

Failure analysis of LLDPE based materials

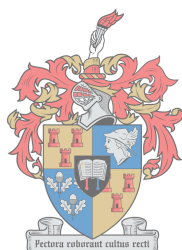
By

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Abstract

In this study the environmental stress cracking resistance (ESCR) of various low density polyethylene (LDPE) and linear low density polyethylene (LLDPE) materials are evaluated. The main purpose was to correlate micro molecular structure, such as molecular weight (MW), molecular weight distribution (MWD), short chain branches (SCB) and crystallinity to the ESCR of these materials.

Initially a suitable method for evaluating environmental stress cracking (ESC) was found. The ESCR test for ethylene based plastics was first used on a LLDPE film. A more fundamental approach was attempted with the modified bending test, adapted from the bell telephone test for the purpose of this study. Several stress crack agents (SCAs) were used with varying Hansen solubility parameters (HSPs). The materials were characterised by DSC, FTIR and high temperature GPC. Scanning electron microscopy (SEM) was used to analyse the morphology of the cracked and delaminated surfaces. Extractable fractions from the bulk were also analysed with DSC and HTGPC. Tensile testing was done on films exposed to SCAs as well as on cracked materials obtained from the modified bending tests.

It was found that additives are easily removed from the material surface during exposure to alcohols and aliphatic solvents. The modified bending test was able to simulate cracking conditions and when a certain polymer solvent combination did result in crack propagation that same combination allowed the extraction of low molecular mass branched polyethylene from the bulk to the solvent. It was found that little change in film properties (thermal and mechanical) were observed after exposure to various SCA's, although heterogeneous layered films did show a diminishing effect (in terms of material performance) when a force was applied on the material. Heterogeneous layered films also showed incompatibility by a delamination effect. When applying a force on a PE film when exposed to light hydrocarbons did show to decrease the yield strength causing the material to deform inelastically, which was attributed to the penetration of these hydrocarbons followed by the untangling PE molecules in the amorphous phase.

Opsomming

In hierdie studie word die omgewingsstreskraakweerstand van verskeie lae digtheid poliëtileen (LDPE) en lineêre lae digtheid poliëtileen (LLDPE) materiale geëvalueer. Die hoofdoel was om mikromolekulêre struktuur, soos molekulêre gewig (MW), molekulêre gewigverdelin , kortkettingtakke (SCB) en kristalliniteit aan die omgewingsstreskraakweerstand van hierdie materiale te korreleer.

Aanvanklik is 'n geskikte metode vir die evaluering van omgewingsstres krake gevind. Die omgewingsstreskraakweerstand -toets vir etileen-gebaseerde plastiek is eers op 'n LLDPE-film gebruik. 'n Meer fundamentele benadering is gepoog met die gewysigde buigingstoets, aangepas uit die kloktelefoontoets vir die doel van hierdie studie. Verskeie stres kraakmiddels is gebruik met verskillende Hans oplosbaarheid parameters . Die materiale is gekenmerk deur DSC, FTIR en hoë temperatuur GPC. Skandeer-elektronmikroskopie (SEM) is gebruik om die morfologie van die gekraakte en gesegmenteerde oppervlaktes te analiseer. Uittrekselbare breuke uit die massa is ook geanaliseer met DSC en HTGPC. Spanningstoetsing is gedoen op films wat aan SCA's blootgestel is, sowel as op gekraakte materiaal verkry uit die gewysigde buig toetse.

Daar is gevind dat bymiddels maklik uit die materiaaloppervlak verwyder word tydens blootstelling aan alkohole en alifatiese oplosmiddels. Die gewysigde buig toets was in staat om kraakomstandighede te simuleer en wanneer 'n sekere polimeer oplosmiddel kombinasie tot kraakvervorming gelei het, het dieselfde kombinasie die onttrekking van lae molekulêre massa vertakte poliëtileen vanaf die massa tot die oplosmiddel toegelaat. Daar is bevind dat klein veranderinge in film eienskappe (termies en meganies) waargeneem word na blootstelling aan verskeie SCA's, hoewel heterogene lae films 'n afnemende effek (in terme van materiaalprestasie) toon toe 'n krag op die materiaal toegedien is. Heterogene gelaagde films het ook 'n delaminerende effek onveroenigbaar getoon. Wanneer 'n krag op 'n PE-film toegedien word wanneer dit aan ligte koolwaterstowwe blootgestel word, het dit getoon dat die opbrengs sterkte veroorsaak dat die materiaal onelasties vervorm word, wat toegeskryf word aan die penetrasie van hierdie koolwaterstowwe, gevolg deur die onophoudelike PE molekules in die amorf fase.

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List of abbreviations

ABS	Acrylonitrile butadiene styrene
ASTM	American Society for Testing Materials
DSC	Differential scanning calorimetry
EPDM	Ethylene propylene-diene rubber
ESC	Environmental stress cracking
ESCR	Environmental stress cracking resistance
ESCR test 1	ESCR test for ethylene based plastics
ESCR test 2	Modified bending test
EVA	Poly (ethylene-vinyl acetate)
EVOH	Poly (ethylene-co-vinyl alcohol)
FTIR	Fourier-transform infrared spectroscopy
HDPE	High density polyethylene
HIPS	High impact polystyrene
HSP	Hansen solubility parameter
HTGPC	High temperature gel permeation chromatography
IPPC	Impact polypropylene copolymer
LDPE	Low density polyethylene
LLDPE	Linear low density polyethylene
LLDPE-g-MAh	Linear low density polyethylene grafted Maleic Anhydride
mLLDPE	Metallocene linear low density polyethylene
MPET	Metalized polyethylene terephthalate
\overline{M}_n	Number average molecular weight
\overline{M}_w	Number average molecular weight
MW	Molecular weight
MWD	Molecular weight distribution
NMR	Nuclear magnetic resonance
PA	Polyamide
PC	Polycarbonate
PE	Polyethylene

PENT	Pennsylvania edge-notch tensile
PEX	Crosslinked polyethylene
PMMA	Poly methyl methacrylate
PP	Polypropylene
PS	Polystyrene
SCA	Stress crack agent
SCB	Short chain branch
SCBD	Short chain branching distribution
SCC	Stress corrosion cracking
t	Thickness of the sample in bell telephone test
T_c	Crystallization temperature
T_g	Glass transition temperature
T_m	Peak crystalline melting temperature
UHMWPE	Ultra-high molecular weight polyethylene
UV	Ultraviolet
w	Width of the holder in bell telephone test

Chapter 1

Introduction and objectives

1.1 Introduction

Polymers have gained great interest in recent years. They have unique properties that make them desirable for many applications.¹ Polymers can be categorized in 2 main groups called natural polymers and synthetic polymers. Polyolefins are classified as synthetic polymers and their use has increased by more than 1000% in the past 50 years.¹ The desirable properties that polyolefins possess include excellent chemical resistance, ease of processing, superior fatigue and impact resistant and furthermore it is relatively cheap to produce.^{2,3} It therefore is an ideal material for blown films used in liquid liners and food packages. Polyolefins can be tailored for specific end uses. This can be done by copolymerizing ethylene with other α -olefins, namely propene, butene, hexene, ect.² The use of a suitable catalyst can also affect the ultimate properties of the product³.

In this dissertation we concentrate on the failure of liquid liners made from LDPE and LLDPE materials. Additionally multi-layered films will be assessed as a means of improving the environmental stress cracking resistance (ESCR) of the barrier films. These barrier films have LLDPE outer layers to ensure the chemical resistance is maintained and the inner layer is meant to act as a toughening component.⁴ The inner layers used in this dissertation are a metallised polyethylene terephthalate (MPET) layer and a polyamide/ethylene vinyl alcohol(PA/EVOH) layer.^{4,5}

Environmental stress cracking (ESC) of polyolefins have been studied for several decades⁶and first reported in polyolefins by Richard⁷ in the 1950s. Unfortunately there is limited information on the ESC for bi-component film systems. The leading cause of failure for these liquid liners is ESC. The films develop pinholes which are preceded by catastrophic failure⁸, it is therefore important to design liquid liners that have high ESCR.

ESC is the brittle failure of thermoplastics. These materials normally undergo ductile failure, but when exposed to a surface active agent together with applied stress fails in a brittle manner⁷. In terms of material properties ESC is the susceptibility of a material to undergo crack propagation if an active environment is present. ESC can occur in amorphous polymers and semi-crystalline polymers.^{6,9} The failure of liquid liners can be quite expensive, for instance, spillage of expensive liquids after catastrophic failure during transport. When

looking at the final product, there are specific sites where ESC commonly occur at. Scheirs¹⁰ postulated that points where stress concentrates at is particularly susceptible to ESC. Such points are sharp radii, thin-thick transitions, surface scratches and in the case of pliable films, folds.¹⁰ Other areas where ESC causes catastrophic failure are: weld lines, adhesive joints, contact between dissimilar polymers and moving parts.^{6,10} Failure can and should be reduced by carefully selecting the polymeric composition and the molding or film blowing parameters to ensure that the end use specifications are met.

Another consideration is the additives and whether they affect the material properties. Usually additives are present in the polymer granules they can however be added in the melt. Additives that are used in film applications are categorized according to their function. Fatty acid amides are usually used as additives and act as antiblocking, release, and slip agents^{6,11}. Additives are added to either assist in the molding/film blowing process or colour pigment is added depending on the desired outcome. According to Wypych¹¹ additives migrate from the bulk to the surface. The rate at which the additives diffuse to the surface is largely dependent on the additive/polymer compatibility, temperature, additive concentration and time.¹¹

There are several standard testing methods used to evaluate ESCR. These Tests can be classified in 2 groups, tests at constant strain and tests at constant stress.^{6,9,12,13} From a practical perspective a method should be chosen that is not too time consuming for some methods take several thousand hours.^{6,14,15} Although the knowledge of ESC has increased significantly in the past 50 years, predictive methods to quantify product lifetime are still lacking.^{16,17}

1.2 Objectives

The main objectives in this study are as follows:

- To find or develop a suitable method for evaluating ESC for LLDPE materials including LLDPE films.
- Determining the effect of SCAs on various LDPE and LLDPE granules.
- To investigate whether multi-layered films have superior ESCR than LLDPE films.
- To determine the PE extractability of SCAs based on polarity.
- Relating extractability to ESCR.
- Evaluating whether the process of ESC has an effect on the material properties.
- To determine the effect of the stress crack agent exposure (without stress) on film properties.

- To study the effects of additives on material properties.

1.3 Dissertation layout

The dissertation will consist of 6 chapters with the following layout:

Chapter 1 contains a brief introduction to ESC where after the objectives will be stated, followed by the dissertation layout.

Chapter 2 describes the concept of material failure due to environmental stress cracking. Polymer failure will briefly be discussed together with environmental effects on polymers. ESC will be discussed in detail; this includes the definition of ESC, the history behind ESC, an illustration of how ESC occurs together with an explanation on the model of failure. Furthermore the factors influencing ESC are discussed.

Chapter 3 outlines the standard testing methods of simulating ESC in order to test the resistance against cracking. The 2 main categories for the testing methods are constant strain testing and constant stress testing.

Chapter 4 provides detailed information on the materials used in this dissertation, as well as the methodology behind experimental work done.

In Chapter 5 the results obtained from the experimental work in chapter 4 is shown and discussed together with conclusive findings from the results. These results include DSC data, tensile data, analysis of extractable material, HT-SEC data and FTIR spectra.

Chapter 6 summarizes the conclusions reached in prior chapters.

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Chapter 2

Environmental stress cracking

2.1 Introduction

Polyolefins are important materials that account for approximately 40% of all polymers produced annually worldwide.^{1,2} These polymer materials generally consist of polyethylene(PE), polypropylene(PP), ethylene-propylene copolymers or so called impact polypropylene copolymer(IPPC) and ethylene-propylene-diene rubber(EPDM).¹⁻³ The polyethylene based materials are classified according to density and aptly named, high density polyethylene(HDPE), low density polyethylene(LDPE) and linear low density polyethylene(LLDPE).² These materials are used as polymer films, pipes, toys, containers, wires and cables.^{2,4,5} The widespread use of olefins are due to their superior properties such as, low cost, processability, high flexibility, low weight, chemical stability and puncture resistance.^{1,3,4,6} The superior performance of polyolefins can be correlated to their chemical composition and microstructure. These properties can be tailored during polymer production to fit a specific end use as required by the customer. For example, the catalyst, monomers and processing conditions chosen during polymerization can significantly alter the material properties^{1,3,7,8}; it is therefore important to keep the end use of the product in mind when deciding on which grade to use.

As mentioned previously a large portion of produced polymeric materials are made from polyolefins due to their superior properties. Material made from polyolefins are expected to perform as intended without failure, unfortunately they can fail unexpectedly during aggressive usage conditions.⁹ Of particular importance is the premature embrittlement and cracking of a plastic due to the simultaneous and synergistic effect of stress and contact with a chemical agent.⁹⁻¹¹ This is called environmental stress cracking (ESC) and is considered the leading cause of material failure.¹⁰ Product lifetime is therefore significantly decreased, and with an increase in the annually usage of polyolefins the frequency of failure could increase. Improving material performance by increasing product lifetime is of utmost importance and this can only be done by understanding the process of failure.

2.2 Material failure

Polyolefins, as mentioned previously, have several beneficial properties making them ideal for moulded parts, liquid liners and cables. Unfortunately these materials have a tendency to

fail through brittle failure or ductile failure.^{12,13} Ductile failure occurs when the material inelastically deforms over a large surface area, losing its original dimensions, and possibly breakage if a sufficient load is applied. Brittle failure occurs at points where stress concentrates; at these points cracks appear that can propagate if sufficient load is applied ultimately leading to catastrophic failure.^{13,14} During brittle fracture minimal material deformation occurs.¹⁴ Once a material has failed certain end use requirements of the material might not be met causing the material to be functionally, structurally and aesthetically unacceptable.¹

Causes of material failure can be classified under five categories and they are: poor material properties, product design flaws, insufficient processing during product fabrication, storage and usage.^{1,15} The composition of the material should have properties that are coherent with the end use specifications, for instance, a product that will experience high impact forces should have a high impact strength etc. Material failure can be related to product design; sharp corners, thick/thin transitions, position of moulding gate are usually points where failures occur.^{1,15} Moulding (processing and fabrication) can be time consuming; speeding up this process can have its drawbacks. The drawbacks are excessive molecular orientation in the moulded product, rapid cooling that can cause built in stresses of the mould and inhomogeneous melting which could all lead to polymer failure. Failure due to storage is a result of physical ageing from oxidation and temperature cycling.¹⁶ Lastly failure during use is a result of overloading, high strain cyclic loading and excessive operating temperature.^{1,15}

The rheological and mechanical properties of polymeric materials are largely dependent on molecular weight, molecular weight distribution, molecular branching, crosslinking, crystallinity and molecular configuration.^{8,16,17} Plastics are also blended with additives which include plasticizers, pigments, fillers, flame retardants, slipping agents and stabilizers.^{18,19} These additives are used to improve the properties of polymeric materials. Such factors should be taken into account due to the strong correlation between mechanical properties and material failure. Molecular composition remains as the most important factor that governs bulk material properties.^{1,3}

Failure analysis can be beneficial in designing the product and to guarantee that it does not fail within a certain period of time. The information gained from analysing a failed specimen can be used to provide solutions to the problem thereby avoiding recurrence. There are four types of failure that polymeric materials undergo, they are, mechanical failure, thermal failure, chemical failure and environmental failure.^{1,20,21}

Polymeric materials made from olefins are generally developed for outdoor use. They tend to have superior resistance to environmental corrosion than similar objects made from metals and alloys.²² However, polyolefins are susceptible to various types of environmental effects including ultraviolet (UV) exposure, humidity, temperature variation, ozone oxidation and pollution.^{1,9} These environmental effects alter the chemical and physical composition of the material leading to embrittlement through crack and craze formation.^{20,23}

In this study we concentrate on liquid liners with LLDPE as the major composition in the films. These liquid liners are used to transport large quantities of liquids (>1000l) that have complex and diverse chemical compositions. The liquids are classified under environmental effect that can cause premature failure during use, resulting in spillage of the liquid being transported. Here we focus on decreasing the frequency of product failure by altering the liquid liners' chemical composition.

2.3 Environmental effects

Environmental factors can be considered as any chemical or physical effect that influences the bulk material properties.^{21,23} The product lifetime can significantly be decreased by these factors. Environmental factors are categorized in two groups as seen in Figure 2.1. Of particular interest is the effect of exposure to an artificial environment. Liquid liners are largely affected by artificial environments because they are in contact with liquid environments during transport.²⁴

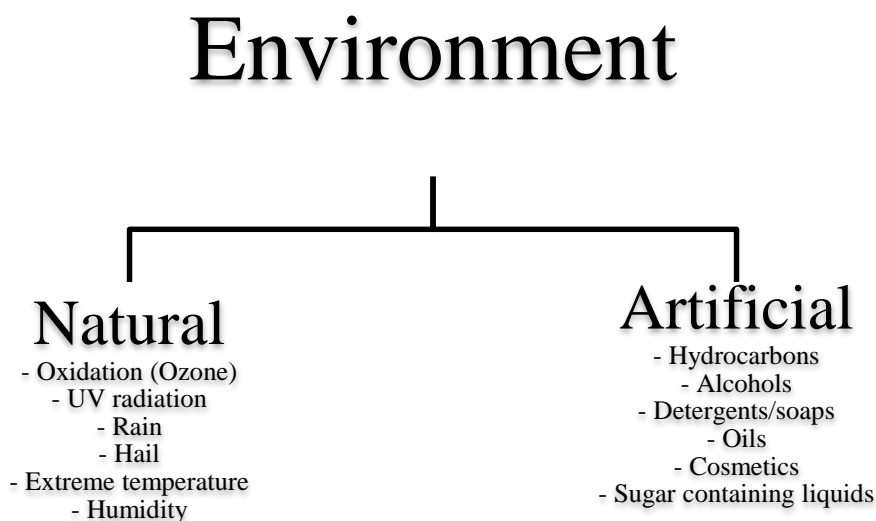


Figure 2.1. Environmental factors influencing material properties.^{1,16,25}

Polymeric materials under a stress field can crack and fail when exposed to certain liquid chemicals.²⁶ Liquids that cause cracking are usually aliphatic solvents, oils, petroleum based substances and surfactants.²⁶⁻²⁸ When exposing a plastic to these liquids while simultaneously applying a stress catastrophic failure may occur. The time to failure is dependent on the liquid/polymer surface tension.²⁹ A low liquid/polymer interfacial tension would result in relatively rapid material failure. Polymer/solvent interaction will be discussed in more detail in Section 2.5.2.

Polyolefins including PE are highly resistant to most acids, soaps and aqueous liquids; however, they do weaken when exposed to strong oxidising agents such as hydrogen peroxide.⁷ Ultimately catastrophic failure is largely dependent on the nature of the environment, the type of polymeric material, exposure time to the environment with stresses and the grade of the material used.¹ As an example branched polyethylene is more susceptible to oxidation than linear polyethylene because branching points have a lower dissociation energy than unbranched points.¹ Additionally, the polymer's crystallinity in a polymer also affects the amount of rate of degradation; a **high** degree of structural order (high crystallinity) perturbs the diffusion of oxygen into the plastic.³⁰ To predict how a material will respond to complex environments can be cumbersome and further research is required to study the effect of the environment on a given polymeric system. This will help to gain a deeper understanding on how a specific polymer system fails.

2.4 Environmental stress cracking (ESC)

2.4.1 Introduction

Environmental stress cracking (ESC) is a process that precedes ultimate failure. Recent estimates suggest that 25% of plastic part failures are caused by ESC.¹³ Plastic materials in use fail prematurely when exposed to certain chemical environments.³¹ ESC of polymeric materials is analogous to stress corrosion cracking (SCC) of metals.³² SCC involves the degradation by chemical reaction. The reaction takes place between the polymer chain and aggressive chemicals, leading to chain scission, cross-linking and embrittlement.^{26,32} ESC of polymer materials is limited to cracking without any chemical reactions, and is governed by diffusion and sorption processes which cause softening and plasticization of the amorphous regions in the material.²⁶

ESC can cause expensive failures and occur after manufacturing, for example, during storage, shipping, at point of sale, or during long term usage.³² Failure has been encountered in various industries, such as, packaging (bottles, films, containers, ect.), electronic (wire and cable insulation), medical (labware and implant components) and automotive industry.^{1,32} Cracking and failure resulting from simultaneous exposure to chemical agents and stresses is a physical process, meaning the composition of the material remains unaltered during cracking. ESC of polyolefins show a physical change in the form of macroscopically brittle cracks that develop on the material surface.^{1,33} ESC can be minimized by carefully selecting which material and material grade to use bearing in mind the environment that the material will be exposed to. Residual stresses that arise from processing are another cause of ESC and should therefore be reduced by choosing milder processing parameters.

2.4.2 Definition of ESC

The term ESC was first defined by J.B. Howard as the “*failure in surface initiated brittle fracture of a polyethylene specimen or part under polyaxial stress in contact with a medium in the absence of which fracture does not occur under the same conditions of stress*”.^{11,32} Wright defined ESC as “*the premature initiation of cracking and embrittlement of a plastic due to the simultaneous action of stress and strain and contact with specific fluids*”.^{1,34}

2.4.3 Historical overview of ESC

ESC has been studied extensively for over 50 years.^{1,32} ESC was first reported for polyolefins by Richard in the 1950s.¹ Since then ESC was reported for several amorphous polymers, such as ABS, PC, PMMA and PS as well as in semi-crystalline polymers (PP, PE, PA, EVOH).³² Research aimed at ESC involve applying a stress on an amorphous or semi-crystalline material in the presence of a surface active chemical.^{26,32,35} The resulting time to failure is then considered as the ESCR.

