

PHYSICAL AGEING BY ULTRAVIOLET  
DEGRADATION OF RECYCLED  
POLYOLEFIN BLENDS

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## **Abstract**

This thesis covers the investigation of the weathering behaviour of mixed waste plastics. It includes a review of the literature on polymer degradation mechanisms with particular emphasis on environmental degradation from ultra violet radiation.

Products manufactured from recycled polyolefin blends were subjected to accelerated weathering conditions and subsequent tests. Field-aged products were tested also.

Samples were analyzed for changes in mechanical, rheological and chemical properties.

Scanning Electron Microscopy and Electron Probe Microanalysis were used to examine samples for both impurities and signs of degradation.

Data obtained in this study, by means of tensile and melt flow tests, with GPC, gloss and colour analyses carried out by Rapra<sup>1</sup>, showed that the effect of UV exposure, whether in the field or artificial environments, was not significant as far as the mechanical properties of the materials were concerned. There was some change in the surface characteristics but such surface effects would not compromise the mechanical integrity of the product when recycled.

During reprocessing of the materials, it is likely that stabilizer is brought to the surface of any new moulding, thus renewing the surface characteristics. Hence damaged or end-of-life products need not be discounted from recycling. However, surface appearance may be an issue.

SEM EDX Analysis was useful in identifying impurities in the recyclate, but there was no conclusive evidence of degradation as a direct result of exposure to UV radiation.

The variation in field-aged materials and the artificially aged materials showed that it is likely that the difference in results for field aged and artificially aged material was due to variability in the source materials and showed that in practice, it is difficult to control the composition of the mix coming from the waste suppliers. This was more significant for the

properties of the materials than any UV exposure. This increase could be due to degradative cross-linking. However, it was more likely to be caused by variability in the batches of raw material.

Chain scission in polypropylene and cross-linking in polyethylene in mixed blends could have a compensating effect on each other and lead to non-degradative effects although evidence for this was inconclusive.

Overall, the study has shown that all the materials tested have generally maintained their mechanical properties with little change under accelerated UV exposure. This has positive implications for the use of plastic recyclate of this nature in manufacturing processes.

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<sup>1</sup> Rapra – Rubber and Plastics Research Association

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Finally, the study would not have been possible without the patience and encouragement from my partner David and son Jonathan.

**Declaration**

I declare that the research contained in this thesis, unless otherwise formally indicated within the text, is the original work of the author. The thesis has not been previously submitted to this or any other university for a degree, and does not incorporate any material already submitted for a degree.

Signed

Date

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## **1. Introduction**

In response to EC Directives, European governments are required to devise policies such as kerbside recycling to reduce levels of industrial and municipal waste.

The recycling of plastics is one area of the waste stream that has had less focus from UK local authorities than others, primarily because of the difficulties encountered when identifying and sorting plastics for recycling. Also, waste reduction targets are based on weight rather than volume. However, EC Directive 94 /62/ EC <sup>[1]</sup>, which set targets that have been incorporated into UK law through the Producer Responsibility Obligations (Packaging Waste) Regulations 1997 <sup>[2]</sup>, which includes sales and transport plastic packaging, proposed a new plastics recycling target of 20% by 2006.

Uncertainty over future oil resources and the recent upward trend in oil prices, as well as a reduction in the use of landfill for waste disposal have increased the need for the recycling of plastic materials.

According to the Waste and Resources Action Programme, six types of polyolefin constitute over 90% of the plastics recycled in the UK. The most common (53%) is low-density polyethylene (LDPE/ Linear LDPE). High-density polyethylene (HDPE) and polypropylene (PP) make up 13% and 21% of the total respectively. Growth in the amount of these polyolefins recycled in the UK is expected to increase by at least 5% per annum <sup>[3]</sup>.

This projected growth in availability of raw materials has intensified the need to overcome barriers to the use of recyclate instead of virgin material in manufacture. One problem identified is the lack of standards for recyclate <sup>[4][5]</sup>. Papineschi <sup>[4]</sup> proposes that universally recognised standards would increase the acceptability of recyclate as a raw material so it can compete with virgin polymers. Also, it would be necessary to develop product specifications to permit the use of recyclate in manufacture whilst ensuring the product is fit for purpose.

The Producer Responsibility Obligations (Packaging Waste) Regulations 2005 addresses the problem of quality control and traceability of recyclates. It provides standard guidance for the accurate identification and quantification of plastics packaging waste destined for

recycling (either in the UK or overseas) and the creation of documented audit trails that will be subject to verification.<sup>[6]</sup> This Protocol was not in effect at the time of sourcing the recycled plastic for this study. However, the exact composition of the original products, such as the amount and type of stabilizers that form the recycle is not specified by the product manufacturers.

Public perception of the use of recycled plastic material was addressed in a survey conducted on behalf of the Waste Resource Action Programme in 2005<sup>[7]</sup>. Of the 460 participants, 77% said they would 'not worry' if food drinks, toiletries and domestic products contained recycled plastics. 86% of consumers felt that it would be 'good if packaging contained recycled plastic. 90% of respondents felt that 'manufacturers and retailers should just get on with producing packaging containing as much recycled plastic as possible'. In focus group surveys, 65% of the participants could see no visible differences between three empty clear plastic containers that comprised 0%, 15% and 50% recycled plastics respectively.

