The plasticisation of plastics using Deep Eutectic Solvents

Thesis submitted for the degree of Master of Philosophy at the University of Leicester in Material Science

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Statement of originality

The experimental work in this thesis has been carried out by the author in the material centre at the University of Leicester between October 2013 and January 2015. The work has not been submitted, and is not presently submitted, for any other degrees at this or any other university.

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The plasticisation of plastics using Deep Eutectic Solvents

Abstract

Owing to the ease of manufacture, versatility of use and relatively low cost, plastics are used in a vast and expanding range of products, from paper clips to spaceships. Plastics are polymers with a range of additives to aid processing and modify the aesthetic, thermal and mechanical properties, depending on their applications. The application of ionic liquids and deep eutectic solvents as an alternative additive for polymers has gained some attention recently due to properties such as thermally stability.

In this study deep eutectic solvents (DESs) were investigated in their application as potential additives for non-polar and polar polymers HDPE, PLA and PET. The mechanical and thermal properties including glass transition temperature, melting temperature, maximum tensile strength, and elongation at break were measured with and without DES additives.

It is shown that with non-polar polymers (i.e. HDPE), the DESs reduce the intermolecular forces between the polymer chains creating more free volume in the polymer, allowing them to flow more easily and resulting in greater flexibility. The interaction of DESs with polar polymers (i.e. PLA), reduces the motility of the polymer chains and makes the materials more brittle.

Plasticisers mainly improve the flexibility of polymers, which can be seen by changes in the glass transition temperature, \( T_g \). This study shows only minor changes in \( T_g \) suggesting that the DESs acted as lubricants rather than plasticisers. This project also reveals how the ratio of DESs affected the properties of the plastic. The mechanical strength decreases with increasing DES content for both HDPE and PLA. It is also shown that DESs enable HDPE to be homogeneously mixed with starch reducing the overall cost of the plastic and making it more biodegradable.
Acknowledgements

This project is a collaborative effort that has been built upon the contributions of many great people:

My parents: Huijuan Wang and Rongjun Qu, who have given me more than enough love and support till this day.

My project supervisor: Professor Andrew Abbott, who has been a great mentor.

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1. Introduction

1.1. Polymers

The term "polymer" is derived from the ancient Greek word polus, meaning "many, much" and meros, meaning "parts". It refers to a substance, of which the molecules consist of a large number of repeated low molar mass base units or monomer residues, which are connected by covalent chemical bonds. The large molecular mass (typically > 10,000 Da) leads to their unique physical properties of polymers.

Polymers that contain only one single type of repeat unit are known as homopolymers, while polymers containing a mixture of repeat units are known as copolymers. The polymers are arranged into a microstructure where the chains interact with themselves and their neighbours to form a variety of crystalline and amorphous regions. Branching of the polymer chain can decrease the packing of the polymer, leading to a greater amount of amorphous micro-structure. A branched polymer molecule has a main chain with one or more substituent side chains or branches. Types of branched polymers include star polymers, comb polymers, brush polymers, dendronized polymers (linear polymers to every repeat unit of which dendrons are attached), ladders, and dendrimers.

Most physical properties are affected by the polymer's architecture including solution viscosity, melt viscosity, solubility in various solvents and the glass transition temperature. The structural properties above define the bulk physical properties of the polymer, which describe how the polymer behaves as a continuous macroscopic material.

The chemical properties of the monomer units at the nano-scale can also affect how the chains interact with each other through various physical forces. At the macro-scale, they describe how the bulk polymer interacts with other chemicals and solvents. Different side groups on the polymer can lend the polymer to ionic bonding or hydrogen bonding.
between chains. These stronger forces typically result in higher tensile strength and higher crystalline melting points of the polymer.

Polymers can be classified by their origin; natural e.g. wool and cellulose, semi-synthetic e.g. cellulose acetate and synthetic e.g. Nylon and PET.

### 1.1.1. Synthetic polymers

Natural polymeric materials such as wood, leather and wool have been used since the beginning of human history, but the domination of synthetic polymers as consumer materials only started with the development of rubber materials at the start of the nineteenth Century.

Since 1930 many thousands of different polymers have been synthesized, but only about 50 have reached large scale commercial production. In 1869, John Wesley Hyatt began experimenting with nitrocellulose, a group of flammable or explosive substances formed by treating paper or cotton with acids. His innovation was to mix nitrocellulose pulp with pulverized camphor gum and heat the mixture under high pressure in a mould; as the product cooled it became celluloid, a versatile substitute for many natural products, which was the first artificial and synthetic polymer up to 1900. In 1907, Leo H. Baekeland — called “the father of modern plastics” — invented a liquid compound of phenol and formaldehyde when used in combination with wood, paper, asbestos, graphite and other substances it produces a solid, non-inflammable insulator which is known as Bakelite. The polymer industry started to achieve a certain degree of maturity shortly before the Second World War with the development of polyolefin, polyesters, and polyamides in the 1940s. The production of plastics in volume has been continuously growing ever since, with polyolefin, polyesters, and polyamides now constituting over 90% of the plastics market.

Pure polymers are rarely processed on their own; they are compounded with other
materials. Standard methods are mechanical blending or melt state mixing. Such compounded products are referred to as ‘plastics’, which means ‘pliable’ in Greek. The compounds may involve flame-retardants, reinforcing agents, other polymers, stabilizers and various processing aids.

Plastics can be classified as either thermoplastic or thermoset determined by their thermal processing behaviour, which in view of processing polymers to products, is the most important classification. Thermoplastics account for 90 weight percent of all polymers produced. They can be melted by heating, solidified by cooling and remelted repeatedly which simplifies their processing. Major types of thermoplastics include polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), polycarbonate (PC), polymethyl methacrylate (PMMA), polyethylene terephthalate (PET) and polyamide (PA, nylon). In comparison, thermosets are hardened by the application of heat and pressure, owing to their cross-linked three-dimensional structure which makes them stiff and brittle. When subjected to high temperatures they decompose and are non-recyclable. Bakelite, epoxides and most polyurethane are examples of thermosets.

The plastics industry is unfortunately known for producing large amounts of waste which can be toxic to biological life. For example, a 1975 National Academy of Sciences study estimated that over six million tons of solid waste was discharged into the sea every year. One study showed that though public interest seems to have been attracted by recent press coverage containing shocking photos of plastic-killed wildlife, 450,000 plastic-related items are dumped daily from ships around the world, including long-lasting synthetic plastic like packing and shipping materials, convenience products, raw plastic, and fishing gear. Animals are killed when they swallow or are entangled in the plastic debris. Many endangered and threatened species are suffering high mortality rates. Besides the significant steps so far to reduce plastic pollution in the seas, attempts
are beginning to deal with the underlying issue of plastic proliferation and the need to substitute biodegradable materials for plastics.

1.1.2 Natural polymers
Natural polymers such as cellulose and starch play a major part of our lives. Classified by source, natural polymers are divided in two types: polymers that come from plants and polymers not come from animals.

The former involves five main organic groups: hydrocarbons, phenols, acetals, amides and esters (Scheme 1) whereas the later contain only two organic groups including acetals and amides (Scheme 2).

Starch is used in raw materials including textiles, paper, adhesives as well as in the laundry and food industries. The extraction of starch from natural materials requires some purification to obtain the pure starch from other components in the starch granule.

\textbf{Scheme 1.1: The types of natural vegetal origin polymers}^{9}.
The extraction of maize starch from maize hull requires a wet milling process. In this process all other components, such as oil, fibre and some proteins, are separated from the pure starch, which has poor mechanical properties in the pure state. The properties of the native starch can be enhanced by chemical and physical modification.

The starch (amylose and amylopectin) is made up of hexagonal chair-shaped ring shaped monomers (glucose). Amylopectin chains have 30 glucose units in each branch whereas amylose chains have between 500 and 6000 units in a chain. The quantities of amylose and amylopectin in each type of plant vary due to hybridisation processes. The existence of hydroxyl groups in the starch structure plays an important role in keeping the starch chain in perfect order due to the ability of hydroxyl groups attracting the rest of hydroxyl groups in the starch pellet.

1.2. Plastics
The use of plastics has grown significantly in recent years. For example production was 99 million tonnes in 1989 which grew to 265 million tonnes in 2010. The Eurozone produced 27.4 million tonnes in 1989, which increased to 57 million tonnes in 1992.
The pie chart below (Figure 1.1) characterizes the different uses of plastics in 1992 by sector.\textsuperscript{12} It is noteworthy that the packaging industry dominates the plastic usage market.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{pie_chart.png}
\caption{The applications of thermoplastics in 2013.\textsuperscript{87}}
\end{figure}

Most of the polymers in Figure 1.1 have a long environmental life and are made from non-renewable materials. These long life polymers, after disposal, are very harmful for the environment and can emit greenhouse gases.\textsuperscript{10}

The extensive use of sheet plastics for applications such as rubbish bags and agricultural wrapping for silage is of considerable environmental concern. There is an urgent need to insert natural materials into the plastic industry instead of petrochemical materials according to the comparison in Table 1.1.\textsuperscript{13}

\begin{table}[h]
\centering
\begin{tabular}{|l|l|}
\hline
Starch based-plastics & Oil based-plastics \\
\hline
Bio-degradable materials. & Non-biodegradable material. \\
\hline
Low cost. & Expensive. \\
\hline
Renewable. & Finite. \\
\hline
Short life. & Long life. \\
\hline
\end{tabular}
\caption{Comparison between starch based plastics and oil based plastics.\textsuperscript{13}}
\end{table}

Plastics are classified as either thermoplastic or thermoset as determined by their thermal processing behaviour. Thermoplastic polymer is a type of polymers that can be heated until they become viscous liquids, and this process can be repeated after they are
cooled down. Thermoset polymers, on the other hand, can only be heated for a short period, as they must reach a suitable temperature until they become viscous liquid. When the liquid solidifies, it becomes difficult to re-use the plastics due to chemical cross-linking. Thermoplastic polymers play a large role in the plastics industry and are used in most of the categories that have been shown in Figure 1.1.