Numerous groups have studied ESC of polyolefins, more specifically the correlation between micro molecular structure and ESCR.^{17,24,36} Work done by Khodabandelou *et al.*²⁸ involves blending PE with HIPS and evaluating fracture behaviour and environmental stress cracking resistance. Blends of LDPE with EVA was also evaluated in terms of ESCR and it was found that by adding EVA an enhancement of the ESCR was obtained.³² Majority of publications

concentrate on only ESC of PE, where different grades are mixed and evaluated. Chen *et al.*³⁷ blended LDPE and HDPE with ultra-high molecular weight polyethylene (UHMWPE) and found that UHMWPE significantly improves ESCR thereby proving that ESCR is molecular mass dependent. Another group determined that the choice of catalyst also affects the ESCR; they concluded that stereoregular polymer compositions have superior ESCR.³⁸ Furthermore Jansen¹³ found that ESCR is dependent on the molecular size of the stress cracking agents (SCA) and concluded that low molecular-weight chemicals are the most aggressive stress SCA's due to the ability of the small molecules to permeate into the molecular structure of the material. ESC also occurs more rapidly at high SCA concentrations.³⁹

Sardashti *et al.*⁴⁰ correlated strain hardening measurements to the ESCR of PE materials and found that short term mechanical measurements can be used to predict long term properties of the material. Unfortunately ESCR tests were found to have limitations in terms of reliability; nevertheless, recent work has focussed on improving the prediction accuracy of ESCR. Work done by Andena *et al.*⁴¹ aimed at improving the accuracy of ESCR testing configurations; their method proved to be valid and was relatable to existing ESCR tests although time to failure varies depending on the testing method used. It is therefore extremely difficult to determine the exact time to failure of a specific plastic product.

2.4.4 Distinguishing characteristics of ESC

Failure via ESC has some distinguishing characteristics^{1,21}, they are:

- ESC originates from a surface flaw; a flaw acts as a stress concentrator where the crack grows and propagates. Notched specimens are more susceptible to ESC than notch-free specimens.^{1,21,42}
- A new surface is created during ESC and is called a fracture surface. The fracture surface typically has a coarse texture. Figure 2.2 shows the ESC surface of a HDPE/EVA blend.⁴³
- Internal or external stresses are present during ESC. Stress is applied externally during use or applied internally during molding.³²
- Lastly a stress crack agent should be in contact with the material. The presence of a SCA promotes premature failure.²⁶

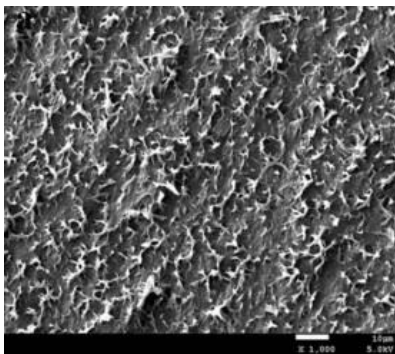


Figure 2.2. Crack surface of the failed sample.⁴³

2.4.5 The occurrence of ESC

ESC occurs in semi-crystalline and amorphous thermoplastic material. Amorphous polymers, such as polycarbonate, have a greater tendency to crack and fail when exposed to SCA. The loose/open structure of amorphous materials facilitates fluid permeation causing rapid ESC.³² Amorphous polymers are more sensitive to ESC at temperatures close to their glass transition temperature (T_g).¹ A larger free volume is seen at temperatures close to the T_g which facilitates fluid permeation into the polymer accelerating the failure process.³² Above the T_g amorphous material act as a viscous liquid meaning the material will deform inelastically without the formation of cracks.¹²

Semi-crystalline polymers such as PE also undergo ESC, even at temperatures above the T_g .¹² Crystalline regions are held together by intercrystalline tie molecules and chain entanglements.⁴⁴ Tie molecules and chain entanglements play an important role in the mechanical properties of the material, through the transmission and dispersion of a load acting on the material.³⁷ ESCR is influenced by polymer microstructure and has been related to the presence of these tie molecules and chain entanglements.^{24,25,44,45} Stress cracking agents act to lower the cohesive forces between the tie molecules, thereby facilitating disentanglement from the lamellae.^{4,32,46} Consequently, cracking is initiated at stress levels lower than the critical stress level of the material. In both amorphous and semi-crystalline polymers ESC is highly dependent on the concentration of the stress crack agent, operating temperature and time, material properties and the stress level.^{1,13,47}

2.4.6 The graphic model of failure

Semi-crystalline polymers can either fail in a ductile or brittle manner. The method of failure is dependent on a stress factor (intrinsic residual stresses and externally applied stresses), environmental conditions and the material properties.³² Brittle failure is preceded by the formation of stress localized microscopic crazes.^{42,47} Inhomogeneities in the bulk localizes the stress eventually giving rise to cracks; the cracks propagate and brittle fracture occurs.^{47,48}

Ductile failure occurs when a relatively high stress level is applied on the material and large scale material deformation is observed.⁴⁹ The necking of polymer films is considered a form of ductile failure.¹⁴ A major difference between the two failure mechanisms is the way energy is absorbed. Energy in the form of a stress is applied on the material; during brittle failure little energy is absorbed to form a crack surface whereas during ductile failure a significant amount of energy is absorbed in order to inelastically deform the material.^{1,14}

ESC is a form of brittle failure and is caused by disentanglement of inter-lamellar links.^{24,50} There are two types of inter-lamellar linkages as seen in Figure 2.3. They are bridging tie-molecules and molecular entanglements.³³ Bridging tie-molecules are polymer molecules that form part of two different adjacent lamellae, thus connecting them through relatively strong covalent bonds.³³ Chain entanglements also connect adjacent lamellae in the form of loose loops and cilia, held together by relatively weak van der Waals forces.^{24,33}

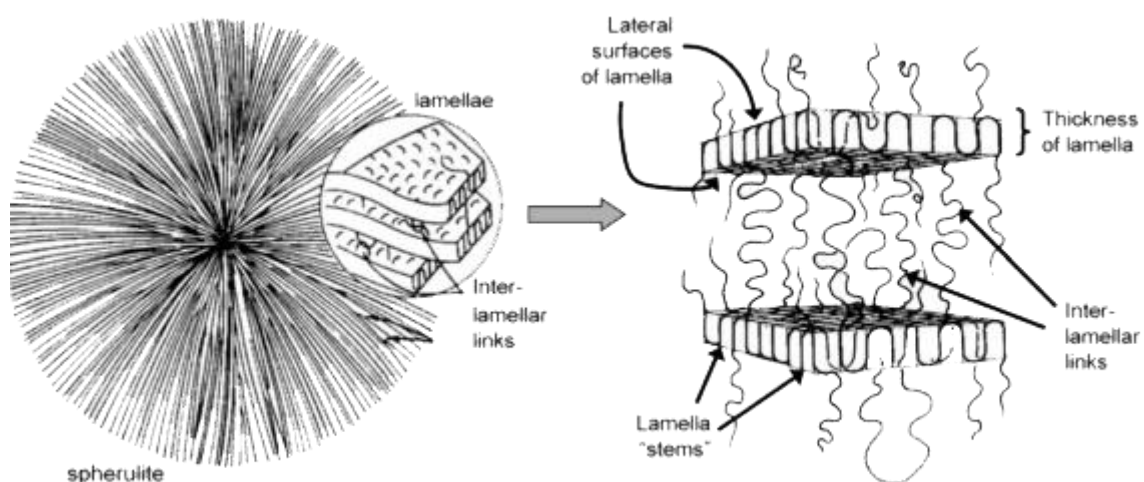


Figure 2.3. Illustration of lamellar connectivity in the amorphous phase.^{24,33}

Inter-lamellar links greatly affect the material's performance. When a tensile load is applied orthogonal to the face of lamellae (Figure 2.4a), the chain entanglements disentangle and the tie molecules stretch.^{32,33} The polymer molecules align parallel to the stress vector whilst adjacent lamellae move apart from one another. At this point tie-molecules cannot be stretched further. Then if sufficient load is applied the lamellae break up into smaller units called "mosaic blocks"(Figure 2.4b).^{32,46} This is considered as a ductile failure process, and occurs when the stress applied is above the yield stress.^{24,46}

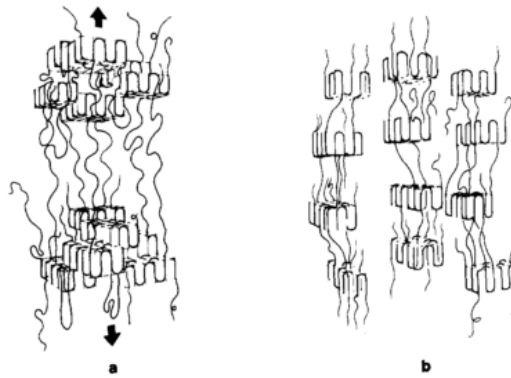


Figure 2.4. Ductile failure mechanism of semi-crystalline material.^{32,33,46}

Alternatively, if a stress below the yield stress is applied over long periods of time then brittle failure occurs. A new crack surface is created orthogonal to the stress direction.¹ The brittle failure mechanism is illustrated in Figure 2.5; the arrows representing a tensile load applied to the material. When a load is applied orthogonal to the lateral lamellar surface (Figure 2.b), the chain entanglements disentangle leaving the tie-molecules as the load bearing.⁵¹ The resulting stress facilitates "pull-out" of tie molecules from the lamellae.^{32,37} As a result, voided areas are created called micro cracks followed by brittle failure (Figure 2.b).⁴² The addition of a stress crack agent accelerates brittle failure by penetrating the amorphous regions and plasticizing it.^{32,52} Plasticization promotes chain untangling in the amorphous areas and "lubricates" the tie molecules.^{32,33} Tie molecule "pull-out" is thereby assisted, resulting in brittle failure earlier and at lower stresses than expected.¹

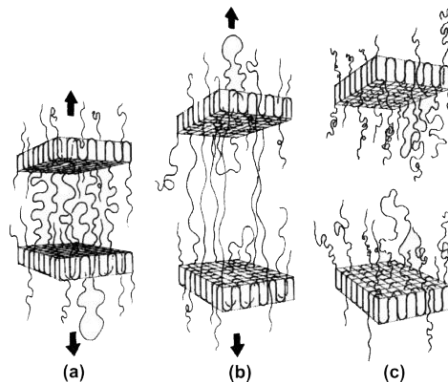


Figure 2.5. Brittle failure mechanism of semi-crystalline material.^{24,33}

The amount of tie molecules and the extent of molecular entanglement have a strong correlation to ESCR. Molecular weight (MW) and short chain branching (SCB) are molecular properties that can indicate the relative amount of inter lamellar linkages.⁴⁷ Cheng²⁴ stated that there is a minimum molecular mass required for a polymer molecule to be considered a tie molecule and that the ESCR increases as weight-average molecular weight increases. Furthermore, short chain branching encourage chain entanglements, improving the ESCR.^{24,47} Ductile failure is preferred over brittle failure because after ductile deformation the material still has the ability to carry a tensile load which is not the case after brittle failure. Brittle failure occurs without visible warning making it impossible to take preventive action during use.

2.4.7 Mechanism of ESC

The Mechanism of ESC is divided in three stages and they are: initiation of a crack by craze formation, crack growth and finally catastrophic failure.

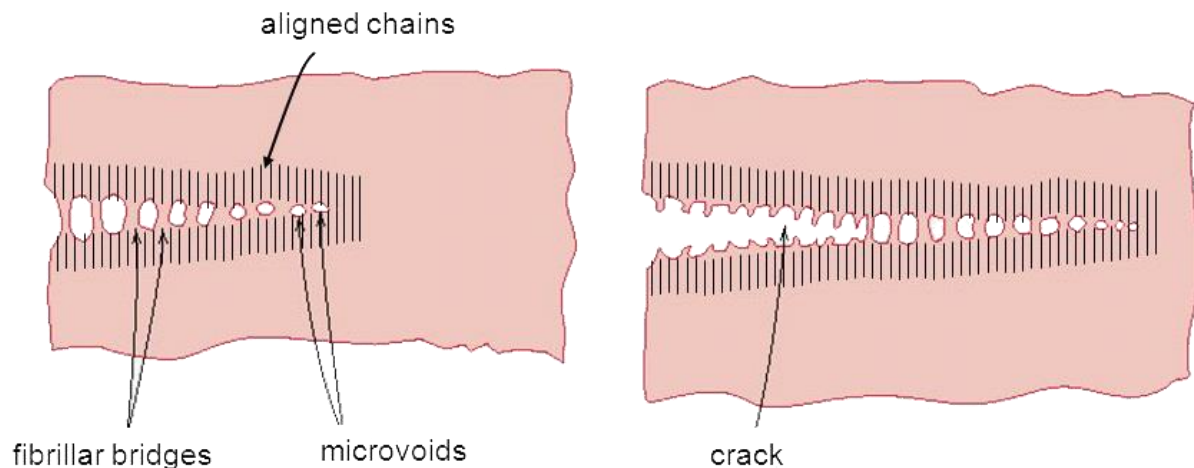


Figure 2.6. Schematic representation of a craze and a crack.⁵³

2.4.7.1 Stage one – Initiation

During the first stage of ESC a crack is initiated by the formation of a craze (also referred to as a micro-crack). Crazes are expanded regions held together by highly drawn fibrils which bridge the micro-crack (see Figure 2.6).³² These crazes are highly voided areas in the material and have a fibrillar structure.^{25,32} The voids in the crazes allow the permeation of surface active liquids into the material thereby plasticizing the fibrillar structure.

To summarize the initiation stage: formation of microvoids, formation of fibrillar bridges and agglomeration of microvoids into stable voids.¹

2.4.7.2 Stage two – Propagation

In the second stage the craze evolves into a crack and propagates. The highly drawn fibrillar structure consists of polymer molecules that are aligned in the stress direction.⁵² In the presence of a SCA these fibrillar structures are plasticized thereby assisting molecular disentanglement and weakening of the fibrils.^{1,37} As a result, fibrillar structures break and a crack is formed. The fibrillar structures break at the centre of the craze where the strain is largest therefore the crack tips can be considered a craze. The crack tips are continuously plasticized due to SCA exposure and as a result, the crack grows.

2.4.7.3 Stage three – Ultimate failure

Stage three is the last stage where ultimate failure occurs; at this point material lifetime is depleted. After stage three of failure the polymer material is unable to fulfil its purpose. As the crack propagates there is less material left to carry the load, as a consequence the stress concentrates at the crack tips. The crack then tears rapidly and as a result the material fails.

2.5 Important factors influencing ESC behaviour

There are several factors that can influence the time to failure. The ESC behaviour can be affected by stress crack agents, stress level, stress type, molecular weight, molecular weight distribution, co-monomer content, type of co-monomer, co-monomer distribution, molecular orientation, temperature, etc.^{1,24,32,47}

ESC is believed to be affected by a combination of material properties, stress and environmental factors (see Figure 2.7).⁵⁴ Material properties include internal and external factors; internal factors are related to molecular properties whereas external factors refer to thermal history and operating temperature.¹ All these factors are highly interrelated when determining the ultimate time to failure and should be taken into account when designing a polymeric product.

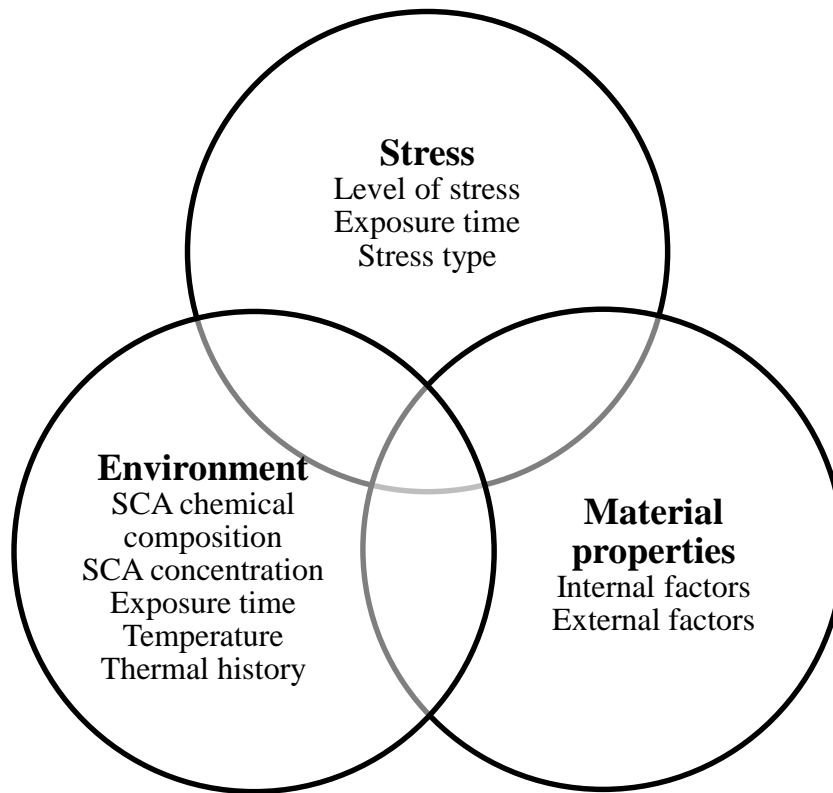


Figure 2.7. Factors influencing the ESC behaviour of plastics.

2.5.1 Stress

Stress is defined as pressure or tension exerted on a material. The material reacts to an applied load by distributing the force in the material thereby balancing the load. These stresses can be internal, external or a combination of both.³² Internal stresses, also called residual stresses, arise during the moulding process.^{3,10,55} External stresses arise during use, handling and installation of the final product; these stresses are tensile or flexural in nature and can be applied sinusoidally.⁵⁶ External stresses can be experienced over a long or short period of time; furthermore, stresses can act on a large area or be localized to a certain spot (stress concentration). ESC occurs over long time periods and the stresses are localized.^{10,41,49} Another consideration is the direction of stress, materials can be stressed uniaxially or polyaxially; polyaxially initiates cracking more rapidly than uniaxially.^{1,32,35} In general, the larger the stresses the more rapidly failure occurs.⁵⁷

2.5.2 Stress crack agents

Liquids and gasses that have the ability to penetrate or be absorbed by a particular polymeric material is considered a stress crack agent (SCA) for that material.^{26,37} The rate of diffusion for liquids into a material is dependent on temperature, exposure time, concentration, molecular size and plastic/liquid compatibility.¹³ SCA are usually liquids such as cleaning agents, lubricants, adhesives, paints, ink, oils, alcohols as well as oil containing consumables.^{11,35,58} These agents act by reducing the inter-lamellar cohesive strength thereby facilitating the “pull-out” and disentanglement of tie molecules and chain entanglements.^{37,43} The presence of relatively small molecules in the amorphous phase increases the molecular mobility of the polymer chains causing a lubricating effect.^{32,33} Ultimately material failure occurs more rapidly than without the presence of a SCA.

An important parameter that determines rate of liquid penetration is the solubility parameters of the polymer and the SCA.⁵⁵ ESC will occur more rapidly if the SCA and polymer have similar Hansen solubility parameters (HSP).⁵⁵ For a particular chemical the HSP can either be estimated through calculation or be determined experimentally, although the HSP have been determined for thousands of chemicals.^{55,59}

The Hansen solubility parameter is a measure of the attractive energy between molecules. Hansen cohesion energy, δ , is quantitatively described by equation 1 and is the sum of dispersion interactions, permanent dipole-dipole interactions and hydrogen-bonding interactions.^{54,55}

$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \quad (1)^{59}$$

A SCA with a solubility parameter relatively close to that of the polymer will thermodynamically favour mixing of the two components meaning the SCA will readily penetrate the amorphous phase of the material.

The effect of liquid penetration and subsequent swelling of the material is amplified as the concentration of the liquid increases. Severe liquid penetration into the polymer bulk could have different effects on the material, these effects include:^{1,60}

- the development of surface compressive stresses that may hinder craze formation,
- plasticization of crazes thereby promoting crack formation and crack growth,
- softening of the bulk resulting in strength reduction,
- more rapid void formation due to strength reduction.

Chemically these SCAs are organic liquids and include the following classes of compounds: aliphatics, aromatics, ethers, ketones, aldehydes, halogenated hydrocarbons, ester, etc.^{1,32,52} SCAs with very high polarity and hydrogen bonding interaction, such as formamide and water are classified as lesser cracking agents.⁵⁴ Alternatively, liquids with weak hydrogen bonding are usually moderate to strong stress cracking agents.³² SCAs are more aggressive at temperatures near to their boiling point.³² Molecular size of the SCAs affect the rate of diffusion into the bulk; smaller molecules can penetrate into the amorphous phase easier than larger molecules.

Typical solvents that cause stress cracking in most amorphous polymers include isopropanol ether, acetone, toluene, carbon tetrachloride, heptane, ethanol, petroleum and chloroform.^{1,32}

2.5.3 Polymer properties

The properties of a polymer material play an important role during ESC and can greatly influence the time to failure. The factors that affect ESC behaviour are categorized either as internal or external factors. Internal factors are inherent to the material bulk which include MW MWD, branching content, branching distribution, branch length, degree of crystallinity, crosslinking density, voids and blends.^{8,17,61} External factors include thermal history, temperature and humidity.⁶²

2.5.3.1 Internal factors

Molecular weight

The physical properties and mechanical behaviour of a plastic is highly dependent on its molecular weight, including the ESCR.^{8,17} Behjat *et al.*¹⁷ determined that higher molecular weight PE's have superior ESCR to that of lower molecular weight PE's. As mentioned earlier, tie molecules and chain entanglements contribute to ESCR. Cheng²⁴ postulated that there is a dependence on the weight average molecular weight and the tie molecule density. Simply put, the longer the polymer backbone, the higher the probability of the polymer to form part of more than one lamella. It is also stated that a minimum molecular weight (18000 g/mol) is required to form a tie molecule.²⁴

Polymers are complex molecules having varying molecular weight; this is referred to as the molecular weight distribution (MWD). A broad MWD indicates that the material has low molecular weight polymer molecules present which have been shown to significantly

decrease ESCR.^{4,35} It therefore stands to reason that material with a high MW and narrow MWD is required for superior ESCR.

Crystallinity

The crystallinity of a material is the fraction in the bulk where polymer molecules are highly ordered and is directly related to the material density.^{24,30} As the density increases the tensile yield strength and stiffness of the material increases.^{24,63} Research has proved that as density/crystallinity increases, the ESCR decreases.^{22,24,44,64} The crystalline phase is considered rigid and stiff and the amorphous phase is flexible. At a high crystallinity the amorphous fraction is small; therefore crystallites are bound together by a relatively small amount of inter lamellar material. The transition from ordered crystallites to disordered polymer chains cause stress concentration at the intermediate phase resulting in a decrease in ESCR.¹ Additionally, less amorphous material means that the density of tie molecules and molecular entanglements present in the material decreases resulting in a lower ESCR.^{33,35}

Short chain branching

Crystallinity and density can be controlled by adding short chain branches to the polymer backbone. Short chain branches (SCBs) are mostly applicable to PEs, where ethylene is polymerized with a small amount of α -olefins.³² These polymers are classified as linear low density polyethylene (LLDPE), meaning the addition of small amounts (1-5%) of short chain branches act by lowering the density of the material. These SCBs are unable to crystallize into lamellae, therefore they are only present in the amorphous phase.^{32,61} Addition of SCBs effectively increase the tie-molecule and molecular entanglement density; improving ESCR.^{24,47} It was found that ESCR is also affected by the type of α -olefin used during polymerization; longer SCBs (higher α -olefins) decreases crystallinity (if comonomer content is similar).⁶⁵ Caro *et al.*⁶⁵ concluded that ESCR increased drastically as the short chain branch length increased from 2 to 4 and 6 carbon atoms because of increased sliding resistance of the polymer chains through the crystal and through the entanglement in amorphous region.