The study addresses fundamental questions about the effect of environmental degradation, and particularly the effect of ultra-violet radiation, on the properties of products made from recycled polyolefins. The properties of products recovered from several years of use outdoors were compared with unused products that were subjected to simulated weathering according to a regime of UV and moisture exposure.

The literature review shows that the mechanical properties of polyolefins can quickly undergo adverse change after severe processing or periods of thermal and light exposure<sup>[8]</sup>. However, polyolefins should, in theory be impenetrable to photodegradation. It is generally assumed that impurities, or chromophores, which absorb UV light, initiate the photo oxidation of commercial polyolefins<sup>[9] [10]</sup>. Many polymers are essentially useless unless stabilizers are added<sup>[11]</sup>. Advances in stabilizer chemistry have extended the use of polyolefins to a wider variety of applications.

During processing, the combination of high temperature and shear forces can lead to chain scission within the polymer and the formation of chain radicals. In the presence of oxygen, these radicals rapidly react to form peroxy radicals, which further propagate to more stable alkoxy radicals that remain present in the polymer sample. <sup>[12][25][26]</sup>

Competing reactions of chain scission and cross-linking are expected to occur in polyethylene samples, where at high temperatures, cross-linking is dominant. In polypropylene, chain scission is dominant. These irreversible effects were expected to affect the melt flow, molecular weight, viscosity and mechanical strength of the polymer. The upgrading method of post-used plastic material by subsequent addition of heat, processing and light stabilizers, known as restabilization <sup>[71]</sup> has been seen to recover mechanical performance to levels comparable with the virgin material.

Chain scission in polypropylene and cross-linking in polyethylene in mixed blends could have a compensating effect on each other and lead to non-degradative effects although evidence for this was inconclusive in this study.

Under natural weathering, the polymer experiences effects such as variable humidity, rain, wind and atmospheric pollutants, all of which affect the rate of polymer degradation. Accelerated weathering has been shown to match the polymer degradation of a naturally aged sample, although this is polymer test dependent. Hence it has been possible to apply a simulation regime typical of the environmental conditions in Northern Europe. It is incorrect to equate hours of accelerated weathering to hours of exposure in the natural environment, because of the inherent complexity and variability of outdoor exposure situations. Factors such as the thermal history of the polymer need to be known, along with the conditions experienced by the sample in use in order to accurately match the environment in accelerated testing.

Although polyolefin degradation has been studied extensively <sup>[12][13][14][15][16]</sup>, most analyses focus on thin film rather than thick specimens <sup>[15][16][17][18][19][20][21][22][23]</sup>. Also,

most test specimens are unpigmented and the majority of these are made of virgin material. Many studies used reaction conditions irrelevant either to any practical processing or end use <sup>[8]</sup>. Furthermore, degradation studies of blended plastics are not as well covered as those of their homopolymers. In order to address these issues, this research focussed on pigmented blended polyolefins from outdoor applications.

### **1.1 Aim and Objectives**

The aim of this study was to investigate changes in mechanical (deformation and fracture) behaviour and rheological properties of recycled polyolefin blends intended for outdoor use that had been subjected to accelerated ageing by UV radiation for a variety of exposure

periods. Comparisons were made with specimens aged ‘in the field’ in order to examine any correlation with degradation in the artificially aged samples. Scanning Electron Microscopy and Energy Dispersive X-Ray Analysis were used to investigate changes in topography and identify any impurities.

The long-term aim would be to contribute to developing methods of standardization and certification applicable to recycled polyolefin material from a series of waste streams.

Part of this study has been published in the journal *Polymer Degradation and Stability* <sup>[24]</sup>.

A copy of the paper is included in the Appendix.

The objectives were to

- Conduct a review of polymer degradation mechanisms with particular emphasis on environmental degradation.
- Investigate the rheological and mechanical behaviour of recycled polyolefin blends by conducting laboratory experiments under controlled conditions.
- Simulate a comprehensive weathering profile using UV cabinet exposure with intermittent analysis and microscopy.
- Identify the problems with correlating data from artificially aged samples with that from naturally weathered material for the prediction of useful lifetimes of products.

The work was part of a larger project at Brighton University funded by the Department of Trade and Industry (DTI) through the Waste Resource Action Program (WRAP). Data from tests carried out by the Rubber and Plastics Research Association (Rapra) for the project were used to support the evaluation of results.

## **2. Polyolefin Degradation**

Polyolefins rapidly lose most of their mechanical properties after severe processing or periods of thermal and light exposure. It is known that during the initial thermal processing cycle the molecular bond forces can be overcome which results in chain scission and the

formation of chain radicals. Since virtually all processing is completed in the presence of oxygen these radicals rapidly react to form peroxy radicals, which further propagate to more stable alkoxy radicals that remain present in the polymer sample <sup>[12] [25] [26]</sup>.

