl esters do not degrade significantly and the residual non-degraded ester suppresses seed growth. After 50 days, the organic material from the compost from the pure TMHT degradation test was recovered by extraction with toluene. The infrared spectrum of

this material was compared to the original TMHT and was found to be almost identical as shown in Figure 6.93.

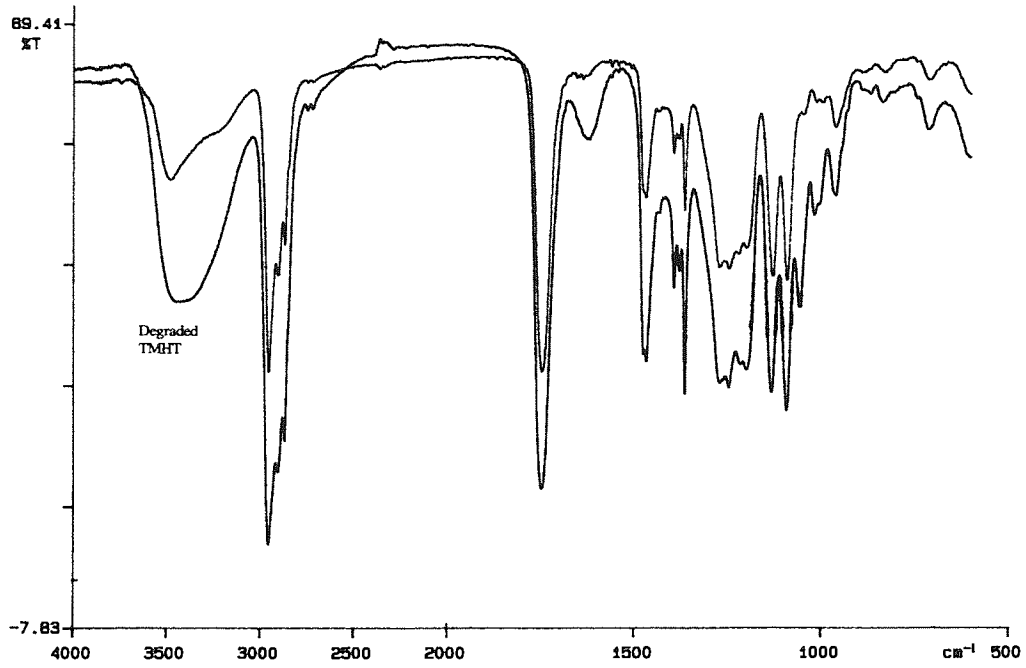


Figure 6.93. Comparison of TMHT to "degraded TMHT"

It has been shown that the pure esters and particularly the copolymer plasticizers produce more carbon dioxide than the background (control) compost strongly suggesting true bio-assimilation. It appears from the cress seed germination tests (Table 6.33 and Table 6.34) above, that all the prepared additives were non-toxic and did not prevent germination and growth of the cress seeds. The only exceptions were TMHT and EHT, which completely suppressed root growth. Although TMHT and EHT inhibited the growth of the seeds, the fact that the seeds exposed to EHT grew after washing with fresh water suggests that EHT and probably TMHT do not kill the seeds but merely suppressed the germination. It is thought that this is related to the hydrophobicity of the particular compound and is connected with the biodegradation results.

Chapter 7

Pilot Plant Production of Biodegradable Plasticizers and Small Scale Extrusion

The work in this chapter was carried out at Robinson Brothers Ltd. West Bromwich.

7.1 Preparation of di-2-ethylhexyl tartrate. (EHT)

As discussed previously the most promising ester plasticizer investigated to this point was TMHT in that the mechanical properties of PLA blended with TMHT were promising. However, some unresolved issues were encountered with its biodegradation and toxicity characteristics. In addition, the preparation of TMHT involves a catalytic hydrogenation stage and its larger scale preparation was not feasible within the time limits of this project. Therefore, EHT was used as an equivalent alternative.

The pilot plant reactions were essentially a direct scale up of the laboratory process. The reaction was carried out in a 50L Lampart glass lined jacketed reactor (Figure 7.94). The contents were heated with pressurised steam and cooled with water which circulated through the jacket. The contents of the reactor were stirred mechanically. It was possible to evacuate the vessel to approximately 2mm Hg and purge with nitrogen.

Tartaric acid (6.4 kg, 0.043 kgmol) and p-toluene sulfonic acid catalyst (150g, 0.79 mol) were charged to the reactor via the manway. The reactor was sealed and a vacuum was applied. 2-Ethylhexanol (11.2kg, 0.086 kgmol) and toluene (31 kg) were charged using a vacuum charge line. The vacuum was released with nitrogen and the reactor contents were heated to reflux. Reflux was continued until the evolution of water had ceased. When the reaction was considered complete, the contents was cooled to 40°C and a water wash was added to remove the catalyst and

excess tartaric acid. The lower aqueous layer was separated and then the washing process was repeated. The remaining toluene was removed by distillation, initially at atmospheric pressure then finally under vacuum. The product was discharged to drums.

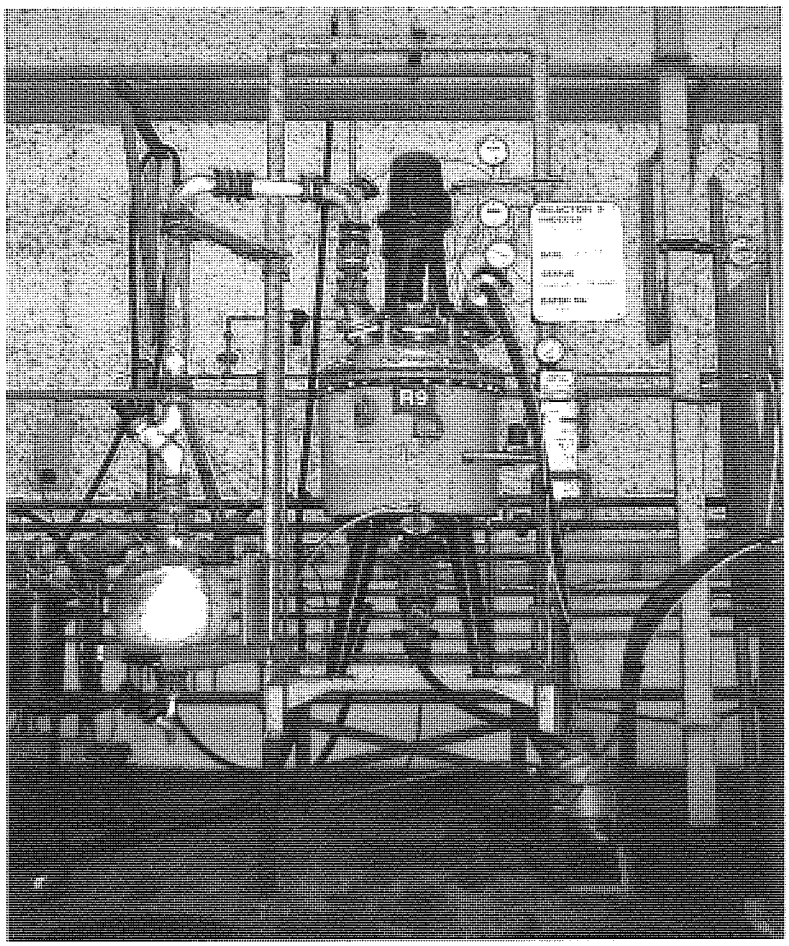


Figure 7.94. 50 Litre Pilot Plant Lampart reactor

The synthesis proceeded smoothly without problems. The yields from the two batches were as expected. The purities of the individual batches were determined using saponification and these were similar to, if not slightly better than the corresponding laboratory experiments. The quantities and yields from the two batches are shown in Table 7.35. The two batches were combined and retested.

Batch Number	Tartaric acid (Kgs)	2-ethylhexanol (Kgs)	Toluene (Kgs)	Weight product (Kgs)	Yield (%)	Purity (%)
010001	6.4	11.2	31	13.0	83	99.5
010002	6.4	11.2	31	14.4	92	97.8
Combined				27.4	-	98.7

Table 7.35. Weights and yields for the pilot plant preparation of EHT

7.2 Preparation of pentaerythritol ethoxylate-*co*-PDLA

The laboratory synthetic method was further refined for the pilot plant synthesis. The use of calcium hydride to dry the toluene solvent (although safe in principle) introduced too many safety issues for it to be used on a large scale. Therefore, an azeotropic distillation procedure was adopted as the preferred method for drying the solvent. The reaction was carried out in the 50 L Lampart reactor described above.

The quantities used for each reaction are shown in Table 7.36 for each experiment. The appropriate quantity of pentaerythritol ethoxylate (PP150™) was charged using the vacuum technique and followed by toluene through the same charge line. An additional 10 kgs of toluene was also charged. The vacuum was released with nitrogen and the contents were heated to reflux and the moisture was removed using azeotropic distillation. When the removal of the water was complete, the excess 10 kgs of toluene was distilled off to further dry the contents. The reactor contents were then cooled to room temperature and purged with nitrogen. The lactide and catalyst were charged via the manway. During this operation, a steady flow of nitrogen was maintained. The reactor manway was then sealed and the contents were heated to 100°C and maintained at this temperature for 6 hours. The toluene was then removed using vacuum up to a maximum liquid temperature of 105°C. The product was

cooled and the viscous copolymer discharged at 40°C. The number average molecular weight of the product was checked using GPC.

	Lactide, Kgs (moles)	**PP150, Kgs (moles)**	**$Sn(Oct)_2$, Kgs (moles)**	**Toluene (Kgs)**
Batch 1	6.5 (0.045)	3.6 (0.0045)	0.1 (0.247M)	40
Batch 2	3.0 (0.021)	1.7 (0.0021)	0.045 (0.11M)	30

Table 7.36. Weights of materials used for the pilot plant preparation of pent ethox-PDLA copolymer.

Two reactions were completed successfully. The first was a full size batch yielding 10 kgs of copolymer; the second was a part batch yielding 4.7 kgs. The GPC molecular weights were 1900 and 1800 and these agreed well this the material prepared in the laboratory

7.3 Synthesis of MeOPEG (750)-*co*-PDLA [1:10]

This compound was unfortunately not synthesised in the pilot plant (as planned) in the same equipment as the pentaerythritol copolymer above due to pressure from commercial products. However, two reactions were completed using a 6 litre Sovirel apparatus similar to the one described previously. The following quantities shown in Table 7.37 were used.

Reactant	Quantity
MeOPEG 750	1287.5g (1.72M)
Lactide	1250g (8.68M)
$Sn(Oct)_2$	20g (0.045M)
Toluene	5L

Table 7.37. Material used for the preparation of MeOPEG (750)-*co*-PDLA [1:10]

The experimental procedure was as close as practicable to that used in the pilot plant.

The reactions appeared to be complete as no lactide crystallised after standing over night at room temperature. The yields from the reactions were 2314 and 2474 grams respectively. Both products were isolated as viscous liquids with GPC molecular weights of 1200 and 1300 respectively, which were slightly lower than expected from the small-scale laboratory results (~1400). When these materials were cooled to less than 20° C, they became soft waxy solids.

7.4 Conclusions: synthesis

The scale up of the copolymer synthesis was successful. The pilot plant equipment provides a more convenient environment for working with and drying solvents on a scale of more than a few litres or tens of grams. The possible effect of moisture was observed in the molecular weights of the MeOPEG-PDLA copolymers prepared on the largest scale possible in the laboratory. The copolymer was formed but the molecular weights were lower than expected. This was thought to be due to some excess moisture that was not removed as efficiently in the laboratory process.

7.5 Extrusion

7.5.1 Polymer master batches

All work described in this section was carried out using PLA supplied by Dow Polymers LLC. The DSC of the Dow PLA is shown in Figure 7.95

35% by weight polymer master batches were prepared using the Prism 16 inch Eurolab twin screw extruder described previously. The plasticizer systems chosen for this work were Pent ethox-co-PDLA 1:10 / EHT and MeOPEG(750)-co-PDLA (1:5) / EHT blends. The EHT and the copolymer were blended in equal proportions before processing.

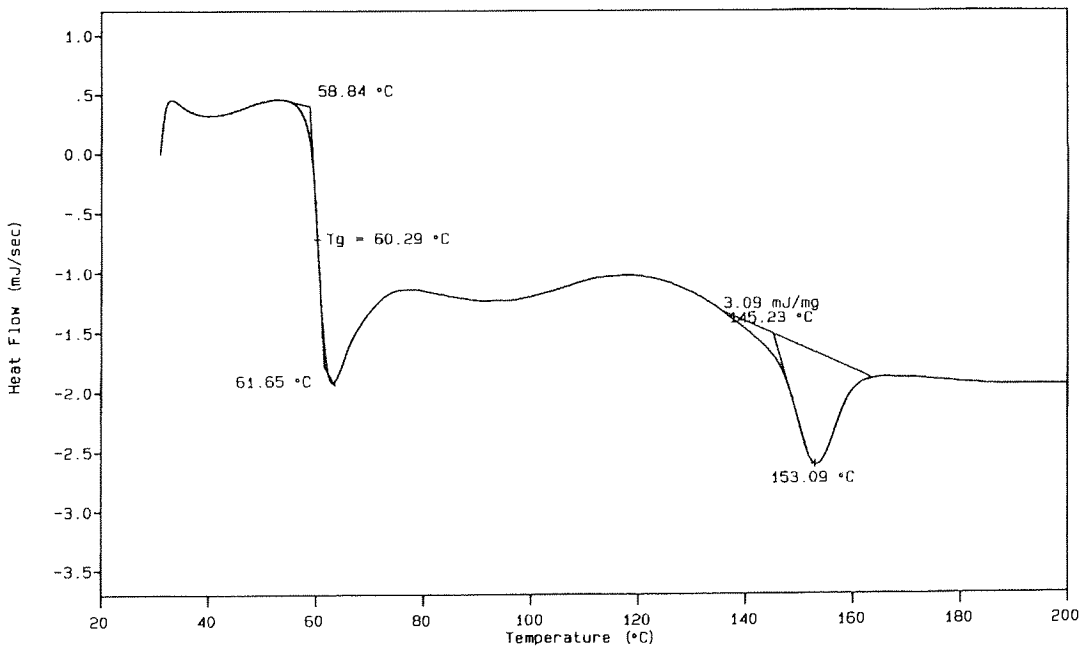


Figure 7.95. DSC of Dow PLA

The copolymer/ ester blend was added using a peristaltic pump at the start of the melting stage to allow time for complete mixing. The polymer was extruded as a

continuous strand and cooled in a water bath. The strand was passed through an air drier and cut into chips. The schematic diagram Figure 7.96 below shows the important system information of the extruder. This information was generated by the in built software.