PEs made from metallocene catalysts have lower short chain branching distributions (SCBD) than those made from Ziegler-Natta catalysts, consequently metallocene LLDPEs have superior ESCR.^{14,38,66} In essence, metallocene polymerized LLDPE (mLLDPE) with higher comonomer content (up to a certain point) and longer SCBs will have a relatively low crystallinity and relatively high ESCR.

Polymer Blends

Different types of polymers, or grades of a specific polymer, could be blended to improve the mechanical properties of a material or to improve its melt processability.³⁸ Blends are made by mixing the components in the melt state. During production of PE films mLLDPE is blended with LDPE to improve processability and to assist the film blowing.³⁸ Chen⁴³ found that adding small amounts (up to 10 wt.%) of poly(ethylene-co-vinylacetate) (EVA) to HDPE or LDPE significantly improved the ESCR. Unfortunately analysis showed that the EVA phase detached from the PE matrix and could act as a stress concentrator affecting the ESCR.⁴³ It therefore is important to blend polymers that are miscible both in the melt and after processing to avoid any phase separation.

Coextruded films are also considered blends where the layers in a multilayer film can have different chemical compositions.⁶⁷ Liquid liners are made from coextruded films and are comprised of a PE laminated polyethylene terephthalate, poly(ethylene-co-vinyl alcohol) (EVOH) or polyamide (PA).⁶⁸ The outer PE layers protect the inner layer from SCAs and oxidising compounds. PE is considered a good moisture barrier; additionally PE is relatively inert which makes it an ideal material to be in contact with the liquid stored in the liquid liners. The non-PE layers act as the load bearing layers, providing the necessary tensile strength to carry the load, and acts as a gas barrier protecting the bag contents from oxygen and other gasses.⁶⁷

PE tends to phase separate from dissimilar polymers such as EVA and EVOH.⁶⁹ To overcome this a compatibilizer is used called LLDPE grafted Maleic Anhydride (LLDPE-g-MAh).⁶⁸ It is either added to the melt or extruded as a tie layer between LLDPE and EVOH. As a tie layer it operates by preventing delamination, which is a form of material failure.

Voids

The presence of voids in a material is a common cause of failure. Voids localize stress in the material thereby causing points of stress concentration.¹³ These points of stress concentration accelerate craze formation (stage one of ESC).³² The larger the voids, the greater the stress concentration causing rapid failure. During crack growth (stage two of ESC) these voids coalesce thus the time to ultimate failure is drastically decreased.¹ Voids also provide an easy path for diffusion of SCAs that then plasticize the material around the voids, enabling void growth to occur more rapidly.⁴² Certain polymer materials are more susceptible toward void

formation during processing (e.g., PC).⁴² Basically, the presence of voids in a material will decrease ESCR.

Crosslinking

Crosslinking is a method used to covalently bind polymer molecules to one another and can be achieved through high energy electron beams, chemical reactions involving peroxides, and ultraviolet irradiation.⁴⁶ Through crosslinking the impact resistance, tensile strength, heat resistance and the ESCR is enhanced. Uncrosslinked material will also be more flexible than crosslinked materials. During crosslinking the molecular mass of the material greatly increases and the crosslinks form a network structure that restricts molecular mobility. It was found that crosslinked PE (PEX) has superior ESCR to that of uncrosslinked PE; this is believed to be due to the increase in molecular mass and the limited molecular mobility.⁴⁶ The drawbacks of crosslinked PE is the loss of flexibility (limiting its applications) and is relatively expensive to produce.

2.5.3.2 External factors

External factors such as thermal history and operating temperature can influence the ESCR behaviour of polymeric materials. It is well known that the cooling rate from the melt affects the degree of crystallinity. If the cooling profile is not homogeneous through the thickness of the material, then one can expect residual stresses through the thermal gradient. Rapid or quench cooled PE has a higher degree of crystallinity than the same material cooled at a slower rate. Above the crystallite melting temperature (T_m) semi-crystalline polymer materials act as a viscous fluid and start to crystallize at a temperature below the T_m called the crystallization temperature (T_c). Crystallization does not only occur at T_c but over a range of temperatures around the T_c and if the material is slow cooled it spends more time in the temperature range where crystallization occurs, consequently, a larger degree of crystallinity is obtained.^{6,44} On the other hand, when quench cooling less time is spent at the T_c and only small crystallites form that leads to an increase in ESCR. The small crystallites means a large amorphous interspherulite boundary and an increase in the number of tie-molecules is acquired, whereas slow cooling has the opposite effect. Slow cooling causes large crystallites to form and small amorphous interspherulite boundaries.³⁵ The remaining amorphous material at the crystal interfaces becomes strained, due to competition of crystallization forces from

adjacent regions and as a result internal strain arises together with the possibility of voids forming.¹ Consequently, a decrease in ESCR is observed for slow cooled material.

Ceteris paribus, time to failure is temperature dependent. The rate of crack growth increases with temperature. Andersen³² stated that there is an exponential decrease in time to failure with increasing temperature and attributed it to the process of chain sliding that occurs during disentanglement which is favoured at higher temperatures. Chain sliding is also assisted by an increase in temperature because the diffusion rate of SCAs increases and penetrate into the material more easily.⁴² The mode of failure is also temperature dependent; semicrystalline resins, such as PE, generally have T_gs below ambient temperature and above the T_g long range cooperative main-chain movement is possible favouring a creep or ductile response.¹³ Below the T_g the material is relatively stiff and fails in a brittle mode. Relating the effect of operating temperature to time to failure is quite complex; for one, stresses at low temperatures could be distributed through the material completely different than at high temperatures. Also, similar deflections at various temperatures can result in differences in applied stress on the material. Lastly, oxidation occurs more rapidly at high temperatures and causes a decrease in ESCR. The operating temperatures for the liquid liners are between 10 °C - 40 °C and are used in the absence of direct sunlight; therefore oxidation is of little concern.

Another external factor that can affect ESCR is the humidity. Materials made from polymers that attract water show a decrease in ESCR on an increasing humidity. These polymers are hydrophilic having strong hydrogen bonding ability and are relatively polar. Such polymers include EVA, EVOH, PA, PMMA and cellulose.⁷⁰ Water vapour is readily attracted into the plastic where it acts as a SCA. Gomes *et al.*⁵¹ found an increase in crack growth rate for PMMA at higher ambient humidity.

2.5.3.3 Other factors

Other factors that might affect the ESCR include the presence of additives in the bulk. Additives such as pigments, fillers, stabilizers, plasticizers, slipping agents and anti-block agents are mixed with the bulk to achieve a desired effect. Incorporating antioxidants and other additives is common practice for inhibiting or decelerating material aging and degradation. Fortunately PE has relatively good resistance to oxidation and chemical exposure.¹⁶ The production process of PE films usually incorporates anti-block and slipping agents as additives. Anti-block additives are used to prevent films from adhering to one

another (usually in the form of solid particles to roughen the surface) and slipping agents decrease the coefficient of friction on the material surface.¹⁹ Slipping agents are homogeneously spread in the polymer matrix in the molten state, thereafter solidification takes place and the slipping agents migrate to the surface where it would fulfil its purpose (see Figure 2.8).¹⁹ SCA's have the ability to extract slipping agents from the bulk surface. It is therefore important that the slipping agents are bio-compatible; they are usually fatty acid amides of which oleamide, erucamide and stearamide are most commonly used.¹⁹ Quantitatively they make up no more than 1 wt.% of the bulk.¹⁹

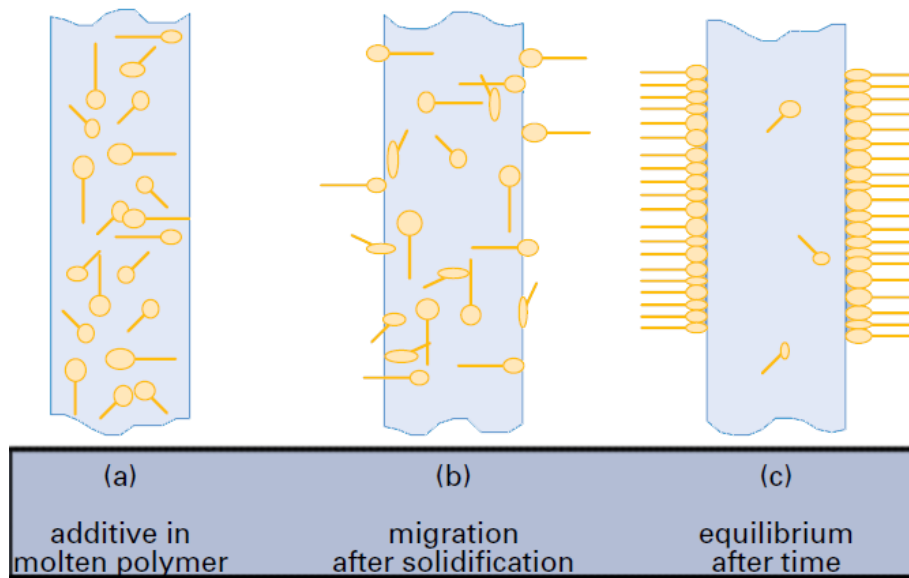


Figure 2.8. Schematic representation of slipping agents' migration.¹⁹

Lamellar orientation could play an important role with respect to the failure process. When a polymeric material is made via film blowing or injection moulding there tends to be preferential alignment of the polymer chains and crystallite lamellae.^{14,57} The alignment is usually in the drawing direction or flow direction (from moulding) also known as the machine direction. Hossain *et al.*¹⁴ discovered that the essential work to failure is larger when the crack propagates through the machine direction than the transverse direction of LLDPE films; interestingly at higher comonomer content this was not the case as the work required was found to be isotropic. Unfortunately in literature there is somewhat controversy concerning the mechanical properties in the transverse direction and the machine direction.

The relationship between material properties and ESCR is tabulated in Table 2.1.

Table 2.1. Material properties that cause changes in ESCR^{1,14,24,32}

ESCR decreases with:
<ul style="list-style-type: none"> • Increasing crystallinity • Increasing molecular weight distribution (MWD) • Increasing organic pigment content • Increasing spherulite size (related to crystallinity) • Decreasing average molecular weight • Decreasing short chain branch length • Decreasing SCB content • Decreasing cooling rate from the melt (related to crystallinity)
ESCR varies with:
<ul style="list-style-type: none"> • Additive concentration • Lamellar orientation • Blend composition

2.6 Concluding remarks

The scope of this study was guided initially by a applied research project funded by the local packaging industry. In essence, it became clear that there was a lack of fundamental understanding regarding the reasons for failures of liquid liners in bulk packaging applications. Within the scope of the problems presented, a study was designed that would (a) approach the problem from a fundamental materials perspective, (b) investigate the effect of additives present or absent in the packaging films and (c) gain a perspective of different film types used within the industry for these applications.

The problem with attempting to conduct this study on a fundamental level was that the materials used within industry were obtained from sources external to the packaging company

that funded the research. There was, therefore, no guarantee that the films used on a week-to-week basis were the same, as many of these materials are multilayer products that may or may not have been produced from the same source polymers under exactly the same conditions. It will be seen therefore, that the approach was first to develop a methodology that could be used to compare (film) materials with regards to their stress crack or flex crack resistance, and then to evaluate material parameters within a more controlled set of materials to gain a fundamental understanding of the effect of these parameters on the crack resistance in the presence of an external agent.

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Chapter 3

Test methods used for evaluating ESCR

3.1 Introduction

The testing of polymeric material is aimed at providing valuable information on how a polymeric material will mechanically respond relative to another. This information is critically important when selecting the type of material for a certain application. In failure analysis the material limitations are evaluated which is a form of quality control.¹ It is done to ensure that a chosen material will not fail during use, to provide a superior alternative material composition that could meet the in service requirements and to investigate the cause of failure.² There are several test methods available to analyse material properties, although selecting the most appropriate methods can be quite cumbersome. It therefore is important to select the most appropriate testing methods while keeping in mind the testing time, testing costs and the accuracy of the test method.³ This is the essence of failure analysis. In this chapter the standard testing methods used to evaluate ESCR will be discussed.

3.2 ESCR testing

Over the past 60 years several standard testing methods for the evaluation of ESCR have been developed.^{4,5} ESCR is defined as the time to failure; the quicker the sample fails the lower its ESCR. It is common practise to state the ESCR test utilised because failure times differ depending on the testing method used. ESCR vary from one method to another due to the severity and nature of the load applied on the sample. The physical dimensions of the specimen also dictate the relative time to failure; a thin film would be more flexible than a thick one therefore at a similar deflection angle the film might not fail whereas a thick specimen would. Generally ESCR tests are done in aggressive conditions to accelerate the testing procedure. Accelerating ESCR tests is achieved by altering testing parameters such as

temperature, stress level, humidity, SCA concentration or adding a notch as a point of stress concentration. The effects of these parameters on ESCR have been discussed in Chapter 2. ESCR tests are aimed at accurately simulating failure conditions imposed on the material during use. ESCR testing can be classified into two groups: tests at constant strain and tests at constant stress.⁶⁻¹⁰ It is important to decide the appropriate strain/stress to exert on the sample, because high strain/stress will result in cracking too quick or failure might occur in a ductile fashion, and at lower strain/stress time to failure will occur after extremely long and impractical times.¹¹

3.2.1 Constant strain testing

3.2.1.1 Bell telephone/bent strip test (ASTM D 1693)

The Bell telephone test was developed by Bell Laboratories and was used to evaluate the ESCR performance of polyethylene cable insulation.^{4,5} Test specimens are injection moulded to the specified dimensions of 38 x 13 x 3 mm, and deflected in a holder into a “U” shape (bent 180°) with the notch pointing outwards longitudinal to the specimen dimensions as seen in Figure 3.1. The holder with the deflected samples is placed in a 10 vol.-% Igepal CO-630 water solution at a temperature of 50 °C. The number of samples that exhibit cracking is recorded as a function of time; cracking is evaluated visually. Test duration should not be less than 48 h. For the material to pass, none of the specimens should have failed during the test. For ESCR quantification the time to failure is defined as the time when 50 % of the samples have failed during the test.

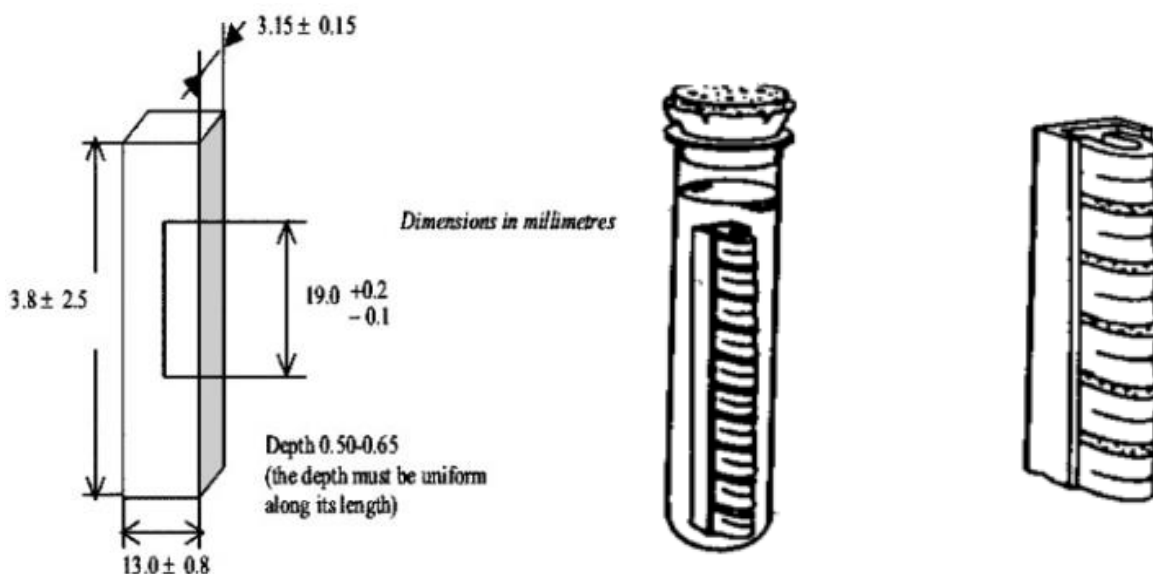


Figure 3.1. Bell telephone test for flexible materials and specimen dimensions.^{5,9}

The maximum surface strain is calculated using the following equation:

$$\varepsilon_{Max} = \frac{t}{w-t} \times 100, (\%)$$

where t is the thickness of the sample and w is the width of the holder.¹²

This method ranks materials according to ESCR; unfortunately it does not aid in the product's lifetime predictions. Therefore, these tests are recommended mainly for quick quality control or relative comparison purposes. The fact that crack or fracture detection is done visually at fixed intervals may give rise to error for it is mentioned in literature that this method does not give results with satisfactory accuracy and repeatability.^{1,5}

3.2.1.2 Three point bending test (ASTM D 790)

The three point bending test is done on rigid materials where the maximum applied strain does not exceed 1%.¹² The test method is illustrated in Figure 3.2 and has 2 variants A and B. Method A allows the adjustment of the deflection via a screw and method B utilise pins with varying thickness that applies incremental deflections (0.3%, 0.5% and 1%).¹² The bent specimens are then submerged in a SCA, and then once cracking is detected a threshold strain can be calculated.

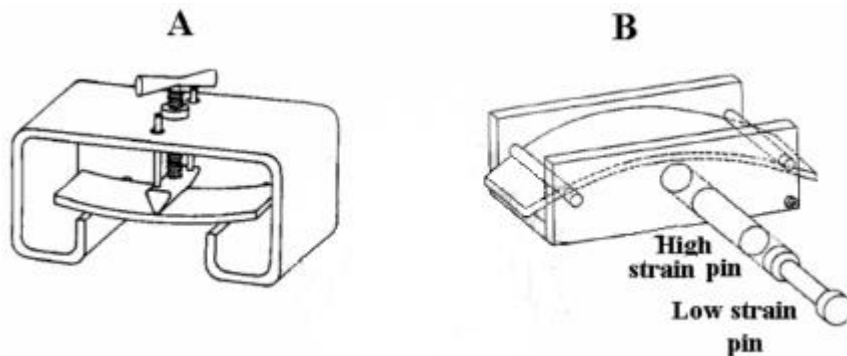


Figure 3.2. Three point bending apparatus used to evaluate ESCR under constant strain.¹²

3.2.1.3 Modified bending test

This method is a variation of the bell telephone test, where the notch is applied transverse of the specimen length instead of longitudinal. The specimen is a typical “dogbone” shape with dimensions of: A - 86 mm, B - 10 mm, C - 5 mm, D - 17 mm, thickness - 1.56mm (see Figure 3.3) and a notch depth of 0.16 mm (~10% of the nominal thickness). The specimen is subject

to a deflective force similar to the Bell telephone test with the notch facing the convex side. Crack growth through the thickness of the specimen is achieved. This is done for 48h at room temperature in a SCA liquid of choice. The sample is then removed and tensile tests are performed on the material; a decrease in breaking strength is then indicative of the extent of cracking.

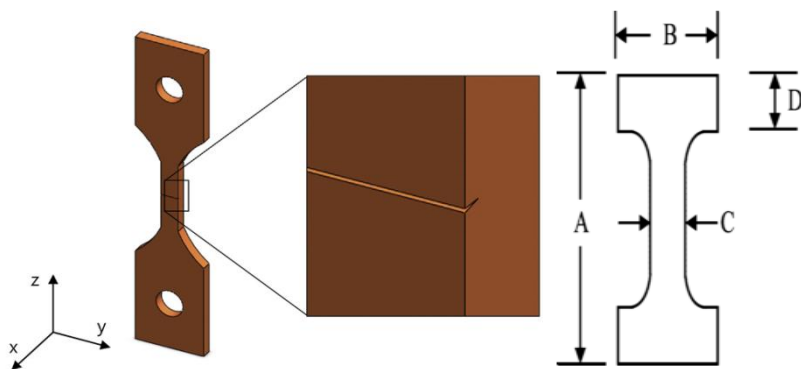


Figure 3.3. Specimen dimensions used during modified bending test.¹³

3.2.2 Constant stress testing

3.2.2.1 Constant tensile load test (PENT, ASTM F1473)

For flexible materials such as LLDPE specimens and films a constant stress test is preferred over constant strain tests. The Pennsylvania edge-notch tensile test (PENT test) was developed by Lu *et al.*¹⁴ and is used for measuring slow crack growth behaviour of polyethylenes. In this test a rectangular specimen is notched on one side, is subjected to a load with one end of the specimen fixed in position while a load is applied to the other end in the form of a hanging weight (see Figure 3.4). The purpose of the notch is to act as a point of stress concentration to ensure a brittle failure mode. A load below the yield stress is applied to ensure brittle failure. The time to failure is the time it takes for the two halves to fully separate and is related to the resistance to the SCG rate. An optical microscope can be advantageous by allowing real time monitoring of the failed surface, unfortunately this does complicate the practical setup of the equipment.

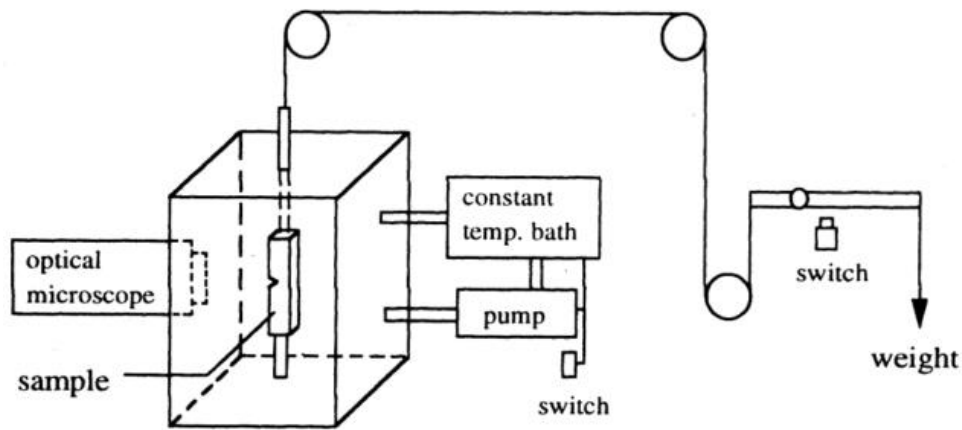


Figure 3.4. PENT test setup.⁵

This method does not include the effects of SCA's therefore the parameters in this test are temperature, applied load and notch depth. Garcia *et al.*¹⁶ modified the PENT method by adding the effects of a SCA in the form of an Igepal CO-630 water solution in an attempt to accelerate SCG and was done with reasonable success.