The severity of degradation is surprising because pure low molecular weight hydrocarbon analogues are generally resistant to oxidation at ambient temperatures and extrapolation to the corresponding polymers would suggest a far higher stability than is actually observed. Also, relatively little chemical change is required to generate major changes in physical properties. This is especially important when the final product is exposed to weathering in outdoor applications, where degradation is initiated by the near-ultraviolet (UV) component of sunlight and oxygen <sup>[8]</sup>.

Like other pure aliphatic hydrocarbons, which do not absorb the UV radiation present in sunlight, polyolefins should, in theory, be impervious to photodegradation. It is generally assumed that chromophoric impurities, which absorb UV light, initiate the photo oxidation of commercial polyolefins <sup>[8] [9] [10]</sup>

The mechanism of polyolefin photooxidative degradation has been studied extensively <sup>[6]–[22]</sup>. The starting reaction is always bond scission in the polymer chain or in some other molecule initiating degradation. Subsequent reactions include cross-linking and the formation of double bonds. Polyethylene undergoes chain scission, branching and cross linking, which occur as competitive reactions, whereas polypropylene undergoes chain scission predominantly <sup>[26]</sup>. Oxidation without UV involvement is much slower than photo oxidation. In almost all polymers photooxidative degradation occurs via a free-radical chain mechanism, initiated by the absorption of UV radiation by chromophores within the polymer. Factors influencing polyolefin photodegradation include molecular structure, polymer morphology (degree of tacticity and crystallinity), internal impurities, specimen thickness, temperature, irradiation intensity and other climatic conditions.

## 2.1 The use of Stabilizers

Polypropylene and many other polymers are essentially unusable unless stabilizers are added <sup>[11]</sup>. Consumption of polyolefin stabilizers in Europe was estimated at 5900 metric tonnes in 1998 and there is a continual demand for new and better varieties <sup>[15]</sup>. The absorption of UV radiation is attributed to chromophores, which are carried through polymerisation or generated during thermal processing. Residual catalyst and polynuclear aromatic hydrocarbon impurities are the chromophores associated with the polymerisation process. Peroxides, hydroperoxides and carbonyl species are the chromophores resulting from imparting energy and initiating the free radical oxidation of the polyolefin.

Based on the knowledge of photo initiation sources and free radical oxidation, light stabilization can be achieved by both physical and chemical processes. The physical stabilizers are additives that absorb or reflect UV radiation. These include benzophenones and benzotriazoles, which dissipate the energy as heat. Chemical stabilizers inhibit the free radical oxidation cycle via catalyst residue deactivation, radical scavenging and hydroperoxide decomposition to non-radical species. The hindered amine light stabilizers (HALS) and hindered benzoates inhibit the degradation process beyond photo initiation. Therefore a combination of these additives can give more efficient and even synergistic stabilization <sup>[8] [15]</sup>.

Usually, mixtures of thermal and UV stabilizers are added at a level of 1% by weight or less. Advances in stabilizer chemistry have extended the use of polyolefins to a wider variety of applications. However, many stabilizers and antioxidants are lost over time through evaporation, blooming or leaching. Consequently it is common practice to add further stabilizers to aged polymer material <sup>[8] [9] [16] [17] [18] [27] [28]</sup>. Addition of small quantities of virgin polymer to recycle can help to maintain most of the mechanical properties, but this is likely due to the presence of stabilizers and additives in the virgin

polymer. Subsequent addition of stabilizers to aged polymer material ('restabilization') can help to recover mechanical performance comparable with the virgin material <sup>[28]</sup>.

An effective stabilizer system requires the combination of several different types of stabilizers working together in a synergistic manner. According to Maia *et al* <sup>[27]</sup>, carbon black is one of the most effective UV stabilizers for polyolefins and is a relatively inexpensive commodity. One drawback to the use of carbon black in recycle is that this stabilizer heavily pigments the resultant material, which tends to restrict its use in manufacture.

## **2.2 Polymer Weathering**

The stability of polymers is essential, especially for outside use, and has attracted much research into degradation reactions and mechanisms <sup>[9][13][18][25][29][30][31][32]</sup>. It is a natural

phenomenon that all materials will undergo some degree of ageing during their lifetime, and specifically polyolefin based plastics have become widely studied owing to their ever-increasing use in outdoor applications <sup>[33][34]</sup>.

One particular aspect of polymer ageing is degradation of the material in question, which usually affects both the chemical and physical properties of the polymer <sup>[34][35]</sup>. The mechanisms that occur during the onset of degradation are well-known and many studies have been conducted into the various reactions that occur during outdoor exposure <sup>[32][34][36][37][38][39][40][41][42][43][44][45][46]</sup>. It is also well documented that weathering of materials, polymers in particular, depend upon the nature of the polymer itself, the conditions of exposure, and the required performance of the end product <sup>[18][32][47][48]</sup>.