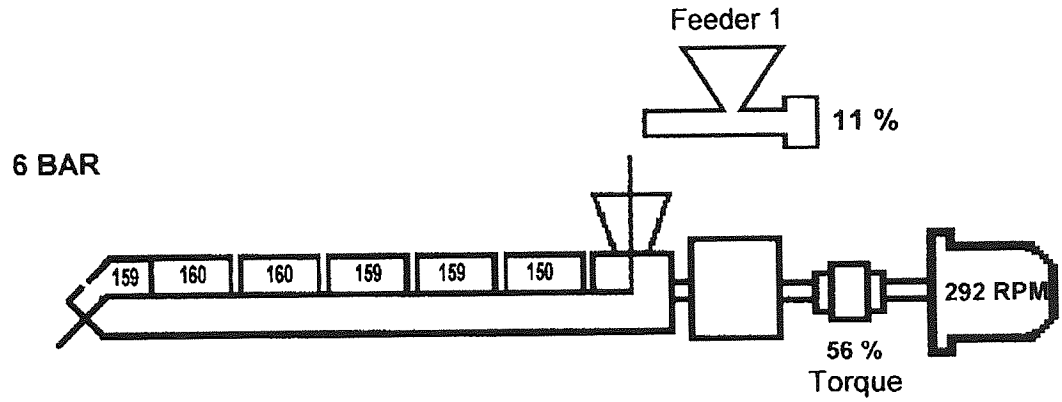


Figure 7.96. Typical system information during processing on the Eurolab 16 inch twin screw extruder

7.6 Preparation of plasticized PLA film from the polymer Master Batch

The 35% master batch was mixed with an equal weight of virgin Dow PLA to give a 17.5% by weight plasticizer and polymer blend. This was extruded using similar conditions to those described previously. The molten polymer was passed through a die designed for sheet film. On this particular equipment, the thickness of the film was controlled by the flow rate of the polymer through the die and haul off speed. Films with a consistent thickness of 100μ to 300μ (0.1-0.3 mm) could be obtained. DSC measurements were made on the plasticized and unplasticized films and these are shown in Figure 7.97 below.

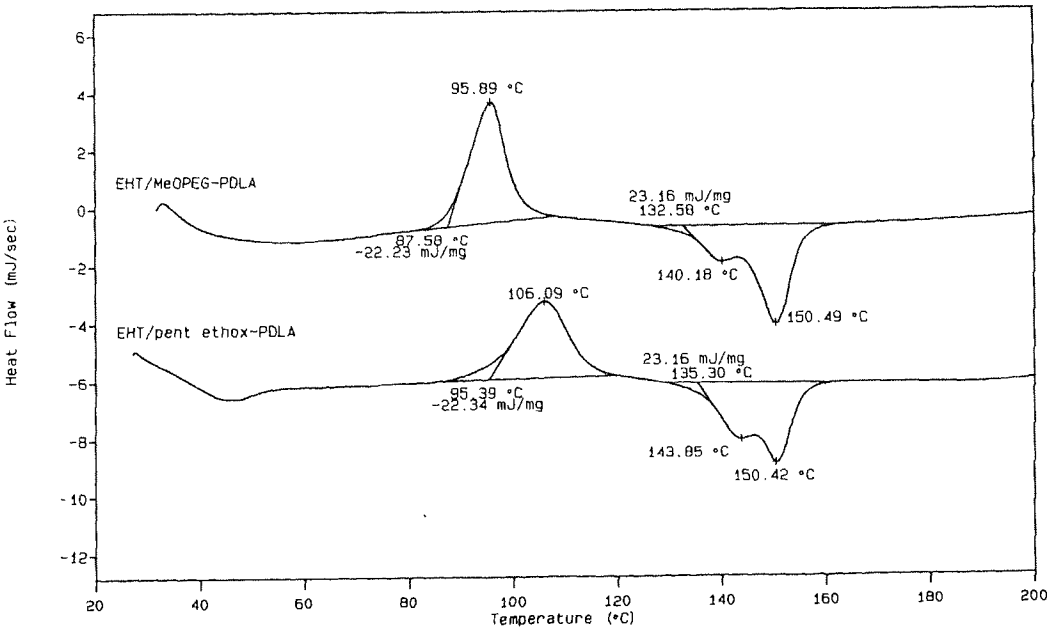


Figure 7.97. DSC of plasticized extruded Dow PLA

The prepared films were completely clear and very flexible. Tensile test specimens were cut from the film (flow direction) and the elongation at break and tensile strengths were measured. The mechanical properties of the extruded film were very similar to the compression moulded film (chapter 5). The samples were retested after 3, 7 and 15 weeks and the results are shown in Table 7.38 and Table 7.39 below

Additives	Elongation at Break (%)	Tensile Strength (Mpa)
Pent ethox-co-PDLA 1:10 / EHT	334	40
MeOPEG(750)-co-PDLA (1:5) / EHT	390	35

Table 7.38. Initial mechanical properties of PLA sheet films

Additives	Time (W)	Elongation at Break (%)	Tensile Strength (Mpa)
Pent ethox-co-PDLA 1:10 / EHT	3	320	45.0
	7	284	39.5
	15	310	44.4
MeOPEG(750)-co-PDLA (1:5) / EHT	3	305	42.0
	7	290	41.6
	15	284	41.7

Table 7.39. Mechanical properties of PLA sheet films after 3, 7 and 15 weeks

The thickness of the particular film had negligible effect on the elongation at break results for either film.

7.7 Conclusions

The scale up of these materials, particularly the PDLA copolymers was successful and the results strongly suggest that further scale up to much larger volumes is possible.

The formation of sheet film with excellent physical characteristics was possible using proprietary polymer processing equipment and techniques. The results have shown that these compounds are suitable for use in conventional equipment and produce a plasticized polymer with properties that could be used for a wide range of items.

Comparison of this chapter (where commercial scale extrusion was carried out using Dow PLA) with chapter 5 (when the majority of the evaluations were carried out using Neste PLA), it can be seen that the improvement in the physical properties of both films are very similar using the novel plasticizing systems. However, it can be mentioned that the virgin polymers from these different suppliers are not identical. The differences between them are discussed in the appendix 10.

General Conclusions

The increasingly damaging effects of stable polymers on the environment are of great concern to governments especially as the opportunities for sending waste to landfill sites are becoming increasingly limited. Various solutions to these environmental problems are under continuous review but with few exceptions. In many cases the cost of recycling and reuse is orders of magnitude higher than the use of virgin polymers such as polyethylene. A solution to the problem is the use of biodegradable polymers that degrade under landfill conditions to carbon dioxide and water. Biodegradable polymers based on poly(3-hydroxybutyrate) and poly(3-hydroxybutyrate-*co*-valerate) have been available for some years but the scope of their application in the market place is restricted by their expense and limited physical properties, such as low elongation at break. This renders them unsuitable for production of packaging films. Other polymers such as poly(ε-caprolactone) are much cheaper to produce, readily biodegradable but whereas these films have a high elongation at break their tensile properties are unsuitable which results from low melting points and glass transition temperatures. Recently Dow polymers have begun production of poly(lactic acid) but like PHB and PHBV the polymer has a high tensile strength and a low elongation at break (<5%). There is a desperate need therefore to improve the properties of existing biodegradable polymers so that their use in a wide variety of applications can be exploited.

A thorough literature survey indicated that various methods have been used in an attempt to modify the properties of PHB. These included the use of plasticizers and blending with other polymers and acheived varying degrees of success. A more sophisticated approach (but more expensive) is to make a copolymer that combines the desirable properties from two or more polymers. This technique is widely used in the medical sector for absorbable stitches.

The aim of this study was to produce novel biodegradable plasticizers in order to modify the physical and mechanical properties of PHB and poly(lactic acid) [PLA] so that they can be used for a wider variety of applications including packaging. Thirteen carboxylic esters were prepared using a variety of carboxylic acid and alcohol combinations by conventional acid catalysed esterification (Table 3.3). The products were characterised using NMR and titrimetric techniques. The carboxylic acids that were chosen for this work occur naturally and this was expected to produce products with low toxicities and that were potentially biodegradable

In order to achieve effective plasticization and compatibility, attention was turned to the design and characterisation of copolymer plasticizers for blending with PHB and PLA to improve the elongation at break without seriously deteriorating their tensile strengths. It was found that PLA copolymers could be prepared by initiation of lactide with R-OH using stannous octanoate as a catalyst. The polymers could be prepared at a moderate temperature with very narrow polydispersities. This was thought to be due to the homogeneous reaction system used. The molecular weights of the copolymers were consistent with the lactide: R-OH mole ratio but it was found that increasing the catalyst concentration tended to lower the molecular weight. This appeared to suggest that other initiating species were present in the catalyst. However, at high concentration the initiation appeared less efficient leading to a proportionally lower molecular wight. The proton NMR of the prepared copolymers were consistent with spectra presented in the literature. However, ^{13}C (S.P.E.E.D) resolved new peaks in the carbonyl region that could be attributed to the carbonyl adjacent to the ethylene oxide of the poly(ethylene glycol) block (Figure 3.35).

The properties (water solubility, solid or liquid etc) of these copolymers could be adjusted by selecting appropriate initiators or adjustment of the lactide: MeOPEG-OH mole ratios (appendix 4). A novel star copolymer was also prepared from an ethoxylated pentaerythritol (PP150) [Figure 3.39].

As well as a variety of MeOPEG-PDLA copolymers a small number of PCL-PLA copolymers were prepared (appendix 2) by the sequential polymerisation of caprolactone then lactide. The evidence for copolymer formation was observed in the NMR and number average molecular weight measurements. The sequential polymerisation of two monomers indicated that the polymerisation (at least to some extent) had living characteristics.

The prepared ester plasticizers were found to have only a marginal effect on the mechanical properties of PHB (Table 4.13). The intrinsic chain mobility and crystallinity of PHB was thought to have a dominant effect on the polymer properties. The low glass transition temperature (~ 0°C) allowed rapid crystallisation at room temperature. Addition of plasticizers further lowered the Tg and in effect aids crystallisation. Therefore, modification of the Tg to a higher temperature (>20°C) might produce better results.

Evaluation of blends of PHB with other conventional polymers like linear low density polyethylene (LLDPE), poly(ethylene)-co-vinyl acetate (EVA), poly(ethylene)-co-carbon monoxide (ECO) and PCL was carried out with limited success. In all cases it was found that phase separation took place with the individual compounds in the blend resulting in inferior mechanical properties. However, valuable information was acquired towards the degradation and physical properties of these blends. It was found that at lower concentrations of PCL the blend shared the properties of PHB but at higher concentrations (>60%) they behaved like PCL.

PHB is a readily biodegradable polymer and it was found that the addition of the ester plasticizers significantly changed the biodegradation rate in terms of the carbon dioxide evolution. It was found that the rate of degradation was related to the structure of the plasticizers alkyl chain and not the carboxylic acid. It appeared that the isobutyl ester esters increased the biodegradation rate, whereas higher alkyl ester

esters slowed the degradation. However, the overall degradation rate of PHB was not inhibited to any significant extent in the presence of plasticizers.
Further work on PHB was then discontinued due to the unavailability of PHB from the supplier. However, the results obtained from PHB were utilised for comparison purposes in the subsequent study on poly(lactic acid).

The major part of this programme was mainly focused on poly(lactic acid) [PLA] due to its availability and versatility of its applications. Virgin PLA (obtained from Neste) is a stiff but strong polymer prepared from L-lactide. This produces a polymer with a stereo-regular structure. This regular structure permits it to form a semi-crystalline material. However, because of its short (C3) chain, PLA has a much higher glass transition temperature than PHB. Consequently, it was found that when the molten polymer was quenched from the melt it was predominantly amorphous and more or less remained in this state at room temperature. The quenched polymer was found to be approximately 18% crystalline and this increased to 46% during heating and reached 66.5% after prolonged annealing at 100°C. The addition of plasticizing additives did not change the percentage crystallinity significantly, however the ester plasticizers did lower the glass transition and the temperature at which crystallisation occurred. During this work, a sample of NatureWorks PLA from Dow was received. This polymer was found to have completely different thermal properties than the Neste PLA. The virgin polymer was almost completely amorphous and did not crystallise during heating. Addition of plasticizers allowed some moderate thermal crystallisation to occur. Stretching the polymer films produced a similar thermal effect as the addition of plasticizers did. It was therefore concluded that the Dow PLA had a structure that was incapable of crystallisation under normal/ elevated temperatures. Addition of plasticizer or stretching the polymer produced a matrix with a regular (crystalline) structure or capable obtaining one during heating.

All of the prepared esters had a significant effect on the mechanical properties of the PLA films when blended at 17%w/w. The elongation at break was increased to around 300% and the tensile strengths were reduced to approximately 35Mpa. The effectiveness of the plasticizers appeared to be related to the presence of hydroxyl groups in the ester. Blending of the prepared copolymers into PLA also had a dramatic effect on the mechanical properties. Evidence from model compound studies suggested that their effects were related to their shape.

Biodegradation studies on plasticized PLA films indicated that the branched chain esters suppressed the carbon dioxide evolution and straight chain esters increased the carbon dioxide evolution (Table 6.30 and Figure 6.79). Biodegradation tests on the pure esters showed that the esters prepared from straight chain alcohols were much more susceptible to degradation than the branched chain esters (Figure 6.80). Both pent ethox-PDLA and MeOPEG 750-PDLA (1:5) were found to be readily degradable (Figure 6.81).

The plasticized PLA films containing the hydrophobic additives TMHT and pent ethox-PDLA retained their flexibility over 108 days when exposed to water at 50°C. The weight lost from these films (17% and 22% respectively) was made up of a significant proportion of low molecular weight PLA in addition to some extracted plasticizer. The film containing the hydrophilic copolymer MeOPEG 750-PDLA (1:5) lost 35% of its original weight and quickly became brittle (Table 6.29). This suggested that the additive was completely extracted coupled with polymer hydrolysis. A comparison of the biodegradation and hydrolysis experiments has shown that the embrittlement of the film (plasticised and unplasticized) is much quicker in compost than in water at similar temperatures. This finding strongly suggests that PLA film either exclusively biodegrades or hydrolyses with biodegradation.