3.2.2.2 Test method for determining ESCR of ethylene based plastics.

PE based films having different layer compositions were tested with this method. The apparatus comprises of a stainless steel bath containing a cylindrical rod for wrapping the test specimen around, and a clamping tool for holding the film securely. A constant load is applied on the sample in the form of a hanging weight; the time to failure is measured with an electronic timing device. When the film breaks the weight drops and the timer is stopped revealing the time to failure.

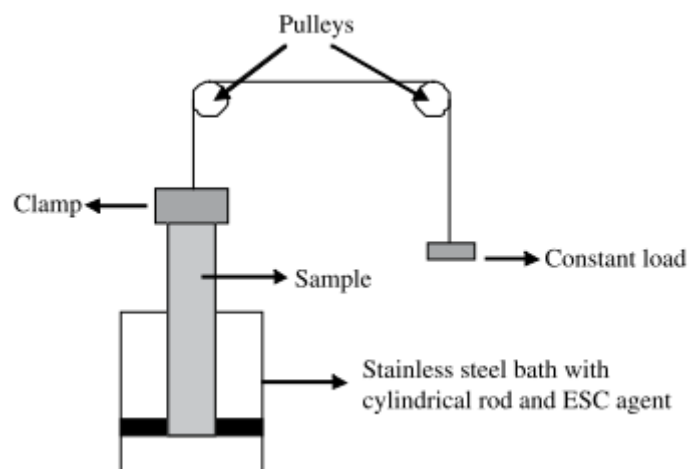


Figure 3.5. Apparatus used for determining ESCR of ethylene based plastics.¹⁷

A load below the yield strength is applied on the film to ensure brittle failure occurs. The specimens are typically unnotched strips and the operating temperatures range from 23 °C to 90 °C.⁵ According to Anderson⁵ the optimum test conditions are: a specimen thickness from 1 to 1.25 mm, a bend radius of 5.5 mm, applied stress of 5 MPa, and a temperature of 75°C.

3.3 Other methods

3.3.1 Test method for determining ESCR of ethylene based plastics.

The aforementioned testing methods all are time-consuming with high variability, therefore Kurelec *et al.*¹⁸ and subsequently Cheng² developed a method where short term mechanical test results give information on the ESCR. They discovered that the hardening stiffness (strain hardening modulus) of PE can be used as a measure of the ESCR. In this method “dogbone” specimens are compression moulded with a thickness of 1.9 mm on which tensile tests are performed at room temperature and a deformation rate (crosshead speed) of 7 mm/min.¹⁰ The tensile tests are done according to ASTM D638 whereby plastic films (>1mm thickness) are pulled until the material breaks. The material undergoes yielding, drawing, strain hardening and finally breaks; strain hardening occurs after drawing and is observed as a linear response on the load-displacement curve. Hardening stiffness is classified as the slope of the strain hardening portion in the load-displacement curve and is directly related to ESCR.

3.3.2 Monotonic creep

The monotonic creep test method is used to determine the relative stress cracking severity of fluids and operates by measuring the strain response at a constant stressing rate. Stress is applied by a water container with a capacity of 75 litres instead of a hanging weight (see Figure 3.6). Water is continuously fed into the container thereby achieving a constant stressing rate. A Moiré fringe extensometer is used to determine material strain. Stress-strain data is plotted for a sample exposed to air and SCA's; a departure of the stress-strain data is observed (see Figure 3.7) and is then called the initiation of ESC.^{4,19}

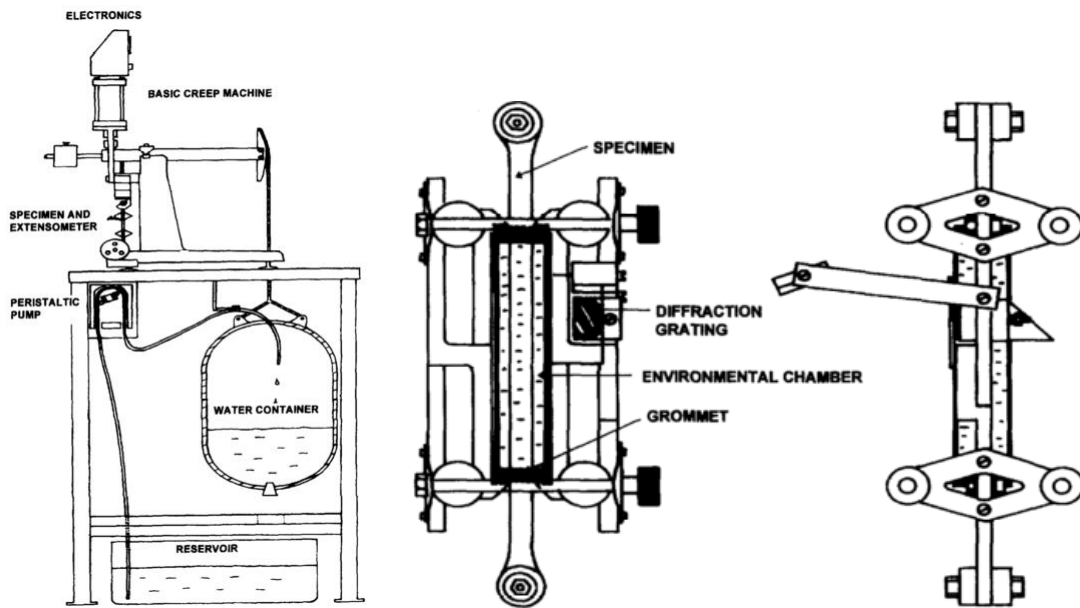


Figure 3.6. Schematic representation of a monotonic creep test setup.¹⁹

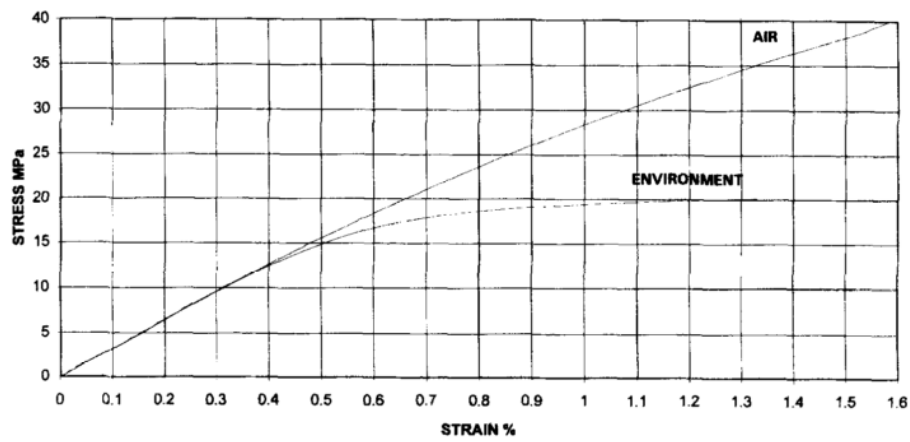


Figure 3.7. Stress-strain curves in air and in an environmental stress cracking fluid.¹⁹

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Chapter 4

Experimental work

4.1 Materials

Materials used in this study are categorized in 2 groups. These are denoted granules and films. The granules are either LLDPE or LDPE samples obtained from Exxon, SASOL, Lotte and Dow (see Table 4.1). These granules have different short chain branch (SCB) length and are used in industry for film blowing applications. These granules are then processed into artefacts used for testing the ESCR.

The first 2 samples (denoted Samples 1 and 2) are classified as low density polyethylenes and are used up to 10 wt. % in films made by STOPAK (the funding body in this research); addition of LDPE is required to get a stable blow-extrusion bulb thereby improving process ability. Sample 3 is LLDPE with 1-butene as comonomer, has a high MFI and is used to produce injection moulded parts. Sample 4 is used 40-90 wt. % in standard monolayer films produced by STOPAK. Sample 5 consists of LLDPE with 1-hexene as comonomer and is used to produce injection moulded parts. Samples 6 is a LLDPE made with a metallocene catalyst and is used up to 30 wt.% in both co-extruded and mono extruded films. Lastly Sample 7 is a 1-octene LLDPE, has so called ultra-low density and is used to produce PE films with superior ESCR. These raw materials were used to produce artefacts used to test the ESCR.

Table 4.1. Commercial granules used in this study.

Sample #	Sample identification	Type	Supplier
1	LDPE HF140	LDPE	Sasol
2	LDPE LD150AC	LDPE	Exxon
3	LLDPE UL 814	1-Butene LLDPE	Lotte
4	LLDPE 1001KI	1-Butene LLDPE	Exxon
5	LLDPE HR472	1-Hexene LLDPE	Sasol
6	mLLDPE Exceed 1018HA	1-Hexene LLDPE	Exxon
7	uLLDPE Attane 4102G	1-Octene LLDPE	Dow

Three commercially sourced films were used in this study all having PE as the major component in the film construction as seen in Table 4.2. Film 1 is mono extruded and is only made from LLDPE whereas the other films are multicomponent; film 2 has layers of poly (ethylene-co-vinyl alcohol) (EVOH) and polyamide (PA) which are “sandwiched” between LLDPE layers. A tie layer is added to the PE/PA interface in the form of LLDPE grafted Maleic Anhydride (LLDPE-g-MAh) as a compatibilizer which prevents delamination.¹ Film 3 is an aluminium metallised polyethylene terephthalate laminate where the PE consists of the octane LLDPE (see Table 4.1). The multi component films have benefits over the mono extruded film; the non PE layers act as oxygen barriers to preserve the bag’s contents and are considered as the load bearing component in the construction.²

Table 4.2. Films used in this study.

Film #	Sample identification	Type	Thickness	Supplier
1	LLDPE	100% LLDPE, mono extruded, 70% 1001KI	80 µm	STOPAK
2	PA/EVOH laminate	14 layer co-extruded PE/TL/PA/EVOH/PA/TL/PE/ PE/TL/PA/EVOH/PA/TL/PE*	112 µm 26/3/2/2/2/3/18/ 18/3/2/2/2/3/26	STOPAK
3	MPET (Metallised Polyethylene terephthalate) laminate	3 layer adhesive laminate, PE/MPET/PE	112 µm 50/12/50	STOPAK

*TL = Tie layer

4.1.1 Sample properties

The polymer used were supplied as granules extruded spherical pellets with radii of approximately 5 mm and are formulated with slipping additives. Material properties are obtained from product datasheets and are listed in Table 4.3. Mechanical testing was done at room temperature in the machine direction according to standard testing methods.

Table 4.3. Properties of LLDPE used in this study*.

Property	Sample						
	1	2	3	4	5	6	7
Density, g/cm ³	0.920	0.923	0.924	0.918	0.939	0.918	0.905
Melt index (190°C/2.16 kg), g/10 min	2.0	0.75	20	1.0	5	1.0	1
Peak melting temperature, °C**	110	111	121	121	128	119	123
Tensile strength at yield, MPa	10	n/a	11.8	n/a	20	9.4	5.7
Tensile strength at break, MPa	37	28	n/a	57	27	50	33
Elastic modulus, MPa	n/a	240	304	220	684	190	90
Dart drop impact, g	128	190	n/a	102	n/a	460	>850
Slip additive concentration, ppm	0	500	n/a	1000	n/a	n/a	n/a

* Information obtained from product data sheets supplied by various suppliers.³⁻¹⁰

**Determined by differential scanning calorimetry (second heating cycle).

4.2 Chemicals

Several liquids were used during the modified bending test to evaluate the SCA's ability to promote crack growth. These liquids include solvent grade isopropanol, methanol and heptane as well as commercial Teepol (produced by Acorn Products (Pty) Ltd), Glühwein (produced by Halewood International South Africa (Pty) Ltd) and lastly distilled water. Glühwein comprises of red wine with added spices of cinnamon, cloves and nutmeg with an ethanol content of 8% alcohol by volume. The Glühwein test was a result of a product failure

experienced in industry during the course of this study. Teepol is a soap with various surfactants and are listed in Table 4.4.

Table 4.4. Teepol composition.

Substance name	CAS #	Amount (%)
Sodium Dodecyl benzene Sulphonate	25155-30-0	5-15
Sodium C12-C15 Alcohol Ether Sulphate	13150-00-0	<5
C9-11 Pareth -10	68439-46-3	<5
2-bromo-2-nitropropanol-1,3-diol	52-51-7	<1

Potassium permanganate (Riedel-deHaën AG D-3026) and reagent grade sulphuric acid (98% purity) were used as etching reagents to remove the amorphous polymer fraction and study the crystalline morphology. Solvent grade methanol and distilled water were used to wash the samples after the etching process.

4.3 Special equipment

Special equipment was required for the test method for determining ESCR of ethylene based plastics discussed in Section 3.2.2.2. A stainless steel bath with cylindrical rod was used and is illustrated in Figure 4.1 and is made of stainless steel which has a relatively high resistance to chemical attack. The films were clamped with the device seen at the top of Figure 4.1 with the aid of rubber sheets to prevent the films from slipping from the clamp. Equipment dimensions are as follows: clamp (20 mm x 40 mm), metal cylinder is 15 mm from the bottom of the tank with a diameter of 10 mm and the tank has a height of the tank is 60 mm.



Figure 4.1. Special equipment used for testing ESCR of ethylene based plastics.

The running hour meter (RHM) timer (designed & manufactured by ICON Electronics c.c.) was used to record the failure time and can be seen in Figure 4.2. This device has a sensor that senses the hanging weight, when failure occurs the weight drops and the timer stops and the time in hours is the ESCR. It can monitor up to 9999 hours and has an accuracy of $\pm 0.05\%$.



Figure 4.2. Running hour meter timer.

4.4 Study of mechanical properties

Tensile tests were conducted on films and notched moulds with a LRX PLUS SERIES Materials Testing Machine (AMETEK, inc.); ASTM D882 was used as the standard testing method. A load cell of 5 kN was used and the crosshead speed was 25 mm/min, 50 mm/min and 100 mm/min. Rubber clamps were used to prevent the film samples from slipping and self-tightening clamps were used for the moulds. Tensile properties were tested along the machine direction. The information gained include the yield strength, stress at break, Young's modulus, elongation at yield and elongation at break. Tensile tests conducted on films had dimensions of: A - 43 mm, B - 10 mm, C - 6 mm, D - 10 mm (see Figure 4.3).

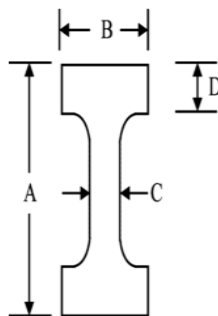


Figure 4.3. Film specimen used during tensile tests.

These dogbone film specimens were exposed to various SCA's for 1 week at ambient temperature where after their mechanical properties were compared to the unexposed films. Exposure involves stirring these specimens in a no. 8 polytop glass vial filled with a liquid SCA. Specimen tests were repeated ten times for statistical analysis.

4.5 ESCR tests

4.5.1 Sample preparation

Pellets were injection moulded into dogbone specimens using a HAAKE Minijet II (Thermo Fisher Scientific Inc.), where after the specimens were visually inspected to ensure that there were no defects. Injection moulding with this device has three parameters that can be set, injection pressure, mould temperature and cylinder temperature. Satisfactory mouldings were obtained with an injection pressure of 350 bar, mould temperature of 80 °C and a cylinder temperature of 200 °C. Notches were cut with a sharp stainless steel blade that was glued between two plastic blocks with part of the blade protruding from it; this is to ensure a constant notch depth is obtained when passing the blade over the sample.

Film test specimens only required to be cut to the desired dimensions which varied according to the test method used, film strips were cut with a razor blade and dogbone film samples were punch pressed.

4.5.2. ESCR test 1 (ESCR test for ethylene based plastics)

This test method was used to evaluate the ESCR of films made mostly from LLDPE and is classified as a constant load test. Test specimens had a length of 200 mm, a width of 20 mm (10 mm in some cases) and thicknesses described in Table 4.2. The weight used varied from 1-2.6 kg depending on the load that was calculated from the yield strength of the films. The weight was altered so that each film was tested at a low % of its yield stress (~30 %) and at a high % of its yield stress (~85 %). Testing temperature was between 15°C and 30°C, at higher temperatures it was found that the SCA's evaporated depleting the tank; the temperature was therefore kept at room temperature. ESC conditions were simulated for at least 24 hours and at most 500 hours. Tests were also conducted in the absence of a SCA in air to ensure the SCA's were contributing to failure. After adding the SCA to the tank the top was covered in aluminium foil to minimise liquid loss from evaporation.

4.5.3 ESCR test 2 (Modified bending test)

In this test, dogbone specimens are deflected as seen in Figure 4.4 in various SCA's. Samples are deflected at an angle of 180° and an end-to-end distance of 20 mm. Samples were deflected and exposed for 48 hours at ambient temperature with a gentle stirring action; during this period crack propagation occurred and was quantified with tensile testing data.



Figure 4.4. Modified bending test setup.

The maximum surface strain (ϵ_{Max}) at the notch was calculated to be 7.5 % and is deemed appropriate to ensure slow crack growth.¹¹

4.6 Morphology studies

Etching is a common technique used for studying polymer morphology.¹² In this study, permanganic etching was done on PE films in order to visualise the crystalline morphology. Several groups have utilised this technique.^{13,14}

4.6.1 Preparation of etching reagent

Potassium permanganate (7g) was dissolved in 100 mL concentrated sulphuric acid. The solution was prepared by adding potassium permanganate very slowly to the beaker containing sulphuric acid, with rapid agitation and both solutions cooled to about 0°C with ice. After adding all the potassium permanganate, the beaker was closed properly and stirred until all the potassium permanganate was dissolved (yielded a dark green solution). The etching reagent was allowed to reach room temperature where after etching commenced.

4.6.2 Procedure of etching process

Specimens made from the LLDPE film with approximate dimensions of 2 cm x 1 cm x 0.008 cm, were cut from the films provided. Each sample was immersed in 10 mL of the etching reagent in a beaker for periods of 1 hour, 2 hours and 4 hours. Afterwards, the films were immersed in clean methanol (three times) and then with distilled water (three times). Lastly the films were dried in a vacuum oven at 45 °C for 4 hours.

4.7 Characterization

4.7.1 Fourier-transform infrared (FTIR) spectroscopy

Attenuated total reflectance (ATR) FTIR spectroscopy was performed using a Nicolet iS10 FTIR spectrometer (Thermo Electron, Waltham, USA) consisting of a sensIR ATR attachment equipped with a diamond crystal. An incidence angle of 45° was used for all measurements. All spectra were collected at a resolution of 4 cm⁻¹ with 64 scans collected for each spectrum and a wavenumber range of 666 cm⁻¹ – 3700 cm⁻¹. An automatic background subtraction was also performed for each spectrum. Thermo scientific OMNIC software was used to analyse the spectral data.

4.7.2 Nuclear magnetic resonance (NMR) spectroscopy

The samples used in the present study were dissolved in deuterated 1,1,2,2-tetrachloroethane to a final concentration of 6 wt%. High-resolution solution ¹³C-NMR spectra were obtained at 120 °C on a 600 MHz Varian^{Unity} INOVA NMR Spectrometer. The following settings were used to obtain the solution NMR spectra: a 90° flip angle of ≈7.4 μs with inverse gated proton decoupling, an acquisition time of 1.8 s and a pulse delay of 15 s. Since only carbon atoms

with T1 relaxation delays of < 3 s were considered, the spectra are considered to be 99 % quantitative.

4.7.3 High-temperature gel permeation chromatography (HTGPC)

Molecular weight and molecular weight distribution was determined with a high temperature Polymer Laboratories PL 220 chromatograph (Polymer Laboratories, Varian Inc., Church Stretton, Shropshire, England). The injection block and column compartment were operated at 150 °C and at a flow rate of 1 ml.min⁻¹. The chromatographic system consisted of 300 mm × 75 mm PLgel Olexis columns (Polymer Laboratories, Varian Inc., Church Stretton, Shropshire, England) and a differential refractive index detector was used. The polymer samples were dissolved at 160 °C for two hours in 1,2,4-trichlorobenzene (TCB) Reagent plus® stabilized with butylated hydroxytoluene (BHT) at a concentration of 2 mg/mL and 200 µl of each dissolved sample was injected into the column. Narrowly distributed polystyrene standards (Polymer standards service GmbH, Mainz, Germany) were used for calibration. Data acquisition and processing was carried out by means of WinGPC software (Polymer standards service GmbH, Mainz, Germany).

4.7.4 Differential scanning calorimetry (DSC)

Thermal analysis was done to determine the degree of crystallinity, peak melting temperature and other thermal events. A TA instrument Q100 DSC (Waters Corp.) instrument was used and was calibrated by measuring the melting temperature of indium metal according to a standard procedure. Measurements were conducted under a nitrogen atmosphere, and at a purge gas flow rate of 50 ml/min. DSC samples were prepared by weighing 5 mg - 10 mg of material in an aluminium DSC pan. PE samples were heated from 25 to 150 °C at 10 °C/min, kept isothermally at 150 °C for 1 minute and cooled to 0 °C at a rate of 10 °C/min, during which time the cooling crystallization curve was recorded. At 0 °C the temperature was kept constant for 1 minute, after which the melting curve was recorded between 0 and 150 °C at a heating rate of 10 °C/min.

Layered film samples were heated from 25 to 300 °C at 10 °C/min, kept isothermally at 300 °C for 1 minute and cooled to 0 °C at a rate of 10 °C/min, during which time the cooling crystallization curve was recorded. At 0 °C the temperature was kept constant for 1 minute,

after which the melting curve was recorded between 0 and 300 °C at a heating rate of 10 °C/min.

4.7.5 Scanning electron microscopy

Scanning electron microscopy (SEM) was used to analyse the topological features of the film surfaces after etching as well as the moulding' fracture surfaces obtained from the modified bending test. Surface imaging was accomplished using a Merlin FE-SEM (Carl Zeiss AG) scanning electron microscope. Prior to imaging the samples were sputter-coated with gold.