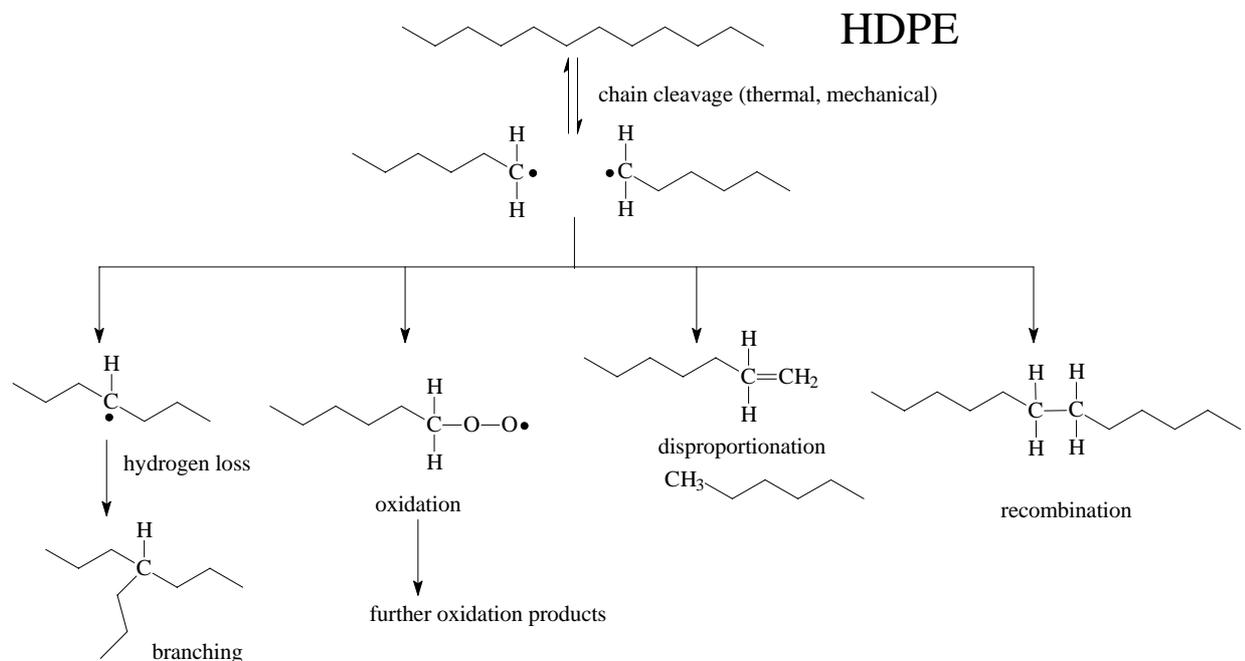
Whilst it would be ideal for all literature samples to contain no additives or UV stabilizers this is not actually possible. Most materials tested in previous studies have some amount of stabilizer or 'restabilizers' in the case of recycled plastics added during the processing stages; very few examples of 'pure' polyolefin polymers have been found to be tested via accelerated or natural ageing methodologies <sup>[29][31][49][50][51]</sup>. Restabilization is the addition of further stabilizers to aged polymer material, in order to improve the long term stability of the recycle for re-use in the original application. <sup>[18][48][52]</sup>

Even the materials that initially have no additives/stabilizers added usually have a percentage of restabilizers added to the recycle. Studies on mixed blends of polyolefins (HDPE and PP), without some additive or compatibilizer present to assist in the preparation of mouldable samples are rare. In either case, homopolymer or blended polymers, most of the weathering data has been acquired using thin film samples of 20–250 µm (0.02 – 0.25 mm) in thickness, thus comparison of every variable is not always possible. Studies on thick samples, such as the closed-loop recycling of plastic crates, have focussed on restabilization techniques to upgrade the material for reuse in the same application <sup>[18][48][52][53]</sup>.

### 2.2.1 Thermal Degradation

It is well documented that the degradation of polymers begins during the initial heat processing stage during product manufacture <sup>[25][14][60][62][54]</sup>. If the molecular bond forces are exceeded then chain rupture will occur, leading to the formation of chain radicals which are well known to initiate degradation (Figure 2.1) <sup>[55]</sup>.

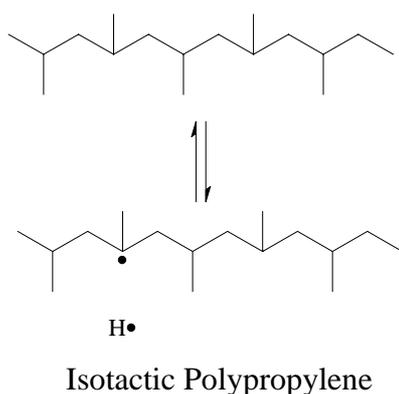
**Figure 2.1: Reactions after thermal processing of polyethylene**



Being organic materials, polymers undergo undesirable chemical changes during their lifetime. This is mainly oxidation and photo-oxidation during the initial processing stage and also during their service lifetime. These irreversible changes cause alteration of physical and mechanical properties of the polymer, sometimes making it unsuitable for reuse in the same application. <sup>[56][57]</sup>

Other reactions that polymers can undergo include cross linking and the formation of double bonds.<sup>[36][ 58]</sup> It is also well documented that extrusion is the most severe form of processing that a polymer can undergo.<sup>[48]</sup> The shear forces and high temperatures lead to the mechanical scission of the polymer chain and results in the formation of chain-end radicals (Figure 2.1).