**1.2.1. Thermoplastics**

Thermoplastics are a class of synthetic polymers that exhibit softening behaviour above a characteristic glass transition temperature (Tg). This behaviour is considered a consequence of the absence of chemical crosslinks in these polymers. The difference between thermoplastic polymers and thermoset plastics is their ability to be softened or fully melted and reshaped upon heating, while remaining chemically and dimensionally stable, which means they can be transformed into any desired shape. This cycle can be repeated at will and permits recycling of thermoplastic articles. Together with the availability of tailored physical properties, this makes thermoplastics highly adaptable for a variety of applications. Compared with more traditional materials such as silicon and glass, thermoplastics offer lower raw material costs and substantially lower manufacturing costs.

Most types of thermoplastics are made from four monomers of petroleum origin: ethylene, propylene, styrene, and vinyl chloride. Ethylene is a simple gaseous hormone that is used in many aspects including plant growth and development. Fruit ripening and flower senescence are the two physiological responses that have been commonly controlled by ethylene, hence the most significant attention involving biology and biotechnology. Today, the control of ethylene effects is one of the most promising approaches regarding genetic engineering. Propene is a colourless gas at room temperature and atmospheric pressure with a weak but unpleasant smell. It has experienced rapid growth, but in the meantime, it is struggling with its status as an
industry by-product sensitive to ethylene's vagaries. Propene can be obtained from a variety of fossil fuels including oil, natural gas, and, to a much lesser extent, coal. It is a by-product of oil refining and natural gas processing. Cracking larger hydrocarbon molecules can produce ethylene, propene, and other compounds. Another source of propene is naphtha cracking intended to produce ethylene, but it can also be produced from refinery cracking which produces a range of products. With the presence of a peroxide initiator, polystyrene is an aromatic hydrocarbon polymer synthesized by the cationic polymerization of styrene monomers. This polymer is found in an amorphous form with relatively high electric insulating characteristics and good mechanical strength.\(^6\)

The thermoplastic polymers used for this project, are as follows:

High-density polyethylene (HDPE) is a polyethylene thermoplastic made from petroleum. It is commonly used in the production of plastic bottles, corrosion-resistant piping and plastic lumber. It is commonly recycled, and known for its large strength to density ratio. The density of high-density polyethylene can range from 0.93 to 0.97 g/cm\(^3\). Although it is only slightly higher than that of low-density polyethylene, HDPE has less branching, which is ensured by an appropriate choice of catalyst (e.g., Ziegler-Natta catalysts) and reaction conditions, giving it stronger intermolecular forces and better tensile strength. The difference in strength exceeds the difference in density, giving HDPE a higher specific strength. It can also withstand rather higher temperatures (120 °C for short periods and 110 °C continuously).

Polylactic acid (PLA) is a biodegradable thermoplastic aliphatic polyester derived from renewable resources (cornstarch, tapioca roots or sugarcane). It had the second highest production volume of any bio plastic of the world\(^15\) in 2010. PLA is used in producing loose-fill packaging, compost bags, food packaging, and disposable tableware. It can also be used as medical implants, as it can degrade into innocuous lactic acid and
gradually transfers the load to the body (e.g. the bone) while the area heals.

Polyethylene terephthalate (PET) is a thermoplastic polymer resin that used in synthetic fibres; beverage, food and other liquid containers; thermoforming applications; and in combination with glass fibre, engineering resins. In its natural state, PET is a colourless, semi-crystalline resin. It is very lightweight, and based on processed methods, PET can be semi-rigid to rigid. It is a strong and impact-resistant material. Clear products can be produced by rapidly cooling molten polymer below the glass transition temperature (Tg) to form an amorphous solid. Like glass, amorphous PET forms when its molecules are not given enough time to arrange themselves in an orderly, crystalline fashion as the melt is cooled. At room temperature the molecules are frozen in place, but if heated above Tg sufficient energy allows them to move again, allowing crystals to nucleate and grow. This procedure is known as solid-state crystallization. To better understand the working mechanism of the plasticization and also for commercial reason, starch came to our attention.

These polymers were chosen to provide a variety of high and low polarity polymers with a mixture of homo- and co-polymer.

The final part of the project will investigate the co-extrusion of a synthetic polymer with a natural polymer using a DES as a common plasticiser. Starch is a naturally abundant branched polysaccharide. It is inexpensive and very abundant in nature (found in plants such as wheat, oats, potatoes and grains). A large amount of starch is located in the centre of the starch granule (endosperm) and the process of starch production affects their size. Amylose is a linear polyanhydroglucose and it consists of glucose units connected with each other via α-(1,4) linkages. The amylose is very flexible due to the presence of α-(1,4) linkages as shown in Figure 1.2.
1.2.2. Thermosets

A thermoset is a polymeric material that irreversibly cures, generally because it forms a 3-D network structure as opposed to a 2-D network which is the case for thermoplastics. The cure can be induced by heat (generally above 200 °C), chemical reaction, or suitable irradiation which results in cross-linking between neighbouring chains. Prior to curing, the thermoset materials are usually in a liquid or malleable form hence easily moulded or used as adhesives. In contrast to thermoplastics, where pellets or powders can be shaped into their final product form by melting and pressing repeatedly, articles of cured thermosets cannot be recycled in a simple way and have to be shaped in a single, discontinuous step by compression or injection moulding.

The polymer resin transforms into rigid thermoset by a cross-linking process. Heat and/or catalysts are added to trigger the molecular chains linking into a rigid, 3-D structure. This process forms networks with a larger molecular weight, and when the melting point is higher than the surrounding ambient temperature, a solid material forms. Meanwhile, these resins consist of a mixture of reactive, low molar mass compounds, which react with each other upon heating and then transform from a fluid
into a solid material. This is the reason why the product formed by thermoset cannot be melted or dissolved any more. Uncontrolled reheating of the material results in decomposition before it can melt. Therefore, a thermoset material cannot be melted and re-shaped after it is cured. This implies that thermosets cannot be recycled, except as filler material.

As a matrix of choice for fibre-reinforced composites, thermoset polymers are used in a wide variety of applications. Compared to thermoplastic polymers, the advantages of thermoset polymers are that they have higher stiffness, higher strength lower creep and thermal resistance compared to thermoplastics. The curing (cross-linking) can be induced by heat (generally above 200 °C), chemical reaction, or suitable irradiation. Prior to curing, the thermoset materials are usually in liquid or malleable form hence easily moulded. For this reason they are also commonly used as adhesives. Contrary to thermoplastics, where small pellets can be melted and shaped into their final product form by pressing, articles of cured thermosets cannot be recycled in a simple way and have to be shaped in a single, discontinuous step by compression or injection moulding. The high mechanical strength and durability of thermoset polymers are exploited in applications such as composite materials, where they form the matrix surrounding carbon or glass fibres.

1.2.3. Processing Methods
In the plastic industry, in order to obtain the suitable shape for use, plastic generally needs to go through a series of processing procedures. Some of the important physical properties which affect the processability of plastics including melting temperature and glass transition temperature. The plastic chips or pellets are usually dried before going to the feeder in order to drive out moisture which could otherwise form bubbles in the plastic as it expands.
Figure 1.3: Block diagrams of the stages in processing thermoplastics, and thermosets or rubbers

Table 1.2 lists the physical properties of some of the most commonly used polymers. It can be seen that polymers such as polyethylene are flexible, ductile and have low mechanical strength so finds application for films and bags etc. Nylon and polystyrene and stronger and more rigid and are used for more structural applications.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Density (kg/m$^3$)</th>
<th>Tensile Strength (N/mm$^2$)</th>
<th>Elongation (%)</th>
<th>Young's Modulus (GN/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC</td>
<td>1330</td>
<td>48</td>
<td>200</td>
<td>3.4</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>1050</td>
<td>48</td>
<td>3</td>
<td>3.4</td>
</tr>
<tr>
<td>PTFE</td>
<td>2100</td>
<td>13</td>
<td>100</td>
<td>0.3</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>900</td>
<td>27</td>
<td>200-700</td>
<td>1.3</td>
</tr>
<tr>
<td>Nylon</td>
<td>1160</td>
<td>60</td>
<td>90</td>
<td>2.4</td>
</tr>
<tr>
<td>Cellulose nitrate</td>
<td>1350</td>
<td>48</td>
<td>40</td>
<td>1.4</td>
</tr>
<tr>
<td>Cellulose acetate</td>
<td>1300</td>
<td>40</td>
<td>10-60</td>
<td>1.4</td>
</tr>
<tr>
<td>Methyl methacrylate</td>
<td>1190</td>
<td>74</td>
<td>6</td>
<td>3.0</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>950</td>
<td>20-30</td>
<td>20-100</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Table 1.2: Physical properties for common plastics
Most the plastics are processed via extrusion, a process used to homogenise and fluidise plastics to create objects with a constant cross-sectional profile. Extrusion can be continuous or semi-continuous and can be done in both hot and cold conditions. An advantage of the extrusion process is that the processing rate can be very large while maintaining product quality.

The material is generally heated above its recrystallization temperature to keep the material from hardening and this allows it to be pushed through a die. Lubrication is required, which can be oil or graphite for lower temperature extrusions, or glass powder for higher temperature extrusions.

Extrusion is carried out in an extruder which contains three parts: a screw (or screws as is the case with twin screw extrusion), a barrel and a die. Once extruded the extrudate is cooled by air or water as it is pulled through the die which causes it to solidify. During extrusion plastics melt by a combination of heating elements and shear heating from the extrusion screw. This is generally done in order to combine different types of polymers and additives before getting the final shape and produce a homogenous mixture. Mixing or conveying elements can also be included in the screw in various conformations to achieve the appropriate mixing. Extrusion is common in the addition of colourants to molten plastic thus creating specific custom colours.

Injection moulding is used for about 25% of processed plastics, which produced plastics in various in size and shapes. It involves two systems: the injection system and the clamping system. The injection system contains a hopper, injection barrel (with reciprocating screw), a hydraulic motor and an injection cylinder. The hopper is used to raise the plastics passing them through the screw inside the injection barrel. The melt zone is the place where plastics melt before they enter the metering zone which compresses the plastics to the required form with support from the hydraulic motor. The metering zone has tips at the end to stop and withdrawal of melted materials when there
is enough plastic. The injection cylinder pushes the screw to inject the melted plastics through the machine into the mould.