4.8 References

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Chapter 5

Results and discussion

5.1 ESCR test 1 (ESCR test for ethylene based plastics)

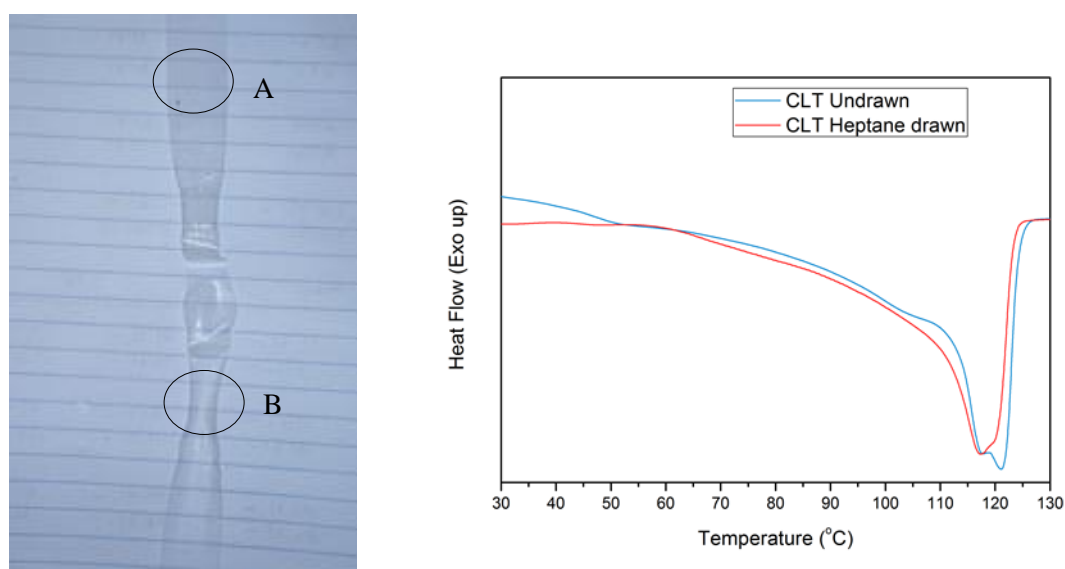
The ESCR was initially evaluated for commercially available 80 μm mono extruded LLDPE film using ESCR test for ethylene based plastics (see Section 4.5.2). A load of 30% that of the yield strength was applied on the LLDPE film (this was done to ensure that brittle failure occurs), the solvent of choice was a 10% vol./vol. solution of isopropanol dissolved in deionised water. After a week there were no visible signs of failure. The concentration isopropanol was furthermore increased step wise (30% vol./vol. per week) to 100% isopropanol which also resulted in no visible signs of failure. This was repeated with a Teepol (soap) solution which revealed similar results as with the isopropanol tests. It was then decided to use 100% solvent grade heptane as the SCA (smaller difference in solubility parameter between material and SCA), again with a 30 % yield load applied. After a week no visible signs of failure presented itself. Lastly the applied load was increased to 80% of the film's yield strength with the chemical environments used similar to that of the 30% yield stress applied tests with one difference; the SCAs were not diluted. Creep rupture (a form of ductile failure) occurred within 2 days only when heptane was used.

The LLDPE film exposed to heptane showed preferential drawing at the sections (B) of the film that was in contact with heptane as seen in Figure 5.11. Weak intermolecular attraction combined with chain entanglements provide strength in LLDPE; when heptane penetrates the LLDPE film chains untangle and intermolecular attraction decreases leaving the tie chains as the only load bearing component in the material. These load bearing tie chains shear the crystallites into smaller ones ("mosaic blocks"), which is confirmed by the DSC thermograms (shown in Figure 5.1) by a decrease in the peak melting temperature of the drawn section (see Table 5.1); higher temperature melting peak shoulder decreases in intensity. The % crystallinity of the drawn section is also lower by 1.1%.

Table 5.1 DSC results of drawn and undrawn sections.

	% crystallinity	T _m
Drawn section	24.0	117.8
Undrawn section	25.1	121.2

The LLDPE film was etched (etched for 1, 2 and 4 hours) and analysed through SEM, unfortunately no distinct morphological features were visible. This could mean that the film has isotropic mechanical properties (all tests were conducted in the machine direction).

**Figure 5.1 CLT specimen with dsc thermograms of undrawn and drawn sections.**

FTIR was done on the drawn section and compared to the undrawn film's FTIR spectrum; the spectra are shown in Figure 5.2 and show that no additives are present on the material surface. Additionally absorbance peaks arose (after being drawn) at wavenumbers of $1100 - 1000 \text{ cm}^{-1}$, 803 cm^{-1} and 1262 cm^{-1} which are indicative of the presence of ethylene in more ordered environments in the deformed polymer. This is a clear indication that the heptane allows for molecular motion during the drawing process and thus creates areas of local order and stress.

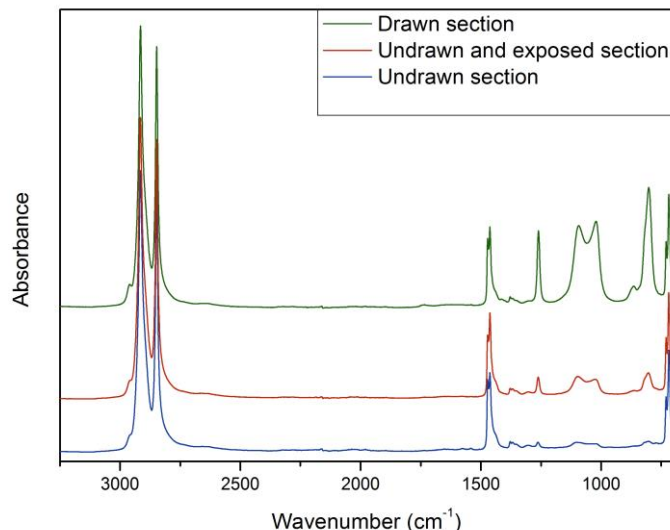


Figure 5.2 Drawn and undrawn FTIR spectra of CLT specimen.

Molar mass analysis was conducted on the drawn section and compared to that of the undrawn section; the chromatograms show that both sections have similar chromatic profiles except that the drawn section has a low molecular mass compound eluting after 24 minutes. This low molecular mass compound is as a result of external contamination of silicone oil.

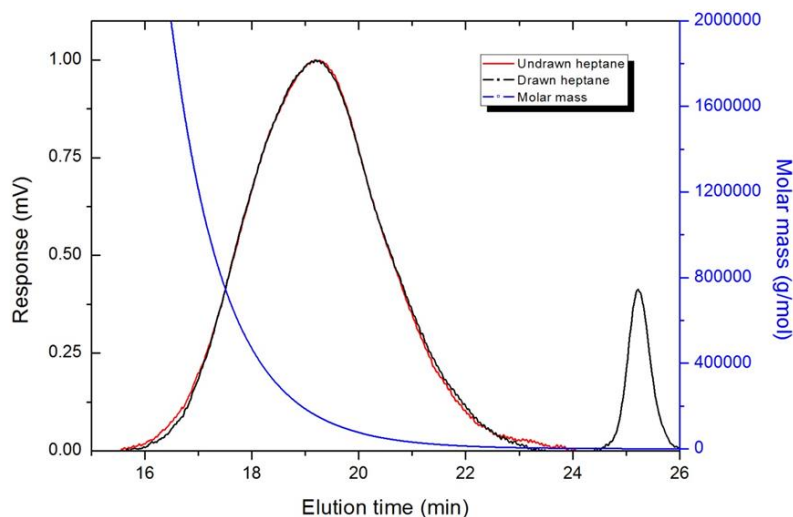


Figure 5.3 Drawn and undrawn HTGPC chromatograms of CLT specimen.

Overall it would seem that the only SCA that has any effect on thin polyethylene-based films is heptane; the reason for the decreased ESCR is the ability of the solvent to penetrate the polymeric film and to facilitate localized chain slippage and building up stress points.

5.2 Polymer granules

As was pointed out in Chapter 2, the variation in fundamental properties and molecular parameters in commercially available films, as well as the failure, for the most part, to develop a rapid and reliable method to evaluate ESCR in these materials, prompted the effort to investigate the effect of fundamental material properties on the ESCR of materials. In this part of the research, therefore, some fundamental differences between polyethylene materials were evaluated w.r.t. the stress crack behaviour of the materials. While it is difficult to get reproducible fundamental material differences in commercial grades, it was decided to focus the study on some grades of materials typically used for the production of blown films for the bulk food packaging industry. Thermal analysis was done on the granules to determine the % crystallinity and crystalline melting temperature. FTIR was performed for the purpose of surface analysis and HT-SEC was used to determine \overline{M}_w , \overline{M}_n and the MWD. The HT-SEC and thermal analysis (first heating) results are tabulated in Table 5.2; 1-butene LLDPE granules (UL814 and 1001KI) as well as 1-hexene LLDPE granules (HR472 and 1018HA) both have high molecular weight and low molecular weight samples. The LDPE's can similarly be differentiated. The calculated % crystallinity and melting temperature for the samples are characteristic for LLDPE materials.

Note that the LDPEs have reasonably similar densities, crystallinities and melting temperatures, with the Sasol HF140 sample having half the molar mass and narrower molar mass distribution compared to Exxon LDPE 150AC.

Despite having the same melting temperatures, the crystallinities of the two 1-butene LLDPEs (Lotte UL 814 and Exxon 1001KI) are different which causes them to have different densities. Overall, it appears as if the Lotte sample has more, but smaller crystallites than the Exxon sample; this is normally indicative of more tie molecules and better expected ESCR.

Similarly, the Sasol 1-hexene LLDPE and the Exceed "super hexene" LLDPE differ significantly with respect to the density, crystallinity and melting temperature.

Obviously the 1-Octene LLDPE has the lowest density of all of the LLDPEs, although the molar mass is similar to the Exceed LLDPE.

Table 5.2 Granule thermal properties and molecular weights.

Material	Density	Mw (g/mole)	Dispersity	% Crystallinity* **	T _m (°C)
Sasol LDPE HF140	0.920	171603	4.51	24.23	109.83
Exxon LDPE LD150AC	0.923	310741	6.41	25.38	111.35
Lotte LLDPE UL 814	0.924	131398	4.34	27.49	121.37
Exxon LLDPE 1001KI	0.918	267828	3.61	24.19	121.86
Sasol LLDPE HR472	0.939	181294	3.4	46.56	127.46
Exxon mLLDPE Exceed 1018HA	0.918	278628	2.52	27.16	119.34
Dow uLLDPE attane 4102G	0.905	271491	3.95	14.88	123.79

* Melting endothermic peak integrated from 70-135°C on second heating cycle.

** 100% crystalline melting heat = 293 J/g.¹

Figure 5.4 represents the FTIR spectra for LLDPE 1001KI granules; both the surface and core spectra are represented. Granules were exposed by stirring the granules in a round bottom flask with sufficient amount of SCA; stirring commenced for 2 days. FTIR is a sensitive technique and is especially suitable for surface analysis; from the results in Figure 5.1 it was possible to distinguish the characteristic vibrations of amides at 3100–3400 cm⁻¹ (N-H stretching vibrations) and at 1645 cm⁻¹ (C=O stretching vibrations) which arises from the presence of additives (fatty acids amides) on the material surface. These are most likely due to slip agents like Erucamide (preferred for film applications), Oleamide or Stearamide. The remaining peaks at 3000–2800 cm⁻¹, 1400–1480 cm⁻¹ and 720 cm⁻¹ correspond to LLDPE C-H bond stretching and bending. Spectra of the granule's surface were compared to the core's spectra and it was found that the additives were only detectable on the granule surface and not in the material bulk as predicted by literature (see Section 2.5.3.3). Injection moulded samples showed the presence of additives on the surface and not in the core of the mould (or at least not enough additives present to be detected with FTIR). The granules that yielded similar information were LD150AC, Attane 4102G, UL814 and HR 472; other samples did not contain additives. FTIR seems to indicate that additives will easily be removed from the surface of (for example) a film made from these materials. While this will then contaminate the medium to which the surface is exposed, it is unlikely that these additives will contribute positively or negatively to the stress crack resistance of these polymers.

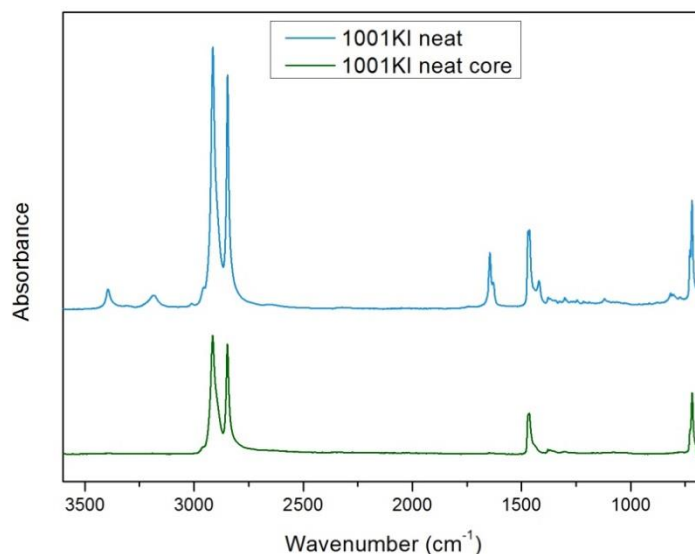


Figure 5.4 LLDPE 1001KI surface and core FTIR spectra.

FTIR spectra were taken of the granule surface after a week's exposure to water, methanol and isopropanol. The spectra in Figure 5.5 indicate that isopropanol and ethanol have the ability to extract the slipping agents from the surface of the granules where water has no effect on the surface composition.

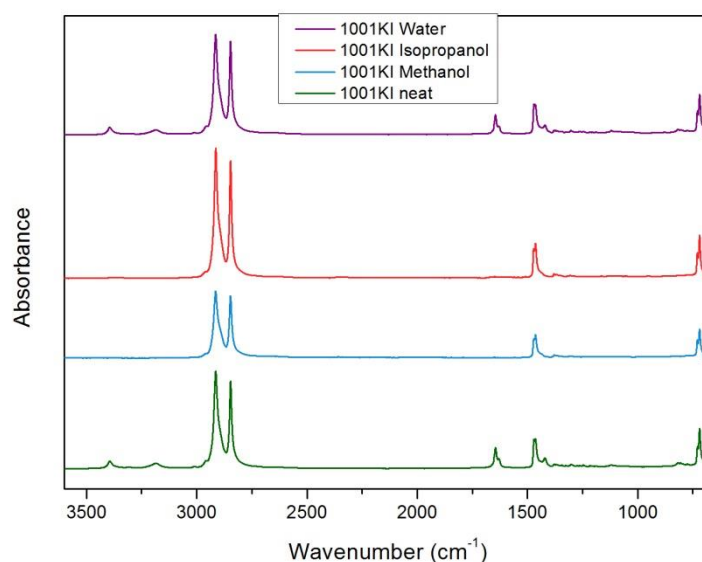


Figure 5.5 LLDPE 1001KI surface neat and after liquid exposure.

The study was extended by including heptane as a liquid SCA because it has a Hansen solubility parameter relatively close to polyethylene (see Table 5.3) and according to theory should have the greatest effect on the material; furthermore, heptane also extracted additives

from the granule surface; see Appendix B. This once again supports the supposition that these additives are easily removed from the surface.

Table 5.3 Hansen solubility parameters of polyethylene and selected liquids.

Chemical	Hansen solubility parameter ($\delta/\text{MPa}^{1/2}$) ^{2,3}
Polyethylene	16.5
Heptane	15.3
Isopropanol	23.8
Methanol	29.7
Deionised water	48

5.3 Modified bending tests

The stress crack ability of selected liquids were evaluated with the modified bending test described in Section 3.2.1.3. The mouldings were analysed with DSC to determine the crystallinity and to relate the moulding's crystallinity to that of the unprocessed polymer. It was found that the moulding's crystallinity remained relatively constant. This means that the moulding is a fair representation of the inherent material properties seeing as the materials were cooled at an appropriate rate after processing. After exposure to the SCAs the tensile properties were evaluated. Notched specimens just exposed to air exhibited the highest breaking force and the specimens exposed to SCAs during the modified bending test exhibited a decreased breaking strength. This decrease is due to crack propagation through the body of the material (see Fig. 5.9). The tensile test plots showing the loss in breaking strength for the 150 AC and HF 140 samples are shown in Figure 5.6 & 5.7. The LDPE with the higher molecular mass (LD 150 AC) required a larger force to break than the low molecular mass sample (HF 140) after the air bending test. The butene comonomer samples showed a similar trend where the high molecular mass 1001KI required a higher force to break than the UL 814 samples. Thus the expected better ESCR for the sample with the apparently smaller crystallites and thus more tie-molecules did not materialise; the overriding factor appears to remain molar mass, thus more chain entanglements which carry the load.

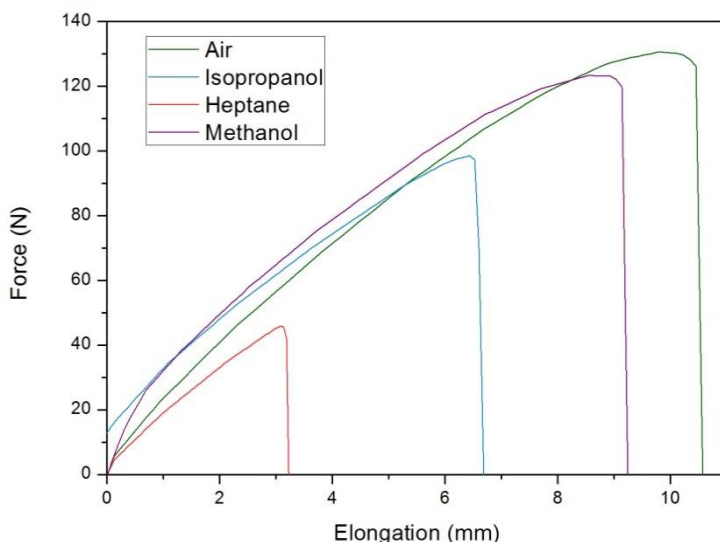


Figure 5.6 Load-Elongation tensile test results after modified bending test for LD 150AC.

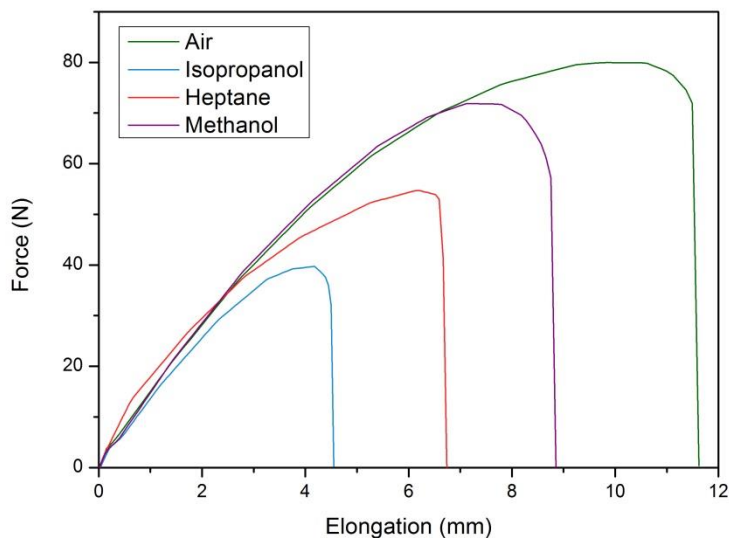


Figure 5.7 Load-Elongation tensile test results after modified bending test for and HF 140.

The decreases in breaking force is tabulated in Table 5.4 and simplified in Figure 5.8; the change in solubility parameter is plotted against the percentage decrease in breaking force. Both LDPEs showed a high cracking tendency when exposed to SCAs with HSPs close to that of LDPE. The 150AC LDPE material showed a larger breaking force drop as the polarity of the SCA decreases. On the other hand, the lower molecular mass HF140 had the highest loss in breaking strength when a slightly more polar SCA (isopropanol) was used. This

tendency is accentuated by the lowest molecular mass UL 814 sample (1-butene LLDPE) and extends to an even more polar SCA (ethanol); the higher molecular mass 1-butene LLDPE 1001KI was highly resistant to cracking. It seems to indicate that low molecular weight LDPE and LLDPE is more susceptible to cracking when polar SCAs are used. Furthermore the superior ESCR of the 1-hexene and 1-octene LLDPE (see Table 5.4) could be attributed to several factors including their longer short chain branches (leading to greater density of chain entanglements), lower dispersity and higher molecular mass. Interestingly the low molecular mass HR 472 showed relatively good resistance to ESC although it has a low molecular mass and relatively high crystallinity. This (much higher) crystallinity appears to have an overriding effect when compared to molar mass. In general, then, the observation can be made (based on the evidence of the presented experimental data) that with samples of similar density (LDPE, 1-butene LLDPE) the molar mass is the determining factor with regards to the ESCR. When comparing 1-hexene LLDPE materials that have a similar disparity in molar mass as the LDPEs, it is clear that the huge difference in density (0.939 vs 0.918) and obviously the associated difference in crystallinity is the main factor influencing ESCR. It must be noted that this is with respect to isopropanol as SCA. The results shown in Figure 5.8 seems to indicate, in general, that for all the samples except the notable outlier UL 814, that the decrease in breaking strength of the samples is less as the solubility parameter difference between the polymer and the SCA increases.

It should also be noted that as the crack grows the strain in the material decreases (due to decreasing specimen thickness) to a minimum threshold where no further cracking is observed.

Table 5.4 Breaking force loss during the modified bending test.

Sample Identification	% decrease in force at break*			
	Air	Methanol	Isopropanol	Heptane
LDPE HF140	0.0	10.0	50.4	31.5
LDPE LD150AC	0.0	5.7	24.2	64.6
LLDPE UL 814	0.0	70.5	44.0	7.7
LLDPE 1001KI	0.0	0.26	1.23	2.1
LLDPE HR472	0.0	4.13	1.48	4.98
mLLDPE Exceed 1018HA	0.0	10.2	6.12	4.41
uLLDPE Attane 4102G	0.0	4.46	6.80	7.86

* Relative to moulds exposed to air during the modified bending test.