It is also well known that among the hydrocarbon polymers, the polyolefins, polyethylene and polypropylene exhibit different degradation processes from each other. Polyethylene undergoes chain scission, branching and cross linking, which occur as competitive reactions, whilst polypropylene undergoes chain scission predominantly.<sup>[56][59]</sup> This is because of the more reactive tertiary carbon in polypropylene as shown in Figure 2.2.



**Figure 2.2: Radical formation in polypropylene**

During the first processing stage of a polymer, it is likely that the moulding process will be carried out in the presence of air. Therefore oxygen will be present and able to diffuse into the molten polymer. As the thermal process causes chain breakage and introduces chain-end radicals this molecular oxygen rapidly converts the carbon based free radical into a hydroperoxide free radical (Figure 2.1).<sup>[25][12][60]</sup>

This radical, and indeed its neutral hydroperoxide (R-OOH), are short lived under thermal processing conditions and decompose rapidly to the more stable alkoxy radical and the hydroxide radical.

From a simplistic perspective the following occurs in saturated hydrocarbon polymers after initial thermal processing:

#### Propagation

- 1)  $R\cdot + O_2 \rightarrow R-OO\cdot$
- 2)  $R-OO\cdot + RH \rightarrow ROOH + R\cdot$
- 3)  $ROOH \rightarrow RO\cdot + HO\cdot$

#### Chain Branching

- 1)  $RO\cdot + RH \rightarrow ROH + R\cdot$
- 2)  $HO\cdot + RH \rightarrow HOH + R\cdot$

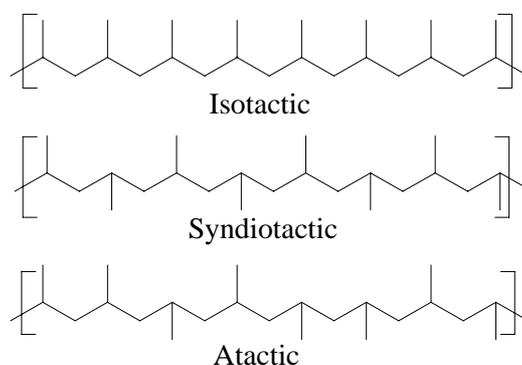
#### 3) Termination

- 1)  $R\cdot + R\cdot \rightarrow$  Inert product
- 2)  $RO_2\cdot + R\cdot \rightarrow$  Inert product
- 3)  $RO_2\cdot + RO_2\cdot \rightarrow$  Inert product

The oxidation cycle is fast and the polymer is either modified by progressive chain scission reactions or cross-linking, resulting in molecular weight alteration and mechanical performance loss. Both cross linking and chain scission are competitive reactions that occur simultaneously during the course of the cycle. Typically for high-density polyethylene, at high melt temperatures, the molecular weight of the polymer decreases because of chain scission reactions being dominant. As the temperature is lowered through the melt processing range (typically 200-160°C) mechanical and thermal stress is applied to the polymer and this results in an increase of molecular weight as chain branching becomes dominant.<sup>[62]</sup> The crystallinity of the polymer is also an important factor.

The morphology of a sample affects the way in which the molecular chains can rotate and move within the polymer structure. This has a direct effect on the strength and toughness of the material. High-density polyethylene is described as being a semi-crystalline

material as it has regions of high crystallinity and regions that are amorphous.<sup>[49]</sup> A highly crystalline material can be considered brittle, as the interface between crystalline regions is weak; in contrast a highly amorphous material will be either rubbery or glassy depending on the glass transition temperature. However, polyolefins are extremely tough because at high stresses the chains unfold from the crystalline regions giving large scale deformations. High-density polyethylene has a combination of these two types of morphology, which makes it an excellent material at room temperature; its properties diminish at low temperatures, as the material becomes glassy and brittle. The crystallinity of polypropylene can vary depending on the polymer's tacticity (Figure 2.3).



**Figure 2.3 Tacticity of polypropylene**

Isotactic and syndiotactic polypropylene are stereoregular polymers, unlike atactic polypropylene. Of these, the isotactic form is the most commercially important <sup>[61]</sup>. Stereoregular polymers, with little or no chain branching are more likely to exist in a crystalline state. The actual degree of crystallinity of polypropylene will depend on the process of manufacture of the polymer. Branching will increase the susceptibility of a polymer chain to thermal oxidation because of the reactivity of the tertiary carbon at the branch point.

Therefore, the order of reactivity of the polyolefin series is: polypropylene > low density polyethylene (branched) > high density polyethylene (linear).<sup>[32]</sup> One of the most studied

areas of polymer degradation during closed-loop continuous recycling is changes in molecular weight distribution <sup>[12][21]28[34][36][41][42][48][49][52][53][54]</sup>

<sup>[56][59][62][63][64][65][66][67][68][69][70][71][72][73]</sup>

A simple example of what occurs during multiple reprocessing steps for a polypropylene sample showed that the viscosity of the sample decreased owing to a reduction in the polymer molecular weight and a narrowing of the molecular weight distribution.<sup>[73]</sup> For samples of high density polyethylene undergoing closed-loop recycling, it has been noted that the changes to molecular weight depend primarily on the catalyst used for polymer production.<sup>[48][59]</sup> For example Table 2.1 shows the physical data for unstabilized high density polyethylenes prepared using different catalysts.<sup>[59]</sup>

HDPE	Mean molecular weight (GPC)	Melting point, $T_m$ (°C)	Density (g/cm <sup>3</sup> )
Phillips	99 000	131	0.952
Ziegler	129 000	129	0.944

**Table 2.1: Physical data for Unstabilized Phillips and Ziegler HDPE**

Following multiple extrusions, at different extrusion temperatures, GPC measurements of molecular weight were again performed and the results are shown in Table 2.2.