1.2.4. Plastics applications

Due to the relatively low cost, ease of manufacture, versatility, and imperviousness to water, plastics are found in countless applications ranging from paper clips to spaceships. They have already displaced many traditional materials, such as wood, stone, leather, paper, metal, glass, and ceramic, in most of their former uses. In developed countries, about a third of plastic is used in packaging and another third in buildings (e.g. piping and facias). Other applications include automobiles (which contain up to 20% plastic), furniture, and toys. In the developing world, on the other hand, the ratios may be different - for example, 42% of India's plastic consumption is reportedly used in packaging.\(^{17}\)

In the car industry, plastics have replaced metal in many areas. This is primarily due to low cost and weight compared to metals. They also stop corrosion, which, when present, can affect the car’s structure; for example, aluminium air intake manifold was double in comparison with the weight of plastics air intake manifold, which caused the inner surface in the plastics manifold was much smoother which can enhance the engine’s performance.

In the last few decades the environmental fate of plastics has become an issue. It has been reported that marine debris, specifically derelict fishing gear, has been a significant and persistent threat to the wildlife.\(^{18}\) During 1996–2005, an extensive multiagency debris removal program was led by the National Marine Fisheries Service (NMFS) and within the North-western Hawaiian Islands alone, 492 metric tonnes (MT) of derelict fishing gear were removed.\(^{18}\) It has been found that ocean currents tend to concentrate water-borne plastics and large concentrations of plastics have been found in the world’s oceans. The so-called Great Pacific garbage patch and North Atlantic
garbage patch have been found to contain fragmented plastic to a concentration of 5 kg km⁻². These particulates are a hazard to all forms of aquatic life. In addition to environmental concerns the sustainability of plastic is an issue as it uses about 6% of the world’s annual oil production.

1.2.5. Polymer Additives
A variety of additives are included with polymers to make what is called a plastic. These include materials which change the physical properties, decrease the flammability, decrease the cost, change the aesthetic appearance and improve processability.

Almost all the polymers currently used need plasticisers; they are small amphiphilic molecules such as alkyl phthalates which decrease the crystallinity of a polymer. This can change the mechanical properties, increasing toughness, strength, tear resistance and flexibility and reducing the brittleness of the polymers. Most of the polymers discussed could not be made without the additives to alter their physical or their visual attributes.

Polymer fillers are materials which bulk out the polymer and are generally the largest constituent by mass. Not only do they reduce the cost of the plastic but in many cases they also improved the product’s thermal or mechanical stability. The most common filler is carbon black although wood flour and chalk are also common. In addition, silicate fillers such as talc, silica, and zeolites function as blocking agents, helping to allow separation of film layers, e.g., in polyethylene films. Metal-containing additives are also sometimes used as antimicrobials (copper, zinc, and silver ions) and as antioxidants (nickel compounds), and they are widely used as polymer colorants (metal oxides and phthalocyanines).
For PVC in particular, polymer additives are essential as additive-free PVC has very limited usefulness. PVC is thermally unstable releasing HCl on heating so additives such as metal stearates and zinc oxide are used as acid-scavenging additives. Without them, PVC not only is subject to slow decomposition, as indicated by yellowing and deterioration, but is even corrosive toward steel.\textsuperscript{20}

Nearly all polymers are flammable and they become even more flammable when highly plasticized as the plasticisers are more volatile than the polymer. Therefore, a variety of inorganic compounds are utilized as flame-retardants and/or smoke suppressants. The simplest and highest-volume fire-retardant additives are aluminium and magnesium hydroxides, which decompose during the fire, removing heat and releasing water vapour.\textsuperscript{21} However, nearly prohibitively large amounts of these additives are needed to achieve the desired effect. Accordingly, these hydroxide materials must act both as fillers and as fire retardants. This combined additive function is desirable in terms of simplicity of formulation and economics. In addition, vapour-phase radical scavengers, combined with halogenated organics, are used in flame-retarded formulations, most notably formed from antimony oxides. Antimony halides appear to form a key link in the radical-scavenging cycle.

Heat and light stabilizers can also be seen as polymer additives. Their values are determined by the compatibility relations with given polymers. It is a known fact that many additives can migrate from one polymeric material into another, and the rate of migration depends on the local diffusion coefficient. In most cases, this process can be expected to be concentration dependent, which means it increases with an increase of the additive concentration. It should also be noted that no transport would occur through crystalline regions, and the additives will be located in the amorphous regions, and stay there.
1.3. Plasticisers

Plasticisers, by definition, are additives that increase the plasticity or fluidity of a material; they make it possible to achieve improved compound processing characteristics while providing flexibility in the final product.²²

Plasticisers can be either non-polymeric materials or polymer impact modifiers. Some forms of copolymerization can produce a degree of internal plasticizing as well. Certain plasticisers can perform other functions, like assisting in viscosity control, dispersion of particulate additives (such as fillers and pigments, and general lubrication of the compound).²³ Plasticisers also function as softeners, extenders, and lubricants, and play a significant role in rubber manufacturing.²⁴ About a million tonnes of plasticisers are consumed by the European plastics market annually.¹¹ The wide variety of ester plasticisers are used include adipates, terephthalates, glutrates, phthalates, and other specialty blends.²⁴

Plasticiser performance is governed by many factors such as solubility parameter, molecular weight, and chemical structure. It was commonly thought that plasticisers work by embedding themselves between the chains of polymers, spacing them apart, thus increasing the "free volume" and significantly lowering the glass transition temperature for the plastic.²⁵ However, it was later shown that the free volume explanation could not account for all of the effects of plasticisation. For plastics such as PVC, the more plasticiser added, the lower its cold flex temperature will be, as a result, it become more flexible and durable.²⁶

Plasticisers evaporate and tend to concentrate in an enclosed space; for example, the “new car smell” was mostly caused by plasticisers evaporating from the car interior. Substantial concerns have been expressed over the safety of some plasticisers, especially because several phthalates have been classified as potential endocrine disruptors with some developmental toxicity has been reported.²⁷
Phthalates account for 92% of all plasticisers and European production is running at about a million tonnes a year with a growing rate around 3.7% per year. The breakdown of use of different types is 11:

- Diethyl hexyl phthalate (DEHP) 51%
- Diisodecyl phthalate (DIDP) 21%
- Diisononyl phthalate (DINP) 11%
- Others 17%

Phthalates have been the target of a worldwide attention in the past few years, from consumer and environmental groups, on grounds of potential carcinogen and possible endocrine modulating effects. Evidence of both has been discovered in tests with rodents, but not in mammals, and there has been some dispute as to whether such results can be translated across the species barrier. Under pressure from lobby groups and faced with inadequate scientific evidence, the first impulse of the EC Commission was to impose an immediate ban on the use of the phthalate plasticisers DINP and DEHP in PVC compounds for products such as teething rings, that are specifically those intended to be put into children's mouths, and a temporary ban on four other plasticisers until 2005, to allow time for evaluation. But to do this it would have had to demonstrate that phthalates present "an immediate and serious risk" - a claim that was rejected by the European Parliament itself in 2014.

The EU Scientific Committee for Toxicity, Eco-toxicity and the Environment (CSTEE), concluded in 1998 on the basis of an extensive review of the available data, that there are safe migration limits for phthalates. In a scientific opinion, the Committee stated that phthalate plasticisers can safely be used in the production of soft PVC toys, provided that migration limits are observed. It suggested guideline migration limits for each of six phthalate plasticisers.
The missing factor in the argument was a scientific basis for testing and measuring content and extractability of plasticisers that would be simple and universally applicable and acceptable. The absence of a suitable test method (and strong pressure from lobby groups) prompted the governments of Austria and Denmark to introduce their own restrictions, and other EU member states indicated their intention to do the same. In the Netherlands, however, the so-called 'Dutch Test Method' was developed, simulating the extraction of plasticisers into saliva when products are sucked or chewed, based on trials with adult volunteers organized by a Dutch Consensus Group. The independent Dutch research and testing institute, TNO, concluded that it would be suitable for routine enforcement of legislation regarding the allowed migration level of diisononyl phthalate (DINP), and it probably could be extended to measuring the migration of other phthalates.

Independent trials have now validated a test that meets the proposed European Union (EU) limits, devised by the UK Laboratory of the Government Chemist (LGC). It provides results consistent with maximum values obtained from the human studies in The Netherlands, and is claimed to provide the only methodology capable of meeting the release value of 9 g/min for a specified plasticizer from a reference PVC compound, proposed as a 'benchmark' by the EU expert committee. It was validated in a trial involving six laboratories, five of which are approved by the EU for testing toys.\textsuperscript{31}

**Working mechanism**

Plasticisers usually cause the polymer matrix to swell and reduce the interaction between the adjacent segments of polymer chains, consequently increasing the segmental mobility and free volume. As a result an increase in flexibility of the polymeric material is commonly observed. It will also function as a forming aid by reducing the glass transition temperature (Tg) of the polymer, thereby promoting the coalescence of the particles.
The degree of plasticisation of a polymer is dependent on the amount of plasticiser and the interactions between the plasticiser and the polymer. Gutierrez-Rocca and McGinity concluded that the efficiency of a plasticiser was related to its chemical structure and the interaction between its functional groups with those of the polymer. Careful selection of the type and amount of plasticiser ensures a uniform product. The deformation of polymeric lattices under specified conditions is one of the most important steps in the process. A sharp increase in mobility of the polymer chains occurs at temperatures above Tg. The relationship between the minimum forming temperature (MFT) and processing conditions is well documented. Plasticisers can also modify the physicochemical and mechanical characteristics of the material, and influence the permeability rate of certain molecules. The plasticiser decreases polymeric intermolecular forces allowing improved polymer mobility which increases the flexibility of the polymer. Increasing the amount of plasticiser could lead to an increase in elongation and a decrease in tensile strength and Young’s modulus.

1.3.1. The polarity of the plastics
Polarity results from head-to-tail association of polymer subunits resulting in polymer lattices in which all of the subunits align in the same direction and the two ends differ structurally. It refers to a separation of electric charge leading to a molecule or its chemical groups having an electric dipole or multipole moment. Polar molecules interact through dipole–dipole intermolecular forces and hydrogen bonds. Molecular polarity is dependent on the difference in electronegativity between atoms in a compound and the asymmetry of the compound's structure. Polarity underlies a number of physical properties including surface tension, solubility, and melting and boiling points.