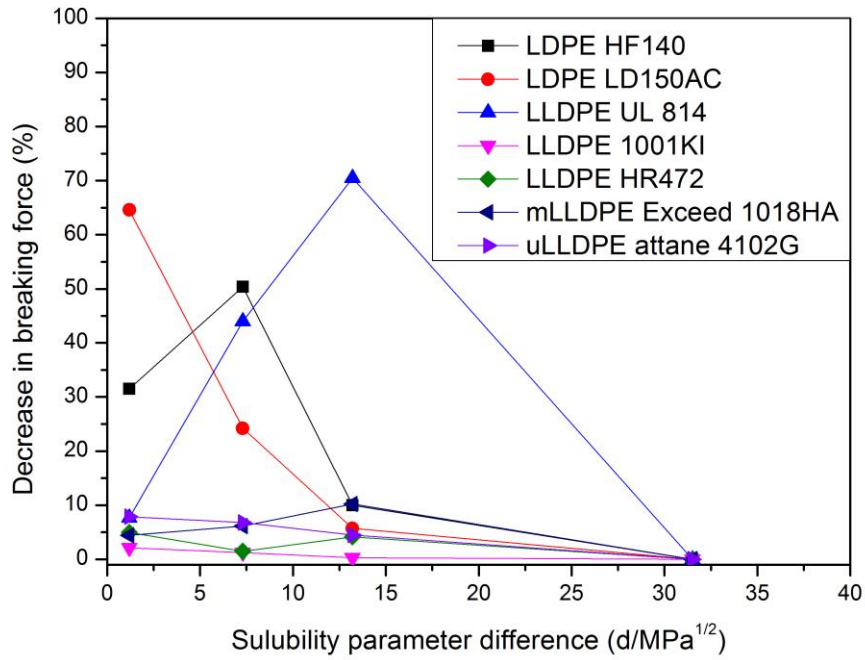


Figure 5.8 Decrease in breaking force during modified bending tests vs solubility parameter difference between LLDPE and the SCAs.

In Figure 5.9 are SEM images taken of the cracked surface (LLDPE 150 AC) that shows two distinct sections; a smooth section that correlates to the notch that was cut and a surface showing fibrous protrusions. Section 2.4.7 describes the formation of fibrillar bridges that arise as a precursor to ultimate failure and confirms that the model of failure during the modified bending test is in fact slow crack growth. Note that these are not fracture surfaces, but cracks that form during the bending tests.

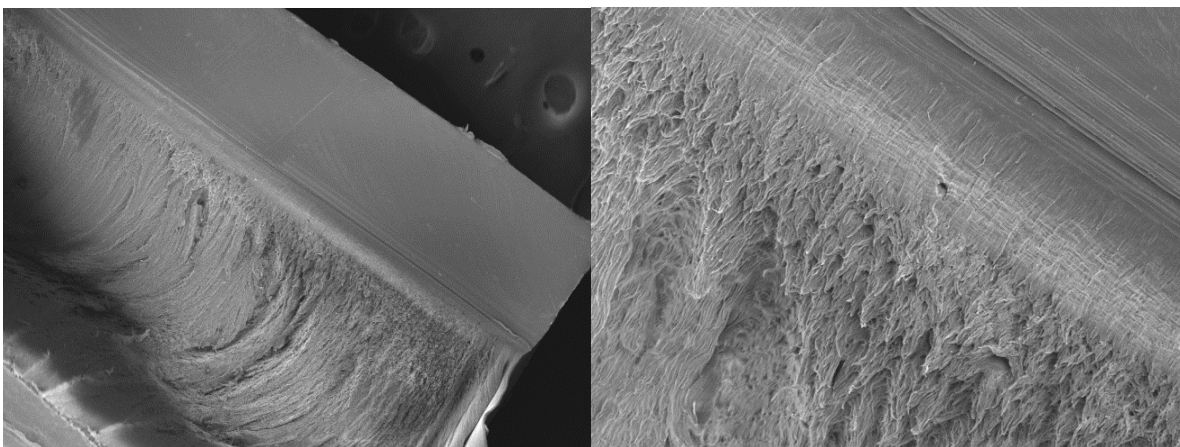


Figure 5.9 SEM image of cracked surface obtained from the modified bending test on LLDPE 150 AC.

FTIR was done on the 150 AC cracked surface and compared to the neat 150 AC granules' FTIR spectrum; the spectra are plotted in Figure 5.10 and show that no additives are present on the material surface. Additionally absorbance peaks arose at wavenumbers of 1100 – 1000 cm^{-1} , 803 cm^{-1} and 1262 cm^{-1} which once again is indicative of the cold drawing of samples resulting in ordered ethylene sequences.

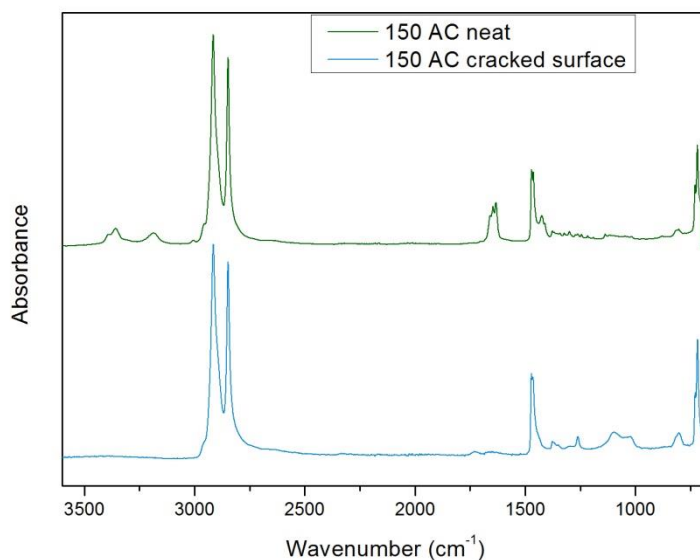


Figure 5.10 FTIR spectra of 150 AC cracked surface and neat surface of granule.

DSC was done on the cracked surface and compared to that of the mould which is plotted in Figure 5.11 where the endothermic peak between 70 °C and 120 °C corresponds to crystalline melting. The data is tabulated in Table 5.5 and show that the cracked surface has a lower peak melting temperature (approx. 1°C) and a crystallinity that is 4.77 % higher which could be due to stress crystallization that may occur during the modified bending; additionally, extraction of amorphous PE could also lead to an increase in crystallinity. Extraction will be discussed in Section 5.4.

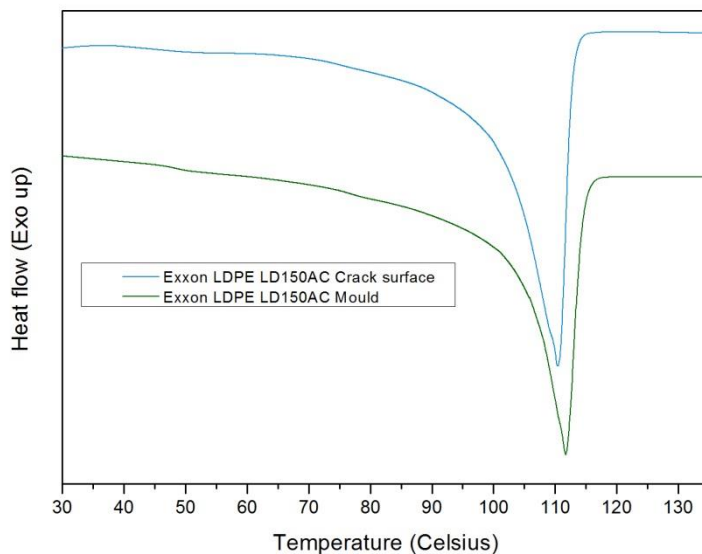


Figure 5.11 DSC thermograms of 150 AC cracked surface and mould bulk.

Exposing the granules to heptane for a week at room temperature also caused a decrease in the peak melting temperature as well as an increase in the crystallinity (see Table 5.5); this could be attributed to an increase in mobility of the amorphous phase, after liquid penetration, allowing further crystallization. The decrease in the peak melting temperatures could be attributed to a decrease in average crystallite size; during swelling from liquid exposure the crystalline/amorphous interface is subjected to a high degree of stress as a result breakage of PE crystals occur.

Table 5.5 LLDPE LD150AC DSC analysis.

Material	% crystallinity*	T _m (°C)
Exxon LDPE LD150AC mould	26.0	111.7
Exxon LDPE LD150AC cracked surface	30.7	110.5
Exxon LDPE LD150AC granule	27.6	109.5
Exxon LDPE LD150AC granule exposed	28.2	109.3

* calculated from the first heating cycle.

The modified bending test successfully produced a brittle crack surface, and the extent of cracking could be determined through tensile tests before and after conditioning. Additionally, analytical techniques such as DSC and FTIR allowed the analysis of the cracked surface which again as in ESCR test 1 showed the preferential penetration of a contaminant (silicone oil). Alternatively to ESCR test 1 an increase in crystallinity was observed on the cracked surface (in ESCR test 1 a small decrease in % crystallinity was observed), probably due to the embrittlement of the cracked surface as opposed to the ductile method of failure

observed during ESCR test 1. It should be noted that the modified bending tests does not successfully correlate molecular structure to ESCR, although lower molecular mass materials did crack more readily. Also the tests do not seem to correlate HSP of the SCA's to stress crack ability as different trends were observed for HF 140 and UL 814.

5.4 Extraction

The granules underwent extraction for the purpose of analysing the extractable material. Initially 5 g of granules were used during the extraction process; unfortunately the yield of extractable material was extremely low. The quantity of granules was therefore increased by a factor of at least 10. Heptane, isopropanol and methanol were used as the solvent (approximately 300 ml per 50 g of granules) during extraction and commenced for 24 hours at room temperature. The yield of the extractables were no more than 0.5% of the initial granule mass. It is therefor highly unlikely that extraction of low molar mass materials could contribute to the decrease in ESCR.

Extracted materials were analysed with DSC to determine the % PE crystallinity and corresponding peak PE melting temperature; see Table 5.6. Only the materials prone to ESC, as determined during the modified bending tests, yielded enough material for DSC analysis (LDPE HF140, LD150AC, LLDPE UL 814 and LLDPE 1001KI).

The DSC thermograms of 1001KI extracted material revealed only a melting endotherm between 60 °C and 80 °C corresponding the melting of additives such as slipping agents (Oleamide, Erucamide and Stearamide).

Table 5.6 Extracted material melting temperatures and % crystallinities.

Material	% crystallinity(PE)/Melting temperature (T_m)		
	Heptane	Isopropanol	Methanol
LDPE HF140	9.41/97.54	24.85/102.31	n/a
LDPE LD150AC	4.71/97.59	9.368/104.05	7.54/106.63
LLDPE UL 814	n/a	19.19/114.94	36.35/118.32
LLDPE 1001KI	additives	additives	additives
LLDPE HR472	n/a	n/a	n/a
mLLDPE Exceed 1018HA	n/a	n/a	n/a
uLLDPE Attane 4102G	n/a	n/a	n/a

n/a – Non-transferable yield, additives $T_m = ^\circ\text{C}$

Thermograms for extractable material LD150 AC and UL814 are represented with their respective neat granules; see Figures 5.12 & 6.13 respectively. It shows that for both granules the melting temperature of the extractable material trends towards that of the neat granule's melting temperatures as the polarity of the solvent increases. The same trend was found for the LDPE HF140 granules. The warm shift in the peak melting temperature indicates that non-polar SCAs preferentially extract highly branched PEs and more polar SCAs extract less branched PE molecules.

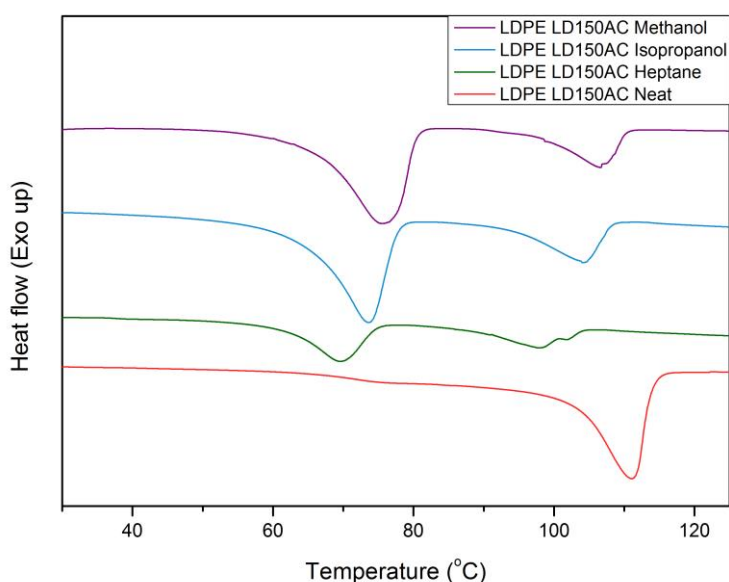


Figure 5.12 DSC thermograms of material extracted from LD150 AC.

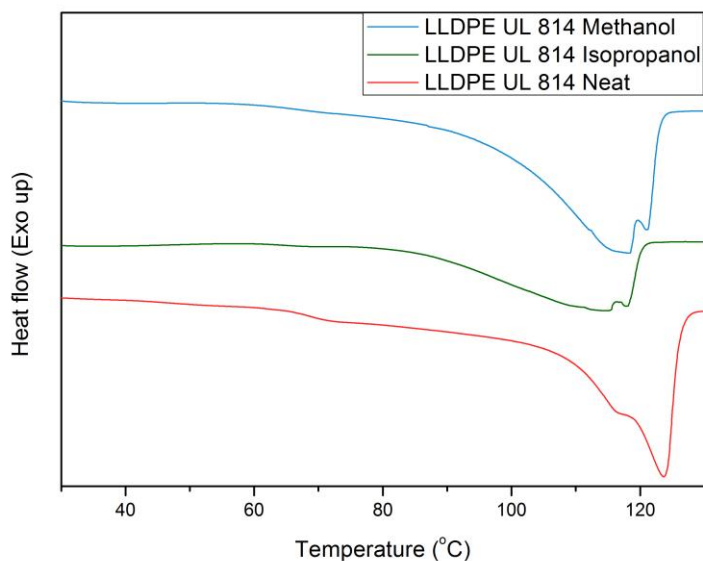


Figure 5.13 DSC thermograms of material extracted from UL814.

The molecular mass of the various PE containing extracted fractions were analysed through HTGPC, the results are tabulated in Table 5.7 below. Comparing the granule molecular mass to the extracted fractions reveals that low molecular mass PE is preferentially extracted. There is no clear relationship between solvent polarity and the molecular mass of corresponding extracted material. However, extraction (and extraction quantity) could indicate that a particular material is susceptible to ESC when in contact with a certain extraction liquid (SCA).

Table 5.7 Extracted materials' weight average molecular mass.

Material	Weight-average molecular mass (g/mole)			
	Granule	Heptane	Isopropanol	Methanol
LDPE HF140	17160	127221	143443	n/a
LDPE LD150AC	310741	202577	241743	213624
LLDPE UL 814	131398	n/a	77540	97269

It is unclear whether an SCA preferentially extracts certain fractions of the bulk. It is evident that in all cases low molecular mass material is extracted preferentially during exposure to ESC agents thereby possibly aiding in ESC.

5.5 Polymer films

Three polymeric films were used in the following section; they will be referred to as polyethylene film, PA/EVOH laminate and MPET laminate. Their compositions are summarized in Table 5.8; all the films have a relatively high molecular weight and intermediate dispersity. The ESCR of these films were analysed in order to see if any relationships could be developed with regards to chemical composition and ESCR. Obviously the film make-up, thickness, molar mass and distribution of the various components also play a role, but these could not be determined. So, using LLDPE as the base material, it would be interesting to see if the addition of other polymers (poly ethylene terephthalate, polyamide or ethylene vinyl acetate) plays a significant role on the ESCR.

Table 5.8 Summary of film properties used in this study.

Sample identification	Thickness	Yield strength (MPa)	% crystallinity / T_m of PE	\overline{M}_w (g/mole)	Dispersity (D)
LLDPE	80 μm	7.39 \pm 0.30	28.69/121.26	265736	3.92
PA/EVOH laminate	112 μm 26/3/2/2/2/3/18/ 18/3/2/2/2/3/26	10.35 \pm 0.37	29.36/117.38	260853	3.53
MPET laminate	112 μm 50/12/50	15.36 \pm 0.542	22.36/122.38	261195	3.67

5.5.1 Film DSC

DSC was conducted on the neat films; melting at 255 °C corresponds to the melting of PET, at 185 °C the melting of PA takes place, melting of EVOH occurs at 210°C and the characteristic melting of PE occurs between 50°C and 130°C. A shift in the baseline below 50 °C could indicate melting of highly branched LLDPE or the glass transition of PET.

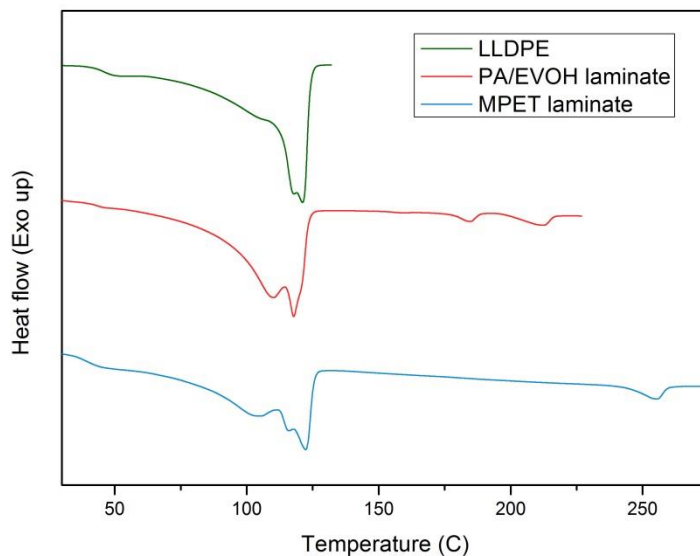


Figure 5.14 DSC thermograms of films (1st heating cycle).

The films were exposed to liquid SCAs and thermally analysed as with the granules, it was found that exposure had little to no effect on the thermal properties of the films.

5.5.2 Film tensile tests

Tensile tests were performed on the three films with LLDPE having the lowest yield strength (7.39 ± 0.30 MPa) and MPET the highest (15.36 ± 0.542 MPa). PA/EVOH and MPET have a significant tensile strengthening effect on the material although only 10.7% by volume is made from it. During tensile testing of the MPET laminate a rapid drop in stress was observed at a percentage strain below 65%, this is the breakage of the inner MPET layer. A second decrease in the percentage strain is from the tear and break of one PE laminate leaving a single PE laminate to carry the load. Visually the film delaminates followed by breakage of the MPET component; breakage damages the PE laminate causing it to tear.

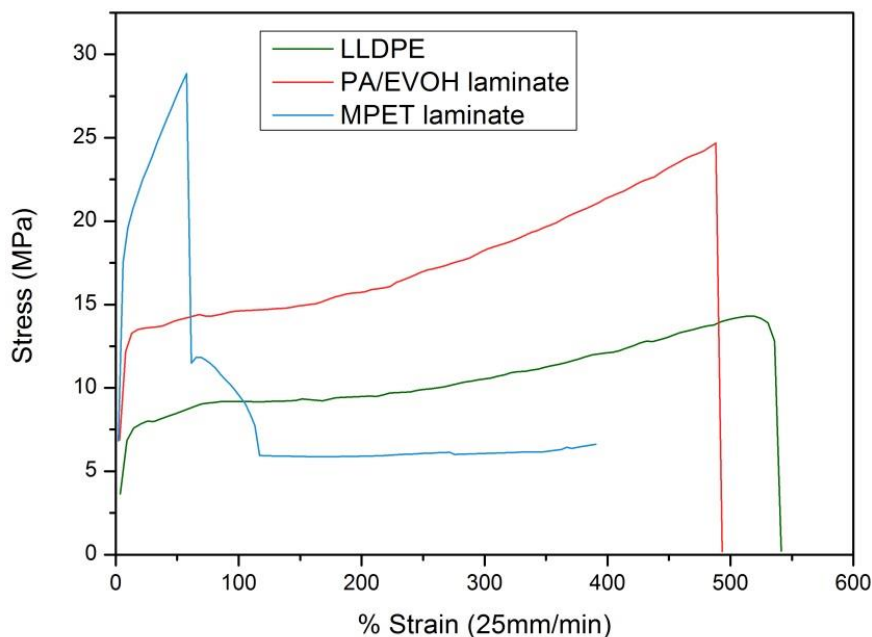


Figure 5.15 Tensile test stress-strain results of films.

In Table 5.9 the laminate tear frequency and the complete breakage frequency is stated as a percentage (percentage of tested specimens that underwent tearing and breakage) for each SCA’s exposure. Isopropanol and Glühwein exposed samples are the only specimens that underwent complete failure; furthermore, the laminate tear frequency is the lowest for the neat sample deformed at 25mm/min. A larger deformation rate showed an increase in the tear frequency as well as with the exposed films meaning that liquid exposure adversely affected the material, specifically at the PE/MPET interface.

Table 5.9 MPET laminate tear and breakage frequency.

Treatment	LLDPE laminate tear frequency	Complete breakage frequency
Neat 25mm/min	20.0%	0.0%
Neat 100mm/min	75.0%	0.0%
Teepol	90.0%	0.0%
Glühwein	45.5%	9.1%
Heptane	50.0%	0.0%
Isopropanol	80.0%	10.0%

Young’s modulus is determined by calculating the slope of the initial linear portion on a stress-strain plot. Tensile tests conducted with a deformation rate of 100mm/min were

compared to tests conducted at 25mm/min both for neat films; all the films responded with higher moduli at a greater deformation rate meaning the material's tendency to deform elastically decreases with increasing deformation rate. Films exposed to several SCAs for 7 days were deformed at a rate of 25mm/min and compared to unexposed films also deformed at 25 mm/min. The LLDPE specimens showed a marginal increase in the Young's modulus after exposure; similarly for the PA/EVOH laminate except for the heptane exposed films which remained constant. For the MPET laminates the moduli remained relatively constant when treated with Glühwein and heptane; isopropanol and Teepol treated films exhibited slightly higher moduli. What is noticeable here is that the change in strength (as measured by the moduli) of the laminated films after exposure to the SCAs mirror that of the LLDPE. The only difference here are the laminates in the presence of Teepol; here the LLDPE appears almost completely unaffected, yet the laminate films are still weaker (in the case of the PA/EVOH notably so) than the unexposed films.