Polymer	Multiple extrusion					
	240 °C			260 °C		
	1 ×	3 ×	5 ×	1 ×	3 ×	5 ×
Phillips	103 000	115 000	121 000	110 000	122 000	126 000

Ziegler	127 000	120 000	119 000	125 000	120 000	113 000
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**Table 2.2: Molecular weights of virgin HDPE after multiple extrusions** <sup>[59]</sup>

From the data above, the Phillips (Chromium) type catalyst polymer shows an increase in molecular weight upon repeated extrusion, independent of temperature, whilst the Ziegler (Titanium) type polymer shows the converse effect. This implies that in the former system cross-linking and subsequent molecular weight increase appears to predominate over chain scission, which leads to a decrease in molecular weight, whilst in the Ziegler polymer chain scission predominates.<sup>[59]</sup> However, cross-linkage and fragmentation are competitive reactions during processing. Thus, it is important to have an idea of the polymer catalyst, where possible, as well as the types and concentrations of stabilizers present, so that experimental observations can be recorded correctly. However, in the case of recycled polymers, the origin of the material is generally unknown.

Melt flow of the reprocessed polymer is characteristic that is often required by manufacturers so they have an idea of how ‘well’ the recyclate can be moulded and is useful for processing comparisons. In the previous example, the Phillips catalysed polymer showed a decrease in melt flow, whilst the Ziegler catalysed polymer remained fairly stable with only a slight increase.<sup>[51]</sup> These findings are in agreement with the molecular weight changes observed. Viscosity measurements have also been studied and these show that, for HDPE, the viscosity of the polymer increases after multiple extrusions which is also in agreement with the increase seen in the polydispersity index for the material,<sup>[49]</sup> i.e. similar to the results seen for the Philips type catalyst previously.<sup>[59]</sup>

A study by Kartalis *et al* examined post-use high density polyethylene bottle crates.<sup>[48]</sup> Although this study was aimed at a restabilization technique, by the addition of different amounts of stabilizer, a non-stabilized sample was reprocessed at the same time for

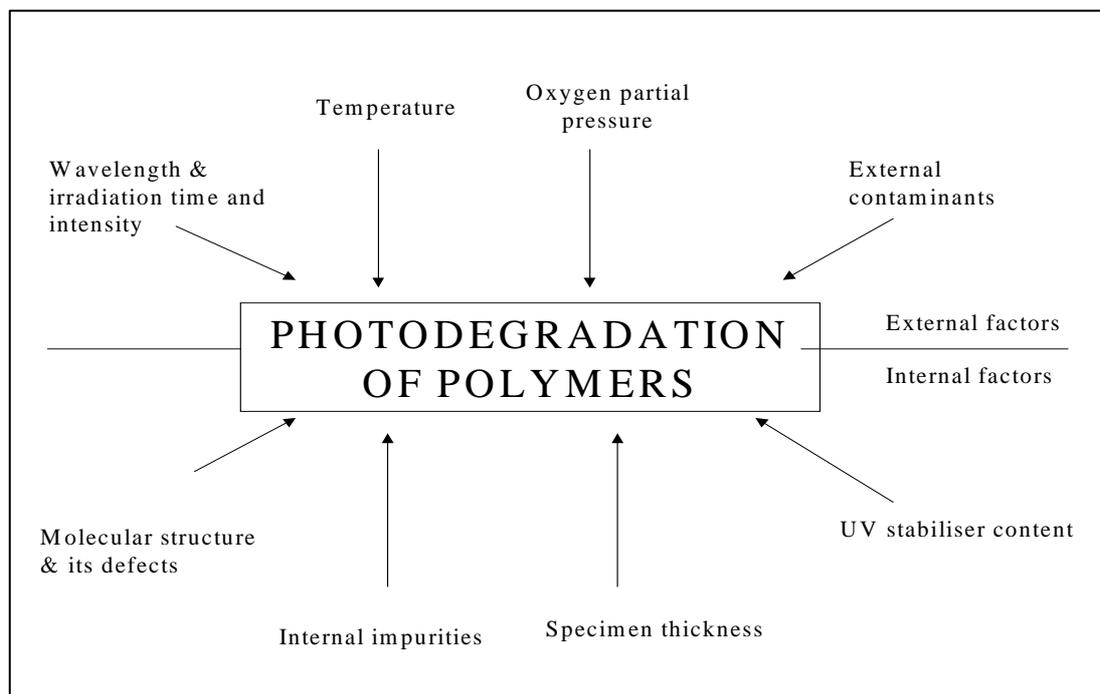
comparison. This work focussed on old crates that had a service lifetime of almost 9 years. There is also a report from Antec'95 by Shaner where a similar study was performed, this time using crates whose average lifetime was 5 years.<sup>[74]</sup> The latter study was intended to assess the number of hours of accelerated weathering exposure related to natural weathering, as will be discussed later. The experiments by Kartalis *et al* showed that the post consumer HDPE sample underwent cross-linking during reprocessing, yielding a harder and stiffer material, which indicated a Phillips type HDPE crate material.<sup>[48]</sup> This material also shows a slight increase in the tensile impact strength as a result of a more compact, cross-linked structure. It is also known that elongation at break decreases with cross-linking, which is again attributed to embrittlement associated with increased cross-linking.<sup>[48]</sup>