It is widely reported and accepted that PLA undergoes thermal degradation at temperatures approaching or above its melting point. Many studies have focused on the thermal degradation characteristics of samples heated in open systems i.e. DSC. The present study has briefly investigated the behaviour of PLA samples under manufacturing conditions i.e. high temperature mechanical processing or extrusion. Under these conditions it was found that PLA underwent a rapid molecular weight reduction to approximately half of it original value but on extended processing only a limited further reduction was observed (Figure 6.82). The addition of the commercial antioxidant Iganox 1076 did not affect this molecular weight reduction, which indicates that PLA does not undergo significant thermo-oxidative degradation as is common with polyolefins.

In many applications such as crop protection film, it is desirable for the polymer to degrade after a specific exposure time in the presence of sunlight. With conventional systems the polymer film disintegrates into small fragments which persist in the soil. If a similar system could be developed for polymers like PLA, then the photo-degraded pieces would be biodegraded even more quickly. This work has shown that PLA undergoes photo-degradation under conditions of UV exposure. Conventional photo-prooxidants like iron salts of dithiocarbamic acid have been found to accellerate the photo degradation of PLA. However, another photo activator, Metone A (Figure 6.69) did not seem to have any effect on the photo-degradation of PLA. These results were explained by the relative reactivity of the dithiocarbamoyl radicals compared to the Metone A radicals formed from ultra violet irradiation of the additives.

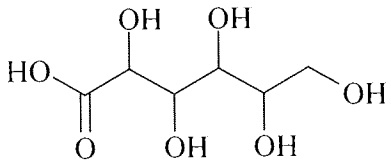
The most promising plasticizers, di(2-ethylhexyl) tartrate (EHT) and pent ethox-PDLA were prepared on a pilot plant scale (~20kg) and MeOPEG (750)-PDLA 1:5 on a large laboratory scale (~2kg). Scale up presented no significant challenges from a synthetic point of view even though the polymerisation system is sensitive to

moisture and impurities. PLA was processed in with equal proportions of EHT/ MeOPEG-PDLA or EHT/ pent ethox-PDLA. Small scale extrusion was carried using a bench top extruder from Thermo-Prism. Initially, several kilograms of a 35%w/w master batch was prepared without problem and this was further diluted with virgin polymer and extruded to produce blends containing the desired 17.5%w/w plasticizer. The plasticized extrudate was blown or extruded into film without any special precautions or techniques. The mechanical properties of all the films were found to be very similar to the compression moulded films prepared in the laboratory.

Overall, this work has shown that the mechanical properties of PHB were difficult to modify by simple plasticizer addition but the added plasticizer did not appear to seriously affect the biodegradation time. Conversely the mechanical properties of PLA were able to be modified to a large extent by the ester plasticizers and copolymers and their effectiveness appeared to be connected with the presence of hydroxyl groups and shape respectively. The present work clearly shows that it may be possible to modify the mechanical properties of PLA for wider applications including packaging by a judicious choice of commercially viable plasticizers and copolymers. These may be used either individually or in combination depending on the application.

Suggestions for Further Work

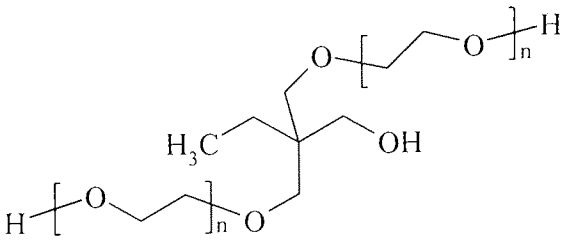
The present study has shown that the tartrate esters act as more effective plasticizers compared to the structurally similar succinate and malate esters. Further work could be directed towards the synthesis of carboxylic esters with more free hydroxyl groups. A starting material for one such compound could be gluconic acid.



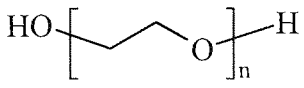
Gluconic acid

Another approach could be the preparation of tartrate or citrate esters using less than the theoretical amount of alcohol required for complete esterification. This would leave some proportion of free carboxylic acid groups free for hydrogen bonding.

It appeared that the plasticizing effectiveness of a particular copolymer was related to its structure and shape. Therefore, a further series of copolymers should be prepared to investigate this. Suggested initiators for these syntheses are: ethoxylated trimethylolpropane derivatives and poly(ethylene glycol) 750.



Trimethylolpropane ethoxylate



Poly(ethylene glycol)

The blends of PLA with conventional polymers e.g. ECO, LLDPE and PCL was not successful due to phase separation, however as an alternative to blending with costly plasticizers, an attempt may be made at blending PLA with other semi-crystalline polymers like nylon 6 (or 6,6) in the presence of a compatibiliser in order to obtain a homogeneous blend.

The mechanisms of biodegradation/ hydrolytic degradation and photo-degradation have not been fully investigated. It is still uncertain whether PLA is degraded by microorganisms or predominantly by hydrolysis. Further work may be directed to establish the mechanism of degradation of PLA.

Although stannous octanoate is considered safe as a food additive by the Food and Drug Administration (FDA) it is suspected of possessing some toxicity [124]. It would be beneficial if the preparation of copolymers of PLA could be catalysed by more benign substances. There are reports that lithium chloride [124] and zinc compounds [125, 126] can act as catalysts for ring opening polymerisations.

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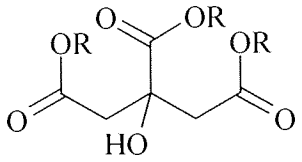
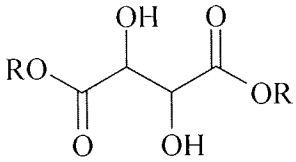
Appendix

Appendix 1. Structures of prepared esters used in this study (chapter 3.1.2)

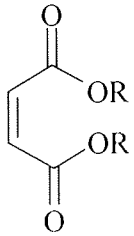
Citrate



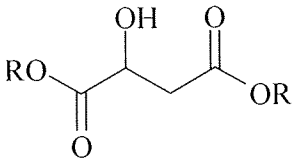
Tartrate



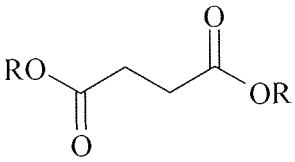
Maleate



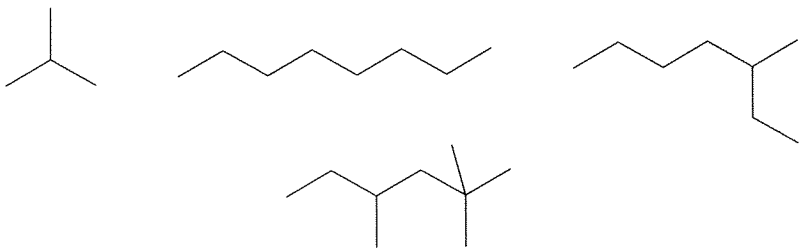
Malate



Succinate

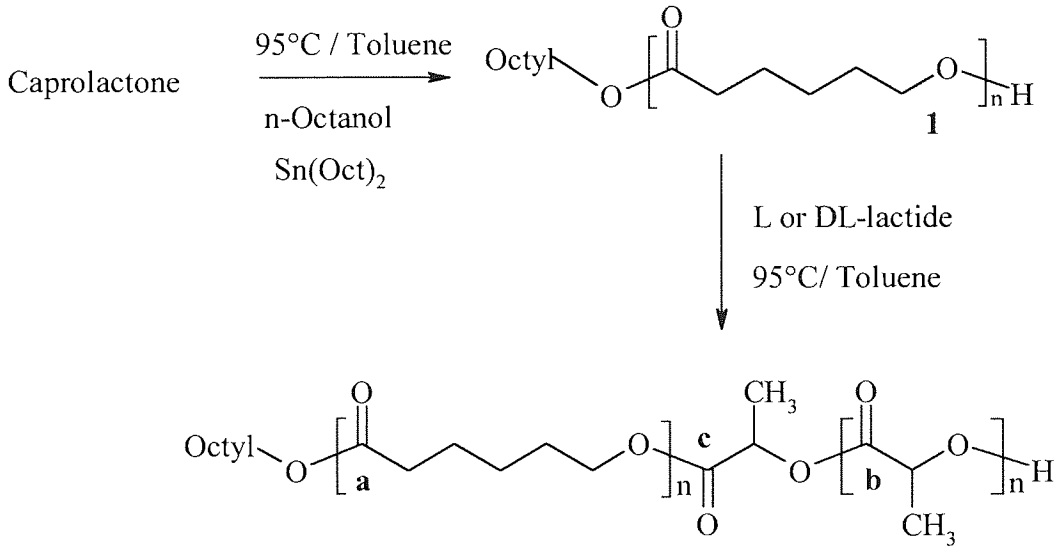


Where R= *iso*butyl, n-octyl, 2-ethylhexyl or 3,5,5-trimethylhexyl:-



Appendix 2 Synthesis of poly(ε-caprolactone)-*block*- poly(lactic acid) copolymers (PCL-PLA) [chapter 3.2.2]

PCL-PLA random and block copolymers have been widely reported in the literature [127]. However, the techniques that are used generally utilise air and/or moisture sensitive reagent such as aluminium alkoxides [128]. In this work, attempts have been made to synthesise diblock copolymers of controlled molecular weight using the techniques and experimental methods developed for the MeOPEG-PLA copolymers. It is known that ε-caprolactone is less reactive than lactide [129], this means that a poly (lactic acid) macro-initiator is not sufficiently reactive to initiate the polymerisation of ε-caprolactone [130,131,132]. To overcome this problem ε-caprolactone was initiated first using a suitable chain control agent (n-octanol) to limit the block length of the poly(ε-caprolactone) segment. After a suitable period of time, an appropriate amount of L or DL-lactide was added to give the desired molecular weight copolymer. The polymer was then precipitated into diethyl ether, which was decanted and replaced with fresh diethyl ether. The residual diethyl ether was removed using vacuum. In these experiments copolymers with approximately equal block lengths and a molecular weight (Mn) in the region of 10000 were initially aimed for using Scheme A.21 below.



Scheme A.21. Synthesis of poly(ε-caprolactone)-*block*- PLA copolymers

Appendix 2.1 Results

Several successful syntheses were achieved giving copolymers with a variety of molecular weights and block lengths (Table A.40). However, the overall molecular weight was difficult to control. It was found that it was relatively easy to complete the ε-caprolactone polymerisation, but the amount of PLA that could be incorporated was variable, resulting in different length PLA blocks. The incompleteness of the PLA polymerisation manifested itself as crystallisation of the lactide monomer when the reaction mixture was cooled to sub-ambient temperatures (-5-10°C). The lactide was recovered by filtration. The proportion of ε-caprolactone incorporated into the final polymer was modified to some extent by using a short reaction time for ε-caprolactone (T_{CL}) and adding the lactide before the ε-caprolactone polymerisation was complete.

CL:Lactyl: OctOH Feed ratio	GPC Mn of PCL Block	GPC Mn after lactide Add^{n}	θ Mn copolymer	^{1}H NMR calc^{d} CL:Lactyl : OctOH ratio	NMR Calc^{d} Molecular Weight
10: 15: 0.22	-	10800	10200	10: 13:0.24	8500
10: 15: 1	1600	2500	2500	10: 6.5: 0.5	3100
10: 20: 0.28	-	6500	9300	10: 17: 0.35	6600
10: 20: 0.28	2200	4750	9300	10: 3: 0.24	5600

Table A.40. Prepared n-octyl-PCL-PLA copolymers.

CL: OctOH Feed ratio	Expected molecular weight	GPC (Mn)	Calculated ^{1}H NMR DP	NMR molecular weight
40:1	4600	4500	63	7200

Table A.41. Molecular weight of a n-OctOH initiated caprolactone polymerisation

Appendix 2.2 NMR Analysis

The NMR spectra showed all the appropriate peaks consistent with the required structure. Initiation with n-octanol was successful and this can be seen in the proton NMR in Figure A.98 and Table A.41. The protons associated with CH_3 the octyl group can be seen at 0.86 and the CH_2OH (1) end group of PCL at 3.6 p.p.m is also clearly visible. These findings are similar in many respects to those of Veld et al [129]. After copolymerisaton with lactide the CH_2OH (PCL) [1] peak was absent, strongly

suggesting the formation of a copolymer. The carbonyl region of the ^{13}C NMR (Figure A.99) spectra shows similar peaks to those that are observed in the MeOPEG-PLA copolymer spectra. Typical full NMR spectra are shown in Figure A.100 and Figure A.101.