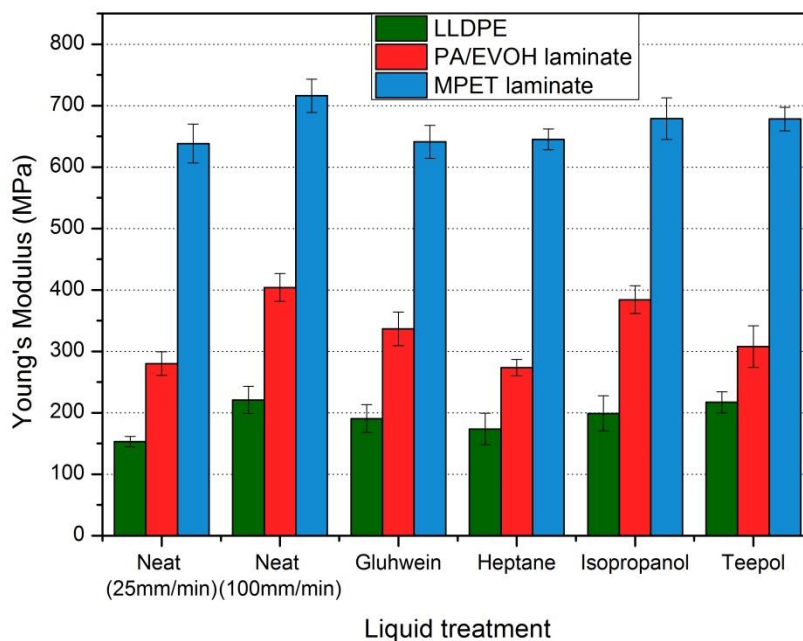


Figure 5.16 Measured Young's modulus before and after liquid treatment.

Lastly, these exposed films showed no significant decrease in the yield strength compared to unexposed films.

5.6 Analysis of failed industrial MPET laminated liquid liner

As stated in an earlier Chapter 4 Section 2.4, Glühwein was added to the list of liquid SCA's; the film suppliers obtained a sample of the MPET laminate that has failed. The MPET

laminated failed section is seen in Figure 5.17 A which shows the disappearance of the silver aluminium colour around the points where pinholes developed. This is because the liquid (Glühwein) enters the material; causes delamination then as a result internal friction accelerates pinhole development. Additionally, the agitation could break up the thin aluminium layer on the film and thereby extracting it. The MPET films that were exposed in Section 5.5.2 did not change colour from silver to transparent as in the real case scenario supporting the fact that internal friction (after delamination) causes the colour transition. The SEM image in Figure 5.17 B is the delaminated surface of the LLDPE laminate which shows the development of surface inhomogeneity in the form of voided areas.

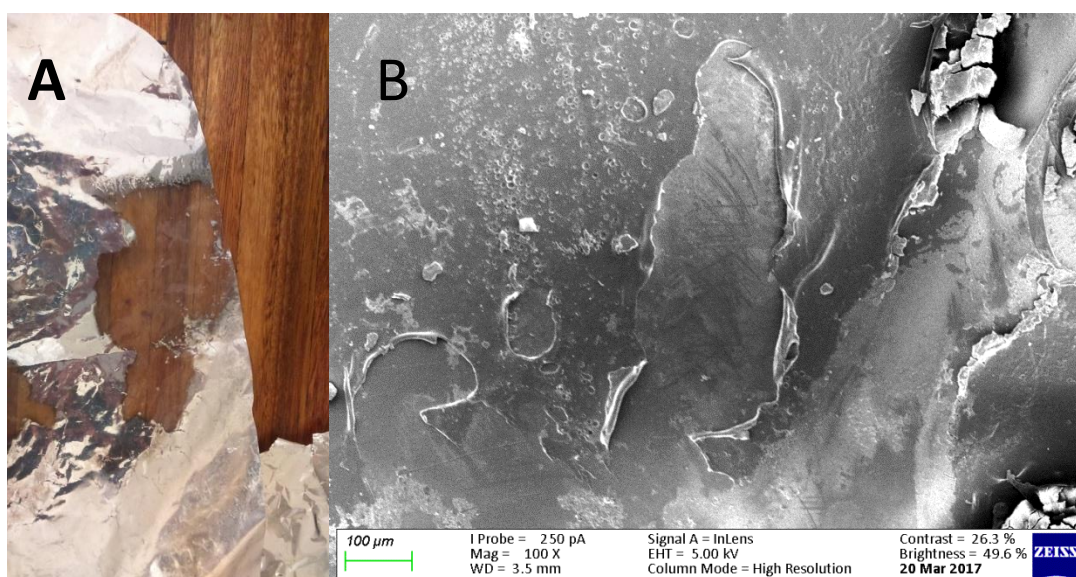


Figure 5.17 MPET failed section (A) and SEM image (B) of the PE delaminated surface.

The pinhole was isolated and two delaminated films were rinsed with deionised water to remove any surface contaminants where after the dried pinhole surfaces were analysed with FTIR spectroscopy. Four surfaces were analysed, they are: 2 outer surfaces of the MPET laminate (non-delaminated surfaces) and 2 inner surfaces of the delaminated surfaces. Laminate 1 and 2 represent the surface in contact with Glühwein initially and the outer surface of the liquid liner, respectively. The outer LLDPE pinhole surfaces showed once again absorbance peaks at wavenumbers of $1100 - 1000 \text{ cm}^{-1}$, 803 cm^{-1} and 1262 cm^{-1} as was the case during the LLDPE CLT and the 150AC cracked surface. These peaks have higher intensity for the LDPE laminate that was initially in contact with Glühwein than the outer laminate, furthermore, laminate 1 had additional peaks at 1650 cm^{-1} and 3400 cm^{-1} indicating the presence of flavonoids at the pinhole surface.

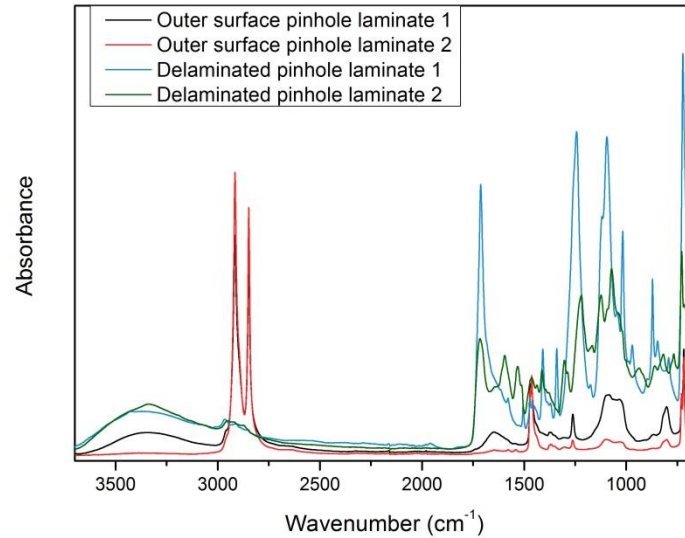


Figure 5.18 MPET failed in Glühwein pinhole surfaces.

The FTIR spectrum of delaminated pinhole laminate 1 is similar to that of polyethylene terephthalate.⁴ Laminate 2 shows somewhat lower absorption intensities compared to laminate 1, possibly due to the presence of metallic aluminium on the surface which does not absorb IR radiation in the range of $3700\text{ cm}^{-1} - 700\text{ cm}^{-1}$.

HTGPC was conducted on the pinhole section and compared to the neat MPET laminate; again it was found that the \overline{M}_n and \overline{M}_w remained constant during the failure process.

DSC analysis (Fig. 5.19) showed that laminate 1 had a melting endotherm at $255\text{ }^\circ\text{C}$ indicative of PET melting; alternatively laminate 2 had no PET melting endotherm. The DSC results together with the FTIR results indicate that delamination preferentially occurs at the polymer aluminium interface, and that this delamination occurs via the intrusion of active components in the SCA in question, in this case flavenoids present in the Glühwein.

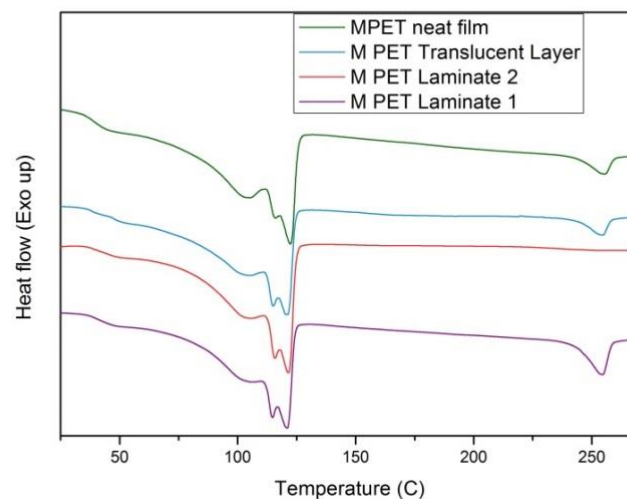


Figure 5.19 DSC of MPET failed in Glühwein pinhole laminates.**5.7 References**

1. Yarysheva, A. Y., Rukhlya, E. G., Yarysheva, L. M., Bagrov, D. V., Volynskii, A. L. & Bakeev, N. F. The structural evolution of high-density polyethylene during crazing in liquid medium. *Eur. Polym. J.* **66**, 458–469 (2015).
2. Casteloes, K. S., Mendis, G. P., Avins, H. K., Howarter, J. A. & Whelton, A. J. The interaction of surfactants with plastic and copper plumbing materials during decontamination. *J. Hazard. Mater.* **325**, 8–16 (2017).
3. Barton, A. F. M. *CRC handbook of solubility parameters and other cohesion parameters*. (CRC Press, 1991).

4. Chen, Z., Hay, J. N. & Jenkins, M. J. FTIR spectroscopic analysis of poly(ethylene terephthalate) on crystallization. *Eur. Polym. J.* **48**, 1586–1610 (2012).

Chapter 6

Conclusions

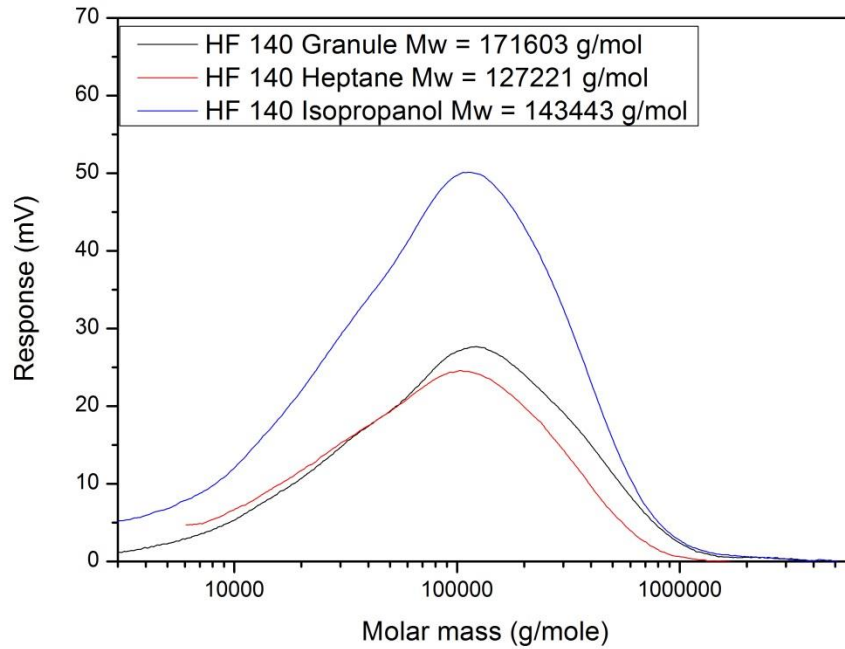
ESCR remains difficult to predict accurately especially when correlating lab scale conditions with that found in the industry. Nevertheless, concluding on the results found during this thesis revealed the following:

- ESCR test 1 (ESCR test for ethylene based plastics) does not seem to be a reliable and quantitative method for testing the ESCR of polyethylene films, although it does predict (from FTIR spectra) that an applied force does promote oil penetration into the film.
- During ESCR test 1 the LLDPE film chains untangle and intermolecular attraction decreases leaving the tie chains as the only load bearing component in the material. These load bearing tie chains shear the crystallites into smaller ones into so called “mosaic blocks”. This failure is called ductile failure and occurred at stresses below the yield stress of that material, therefore a penetrating liquid decreases the yield stress.
- The molecular mass of the bulk of the material remains largely unchanged as an extremely small quantity of lower molecular mass material is extracted during exposure to a SCA.
- Extracted PE material have lower melting temperature than the bulk which indicate that branched PE is preferentially extracted.
- Extraction (and extraction quantity) could indicate that a particular material is susceptible to ESC when in contact with a certain extraction liquid (SCA).
- A brittle fracture mechanism was achieved with the modified bending test seen as the formation of fibrillar structures on the cracked surfaces with an increase in crystallinity of the same surface (as compared to the bulk).
- The modified bending tests reveal that lower molecular weight polyethylenes are more susceptible to ESC, although a trend between cracking extent and HSP of SCA’s is difficult to determine.
- Additives are only present on the material surface due to migration.
- Additives such as oleamide, erucamide and stearamide are easily removed from the surface with alcohols and aliphatic SCA’s.

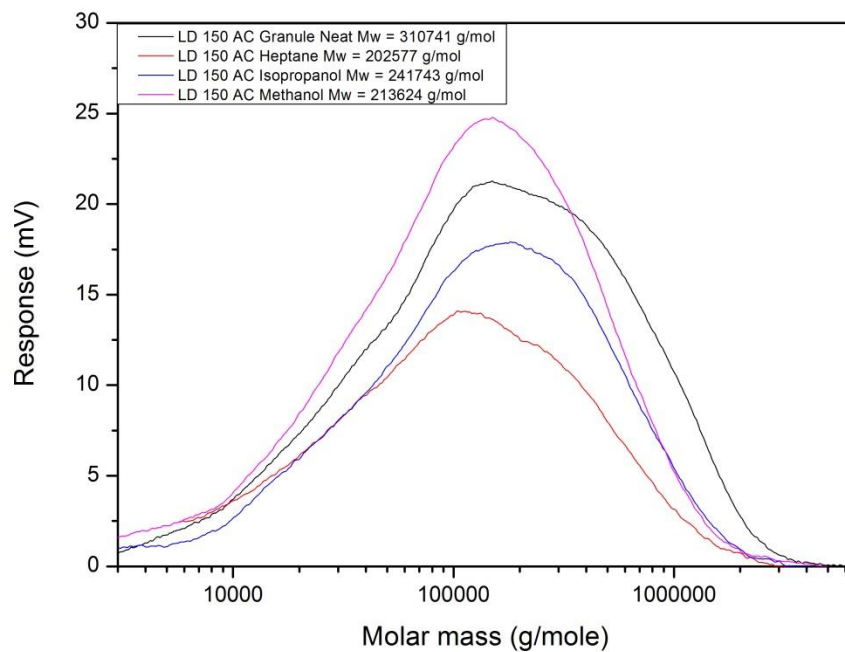
- Films only exposed to liquid SCA's reveal that exposure had little to no effect on the thermal properties of the films.
- Marginal changes were observed in the Young's moduli after exposure to SCA's for various commercial films.
- No change in the film's yield strength was observed after exposure to SCA's.
- Heterogeneous layered films (particularly MPET) delaminate rapidly in industry and as a result cause pinholes to develop which is followed by catastrophic failure. Therefore heterogeneous layered films should be avoided although they have higher yield strengths.
- Delamination of heterogeneous layered films are due to phase immiscibility as well as attraction of SCA's to the layer interfaces.

Appendix A: GPC DATA

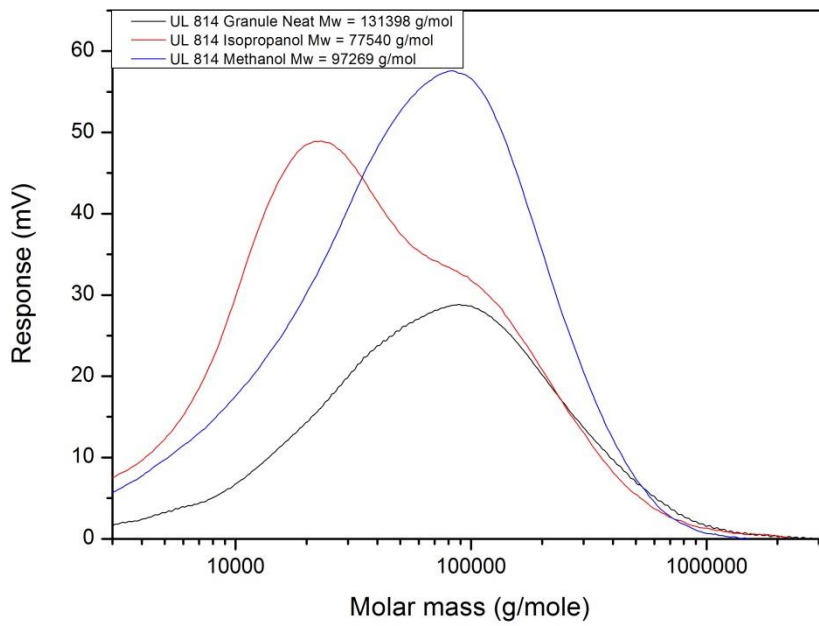
HF 140 extraction HT - SEC



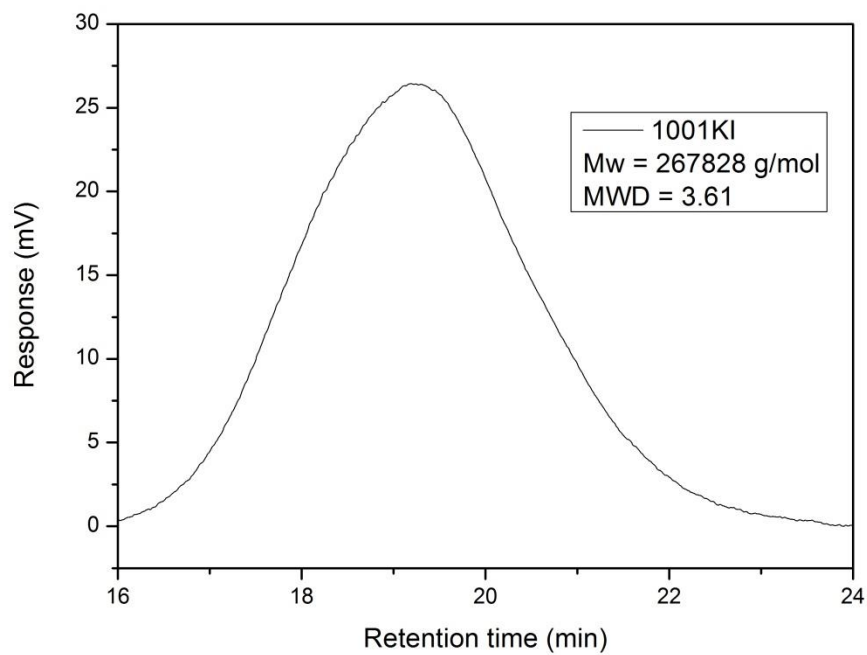
LD 150 AC extraction HT - SEC



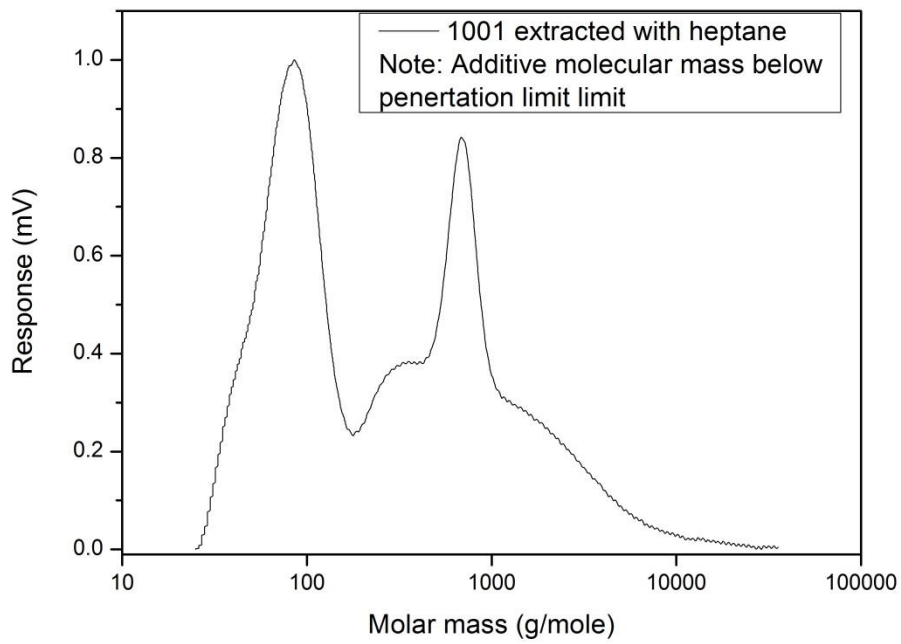
UL 814 extraction HT - SEC



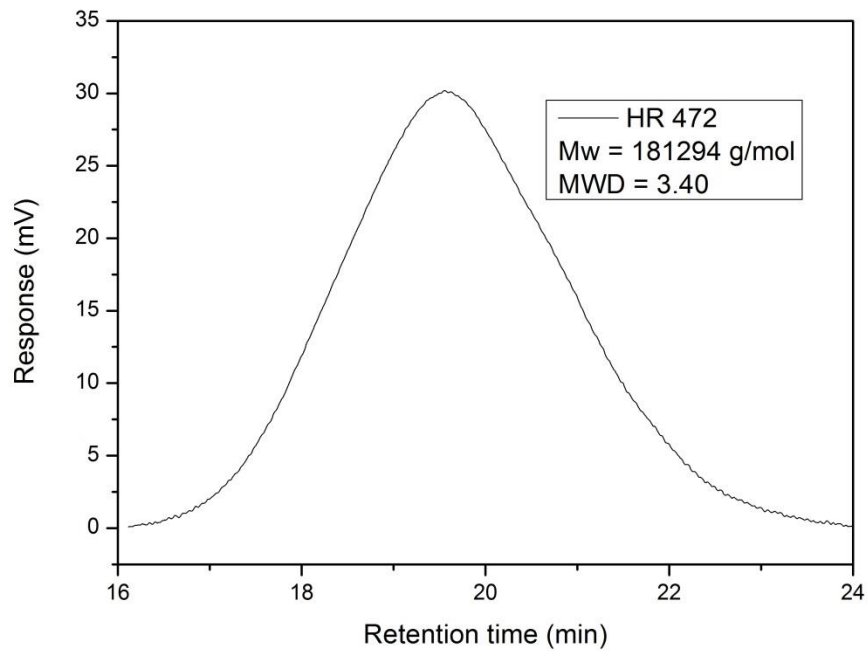
1001 KI Neat HT - SEC



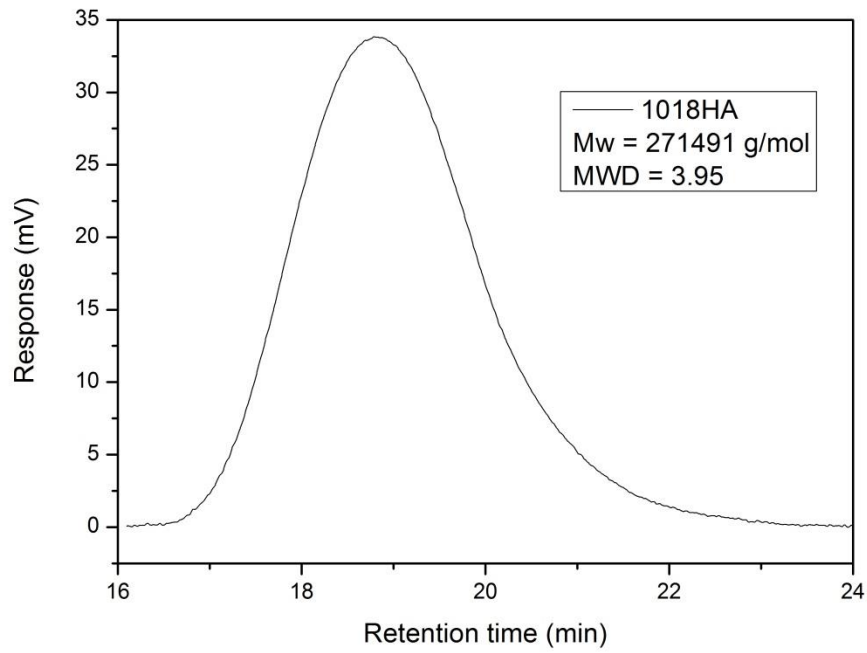
1001 KI Heptane extracted material HT - SEC