Electrons are not always shared equally between two bonding atoms; one atom might exert more of a force on the electron cloud than the other. In which case can make a
dipole-dipole intermolecular force. This "pull" is termed electronegativity and measures the attraction for electrons a particular atom has. The unequal sharing of electrons within a bond leads to the formation of an electric dipole: a separation of positive and negative electric charge. Partial charges are denoted as $\delta^+$ (delta plus) and $\delta^-$ (delta minus). Ingold and Usherwood introduced these symbols in 1926.\textsuperscript{36}

Atoms with high electro-negativities such as fluorine, oxygen, and nitrogen exert a greater pull on electrons than atoms with lower electro-negativities. In a bond, this can lead to unequal sharing of electrons between the atoms, as electrons will be drawn closer to the atom with the higher electronegativity.

Bonds can fall between one of two extremes - being completely nonpolar or completely polar. A completely nonpolar bond occurs when the electro-negativities are identical and therefore possess a difference of zero. A completely polar bond is more correctly called an ionic bond and occurs when the difference between electro-negativities is large enough that one atom actually takes an electron from the other. The terms "polar" and "nonpolar" are usually applied to covalent bonds, that is, bonds where the polarity is not complete. To determine the polarity of a covalent bond using numerical means, the difference between the electronegativity of the atoms is taken. On the Pauling scale, if the result is less than 0.4, the bond is generally nonpolar covalent. If the result is between 0.4 and 1.7, the bond is generally polar covalent. If the result is greater than 1.7 the bond is generally considered ionic.

While the molecules can be described as "polar covalent", "nonpolar covalent", or "ionic", this is often a relative term, with one molecule simply being more polar or more nonpolar than another. However, the following properties are typical of such molecules.
1.3.3. Issues with current plasticisers
Common plasticisers are o-hydroxybiphenyl (HBP) and bis (2-ethylhexyl)phthalate (DEHP). HBP consists of two linked benzene rings and a phenolic hydroxyl group, and is on the list of chemicals recognized as carcinogens by the state of California. It was found at a concentration of 23 μg/L in the effluent of our anaerobic membrane bioreactor treating simulated municipal solid waste. But some authors have reported a concentration of 2 μg/L in actual landfill leachate.

DEHP is the most important phthalate, it is produced on a massive scale due to its good plasticizing properties, and is known to be a disruptive endocrine compound and has carcinogenic and mutagenic effects. DEHP was reported to be poorly biodegradable under anaerobic conditions, while other authors found that it could not be removed by aeration, coagulation/sedimentation or biological treatment. Gavala et al. showed that degradation of DEHP occurred in a digester treating primary sludge, but accumulation of high levels of DEHP (more than 60 mg/L) had a negative effect on DEHP removal rates as well as on the biogas production.

O'Connor et al. showed that DEHP exhibited a relatively high toxicity to methanogenesis over 100 mg/L. It was found in a lab-scale anaerobic bioreactor effluent at a concentration of 1 mg/L, and its concentration decreased in the aerobic polishing step placed after the anaerobic bioreactor. Jonsson et al. found phthalic acids at concentrations of 50 mg/L in landfills and observed that the concentration decreased over time.

Another example of a commonly found plasticiser is 2,6-di-tert-butyl-4-(dimethylaminomethyl) phenol (MAMP) which is an antioxidant and stabiliser used as an oxidation inhibitor in natural and synthetic elastomers, polyolefin plastics, resins, adhesives, petroleum oil and waxes. Little is known regarding their biodegradability in the environment and even less about their toxicity towards
methanogens. Methanogens are known to be the most sensitive trophic group in the anaerobic process, and any inhibition of their metabolism could cause an anaerobic digester to fail. Anaerobic digestion is becoming widely used to treat waste, and it is therefore important to know at which concentration these plasticisers will become an issue. Because some plasticisers can accumulate in the environment, it is important to know if these could have an effect on methanogens during the anaerobic treatment of leachate. This is particularly relevant in the case where plastics or industrial wastes are present in the municipal solid waste landfill.

1.4. Ionic Liquids

Ionic liquids are pure compounds which consist only of cations and anions (i.e., salts). They should melt at or below 100 °C and many are liquid at 25 °C, hence the name room temperature ionic liquids. In the past 20 years, ionic liquids have been widely used in the fields of catalysis, electrochemistry, and material chemistry. Therefore considerable attention has been paid to these low temperature molten salts. Early research focused on the formation of ionic liquids by mixing metal salts, mostly zinc, aluminum, tin and iron chlorides, with quaternary ammonium salts. Although both salts have very high melting points, their proper mixing leads to the formation of a liquid phase, the so-called eutectic mixture. These eutectic mixtures are generally characterized by a very large depression of freezing point, generally greater than 150 °C. With the introduction of the concept of green chemistry in the early 1990’s, the search for metal-free ionic liquids (ILs) has become of growing interest. In this context, a lot of studies were dedicated to the design of ILs by combining organic cations with inorganic anions. ILs have emerged as a new class of promising liquids and the possibility to chemically modify the cationic moiety almost infinitely has led to their description as designer solvents. The large choice of cations and anions allow tuning of the physical properties such as melting point, solubility, viscosity, density, conductivity, and refractivity, among others. For instance, in 2009, Seddon and co-workers have
reported that $10^{18}$ different ILs can be theoretically produced, 250 of them being already commercialised.\textsuperscript{19}

Owing to their low vapour pressure and high boiling point, ILs were qualified as green solvents. However, the “green credentials” of these neoteric solvents is now largely contested in the current literature. Indeed, many reports pointed out the hazardous toxicity and the very poor biodegradability of most ILs. ILs with high purity are also required since impurities, even in trace amounts, affect their physical properties. Additionally, their synthesis is far from environmentally friendly since it generally requires a large amount of salts and solvents in order to completely exchange the anions. These drawbacks together with the high price of common ILs unfortunately hamper their industrial emergence and new concepts are being developed to produce a more rational way of making ionic fluids. Ionic liquids have gained a lot of interest around the world due to the various properties they exhibit. They are, non-combustible making them safer to handle and can be readily recycled.

### 1.5. Deep Eutectic Solvents

A Deep Eutectic Solvent (DES) is composed of two or compounds; a quaternary ammonium salt and either a metal salt or a hydrogen bond donor.\textsuperscript{48} Carboxylic acids, amides and alcohols are examples of appropriate hydrogen bond donors. The first of these systems to be described was the choline chloride (ChCl)/ urea system mixed in a 1:2 mole ratio.\textsuperscript{49} The hydrogen bond interactions decrease the lattice energy of the components to form a eutectic mixture with a melting point lower than those of individual constituents. DESs are normally in liquid form at temperatures lower than 100 °C. Generally, DESs are less expensive and less toxic than conventional ionic liquids. These DESs exhibit similar physical as well as chemical properties to the traditional ionic liquids, with much cheaper and environmentally friendlier quality. Owing to these outstanding advantages, DESs are now gaining interest in many fields
of research including metal deposition, electro polishing, metal oxide processing and some of these applications have been scaled up to > 1 tonne.50

Most DESs exhibit comparatively high viscosities at room temperature, with the exception of ChCl–ethylene glycol (EG) eutectic mixture. The high viscosity of DESs is mainly due to the presence of the widespread hydrogen bond network between each component, which results in a lower mobility of free species within the DES.51

In the field of catalysis and organic synthesis, it is clear that DESs will definitely contribute to the design of eco-efficient processes. In particular, the possibility to (1) selectively and conveniently extract products of the reaction from the DESs phase, (2) adjust the pH of DESs, (3) dissolve not only organic and inorganic salts but also transition metal-derived complexes or nanoparticles and (4) recycle these media is among the most promising advantages of DESs. It is our opinion that development of DESs in the field of catalysis will also be drastically boosted by the need to urgently design innovative processes for the catalytic conversion of biomass. Indeed, imidazolium-based ILs have the unique ability to dissolve large amounts of cellulose and more largely lignocelluloses opening promising routes for the saccharification of biomass. However, it is also clear that the price and toxicity of ILs represent two serious drawbacks that hamper the scale-up of these processes. We are fully convinced that the recent progress made in the field of DESs for the catalytic conversion of carbohydrates will definitely open soon new methodologies for converting lignocellulosic biomass in a more rational way.

In the field of materials chemistry, it is also apparent that ILs can be advantageously replaced by cheap and safe DESs for the ionothermal synthesis of a wide range of inorganic materials with different textures and structures. Although a proper selection of the exactly required DESs still remains a big challenge, the works described above have
clearly demonstrated that very important materials, from microporous zeolites\textsuperscript{52} to carbon materials, can be synthesized in DESs. The very recent use of DESs for material synthesis demonstrates the exceptional potential of these media for the generation of novel structures and engineered materials. In these syntheses DESs may play different roles such as solvent, structure-directing agent, water inhibitor, reactant for structure crystallisation, etc.\textsuperscript{53}

One of the most widespread components used for the formation of these DESs is choline chloride (ChCl). It is a very cheap, biodegradable and non-toxic quaternary ammonium salt, which can be either extracted from biomass or readily synthesised from fossil reserves (million metric tons) through a very high atom economy process.\textsuperscript{54} In combination with safe hydrogen bond donors such as urea or renewable carboxylic acids (e.g. oxalic, citric, succinic or amino acids), ChCl is capable of rapidly forming a DES.

As compared to the traditional ILs, DESs derived from ChCl have many advantages, such as:

(1) Low price.

(2) Chemical compatibility with water (i.e. easy storage).

(3) Easy to prepare—since DESs are obtained by simply mixing two components, thus by-passing all problems of purification and waste disposal generally that encountered with ILs.

(4) Most of them are biodegradable, biocompatible and non-toxic, reinforcing the greenness of these media.
Clearly, DESs cannot replace ILs in all fields of chemistry but their low ecological footprint will contribute to the industrial emergence in the near future. The topic of DESs has recently been reviewed in depth by Smith et al.  

1.6. Ionic liquids as plasticisers

ILs have been proposed as novel alternative plasticisers, which have shown promising results in the early stages of investigation, especially those containing imidazolium or pyridinium cations. Ideally, plasticisers exhibit most of the following characteristics: low volatility, low leachability, high and low temperature stability, thermodynamic compatibility with polymer, low cost and minimal health and safety concerns.

ILs exhibit many of these characteristics, with some of them better than traditional plasticising agents. With over 4 million tons of plasticisers produced annually, the development of ILs will create an alternative for plastic processing, and may expand the market to include a number of new applications.