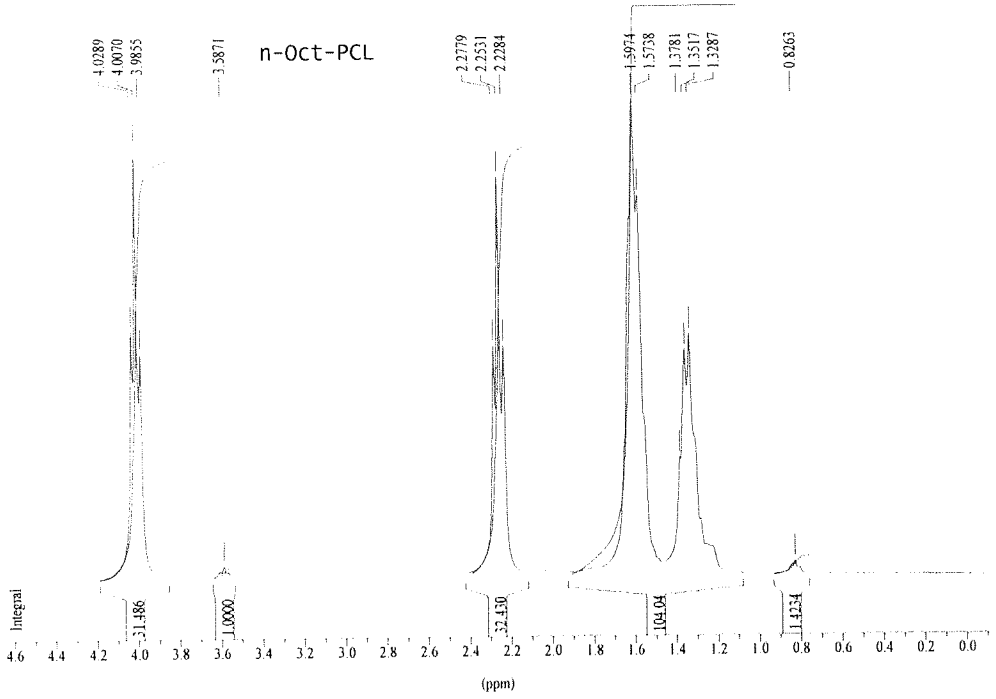


Figure A.98. n-Octyl-PCL

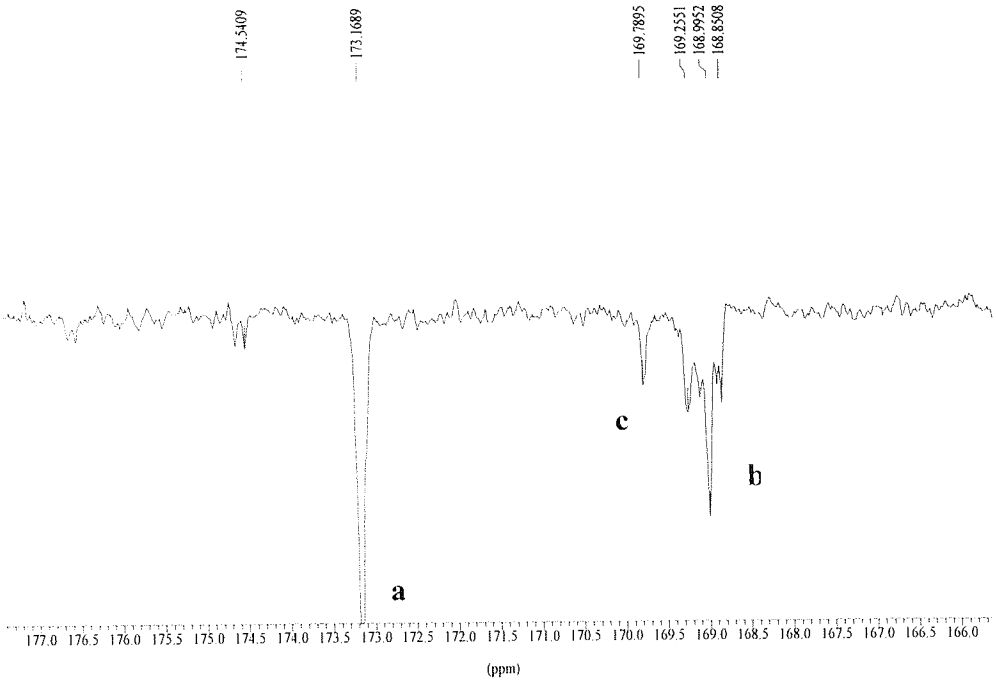


Figure A.99. n-Octyl-PCL-PLLA (Mn ~ 2500) [carbonyl region]

Carbonyl carbon	Chemical shift (p.p.m)	Assignment
a	173.1	Caprolactone C=O
b	169.3	PLA C=O
c	169.8	PLA-PCL junction

Table A.42. Chemical shifts for n-octyl-PCL-PLLA copolymer (carbonyl region)

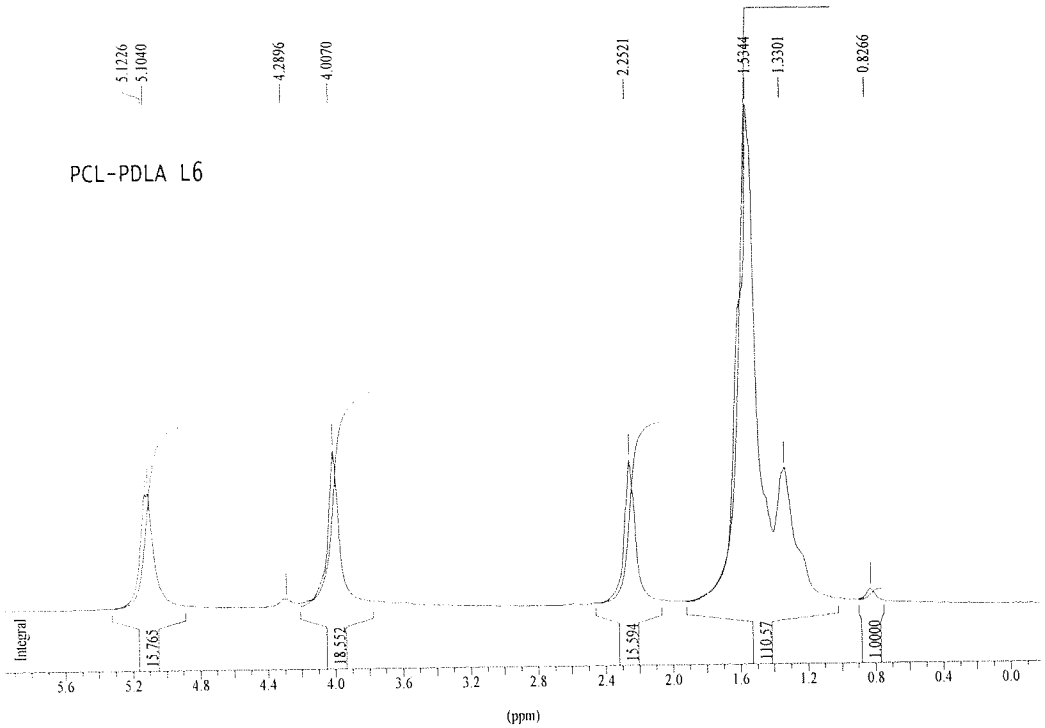


Figure A.100. ^{1}H NMR of a typical PCL-PDLA copolymer

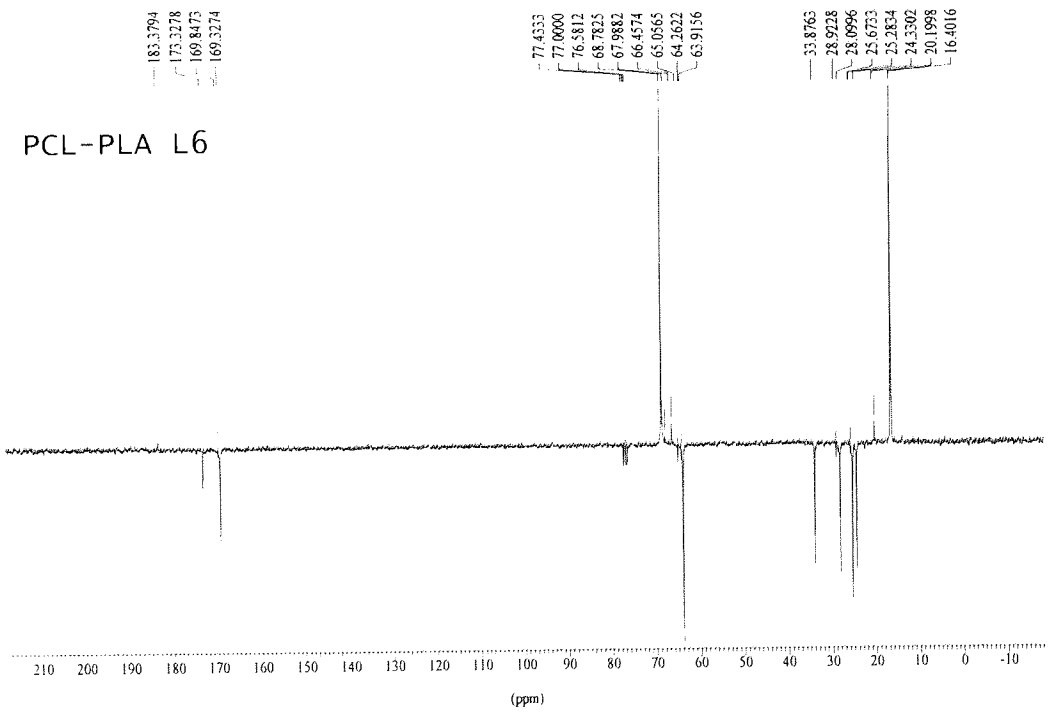


Figure A.101. ^{13}C NMR of a PCL-PDLA copolymer

Appendix 2.3 DSC Analysis

This technique was used to determine the effect of the molecular weight on the thermal properties of the copolymer and also the miscibility of the individual PLA and PCL blocks.

Differences were observed in the thermal properties of the octyl-PCL-PDLA copolymers depending on the length of the respective blocks. Because of its regular chain structure and flexible monomer unit poly(ε-caprolactone) is a crystalline material and it has a very low glass transition temperature (Tg ~ -60°C) and melting point (~ 60°C). Consequently, thermal analysis usually only detects the transition associated with the melting point and possibly the glass transition. This is because crystallisation is able to occur during rapid cooling (quenching).

The Synthesised PCL-PLA copolymers (Figure A.102) showed a variety of thermal transitions depending on the exact polymer composition. It can be seen clearly that the PLLA copolymer (Mn 4750) exhibits phase separation, whereas the copolymer (Mn 6500) with a short PLLA block shows only a double melting transition corresponding to PCL. However, the PDLA copolymer (Mn 10800) has a crystallisation exotherm at 19°C and a melting transition at 48°C corresponding to melting point of PCL.

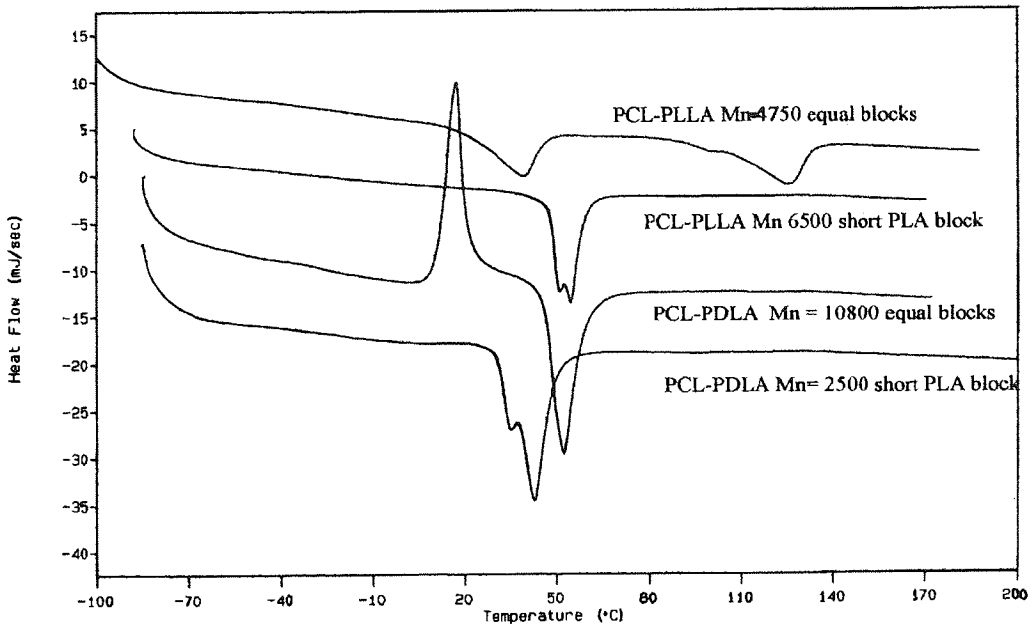


Figure A.102. DSC of n-octyl PCL-PLA copolymers

To assess the melting characteristics of the individual low molecular weight PCL and PLLA blocks, they were synthesised independently using n-octanol as the initiator for PCL and n-butanol for PLLA following the standard method described previously. These initiators were chosen to minimise any effects of the alkyl end group.

Copolymer	GPC Molecular Weight
n-octyl PCL	4500
n-butyl PLLA	5000

Table A.43. Alkyl terminated PCL and PLLA homo-polymers

The DSC thermograms of the prepared homo-polymers are shown in Figure A.103 and Figure A.104 below.

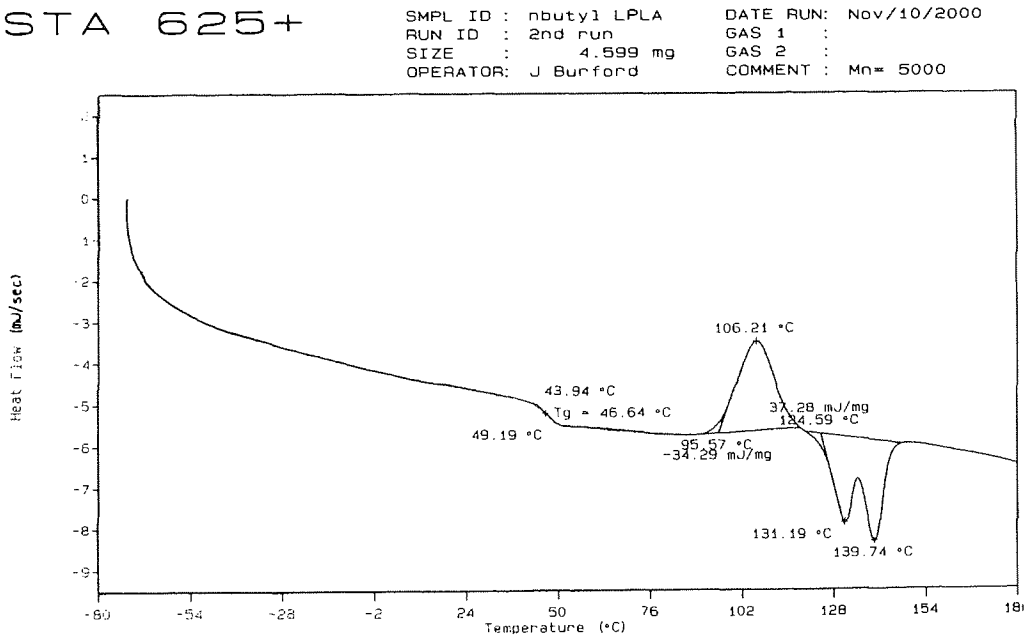


Figure A.103. DSC of n-butyl-PLLA

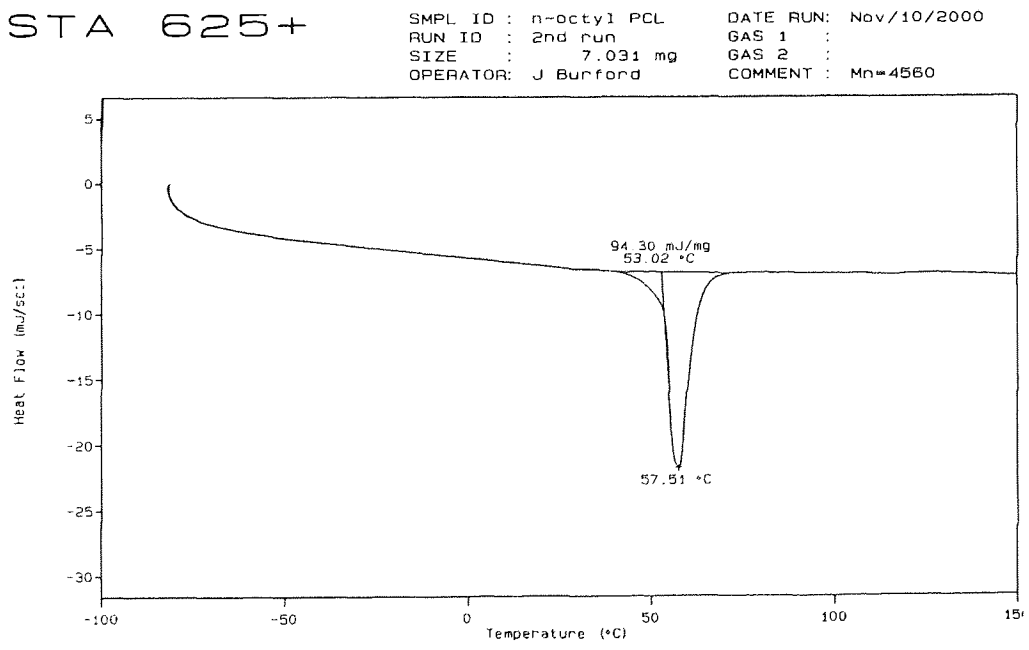


Figure A.104. DSC of n-octyl-PCL

Appendix 2.4 Discussion

The synthesis of ε-caprolactone homo polymer was successful but the reaction time required to achieve an equivalent molecular weight to that of poly(lactic acid) was much greater. This was consistent with the reported lower reactivity of ε-caprolactone.