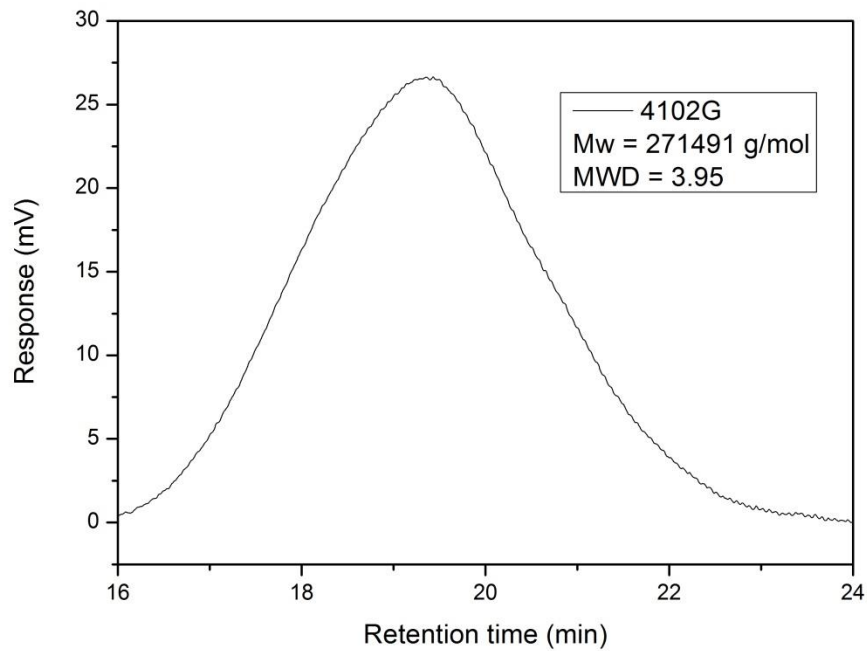
LLDPE HR 274 Neat HT - SEC



LLDPE 1018 HA Neat HT - SEC

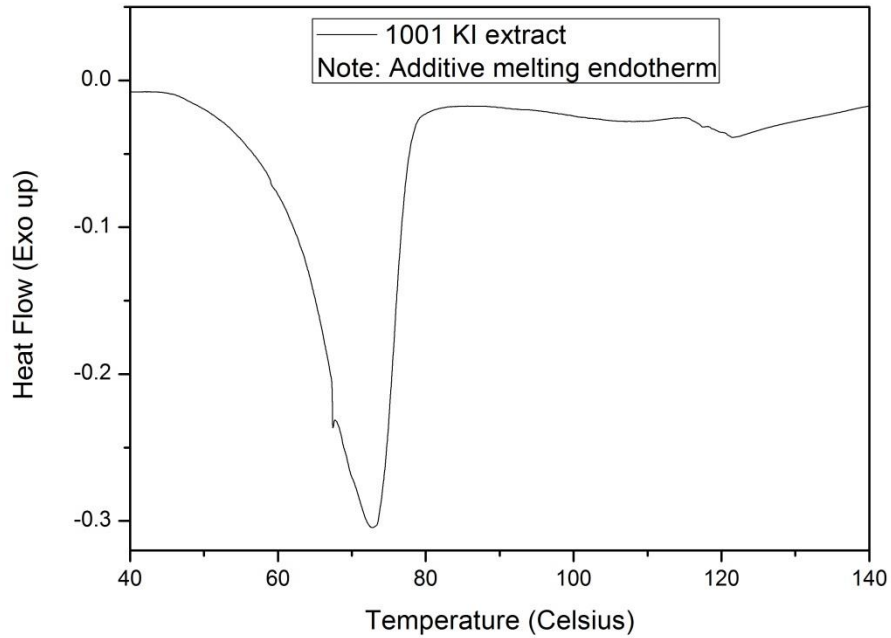


LLDPE 4102G Neat HT - SEC



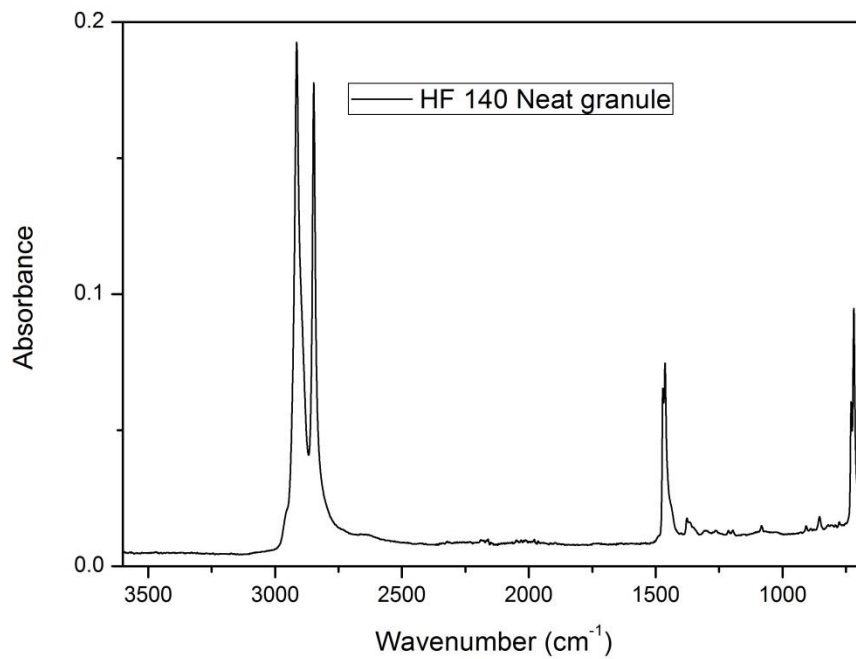
Appendix B: DSC DATA

1001 KI Heptane extracted material DCS melting

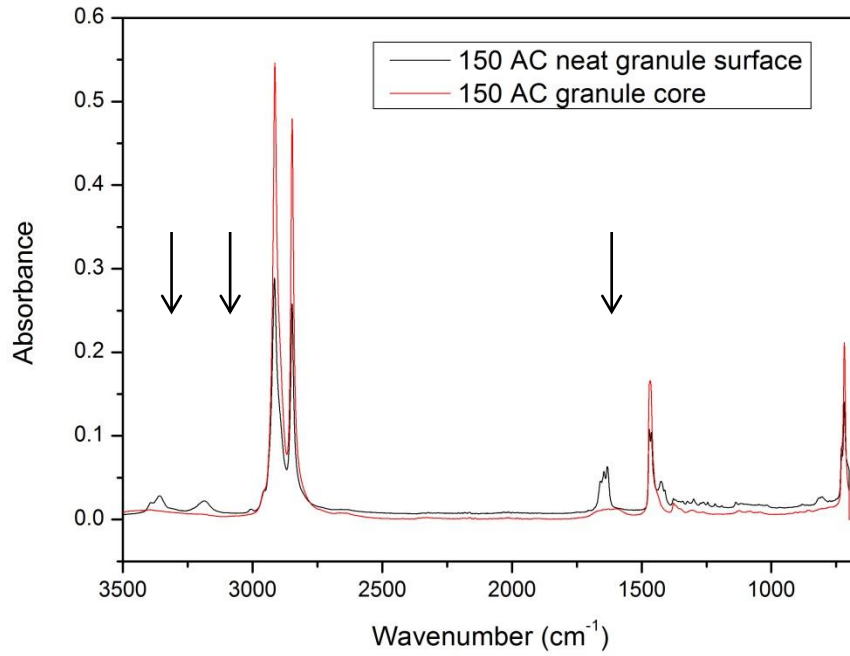


Appendix C: FTIR DATA

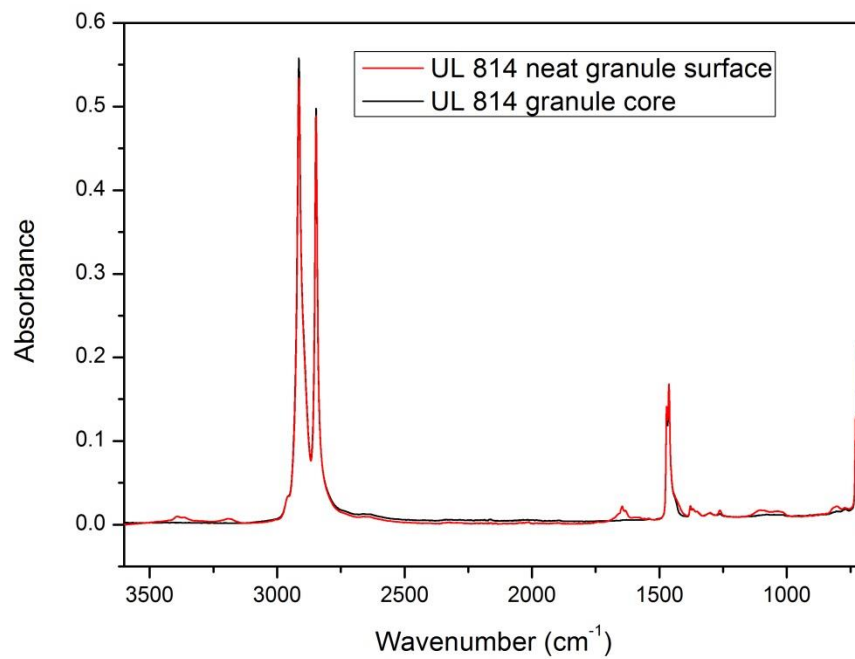
LDPE HF 140 Neat granule surface FTIR



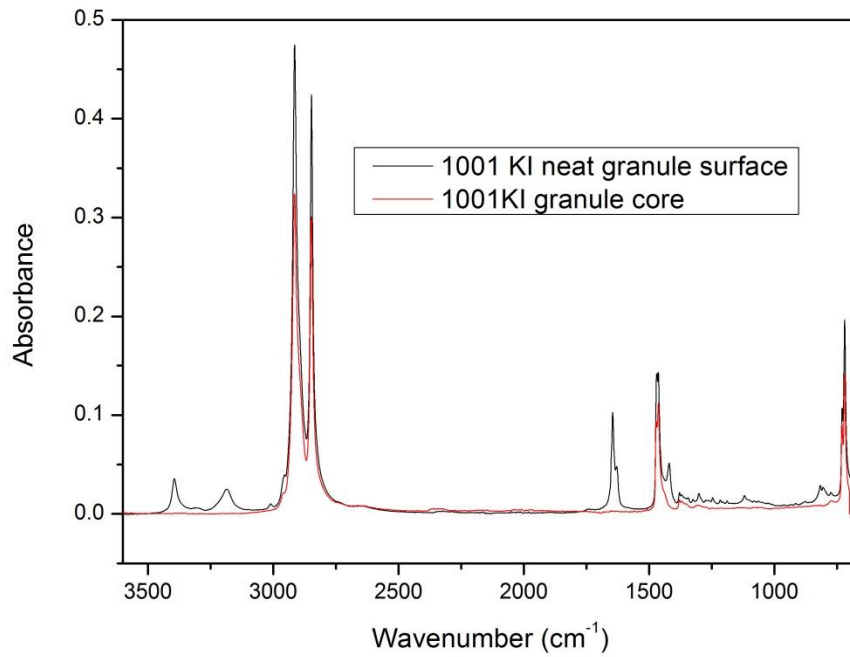
LDPE 150AC Neat granule surface vs core FTIR



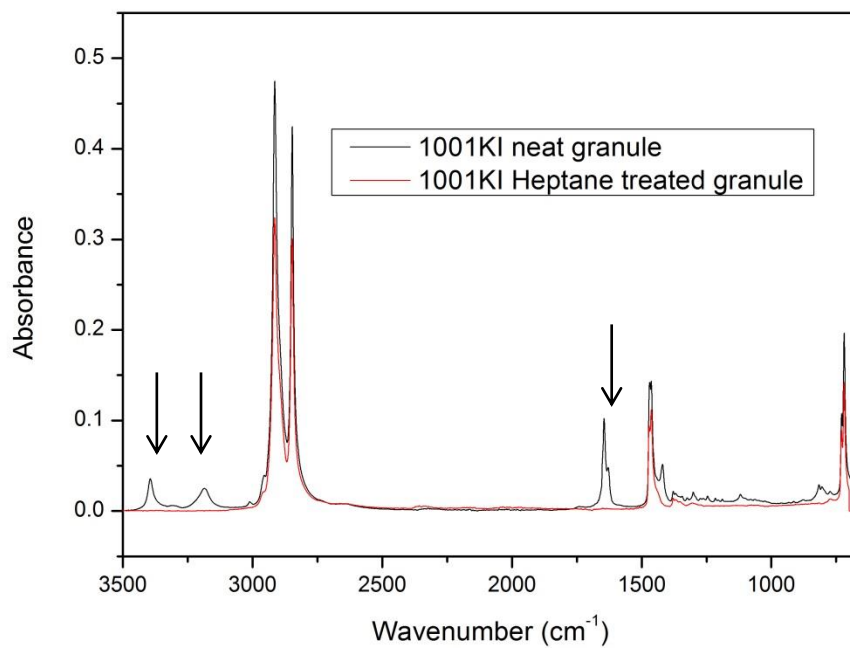
LLDPE UL 814 Neat granule surface vs core FTIR



LLDPE 1001 KI Neat granule surface vs core FTIR

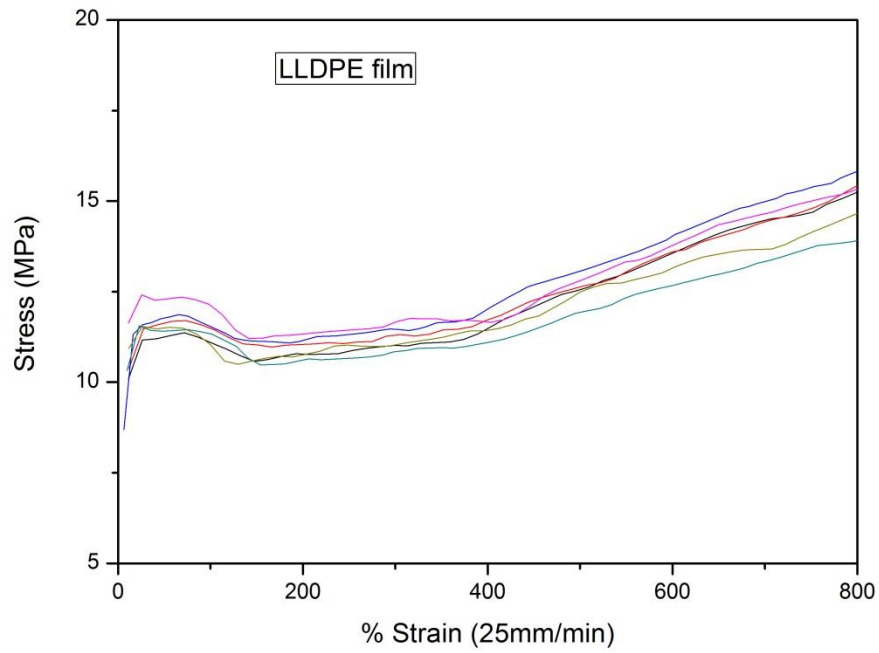


LLDPE 1001 KI Neat granule surface vs Heptane exposed surface FTIR

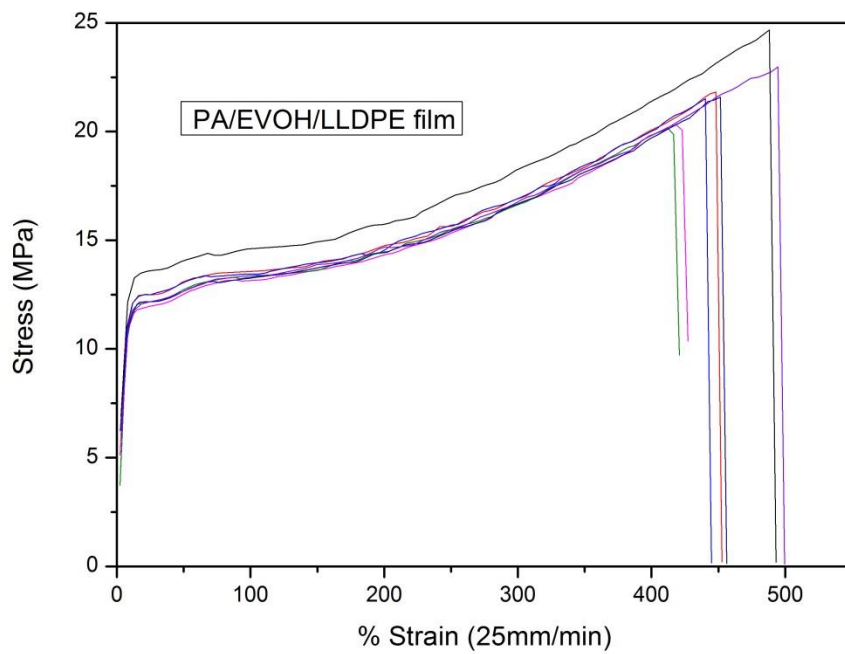


Appendix D: FILM TENSILE TEST DATA

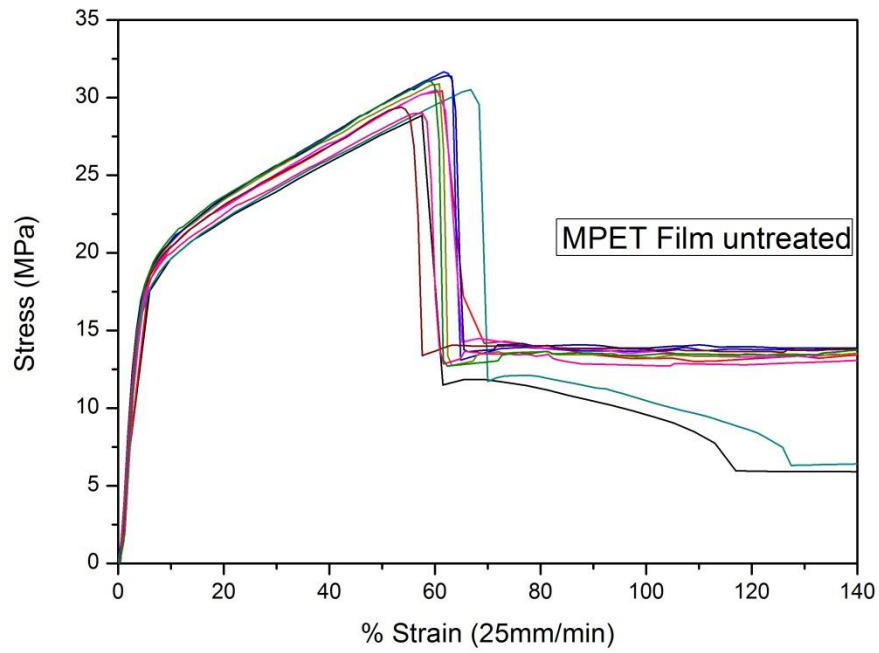
LLDPE Film tensile test data



PA/EVOH/LLDPE Film tensile test data

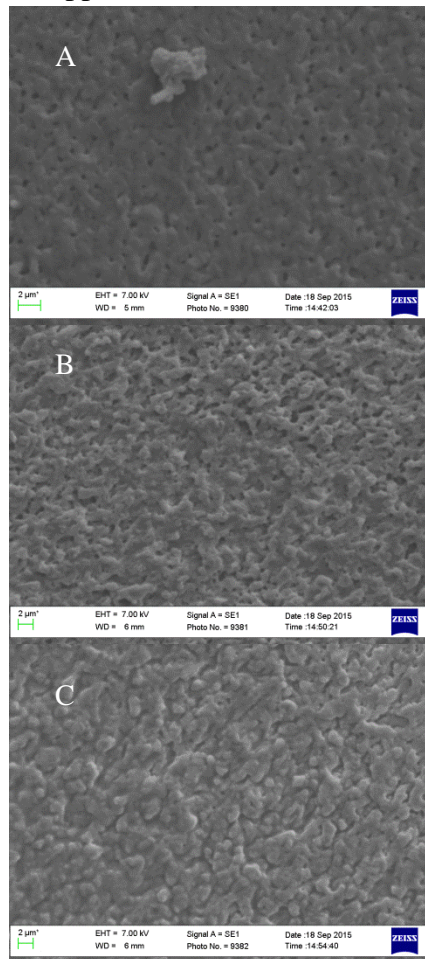


MPET Film tensile test data



Appendix D: SEM DATA

LLDPE film etched for
 (A) 1 hour,
 (B) 2 hours,
 (C) 3 hours.



Appendix E: Constant load results

SCA	Concentration	30% yield strength	80% yield strength
Isopropanol/water	1: 9 vol%	No visual failure	No visual failure
Isopropanol/water	4: 6 vol%	No visual failure	No visual failure
Isopropanol	Solvent grade	No visual failure	No visual failure
Teepol (surfactants)	n/a	No visual failure	No visual failure
Heptane	Solvent grade	No visual failure	Ductile failure