Some work has been carried out using ionic liquids as plasticisers, as has been shown in a number of earlier publications. Ionic liquids can be made into hydrophobic or hydrophillic formulations depending on their application. This ability to tune the polarity could make them useful for polymer plasticisers which vary in their polarity depending upon the type of monomer. The incorporation of ionic liquids into plastics has been driven by the need to produce conducting membranes and most studies to date have been attempting to make membranes for fuel cells. They have been used as solvents for liquid–liquid extraction, organic synthesis, electrochemical research, polymerization reaction, chromatography, and catalysis.

The first attempt to use ionic liquids as a plasticiser was by Puyu who used 1-butyl-3-methylimidazolium hexafluorophosphate to modify poly (methyl methacrylate). It was found that the ionic liquid could be well mixed with the polymer,
reducing $T_g$ and improving the thermal stability.

As plasticisers, ILs were then found to be used as in polymer materials including PMMA, PLA, polyamides, and suspension-polymerized PVC, except for PVC paste resin. One common type of ionic liquids is based on alkyl imidazoliums as cations, paired with a counterion, such as chloride, bromide, hexafluorophosphate, or other anions. They were found to be capable of not only lowering the $T_g$ of PMMA, but also improving the high temperature stability and providing a wide temperature range for flexible PMMA-based plastics. Using PVC for example, as a widely used polymer for a range of medical devices including in endotracheal tubes and catheters, the unique flexibility of PVC in such applications is commonly derived from the use of phthalate esters as plasticisers. However, the possible carcinogenic and reprotoxic effects of phthalates has been a concern for some decades because of their identification as an environmental contaminant. To solve this problem, a design and use of novel dual functional ionic liquids, two dual functional ionic liquids, 1-ethylpyridinium docusate and tributyl(2-hydroxyethyl)phosphonium docusate, was reported to act as a plasticiser for PVC. The glass transition temperature of even a rigid PVC can be tailored as a function of IL loading, such that a decrease in $T_g$ of up to 45°C is achievable and thus device flexibility may be engineered.

Many ILs, especially the ones based on imidazolium cation, have also been shown to be capable of dissolving polysaccharides such as starch and thus can be used as an excellent media for polysaccharide plasticisation and modification. Moreover, the use of ILs could also allow the development of starch-based ionically conducting polymers or solid polymer electrolytes. Most of the work done before in this area involves processing in solution, though melt processing is seen to be more suitable for industrial production as it requires less solvent and higher efficiency. Sankri et al. and Leroy, et al. pioneered the use of an IL (1-butyl-3-methylimidazolium chloride) as a new plasticiser
in melt processing of starch-based materials and showed improvements in plasticisation, electrical conductivity, and hydrophobicity.

Recently, Abbott et al. showed that DESs, can be used as efficient new plasticisers of starch$^{64,65}$. A significant decrease in the energy needed for melt processing was observed. The materials displayed improved tensile strength and did not recrystallise on storage.$^{66}$ The starch plastics had reduced water sensitivity and acted like true thermoplastics which could be recycled without significant loss of mechanical properties.$^{64}$ The thermoplastic starch was also demonstrated as a binder for wood particles to make a thermoplastic material, which could be recycled.$^{65}$ Mixtures of glycerol and quaternary ammonium salts were also used to plasticise starch and this DES had the advantage that it can be made with a Sheldon E-factor of zero.$^{67}$ The optimization of the plastic was made and it was shown that the properties could be made similar to those for HDPE.

1.7. Research aims

This project focused on the use of DESs as alternative plasticisers with three types of plastics (HDPE, PET, PLA) which had different polarity. The aim was to determine the effect of incorporating an ionic component in polymers of different polarity. Each polymer was extruded with different amounts of DES to see the effect of loading. The mechanical and morphological changes occurring in the polymers with DES incorporation were determined.

In addition to the effect of DESs on the mechanical properties attempts were made to use the ionic fluids as media to enable the blending of different types of polymers. One issue with polyethylene is its slow environmental decomposition. Attempts were made to blend starch with HDPE by blending them both with DESs. Attempts were made to break down these polymers in boiling water to investigate their decomposition.
2. Experimental Procedures

2.1. Polymers
The polymers used in this thesis are HDPE (high density polyethylene), PLA (polylactic acid) and PET (polyethylene terephthalate) from Artenius Tech Polymers and were used as received.

2.2. Formation of DES
Ethaline was prepared using choline chloride (ChCl) (Sigma-Aldrich, >98%) and ethylene glycol (Fischer Scientific, >98%) which were mixed together in a 1:2 molar ratio respectively. The liquid was then put into a Thermo Scientific Heraeus oven (50 °C, overnight). To finish off the melting process, the partially melted mixture was placed on a hotplate-stirrer (50 °C), and the top of the beaker was sealed with Para film. After the melting process was complete the resulting Ethaline 200 DES was stored in a sealed bottle at 50 °C. The same procedure was used for preparing Glyceline 200 but replacing ethylene glycol with glycerol (Sigma-Aldrich, >99%). Reline 200 was made by the same process as Ethaline 200 but replacing ethylene glycol with urea (Sigma-Aldrich, >99%).

2.3. Sample preparation

2.3.1. Different composition
Ethaline, Glyceline and Reline were prepared as 1, 3, 5% dispersions by weight in HDPE and as 1, 2 and 3% dispersions in PLA, PET.

2.3.2. Extrusion procedure
The set up for the extruder is shown schematically in Figures 2.1 and 2.2. All the plastic/DES mixtures were extruded using the screw configuration shown in Figures 2.3 in a Prism TSE 24 TC self-wiping extruder (100 RPM, 95 RPM, 1.0) with a Prism volumetric feeder and an air swept face-cut pelletising system. The extruder has 5 temperature-controlled zones; all samples were extruded using the following
temperature profiles.

Figure 2.1: Schematic diagram of the extrusion process

Figure 2.2: Configuration of the temperature zones in the extruder.
Table 2.1: The temperature profiles for different mixtures during extruding

<table>
<thead>
<tr>
<th>Zone</th>
<th>5 (°C)</th>
<th>4 (°C)</th>
<th>3 (°C)</th>
<th>2 (°C)</th>
<th>1 (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE</td>
<td>120</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>PLA</td>
<td>140</td>
<td>140</td>
<td>165</td>
<td>165</td>
<td>165</td>
</tr>
<tr>
<td>PET</td>
<td>210</td>
<td>220</td>
<td>240</td>
<td>240</td>
<td>250</td>
</tr>
</tbody>
</table>

The extrusion pressure for all samples varied but the screw speed was constant for all samples.

2.3.3. Powder grinding
HDPE and starch samples (both pre-modified with DES) were ground using a coffee grinder into a fine powder. The sample powders were mixed in different ratios containing 30 wt% and 40 wt% starch.

Table 2.2: The percentage and weight of the starch and HDPE sample in their mixtures.

<table>
<thead>
<tr>
<th>Glycine in HDPE/°C</th>
<th>Glycine in starch/°C</th>
<th>HDPE sample/°C</th>
<th>Starch/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>75</td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>3</td>
<td>75</td>
<td>70</td>
<td>30</td>
</tr>
</tbody>
</table>

2.3.4. Compression moulding
The powdered mixture or extruded pellets were placed between two copper plates (Figure 2.4) lined with anti-stick silicone sheets with a 1 mm copper separator as shown on the middle between the two copper plates (10 cm square aperture). The sandwich
was then placed in a hydraulic press (Fontune Grotnes Laboratory Press TH400 (Figure 2.5) and a force of 120 kN was placed on the sample for 10 minutes at different temperatures (Table 2.3).

Table 2.3: The temperature at which the samples were pressed

<table>
<thead>
<tr>
<th>Mixture</th>
<th>HDPE</th>
<th>PET</th>
<th>PLA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>150</td>
<td>165</td>
<td>250</td>
</tr>
</tbody>
</table>

Figure 2.3: The 1 mm copper separator and the two copper plates

The sample was then cooled back to room temperature in 5-10 minutes in the press with the force still applied. Once cool, the sample was removed from the press and then the mould. Three sheets were made for each mixture with dimensions as appeared in Figure 2.4.
2.3.5. Tensiometer
All the materials prepared above were mechanically tested using an Instron 3343 tensiometer fitted with a 500 N load cell. All samples were pressed into small sheets using the procedure discussed above, then using a mechanical 'dog bone' press (Ceast Hollow Die Punch, Type 6051) to cut test shapes (test area size: L 1/4 30 mm, W 1/4 4 mm, D 1/4 1 mm) (Figure 2.6).

![Figure 2.6: The dimensions for tensile test shapes](image)

The material strain and stress was controlled by Instron Bluehill 2 software and average values were taken from 8 or more samples. In every case the thickness of each sample was measured using a micrometre and subjected to a strain rate between 2–10 mm min\(^{-1}\).

2.3.6. Differential scanning calorimetry (DSC)
Differential Scanning Calorimetry (DSC) was used to evaluate the thermal behaviour of
the plastics. The Mettler Toledo DSC1 was used to test the material pellets in 3 stages, starting from a low temperature until it passed the Tg. The results were analysed with STRe software. Samples (5-10 mg) were placed on the standard aluminium DSC pan and weighed accurately. The lid of the pan was pierced with a pin before it was pressed together with the pan, which is required to prevent the gas pressure build up inside. The sample was placed within the furnace next to an empty pan (with pierced lid) and used as a reference. Testing conditions were as follows:

Table 2.4: The temperature profile for different samples during DSC test

<table>
<thead>
<tr>
<th>Stages</th>
<th>Increase (at 10 °C/ min)</th>
<th>Held (for 5 min)</th>
<th>Decrease (at 20 °C/ min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE</td>
<td>-160 to 150 °C</td>
<td>150 °C</td>
<td>150 to 25 °C</td>
</tr>
<tr>
<td>PLA</td>
<td>-15 to 170 °C</td>
<td>170 °C</td>
<td>170 to 25 °C</td>
</tr>
<tr>
<td>PET</td>
<td>0 to 270 °C</td>
<td>270 °C</td>
<td>270 to 25 °C</td>
</tr>
</tbody>
</table>

2.3.7. Differential mechanical analysis (DMA)

Dynamic Mechanical Analysis measurements were carried out using a Mettler Toledo DMA1 STARE system, operating in the single cantilever bending mode using titanium clamps (Figure 1-). Tests were performed at 1 Hz and the temperature was ramped from -70 °C to 160 °C at a rate of 3 °C/min, and the displacement was set to 10 µm. The dimension of each sample was 2 mm in length and a cross section of 4 x 4 mm. These dimensions were measured accurately by a micrometer before every experiment.
Figure 1-7: A diagram showing the single cantilever mode in DMA.
3. Results & Discussion

HDPE is clearly a non-polar polymer and plasticisers such as phthalates will clearly interact through van der Waal’s interactions. It would not necessarily be expected that DESs would mix well with HDPE but in all cases extrusion produced mixtures. Conductivity measurements showed that the materials were non-conducting which suggests that the DES does not form continuous liquid channels through the plastic. There are numerous parameters which can be measured to provide information about the interaction between the DES and polymer;

Material appearance, including colour, transparency, and homogeneity, is an important property as it provides information on the quality and applicability of material. The mechanical properties of a material are crucial parameters as they describe the future use of the material. The parameters which are measures are the tensile strength, tensile strain and chordal modulus. These provide information about the strength, ductility and flexibility of the plastics.