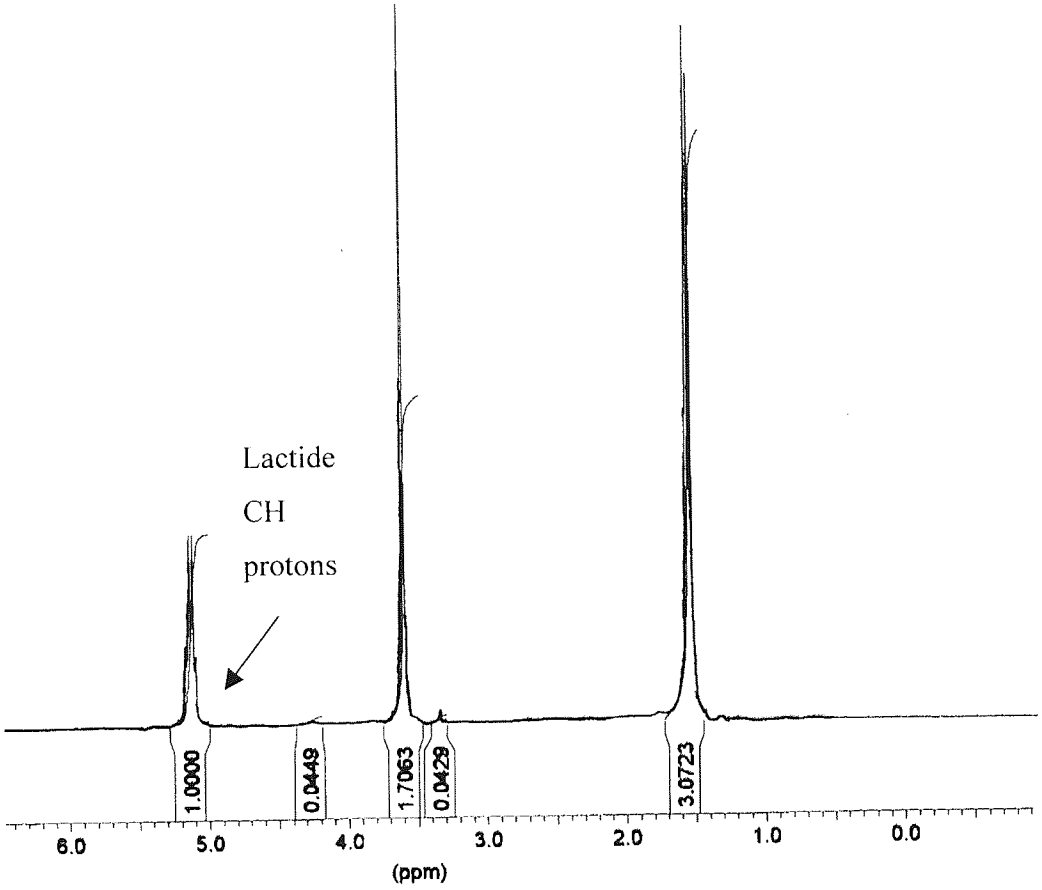
Synthesis of poly(ε-caprolactone)-*block*-poly(lactic acid) copolymers of controlled molecular weight was generally successful. However, the incorporation of the lactide monomer was not complete in most cases. It is suspected that the long reaction times required to complete the ε-caprolactone polymerisation may allow the catalyst to become 'deactivated' by reaction with impurities, particularly water. The ε-caprolactone macro-initiator would be expected to be less reactive than ROH (alcohol or water) this would favour competitive initiation of lactide producing a mixture of copolymer and homo polymer. However, no evidence for homo polymers was observed in the NMR spectra except for the lower than expected incorporation of lactyl units relative to the GPC molecular weight. In addition, it has already been shown that polymerisation of lactide using this catalyst system is rather easy and always complete. Therefore, the recovery of lactide at the end of the reactions would strongly suggest catalyst deactivation or very slow initiation under these conditions rather than PLA homo polymer formation. It is suggested that the caprolactone polymerisation will generally run to completion over the 10 to 20 hour reaction period regardless of the presence of lactide. The lactide initiation by the caprolactone macro-initiator is rather slow under these conditions. Evidence for this is taken from (Table A.40) [forth entry] where the lactide was added well before the caprolactone reaction was complete (GPC Mn =2200). At the end, still relatively little lactide was incorporated (and recovered) but the molecular weight had increased by much more than could be accounted for by the lactide. It is expected that an increase in temperature would favour a more successful reaction.

The DSC thermograms of PCL-PLA copolymers show a similar pattern to those of Barakat and coworkers [128] for poly(ε-caprolactone-*block*-glycolide) polymers. They observed crystallisation of the glycolide blocks above a certain chain length, explained by the partial miscibility of short blocks. It would appear from the results above (Figure A.102) that the crystallisation in the PCL-PDLA (Mn 10800) copolymer is due to the caprolactone block rather than the PLA block (Figure A.103). Indeed, for such copolymers the PDLA block would be expected to be amorphous. From these results it is suggested that the amorphous nature, high glass transition temperature and block length of PDLA are important. The long glassy block of PLA can 'lock' the PCL chains during cooling preventing them from crystallising. However, recrystallisation occurs during heating because of specific properties associated with the particular polymer. This effect has not been seen with short PDLA or crystalline PLLA copolymers. Perhaps, because short blocks (relative to the PCL block length) have little effect on the crystallisation of the PCL chains. In addition, crystalline PLLA chains may also phase separate, perhaps reducing their effect further. Indeed, Qian et al [133] in a recent publication says "*introduction of a PLLA block into the polymers [PCL-PLA] makes worse conditions for crystallisation of the PCL and results in the decrease of its melting endotherm*".

Appendix 2.5 Conclusions

The synthesis of PCL-PLA copolymers using the developed polymerisation procedure will allow (with further development of the reaction conditions) large scale synthesis of copolymers of this type. This class of materials will be useful as potential compatiblising agents for the otherwise incompatible PCL and PLA blends.

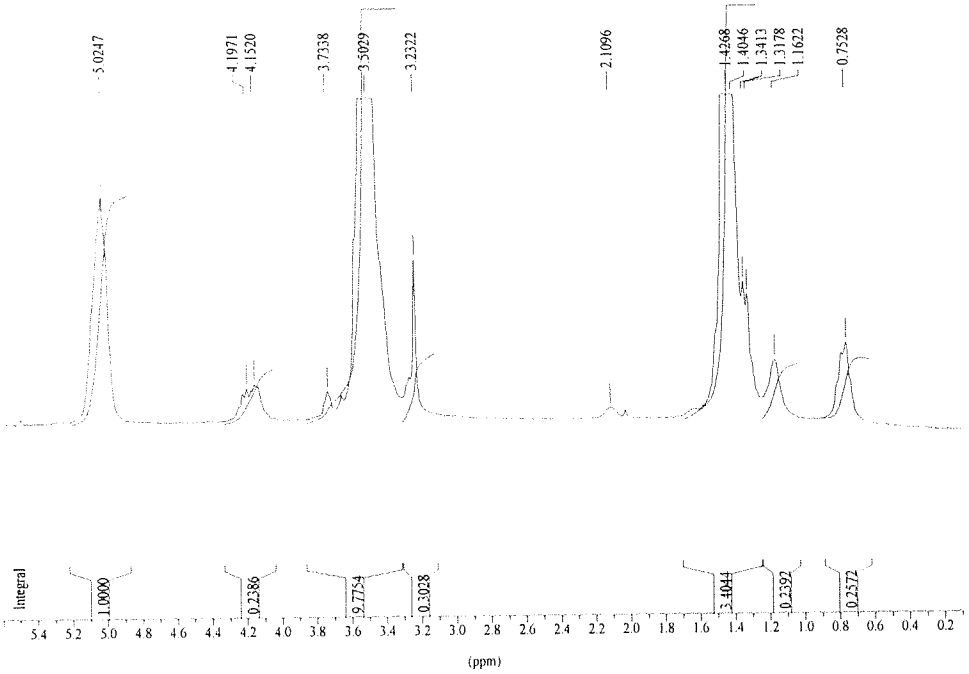
Appendix 3. Proton NMR spectrum indicating the absence of lactide (chapter 3.2.3)



Appendix 4 Summary of prepared MeOPEG-PDLA copolymers (chapter 3.2.3)

PEG Mwt	Lactide: MePEG-OH Mol ratio	% Yield	Theoretical Mwt	GPC (Mn)	Mw/ Mn	Properties
350	70: 1	84	10400	12600	1.2	Solid
350	55: 1	90	8270	9940	1.5	sl.sticky solid
350	28: 1	89	4400	5600	1.1	V .soft solid
350	10: 1	40	1790	2712	1.3	V .visc.oil
350	5: 1	-	1070	1124	1.4	Visc oil
750	70	89	10800	14800	1.1	Hard Solid
750	55	85	8670	10311	1.1	Sticky solid
750	28	84	4700	5050	1.2	Solid
750	10	70	2200	2433	1.2	V. visc. Oil
750	5	-	1470	1439	1.1	Less visc. Oil
2000	70	75	12100	11800	1.2	Soft solid
2000	55	72	9920	12600	1.6	Soft gum
2000	28	80	6030	7500	1.2	Solid
2000	10	80	3440	3971	1.1	Solid
2000	5	90	2720	3014	1.1	Solid
5000	70	90	15080	17000	1.2	Solid
5000	55	74	12900	8000	1.2	Solid
5000	28	96	8960	9500	1.2	Solid
5000	10	73	6440	7992	1.1	Solid
5000	5	93	5720	7950	1.2	Solid

Appendix 5. MeOPEG-PDLA copolymer 1:1 catalyst: PEG ratio T=1.5 hours (chapter 3.2.5)



Appendix 6 2-Butanol initiated polymerisations (chapter 3.2.9)

Using a low molecular weight initiator such as 2-butanol allowed the preparation of a polymer, which essentially resembled a homo-polymer as closely as possible with minimal interference from the initiating end group. As already mentioned the calculation of the molecular weights by NMR of homo-polymers is difficult because of the problem associated with detecting end groups in high molecular weight polymers. This method allowed a successful molecular weight calculation while emphasising the control of molecular weight by R-OH type initiators. The degree of polymerisation was calculated using the ratio of C-H end chain proton (PLA) at 4.28 p.p.m to those of the in chain protons at 5.1 p.p.m.

Lactide : BuOH mole Ratio	Integration of end chain proton (PLA)	Integration of in chain proton (PLA)	Degree of polymerisation
5:1	0.0991	1.00	10.1

Table A.5. Degree of polymerisation for 2-BuOH initiated PLA

Appendix 6.1 Reaction rate

A survey of the current literature [45, 46, 134] suggests prolonged reaction times (in excess of ten hours) at temperatures in the region of 140°C. To investigate the rate of a 2-butanol initiated polymerisation, aliquots of reaction mixture were periodically removed from the reaction using a syringe inserted through a rubber septum. The samples were immediately diluted to a suitable concentration and injected into the GPC instrument. The increase in the number average molecular weight over time is shown in Figure A.105 below.