A set of trials by Bernardo *et al* looked at the melt flow properties of recycled HDPE and PP, together with addition of small amounts of virgin polymer into the recyclate.<sup>[75]</sup> This work concentrated on samples of polypropylene with two mixtures of virgin and recycled polymer (10% and 30% virgin polymer respectively) and analysed the melt flow of these materials in comparison to pure recyclate. The results of these trials showed that increasing the amount of virgin material in the mixture led to an increase in MFI values. Models of the behaviour of recyclate with addition of various amounts of virgin polymer to recyclate show that the amount of recyclate remaining after continued reprocessing cycles diminishes after each step. For example, if 32% of reprocessed material and 68% of virgin are used as a binary mixture, after 10 cycles only 0.004% of material from the first cycle will remain.<sup>[75]</sup> This implies that the properties of the melt flow can remain fairly constant in comparison with 100% recyclate in a closed-loop processing.

### **2.2.2 Weathering Degradation**

Weathering encompasses many different natural phenomena, such as oxidation, light and heat. Add to these the complex nature of the physical environment and factors such as

humidity, rain, wind and the physical atmosphere, further complicate the process of natural weathering of polymer samples (Figure 2.3).<sup>[32][44]</sup>



**Figure 2.4 Factors affecting the oxidative photodegradation of polymers**

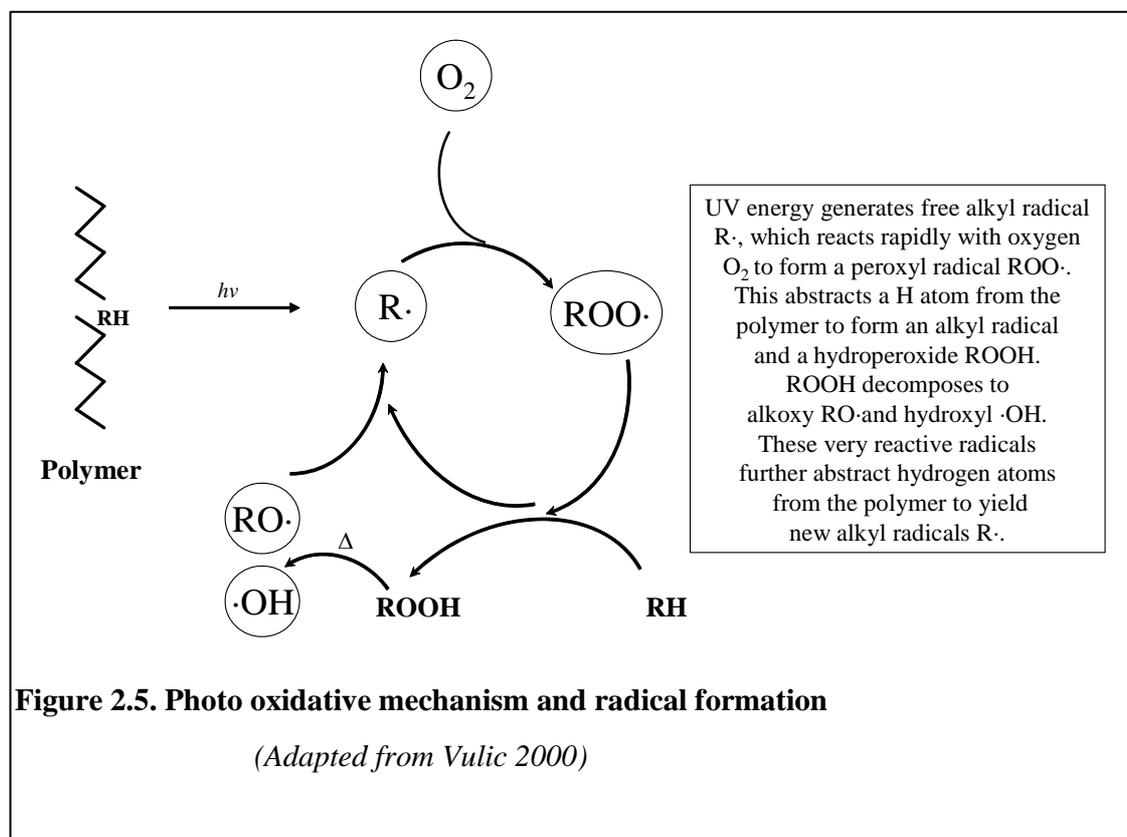
The ultraviolet (UV) contribution from solar radiation is believed to be a major factor in polymer degradation<sup>[8][9][10]32[76]</sup>. The portion of UV light with high enough energy (290–400 nm, an energy of between 412–300 kJ/mol) to break molecular bonds and induce photo oxidation is only about 4–6 % of the mean annual radiation on Earth.<sup>[76]</sup> This high energy UV light is capable of initiating bond scission within the polymer backbone, which leads to further chemical modification of the bonds via rupturing and chain reactions through the formation of radical species.<sup>[32][54]</sup> This description is ‘typical’ of polymer systems in general but saturated hydrocarbon materials, such as the polyolefins, do not absorb light above 250 nm. However, these materials do degrade through photo–oxidation and there are a number of reasons why this occurs.