The ultimate tensile strength of a material is defined as the maximum tensile stress required to break a material. The maximum elongation is defined as the relative change in material length compared to its original length. The chordal modulus is the slope of the stress-stain curve in the low deformation region. These parameters are shown schematically in Figure 3.1.
The glass transition temperature defined the temperature at which a material changes from a hard brittle material to a rubber-like material. This, as well as the melting temperature, is the most important thermal parameter for a plastic material, as it allows a working temperature range to be established and comparisons to commercial plastics be made.

3.1. High density polyethylene (HDPE)

The mixtures here contained DESs as plasticisers and HDPE as thermoplastic biopolymer. In order to allow for probing the degree of plasticisation, pure HDPE were equally pressed and treated in similar manner as those containing ionic liquids to develop compression mouldable materials. Initially, HDPE was mixed with 1, 3 and 5 wt% DES before extrusion but only 1 and 3 wt% were miscible with the plastic and the data for 5 wt% were discarded.

3.1.1. Sample color comparison

The appearance of the extruded HDPE materials is shown in Figure 3.2. Both Ethaline and Reline produce a slight yellow colouration to the plastic whereas Glyceline is white.
but the colour density is inhomogeneous. As the ratio of the DESs to go up, the homogeneity goes down, and the colour intensities in the inhomogeneous regions. This appears to be very random and uneven, which may be attributed to non-even distribution during the mixing and the extruding process, which is to be expected as no specific orientation can be achieved with the process utilized to form these materials.

<table>
<thead>
<tr>
<th></th>
<th>Ethaline</th>
<th>Glyceline</th>
<th>Reline</th>
</tr>
</thead>
<tbody>
<tr>
<td>1%</td>
<td><img src="1" alt="Image" /></td>
<td><img src="2" alt="Image" /></td>
<td><img src="3" alt="Image" /></td>
</tr>
<tr>
<td>3%</td>
<td><img src="4" alt="Image" /></td>
<td><img src="5" alt="Image" /></td>
<td><img src="6" alt="Image" /></td>
</tr>
</tbody>
</table>

Figure 3.2: Colour comparison between different HDPE sample sheets

This is logical as the high content of the ionic liquids may cause some of the polymer pellets to stick to each other or on the feeder of the extruder, and causing those pellets to be surrounded by more liquids and causing stronger chemical reaction, hence heavier colour of the pellets. This leads to an increasing risk of the material not properly forming under heat and pressure. As the different colour of the pellets might lead to uneven distribution of the darker spots on the sheets. To have a better understanding of the form of DES inside the sample, the density of the HDPE samples were measured. The density of the HDPE sheet without plasticiser was found to be 0.994 g cm$^{-3}$
whereas that containing 1% Glycine was 0.948 g cm\(^{-3}\). This is an unusual result as the density of pure Glycine is 1.30 g cm\(^{-3}\) so the plasticised HDPE should be more dense than the unplasticised polymer. This would suggest that the DES is increasing the free volume of the plastic and this should therefore decrease the glass transition temperature and rigidity of the plastic.

The conductivity of all samples was tested and showed no current flow through the sample.

\[ \text{Figure 3.3: Typical Stress-Strain curve for pure HDPE and HDPE containing 1 wt\% Glycine.} \]

\[ \text{3.1.2. Mechanical analysis} \]

Figure 3.3 shows a typical Stress Strain curve for pure HDPE and HDPE containing 1 wt% Glycine. It can be seen that the DES increases the elongation at break but has
only a small effect on the ultimate tensile strength. The chordal modulus is also decreased showing that the DES is acting as a plasticiser. Figures 3.4 and 3.5 show the ultimate tensile stress (UTS), percent elongation at break obtained for the three DESs listed above at 1 and 3 wt% loading. Each result was taken as the average from 10 samples. It is interesting to note that the error bar for most samples containing DES is smaller than that for the blank sample. This shows that despite the apparent visual inhomogeneity of the samples in Figure 3.2 it does not significantly affect the mechanical properties of the plastics. As will be shown below it is quite common for 1 to 2 wt% plasticiser to decrease the UTS by 40 to 50 %.

![Figure 3.4: Chart showing a comparison of the maximum tensile strength of the blank samples and HDPE plasticised by 1,3% of all three DES (from left to right, Ethaline, Glyceline, Reline)](image-url)
Figure 3.5: Chart showing a comparison of the true elongation at break of the blank samples and HDPE plasticised by 1,3% of all three DES (from left to right, Ethaline, Glyceline, Reline)

There are many factors which could affect the strength of the HDPE materials and these include the pre-treatment, composition, water content, extrusion temperature, residence time in the extruder, pressing time and pressing temperature.

As can be seen from Figure 3.4, there are no significant variations in the tensile strength within each type of material. It is notable that all the samples, regardless of additives type or content, showed similar strengths to unmodified HDPE. Plasticisers would normally be expected to decrease the strength and increase the elongation at break and this would be proportional to the amount of plasticiser added as shown below.

It can clearly be seen that all three DESs help to enhance the ductility of the plastic (Figure 3.5). All three DESs approximately double the elongation at break of the plastics with 1 wt % additive compared to the sample without DES. When more DES is
added the ductility returns to values similar to those without additive suggesting that possibly a large plasticiser content leads to inhomogeneous mixtures.

While all three DESs are beneficial as plasticisers, the use of Glycerol-based liquids is beneficial as it is a waste product in the production of long-chain carboxylate salts used as soaps. It is also a by-product of the production of biodiesel via transesterification of oils and fats. The toxicity of DESs has recently been characterized and it was found that they are extremely benign having toxicity which is the sum of the consummate parts.\textsuperscript{68}

Polyethylene, as a non-polar high crystallinity polymer with good melt flow property for easy moulding, is usually processed without plasticiser, since the addition of a plasticiser can lead to a general decline in the physical properties of the products. However for some products, such as films, sometimes it is appropriate to add a small amount of oleic acid amide as processing aids and to make the product smooth and has a improved performance.\textsuperscript{69} As flame retardant, chlorinated paraffin is also a common additive for polyethylene.\textsuperscript{70} Other examples include: dioctyl phthalate, DOP, in low density polyethylene, in the production of microporous film, in a composite based on chlorinated polyethylene, and in the hotmelt adhesive for the pavement marking, glycercyl tribenzoate in adhesives polyethylene polyethylene foams and in a biodegradable formulation. In addition sunflower oil is used in biodegradable formulations containing starch and waxes are used for the production of porous films.\textsuperscript{71}

As shown above, there several applications for plasticisers in polyethylene formulations. Smaller amounts ( < 10 wt%) are added e.g. to make hotmelt adhesives\textsuperscript{72} and the plasticisation of pipe materials.\textsuperscript{73} It has been shown that up to 30 wt% of plasticiser can be added to polyethylene.\textsuperscript{74}

It is useful to note that while elongation increases of 100% are relatively common for plasticisers, it is usually a significantly higher plasticiser content that is required to see a
noticable increase in the elongation at break.

The data above show that all 3 DESs increase the elongation at break for HDPE which suggests that they act as a plasticizer. The data in Figure 3.6, however show that the chordal modulus also increases when the DESs are added to the polymer which shows that the polymers are more rigid than without modifier. This suggests that they have some anti-plasticiser properties.

![Figure 3.6: Chart showing a comparison of the tensile chordal modulus of the blank samples and HDPE plasticised by 1 and 3 wt% of all three DES (from left to right, Ethaline, Glyceline, Reline)](chart)

The chordal modulus data has a significant error bar associated with it. As can be seen from Figure 3.3 there is considerable uncertainty associated with the position where the chord is made to the stress-strain curve. Qualitatively the flexibility of all of the samples feels similar showing that despite the large error bar the flexibility of the plastics is roughly constant when the plasticiser is added.
Overall there is only a small loss of maximum tensile stress throughout the range of materials amplifying the increase in chordal modulus is characteristic from the elongation that occurs. The unmodified HDPE is likely to be stiffer than the materials containing ILs due to the superior ductility of the modified samples. Similar to the elongation data, it is clear ILs have a profound effect on these samples.

3.1.3. Glass transition temperature
The glass transition temperatures of HDPE modified with DES were determined using DSC and that data are shown in Table 3.1. The value of the unmodified HDPE was similar to that of the starting material and is typical for HDPE (-81 °C) confirming that the methodology is correct. It can be seen that almost all of the DESs plasticised HDPE have glass transition temperatures that are decreased by up to 9 °C. This is a typical value for this amount of plasticiser.

Table 3.1: Effect of plasticiser type and concentration on the glass transition temperature of HDPE as determined using DSC

<table>
<thead>
<tr>
<th></th>
<th>Ethaline</th>
<th>Glyceline</th>
<th>Reline</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-81.3</td>
<td>-81.3</td>
<td>-81.3</td>
</tr>
<tr>
<td>1 wt%</td>
<td>-85.4</td>
<td>-84.0</td>
<td>-82.7</td>
</tr>
<tr>
<td>3 wt%</td>
<td>-89.3</td>
<td>-80.0</td>
<td>-87.7</td>
</tr>
</tbody>
</table>

It has previously been shown that DSC traces occasionally exhibit an upper and lower Tg, a phenomenon dependent upon the amount and type of plasticiser. No distinct melting temperatures were observed for any samples although an indication of that can clearly be seen from the DMTA data in the Appendix A1. In all cases samples show evidence of decomposition at approximately 140°C.