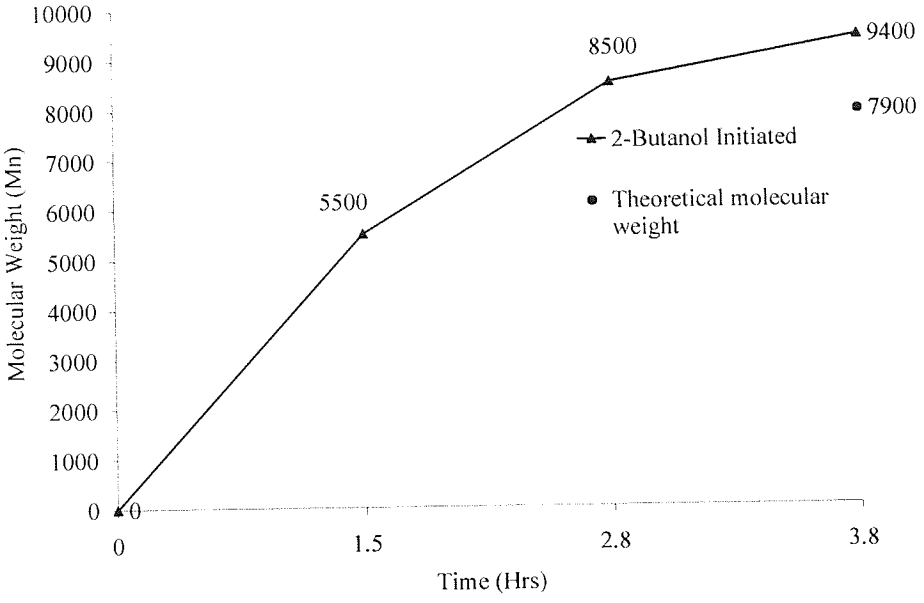
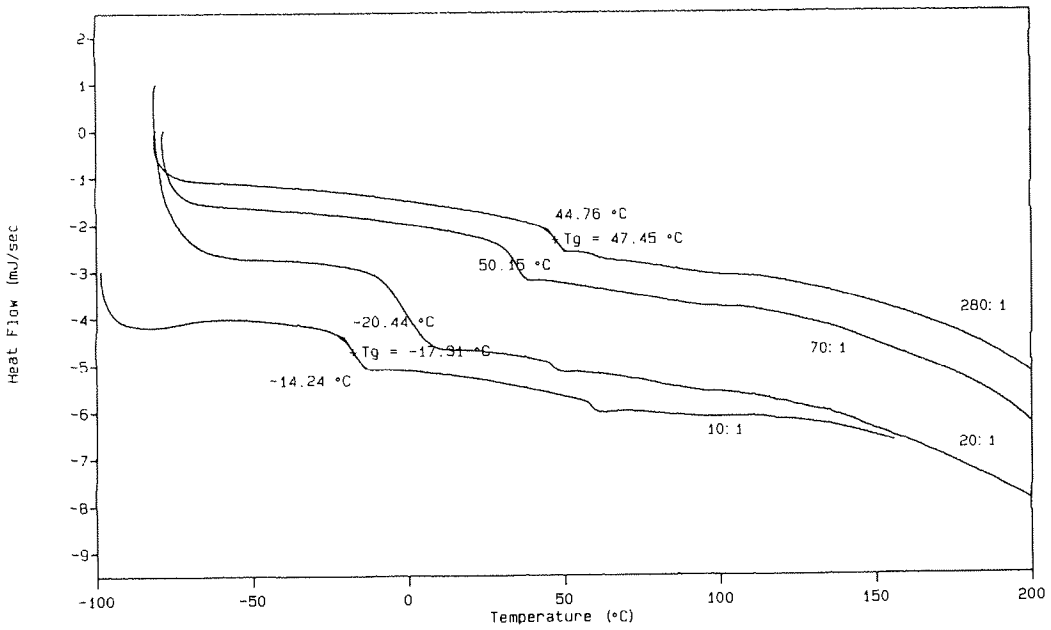


Figure A.105. Increase in molecular weight of PDLA initiated by 2-butanol

The reaction rate was found to be similar to the polymerisations initiated with poly(ethylene glycol) methyl ether and much faster than a homo-polymerisation initiated with tin II octanoate alone. This result is further confirmation that this type of copolymerisation reaction is faster under homogeneous conditions than heterogeneous conditions and ROH is an efficient initiator.

Appendix 7. DSC thermograms of pent ethox -co-PDLA prepared copolymers



Appendix 8 PLA blends (chapter 5.11)

Using a similar methodology to the PHB blends described previously it was felt that the physical, mechanical and degradation properties of PLA could be modified by melt processing with PCL, LLDPE and ECO.

PLA was melt processed in a torque rheometer with either, PCL, LLDPE and ECO at 180°C for 10 minutes with or without ester plasticizer. The effectiveness of the blend was measured using DSC and mechanical strength measurements.

Appendix 8.1 Blends with PCL

Blends of PLA (Neste) and PCL at various concentrations with and without ester plasticizer (EHT) were prepared using the same conditions as those for the PHB blends in chapter 4.4. Tensile strength, elongation at break and DSC measurements were used to assess the compatibility of the polymers.

Appendix 8.1.1 Results

The results for the mechanical properties and DSC measurements are shown below in Figure A.106 and Figure A.107 respectively.

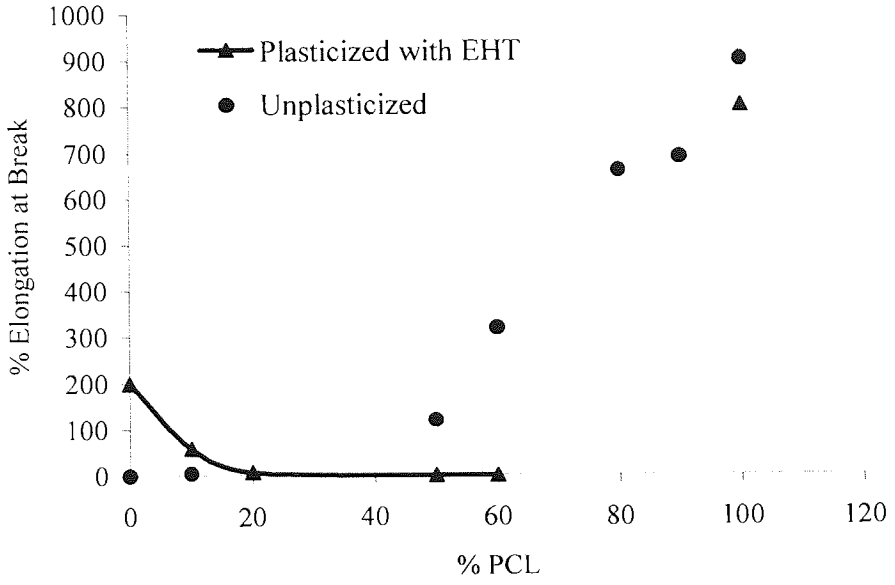


Figure A.106. Comparison of plasticized and unplasticized blends of PLA and PCL

Interestingly, the plasticized PLA blends containing greater than 10% PCL had no mechanical strength what so ever. The processed molten polymer had a very low viscosity and when it solidified it had a crumbly texture and broke easily between the fingers. The DSC results could not detect any increased compatibility between these blends and the unplasticized ones (Figure A.107 and Figure A.108).

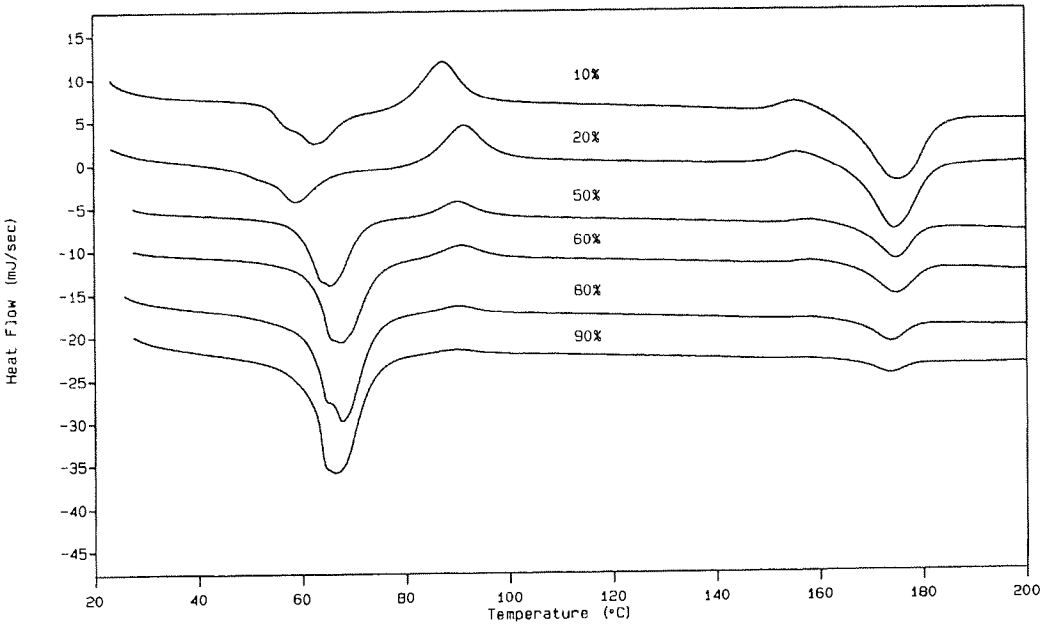


Figure A.107. DSC of PLA containing different concentrations of PCL (unplasticized)

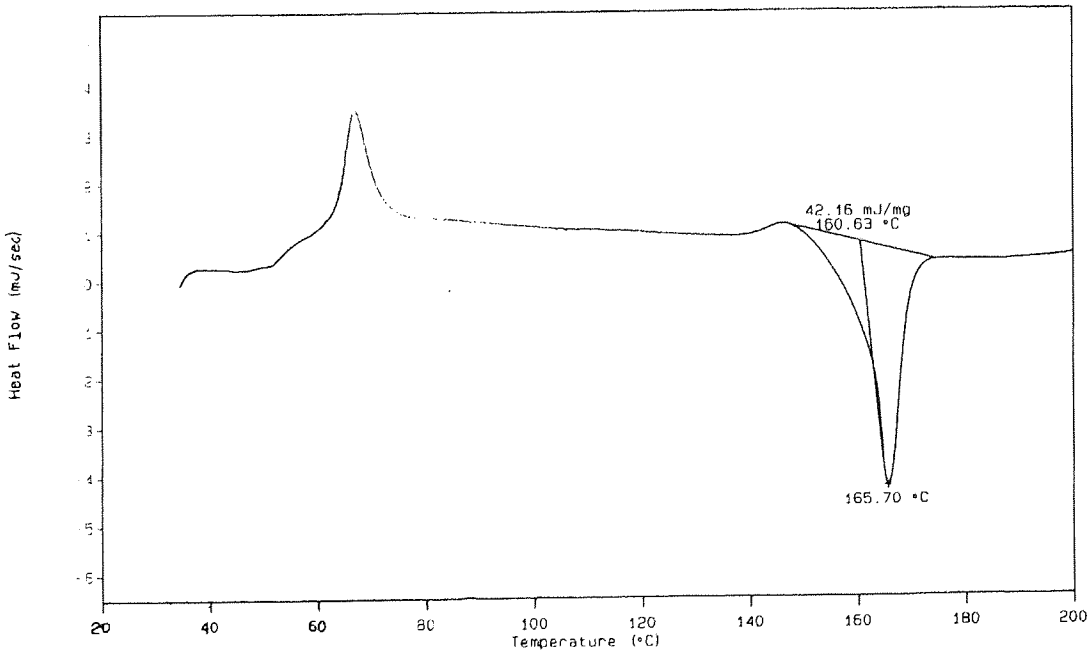


Figure A.108. DSC of PLA blended with 20% PCL plasticized with 17% EHT

Appendix 8.2 Blends with LLDPE and ECO

LLDPE and ECO were blended at concentrations of 5, 10 and 20%. In some blends, 20% TMHT was added as a plasticizer and compatibilizer.
The plasticized blends containing 20% LLDPE or ECO were also tested for their hydrolytic stability under mildly acidic and basic conditions.

Appendix 8.2.1 Results

It was apparent from the DSC results (Figure A.110 and Figure A.111) that both the LLDPE and the ECO were incompatible with PLA. The addition of plasticizer appeared to have no effect on the compatibility. However, the PLA part of the polymer was plasticized as seen previously and this resulted in the elongation at break of the blends having similar values (260% [LLDPE] and 270% [ECO]) to those of the PLA alone.