The glass transition temperature was also determined by dynamic mechanical analysis (DMA) the raw data for which are shown in Appendix A2 and a summary of Tg values
are shown in Table 3.2. The Tg values are clearly seen as a broad peak. Whilst the Tg values were marginally different to the DSC data, it is normal as they are measuring slightly different properties of the polymer. Looking at the DTA data, they followed a very consistent yet similar trend. It can be seen from both graphs that the results seem to be very consistent and there are no significant difference between the blank group and the plasticized materials. Which showed an intriguing possibility that instead of plasticiser, the DESs were actually acting as lubricant which can change the workability and flexibility of polymers without changing the glass temperature. The Abbott group has recently shown that DESs act as extremely effective lubricants which are comparable with mineral based lubricants.\textsuperscript{75} Abolibda has also shown recently that the use of DESs as plasticisers in starch increases the melt flow rate which confirms that they can act as lubricants for polymers.

Table 3.2: Effect of DES type and loading on the glass transition temperature of HDPE as determined using DMA

<table>
<thead>
<tr>
<th>wt% DES</th>
<th>Ethaline</th>
<th>Glyceline</th>
<th>Reline</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>-156.4</td>
<td>-156.4</td>
<td>-156.4</td>
</tr>
<tr>
<td>1%</td>
<td>-117.8</td>
<td>-119.65</td>
<td>-121.1</td>
</tr>
<tr>
<td>3%</td>
<td>-122.7</td>
<td>-120.5</td>
<td>-117.35</td>
</tr>
</tbody>
</table>

\textbf{3.2. Polylactic Acid (PLA)}

The second polymer to be studied was polylactic acid, the structure of which is shown in Figure 3.7. PLA has a carbonyl group and is capable of accepting a hydrogen bond from the DES. It can be thought of as more polar than HDPE and so it might be expected that the DES would have a more significant effect upon the mechanical properties of PLA.
Comparing Figures 3.1 and 3.8 it can be seen that PLA has a much higher UTS and a much smaller ductility than HDPE which would be expected as the former is a more polar polymer which is capable of hydrogen bonding. The elastic region for PLA is much more linear than that for HDPE.
3.2.1. Mechanical analysis

In contrast to the results for HDPE, DESs were found to have a significant effect upon the tensile stress of PLA. It was also shown that there was a significant variation within the three DES modifiers. It can be seen from Figure 3.9 that the UTS for all of the DESs tested were lower than the control with no additive. While a decrease in UTS would be expected for most plasticisers, Figure 3.10 shows the elongation at break is also considerably lower than the control meaning that the materials are becoming more brittle. This was observed by the fact that the 1% and 2% Reline samples were too brittle to apply any mechanical force to so they could not be tested. For PLA the DESs could be said to be extremely effective anti-plasticisers. They function probably by hydrogen bonding across the carbonyl groups effectively cross-linking neighbouring chains. This would tie in with urea being the strongest hydrogen bond donor and therefore be able to crosslink the most. The interesting observation that the brittle

Figure 3.8: Typical Stress Strain curve for pure PLA and PLA containing 1 wt% Glyceline

Figure 3.9: Chart showing a comparison of the maximum tensile strength of the blank samples and PLA modified by 1,2,3% of all three DES (from left to right, Ethaline, Glyceline, Reline)
behaviour is decreased by adding more DES can be explained by there being sufficient liquid to lubricate between the chains.

Figure 3.12: Chart showing a comparison of the maximum tensile strength of the blank samples and PLA modified by 1, 2, 3% of all three DES (from left to right, Ethaline, Glyceline, Reline)

It is a known fact that in most occasions the addition of small amounts of solvent to a polymeric system leads to a decrease of the glass transition temperature (Tg) with a softening effect of the polymeric materials. This “plasticisation” phenomenon as discussed above is widely exploited in applications and has been the subject of various experimental and theoretical studies. The study of anti-plasticisers, however, has gained some attention as well, as a special class of molecules with the ability to lower the glass transition, while simultaneously increasing the elastic moduli (or stiffness) of polymeric materials in the glassy state. Examples of anti-plasticiser/polymer pairs include tricresyl phosphate in polysulfonate and dibutylphthalate in polycarbonate.
Various theories of the anti-plasticisation mechanism have been suggested. One dominant idea is that the anti-plasticiser interacts strongly with the polymer chains and acts as a cross-linking agent. Another theory is that the strong interaction between the anti-plasticiser and the polymer has also helped to form an adsorbed layer of solvent that slows down fast molecular motions. It has also been suggested that anti-plasticiser molecules fill the space that allow the polymer to move freely volume, and a number of models have been introduced based on this point. But recently, this free-volume concept has been challenged by Ngai et al. and Rizes et al., so the interpretation of this phenomenon remains unresolved, even from a qualitative standpoint. We must also consider the possibility that this phenomenon may have more than a single cause and all theories mentioned above may each be partially correct.

Thermoplastic polymers such as PLA, with stiff, bulky side groups or back-bones, are found to exhibit a large degree of packing frustration and are thus more fragile polymers. PLA can easily interact with ILs by forming hydrogen bond in between the polymer chain thus making crystallites which become localized into regions of space. A slight reduction of Tg would be expected to occur, and in addition such particles would be expected to increase the density and the stiffness of the mixture in the glassy state. Such additives should therefore lead to an increase of the fragility.

Interestingly Glyceline behaves very differently to Ethaline and Reline. Urea (Reline) is the strongest hydrogen bond donor and ethylene glycol (Ethaline) and glycerol (Glyceline) should have relatively similar hydrogen bond strengths. It is therefore not evident why the differences occur between the three liquids. It should however be noted that the same trend is observed for the plasticization of starch with the same three liquids with Glyceline imparting by far the highest strength to the plastic. Ref Tariq
Figure 3.13: Chart showing a comparison of chordal modulus of the blank samples and PLA modified by 1,2,3 wt% of all three DES (from left to right, Ethaline, Glyceline, Reline)

As would be expected for a brittle material the chordal modulus increases with the addition of DES. This is because the polymer chains are less able to flex as they are hydrogen bonded to their neighbours. This should manifest itself in an increase in the glass transition temperature with added DES.

3.2.2. Glass transition temperature
Table 3.3 shows the glass transition temperatures for PLA mixes with three different DESs at three concentrations. The raw data are contained in Appendix A3. The glass transition temperatures of the PLA samples were higher than those of polyethylene due to the hydrogen bonding. Like HDPE, however Tg does not show big difference for PLA after being plasticised.
Table 3.3: Effect of plasticiser type and loading on the glass transition temperature of PLA as determined using DSC

<table>
<thead>
<tr>
<th>PLA + wt% Plasticiser</th>
<th>Ethaline</th>
<th>Glyceline</th>
<th>Reline</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>57.05</td>
<td>57.05</td>
<td>57.05</td>
</tr>
<tr>
<td>1%</td>
<td>50.00</td>
<td>54.54</td>
<td>54.05</td>
</tr>
<tr>
<td>2%</td>
<td>50.51</td>
<td>55.01</td>
<td>57.82</td>
</tr>
<tr>
<td>3%</td>
<td>49.25</td>
<td>53.89</td>
<td>54.82</td>
</tr>
</tbody>
</table>

3.3. Polyethylene terephthalate (PET)

The third polymer tested was polyethylene terephthalate, the structure of which is shown in Figure 3.14. PET is probably the most widely used polyester being used extensively for polyester fibres and plastic drinks containers. As with PLA, PET has a carbonyl group and is capable of accepting a hydrogen bond from the DES. PET could be expected to act in a similar way to PLA but the aromatic ring in the chain could change the flexibility of the polymer.

![Figure 3.14: Polyethylene terephthalate](image-url)
3.3.1. Mechanical analysis

Despite repeated attempts it was not possible to create a sheet of DES modified PET as in all cases the samples were too brittle to enable dog-bone samples (Figure 2.5) to be cut from the sheet. In all cases the samples shattered when removed from the mould. Two different approaches were made to slow down the cooling procedure hence prevent the sheets from shattering, however, neither was successful. A typical sample of plasticized PET is shown in Figure 3.15.

3.3.2. Glass transition temperature

It was however still possible to measure the glass transition temperature of the plasticized samples. The glass transition temperature of PET showed only slight differences after modified (Table 3.4). But unfortunately it is lacking additional data to compare due to the difficulty of forming sample sheets. Also, with some of the plasticised samples, it appears to have another bump after it passed the glass transition temperature, which might be caused by polymer recrystallising. The raw data are shown in Appendix A4.
Table 3.4: Effect of plasticiser type and loading on the glass transition temperature of PET as determined using DSC

<table>
<thead>
<tr>
<th>PET + wt% Plasticiser</th>
<th>Ethaline</th>
<th>Glyceline</th>
<th>Reline</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>68.76</td>
<td>68.76</td>
<td>68.76</td>
</tr>
<tr>
<td>1%</td>
<td>61.33</td>
<td>68.9</td>
<td>63.88</td>
</tr>
<tr>
<td>2%</td>
<td>59.03</td>
<td>70.05</td>
<td>63.70</td>
</tr>
<tr>
<td>3%</td>
<td>58.26</td>
<td>69.35</td>
<td>63.68</td>
</tr>
</tbody>
</table>

3.4. Comparison

The combination of DESs with thermoplastic matrix in general presents a question associated to the compatibility between the polar and non-polar parts of the polymer and solvents. It can be seen from data above that DESs have a marked effect upon the mechanical properties of all of the polymers tested. The two polymers with the ester linkage, PLA and PET can both be considered as polar polymers and in both cases the DESs tended to make them more brittle than without DESs.

In contrast the DESs all acted to plasticise HDPE despite it being a non-polar polymer. This is thought to occur because the DES lubricates between the polymer chains enabling slip and increasing the ductility at break. The fact that they do not act as true plasticisers can also be observed by the fact that the UTS is not changed significantly whereas the chordal modulus increases showing that the DES imparts stiffness to the polymer structure.

There are differences observed in the effect of each of the DESs which are still not fully understood but they are similar to work already published on plasticising starch. Figure 3.16 shows mechanical strength data by Abbott et al. for starch with the same DESs tested in the current study\textsuperscript{83}. It can be seen that Glyceline produces the strongest but least ductile material whereas Ethaline is the reverse.
Figure 3:16: Representative stress-strain curves for starch modified with choline chloride with either; urea, ethylene glycol or glycerol. Samples were extruded at 130 °C, 100 rpm and a die pressure of c.a. 20 bar before being pressed at 145 °C, 110 kN for 10 min\textsuperscript{83}.

For PLA and PET, the DESs appear to act as an anti-plasticiser making the materials more brittle. They significantly decrease the extension at break and the UTS. The DESs do not significantly change the glass transition temperatures of any of the polymers showing that they are not increasing chain flexibility. True plasticisers would tend to show greater solubility in the polymer. The observation that any more than 2% DES tends to shed from all the polymers suggests that they function by filling up the void volume of the material.

To see if the DESs form a continuous layer within the polymer the resistance of the polymers was tested. The digital voltmeter showed no electrical conductivity within the sample showing that there is no continuous pathway of DES through the sample. This suggests that the DES could exist as discrete pockets of liquid distributed throughout the plastic.
3.5. **Homogenisation of HDPE and thermoplastic starch**

One of the issues with polyolefin polymers is their slow environmental degradation due to the inability of enzymes to degrade saturated hydrocarbons. One mechanism to achieve higher rates of mechanical degradation would be to incorporate starch within the polyolefin structure.

Starch is a low cost, hydrophilic and biodegradable renewable resource with limited mechanical performance. Its ductility can be improved by adding plasticiser such as glycerol to water-swollen starch granules in the presence of heat and a high shear. The resulting plasticized starch is known as thermoplastic starch (TPS). It can be melt-blended with polyolefin, such as polyethylene (PE), to improve its mechanical properties of the starch. In general, however homogenization of the two polymers only occurs with polymeric stabilisers. Polyethylene/maleic anhydride graft (PE-g-MA) copolymers containing 0.4 and 0.8 mol % anhydride groups were used by Bikiaris and Panayiotou. In a previous article on HDPE/TPS blends,\(^5^9\) it was shown that the glycerol-rich domains of TPS dispersed phase migrated to the interface, and played a lubricant role, which resulted in very high mechanical properties. The area of starch polyolefin blends has been reviewed by Hamad *et al.*\(^8^2\)

In this study it is proposed that since both starch and HDPE can be modified using DESs this would be a suitable method to simply homogenise the two polymers. Two different methods were tested to test the ability of the DES to enable mixing. Firstly the two types of polymer (HDPE + 1 wt% Glyceline and Starch with 25 wt% Glyceline) were ground separately and then the fine powders were pressed together at 120 °C to form a coherent film. Two samples were made; one with 30 wt% modified starch and a second with 40 wt%. The tensile strength and elongation at break were measured and the data are shown in Figure 3.17. It can clearly be seen that the blended materials are both considerably weaker than either HDPE or TPS showing that the strength is
governed by the interfaces between the two materials. While this may be viewed as a poor material from a mechanical perspective it does have the advantage that it should mechanically fragment much more rapidly as the starch granules are much more accessible.

![Figure 3.17: tensile and elongation data from modified HDPE:modified starch=7:3 (before extrusion)](image)

This experiment was repeated by extruding the two modified polymers together. This should clearly enable more homogeneous blending but will render it slower to degrade. Starch was plasticized with Glyceline and blended with HDPE in a one-step extrusion process at 150°C. Blends were prepared in two ratios, one mixture containing 30 wt% of TPS and 70 wt% of HDPE, one containing 40 wt% of TPS and 60 wt% of HDPE.

![Figure 3.18: tensile and elongation data from modified HDPE:modified starch=3:7 and modified HDPE:modified starch=4:6 (after extrusion)](image)
Direct comparison with PE/TPS starch from the literature is complex due to the presence of complex co-polymers in most cases. Otey and coworkers\textsuperscript{69,70}, used HDPE blended with TPS using poly(ethylene-co-acrylic acid) as a modifier. They tested blend up to 40 wt\% TPS and found that as in Figure 3.18 the more TPS the lower the UTS of the blend. UTSs of typically 6 to 16 MPa were presented which compare well to those presented above. The elongation at break was also reported to be in the region 40 to 65\% which again are comparable. Research shows that when blended with thermoplastic, starch powder tends to degrade during processing\textsuperscript{71}. Psomiadou \textit{et al.}\textsuperscript{72} also studied PE/starch blends. With higher starch loadings, poor strain values were observed due to weak adhesion between the filler and matrix. The specimens failed during neck propagation, which indicated fracture.

In a previous study, it was demonstrated that high tensile strength was obtained for modified HDPE/TPS blends due to a double mechanism at the interface that related to the formation of glycerol and copolymer layers\textsuperscript{59}. A similar improvement of the mechanical properties of LDPE was reported with varying proportions of plasticised tapioca starch in presence of a compatibiliser (poly(ethylene-co-glycidyl methacrylate))\textsuperscript{60}. With the amounts of TPS at HDPE contents increasing from 30 wt\% to 40 wt\%, the micrographs of impact and tensile fractured surfaces showed a brittle–ductile failure transition. Regarding the literature on polyolefin/TPS blends, a few articles dealing with the mechanical performances of such blends have been reported\textsuperscript{61}, but these did not address the failure mechanisms.
An interesting observation was made after the extrusion process, which was that the co-polymer was extremely effective at cleaning the extruder. The remaining sample chips were easily peeled off and fell off after soaking in hot water.

A sample sheet (with 30% modified starch and 70% modified HDPE) was put into a beaker with 60ml of boiling water on a hot plate (to keep a steady temperature) for 3 hours. The sample was then removed and dried at room temperature. Figure 3.19 shows that the sample became whiter and less translucent than before suggesting that some of the starch was removed. The sample was weighed before and after the experiment and it was found that the mass decreased from 5.40 g to 4.81 g (11%). Clearly the HDPE is insoluble, the starch is partially soluble and the DES is totally miscible with water. A mass loss is most likely due to a loss of DES from the material. The DES only accounts for 8.2% by mass of the material so it is clear that some of the starch has also been removed from the sheet. To see the effect of boiling on the structure a series 3D microscope images were taken as shown in Figure 3.20.

It can be seen that the sample surface prior to boiling was extremely smooth but it became rough on boiling with what appears to be multiple visible holes in the surface. This suggests that the samples will degrade in the environment when exposed to water.
In addition the materials became more brittle after boiling showing that they will mechanically degrade more rapidly than pure HDPE which is one of the major environmental issues.

Figure 3.20: 3D microscope images of a sample of 70% HDPE-30% starch before (left) and after (right) boiling in water for 3 hours

The main issue with polyethylene it its longevity in the environment. Many of the issues are related with its ingestion into animals. Low resolution microscopy shows that after immersion in water, mechanical action makes the plastic begin to flake into sub µm thick layers as shown in Figure 3.21. This suggests that the mix of HDPE and starch is homogeneous. To show that this is the case DSC was carried out on a sample the 30% modified starch and 70% modified HDPE. It was found that although both components had a Tg of -84°C the composite had a Tg value of -113.4°C, showing that they co-plasticised each other to produce a homogeneous mixture.

Figure 3.21: Low resolution microscopy (x24 magnification) of the sample shown in Figure 3.23 (right)
4. Conclusions

This study has shown that HDPE, PLA and PET can be mixed with deep eutectic solvents to form modified polymers. In all cases the DES was shown to significantly change the mechanical properties of the plastic although in no cases was the glass transition temperature significantly affected. HDPE extruded with DESs was found to have similar strength but increased ductility and increased stiffness showing that the DES acted more as a lubricant than a plasticizer.

When mixed with polar polymers (PLA and PET) the DESs acted as anti-plasticisers decreasing both the UTS and elongation at break. The polymers became brittle and in most cases more rigid. The DESs are thought to act by filling the free volume of the polymer decreasing the volume for the chains to rotate in and hence decreasing the flexibility of the polymer.

The DESs were found to be effective agents for homogenising polymers of different polarity. It was shown that starch which had been plasticised with DESs could be blended with HDPE which had been similarly modified. The pressing time and temperature were found to be relatively unimportant so it was be concluded that the extrusion conditions are the important part in controlling the ability of the salt to plasticise the starch/glycerol mixture.
5. **Future work**

The most interesting results from this study have been the ability of DESs to homogenise polymers of different polarity and this would probably be the most useful area to follow up. It would be useful to determine the mechanism by which the polymer chains are homogenised and this could be done using X-ray diffraction to study the crystallinity of the two phases as a function of DES composition. Following this optimisation of the extrusion conditions could be carried out to determine how suitable these materials could be for polyethylene modification. It would be interesting to see the extent to which polar and non-polar polymers could be blended using this approach. It may also be interesting to see if this approach could be used to blend natural fillers with polyolefins to improve the biodegradability of composites.

Carbohydrate-based materials have been extensively studied within the group. Recent research, within the group, has shown that some ionic liquids can modify collagenic materials due to their charged structure. It has been shown that leather can be modified by this approach and particulate materials can be infused into the collagen structure which is swelled greatly by DESs.

Studies have also shown the use of DESs to modify materials such as gelatine and a variety of materials with different viscoelasticity could be produced. The conducting properties of DESs could also be used to make conducting membranes. It is thought that acidic DESs could be used to dissolve significant amounts of proteins. One of the reasons is the unfolding of the protein chains, and surprisingly the proteins remain stable for long periods of time and can be reprecipitated by treatment with aqueous salt solutions. This may be an interesting method by which to make novel biomaterials.
6. References


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7. Appendix

Figure A1: A comparison of the glass transition temperature of the blank samples and HDPE plasticised by 1,3% of all three DES (from top to bottom, Ethaline, Glyceline, Reline) using DSC

Figure A2: A comparison of the glass transition temperature of the blank samples and HDPE plasticised by 1 and 3% of all three DES using DMA
Figure A3: glass transition temperature of the blank samples and PLA modified by 1,2,3% of all Ethaline using DSC as example

Figure A4: glass transition temperature of the blank samples and PET modified by 1, 2 and 3 wt% of Ethaline using DSC as example