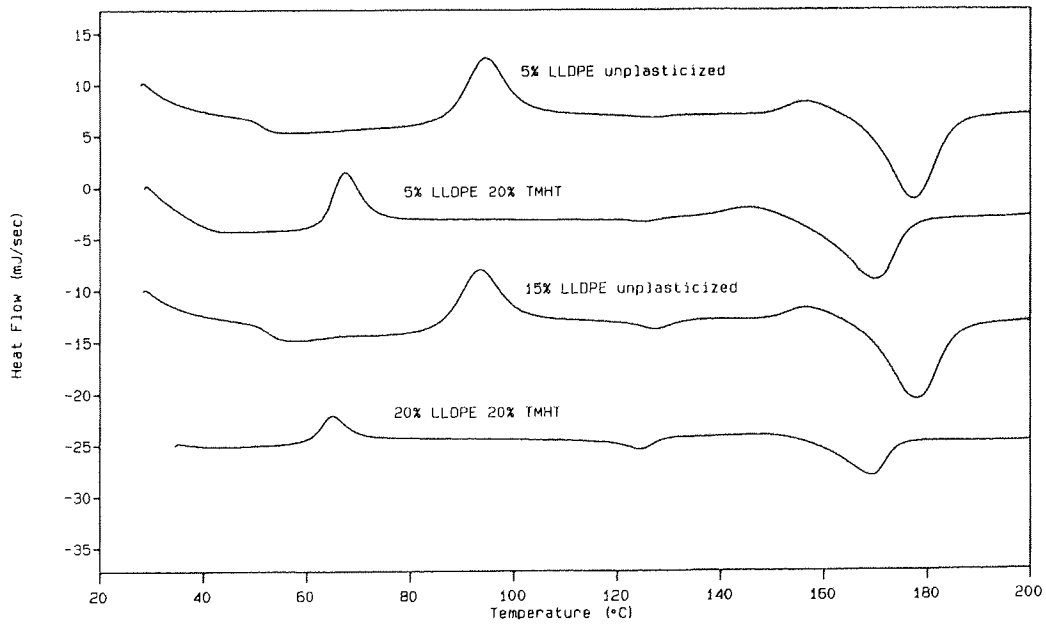


Figure A.109. DSC of PLA- LLDPE blends

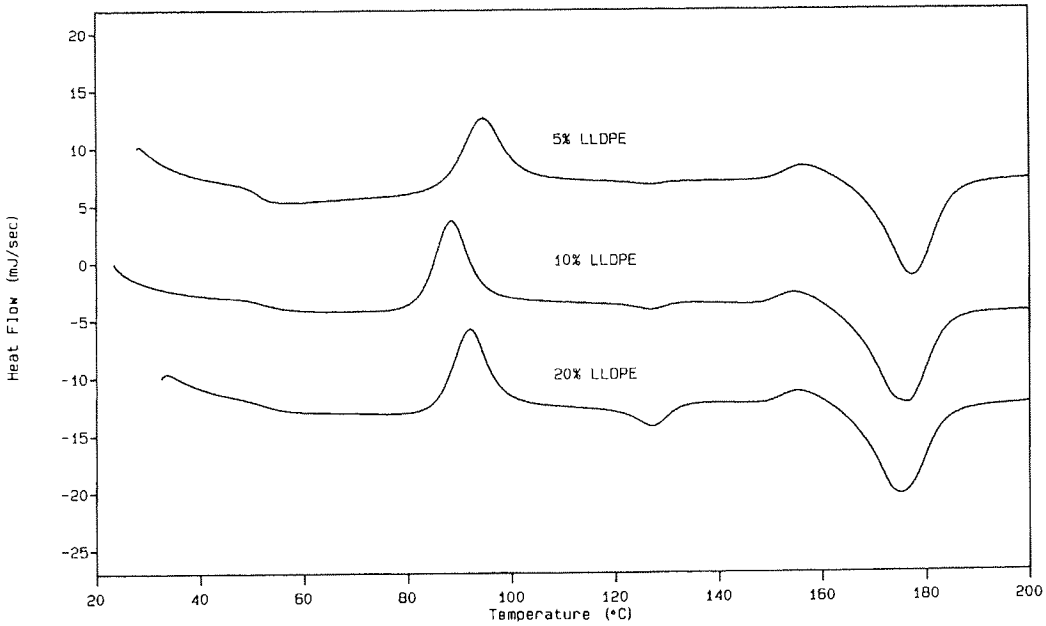


Figure A.110. DSC of unplasticized PLA-LLDPE blends

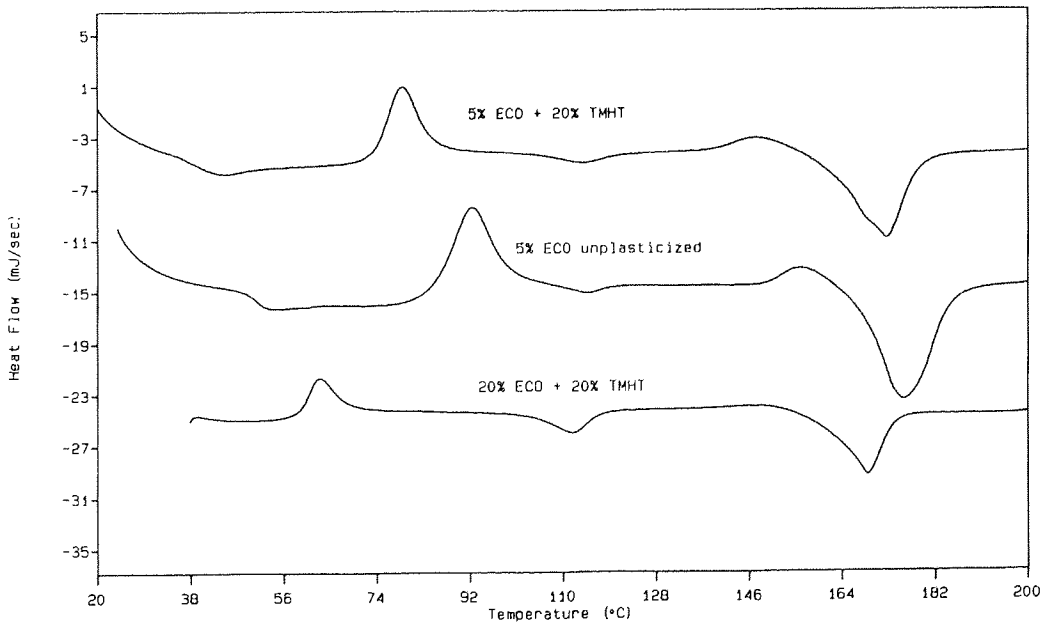


Figure A.111. DSC of PLA- ECO blends

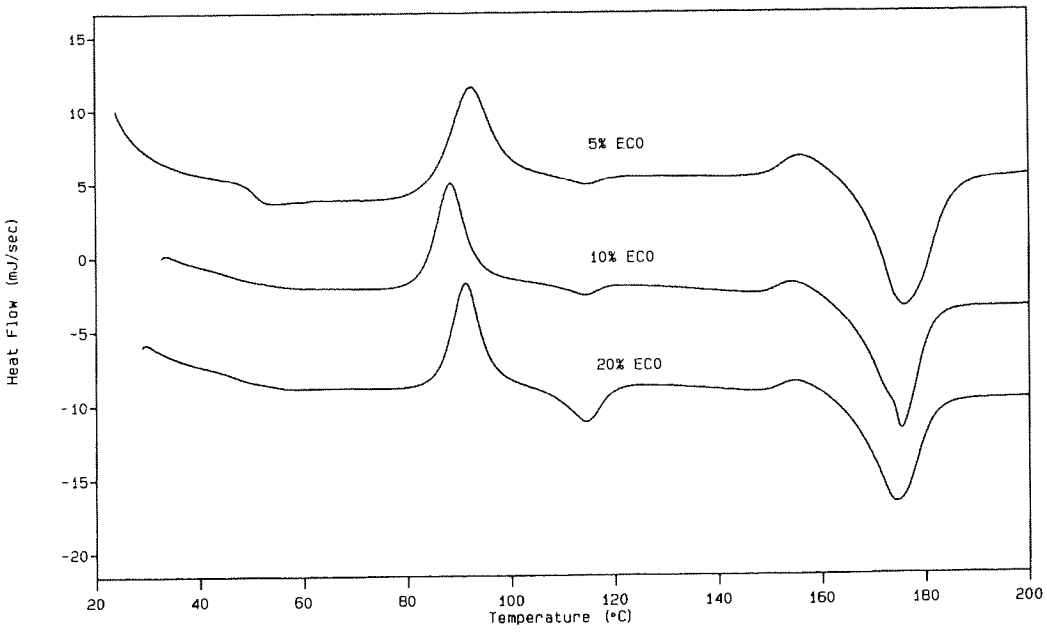


Figure A.112. Thermal properties of unplasticized PLA-ECO blends

The hydrolytic stability of the plasticized LLDPE and ECO blends were similar to, if not better than the corresponding PLA/ TMHT blend (Figure A.113 and Figure A.114).

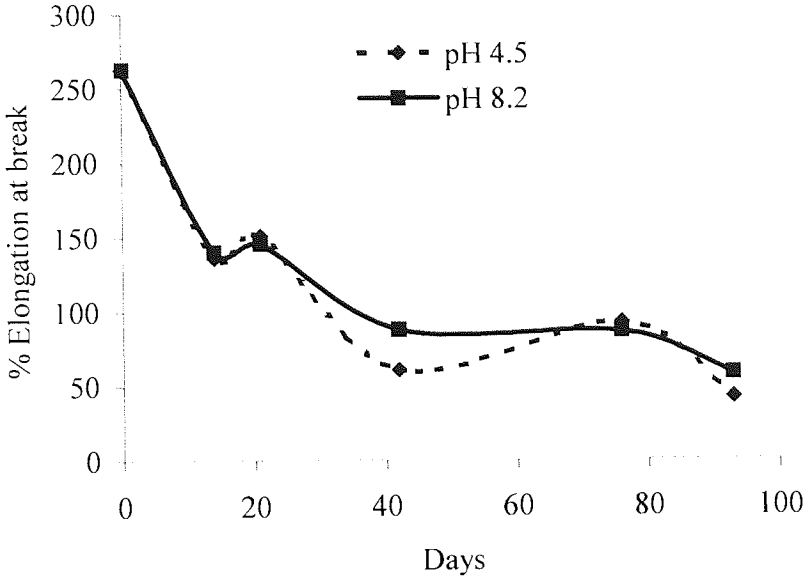


Figure A.113. Hydrolytic stability of plasticized PLA / LLDPE blend

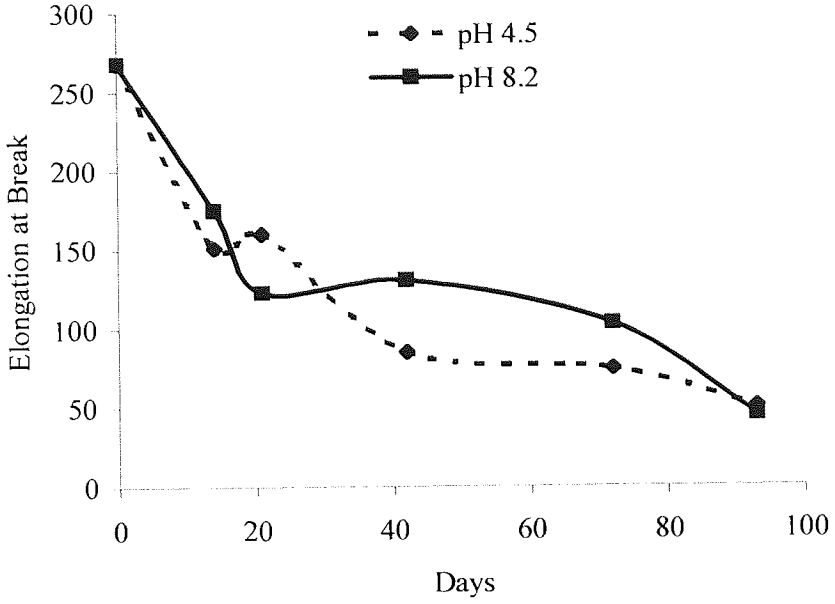


Figure A.114. Hydrolytic stability of plasticized PLA / ECO blend

Appendix 8.3 Degradation

The polymer blends: PLA/ECO/TMHT, PLA/LLDPE/TMHT and PLA/PCL were briefly assessed for their hydrolytic stability and rate of biodegradation using the batch composting method. The percent weight loss and molecular weight changes were monitored.

Appendix 8.3.1 Results

It was found that when PLA was blended with ECO (or LLDPE) and plasticized with TMHT the degradation rate appeared to be much quicker than the degradation rate of plasticized PLA or unplasticized PLA (Table A.44). However, the reduction in the molecular weight (of the PLA part) was similar to PLA or the PLA/TMHT blends (Table A.45). The LLDPE and ECO were insoluble in the GPC solvent

(chloroform) and therefore any changes in molecular weight of these polymers could not be determined.

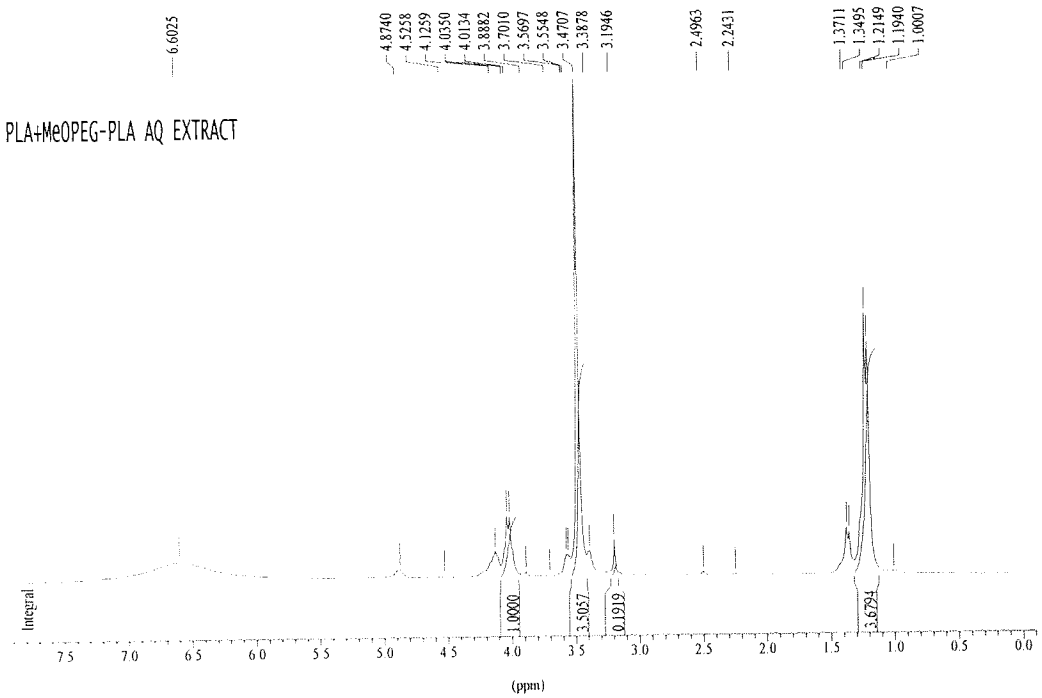
	Time (Days)			
Weight % PLA:ECO:TMHT	**7**	**14**	**21**	**28**
79: 4:17	5.6%	9.6%	12.9%	31.2%
75: 8:17	7.8%	11.0%	23.8%	29.6%
71:12:17	8.3%	25.5%	~30%	35.3%
67:17:17	11.3%	12.6%	16.1%	17.0%
Weight % PLA:LLDPE:TMHT				
79: 4:17	8.7%	39.9%	-	45.8%
75: 8:17	12.8%	35.2%	-	25.6%
71:12:17	9.9%	34.8%	-	44.5%
67:17:17	12.0%	27.2%	-	33.6%
PLA control	-	3.2	-	3.8
PLA/ TMHT 17% wt.	6.4	11.1	-	22.4

Table A.44. Percentage weight loss from PLA/ECO/TMHT plasticizer films in compost at 58±2^{0}C

	Time (weeks)			
	0	**1**	**2**	**3**
PLA/ECO/TMHT	48400	17700	3300	2400
PLA/LLDPE/TMHT	48500	-	8900	2100
PLA/TMHT	31700	12500	4500	-
PLA control	34000	16800	6900	2600

Table A.45. Molecular weight change of plasticized PLA/ ECO and PLA/LLDPE blends

Appendix 9. Residue from hydrolytically degraded MeOPEG-PLA plasticized PLA (chapter 6.4.1)



Appendix 10. Comparison of Neste and Dow PLA polymers (chapter 7.7)

Comparison of the DSC thermograms of the virgin Dow and Neste polymers clearly shows significant differences between them. The DSC of the Dow polymer was regarded as unusual. Some important points are.

1. The magnitude of the glass transition.
2. The absence of any significant crystallisation during heating.
3. The energy content of the melting transition.
4. The melting point of the Dow polymer with respect to the Neste material.

It is known that the glassy state (by definition) occurs in the amorphous parts of the polymer matrix. Therefore it can be inferred from 1 and 4 above that the magnitude of the glass transition and the almost virtual absence of a crystalline melting point, that the polymer is predominantly amorphous. In addition, the absence of any detectable crystallisation suggests the polymer is unable to crystallise during heating.

The addition of plasticizer to the Dow polymer significantly increases the thermal crystallisation and the energy of melting (Figure A.115) to that approaching the unplasticized Neste PLA. The ability for the plasticized polymer to undergo these transitions, particularly crystallisation indicated increased chain mobility.

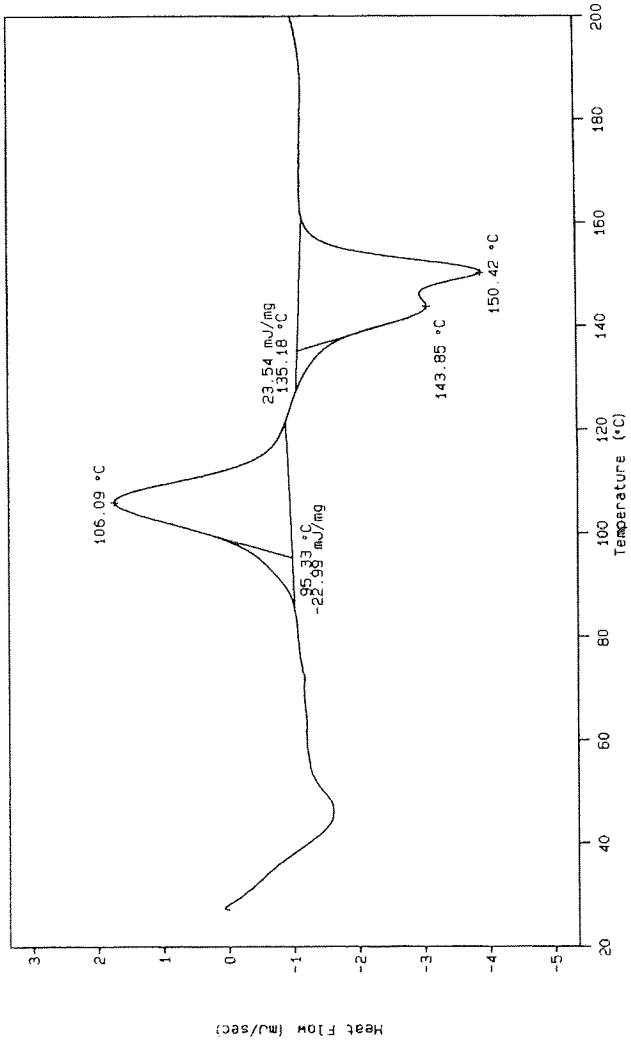


Figure A.115. Typical DSC of plasticized Dow PLA

An interesting phenomenon is observed when the stretched parts of the plasticized and unplasticized (Dow and Neste) PLA samples are analysed by DSC.
The stretched virgin Neste PLA, (Figure A.116) results in a DSC resembling "plasticized PLA" in terms of its crystallisation temperature. This suggests less energy is required to crystallise the polymer.

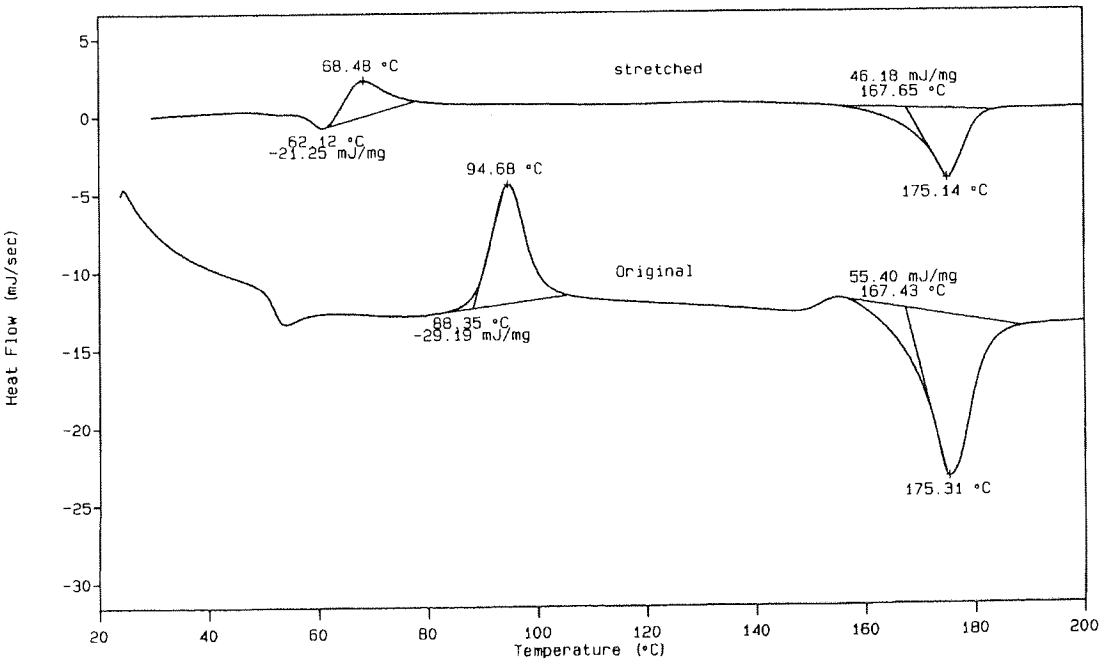


Figure A.116. Effect of stretching on the thermal characteristics of unplasticized Neste PLA

Moreover, when a sample of plasticized Neste PLA is stretched, the resulting DSC (Figure A.117) indicates that the sample has reached its maximum crystallinity (as none is observed during heating). This suggests that the film has crystallised on stretching.

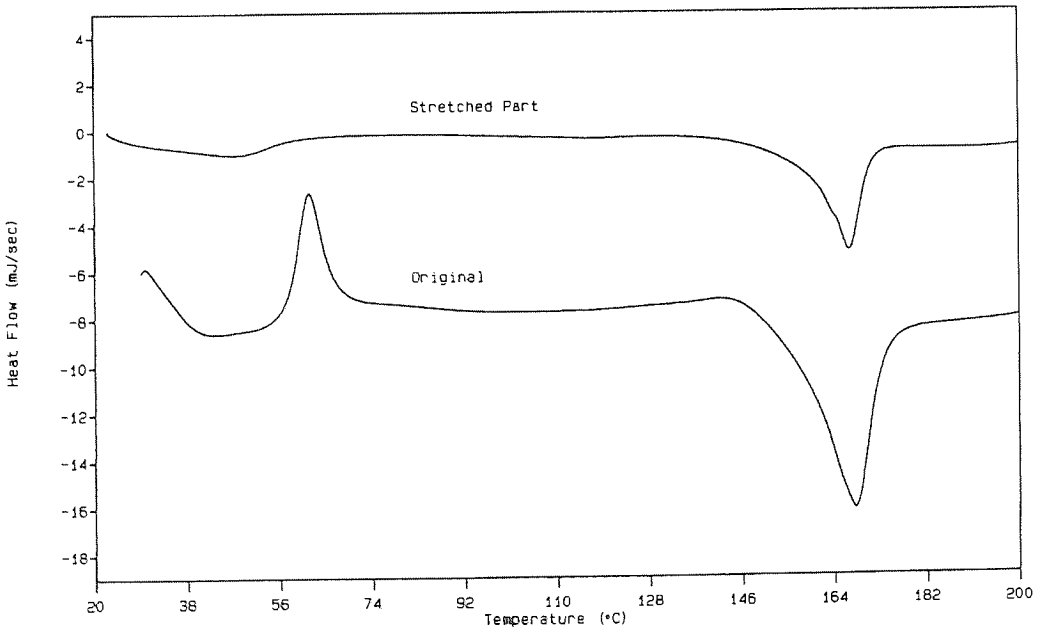


Figure A.117. Effect of stretching on plasticized Neste PLA film

A somewhat similar but less dramatic effect is observed when the unplasticized Dow polymer is stretched (Figure A.118). It is clearly seen that there is a somewhat more pronounced pre-melt crystallisation exotherm in the stretched sample. It could be imagined that as this moves towards a lower temperature it could sharpen and become a more definite crystallisation.

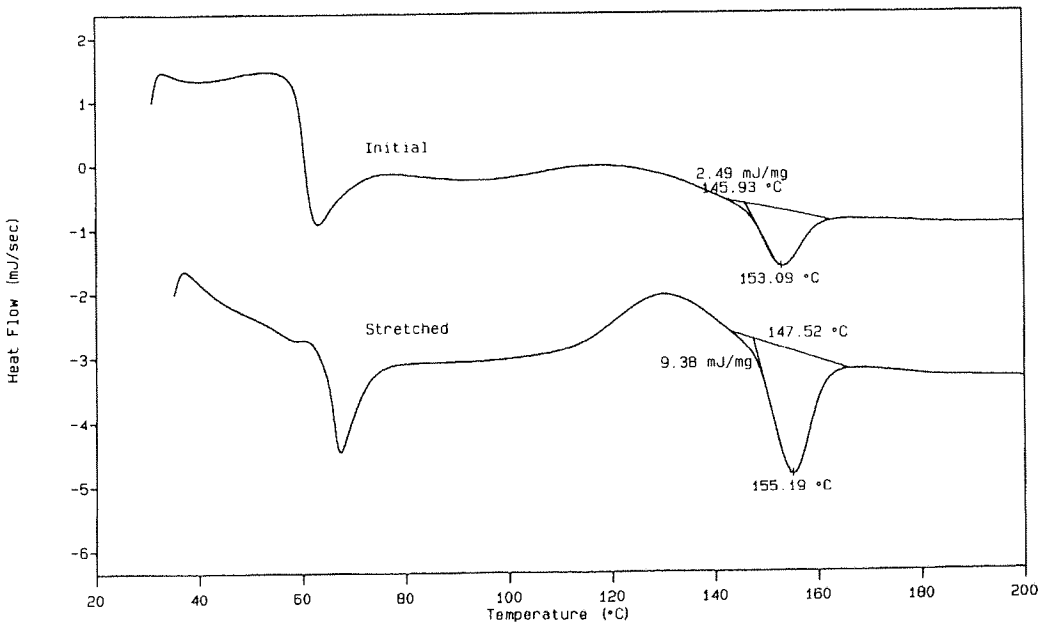


Figure A.118. Effect of stretching on unplasticized Dow PLA film

Similar stretching of a corresponding plasticized sample lowers the crystallisation temperature even further (Figure A.119) but not as significantly as seen in the Neste polymer. In fact the thermal properties of the stretched unplasticized Dow sample resemble the unstretched plasticized Neste PLA

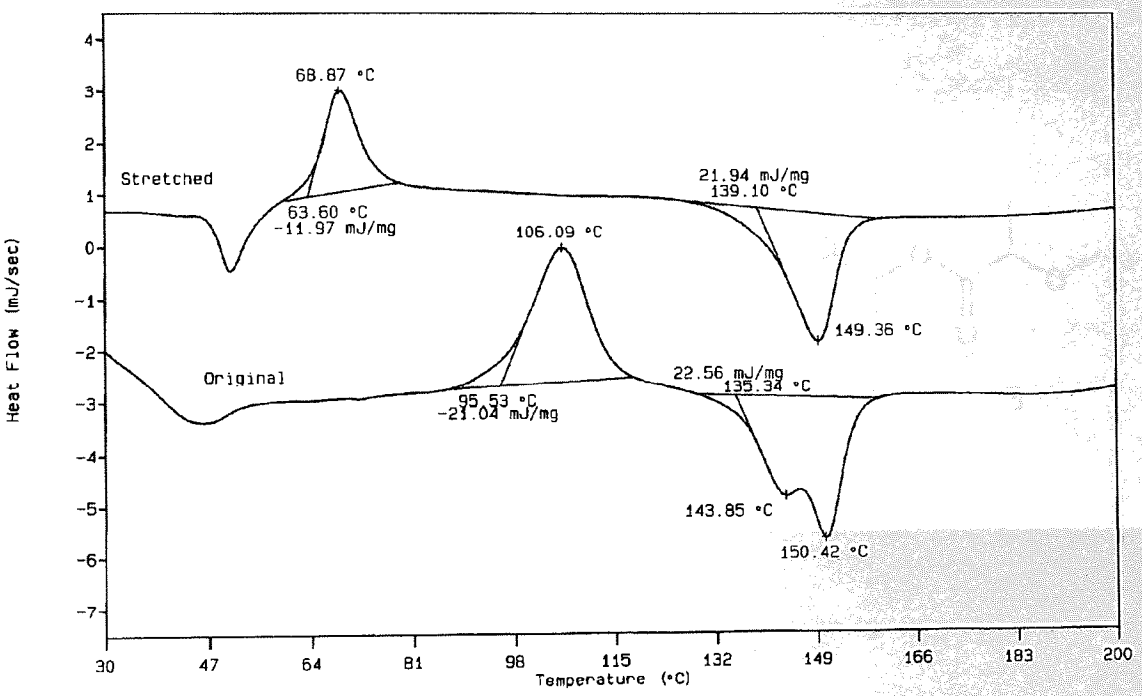


Figure A.119. Effect of stretching plasticized Dow PLA

It is expected that the Dow PLA is manufactured in such a way as to produce a much more amorphous polymer (but maintaining a predominantly L configuration) than the L-PLA supplied by Neste. An explanation for the apparent high amorphous character of the Dow polymer is that simply the polymer could have a predominantly (R,S) configuration. However, it is known that this polymer was manufactured by the NarureWorks process, which uses fermentation techniques to produce the lactic acid and would therefore be expected to be of the natural L (R)

configuration. Moreover, a polymer formed from a racemic lactide with an R,S structure (i.e. amorphous) would be expected to be very soft and have poor mechanical properties. Therefore, a reasonable explanation that would fit with the observations (including the depressed melting point) would be that a proportion of (R, S)-lactide was added during the manufacturing process to form a polymer that can be represented in Figure A.120 below.

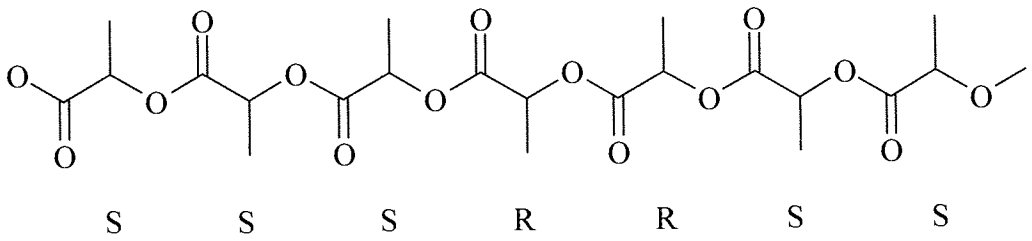


Figure A.120. Possible structure of Dow PLA