During processing, manufacturing, the polymer can undergo some fundamental, irreversible, changes to the polymer structure <sup>[10][12][18][25][28][34][35][36]</sup>. Cross-linking, chain scission and the formation of double bonds have been observed in materials manufactured from virgin polyolefin. <sup>[37][45][49][52][60][63][69][71][75][77]</sup> Likewise, impurities in the polymer itself, from residual catalyst for example, or the addition of additives or pigments, can also affect the nature of product towards UV light. <sup>[18][48][59]</sup>

Any of the above factors can seriously affect the lifetime performance of the product towards UV light and hence photochemical degradation through ‘typical’ radical species. All of these radical reactions proceed via three stages: initiation, propagation and termination. There are however, subtle differences in the photochemical degradation of polyethylene and polypropylene; in the case of the former, cross-linking reactions are said to prevail over chain scission reactions. <sup>[10]</sup>

#### **2.2.2.1 Photochemically initiated degradation**

It has been well documented in the literature that polyolefin materials will degrade through a photo-oxidative reaction path, as shown in Figure 2.1. This example shows what can happen to high-density polyethylene under typical thermal processing conditions, mostly chain scission, which yields a chain terminal radical that can undergo further oxidative reactions. The extra branch point evenly distributed along the polymer backbone, which owing to its tertiary carbon atom renders the hydrogen atom highly reactive, augments the susceptibility of polypropylene to these oxidation processes.



The fundamental process that is believed to be the most significant in the mechanism of photo-oxidative degradation is the formation of hydroperoxides. These form more readily with polypropylene materials than they do with polyethylene, owing to the more reactive tertiary carbon atom, and therefore the degradation of polypropylene occurs more rapidly.<sup>[10][55]</sup>

The hydroperoxides (formed during propagation) are highly unstable and provide the necessary mechanistic route towards chain scission and cross-linking reactions, similar to that observed in thermal degradation (Figure 2.5).

Polypropylene samples are more readily oxidised than their polyethylene counterparts, and undergo more rapid chain scission reactions (molecular weight loss) whereas polyethylenes may also undergo cross-linking reactions (molecular weight gain).<sup>[78]</sup> As would also be expected the temperature at which the photo-oxidation occurs is also important; it is often cited that a 10°C rise in temperature doubles the rate of decomposition.<sup>[55]</sup> However, there are many other external factors associated with outdoor polymer degradation (humidity etc.) as well as the polymer sample itself: sample thickness, degree of branching, melt flow index.<sup>[47][55]</sup> There are also reports that the degree of tacticity of polypropylene samples also has an effect on the degradation rate of the polymer sample, regardless of variable external factors.<sup>[79]</sup> The comparison of in field versus accelerated weathering testing is very complex, and the remainder of this section intends to highlight advances in this essential testing methodology.

### 3. Natural and Accelerated Weathering

#### 3.1 Irradiation (Natural)

The actual UV radiation affecting outdoor polymers is not constant; the latitude, season, time of day, cloud coverage all play a factor in the amount of radiation the polymer sample is exposed to ultimately. Therefore, samples of the same polymer batch (to account for inherent impurities – chain scission in processing etc.) will most likely have different degrees of photo-oxidation if studied at different latitudes or during different seasons.<sup>[76]</sup> For example, it has been noted that polyethylene samples degraded faster in the summer months owing to the greater intensity of solar radiation, shorter wavelengths of light penetrating the atmosphere (higher energy) and a higher ambient temperature compared with other seasons.<sup>[10]</sup> This is of course a reasonably apparent observation to make, but of more interest is the observation by Satoto et al <sup>[76]</sup> that there was a close correlation between temperature and degradation, whereas the correlation between irradiance and degradation was negligible in samples sited at different latitudes. In this paper they observe that for ‘light’ (or white) coloured materials, the main factor affecting degradation is the ambient temperature of the polymer sample being studied. This implies that the solar radiation induces the photodegradation process, but after the formation of the hydroperoxide species the temperature actually controls further degradation. In light of this observation it should be noted that diffusion of oxygen into the polymer is an important process regardless of which factor contributes to the main degradation process.

It is also well known that any chemical transformation (such as hydroperoxide formation) will occur faster at elevated temperatures, and oxygen absorption is no different; it is a diffusion controlled event which is made faster by elevated temperature and also by greater mobility of polymer chains at the surface.<sup>[41][42][80][81]</sup> This does not necessarily mean that temperature is the only factor affecting degradation, but further correlations between irradiance levels and degradation need closer investigation. It should be noted here that

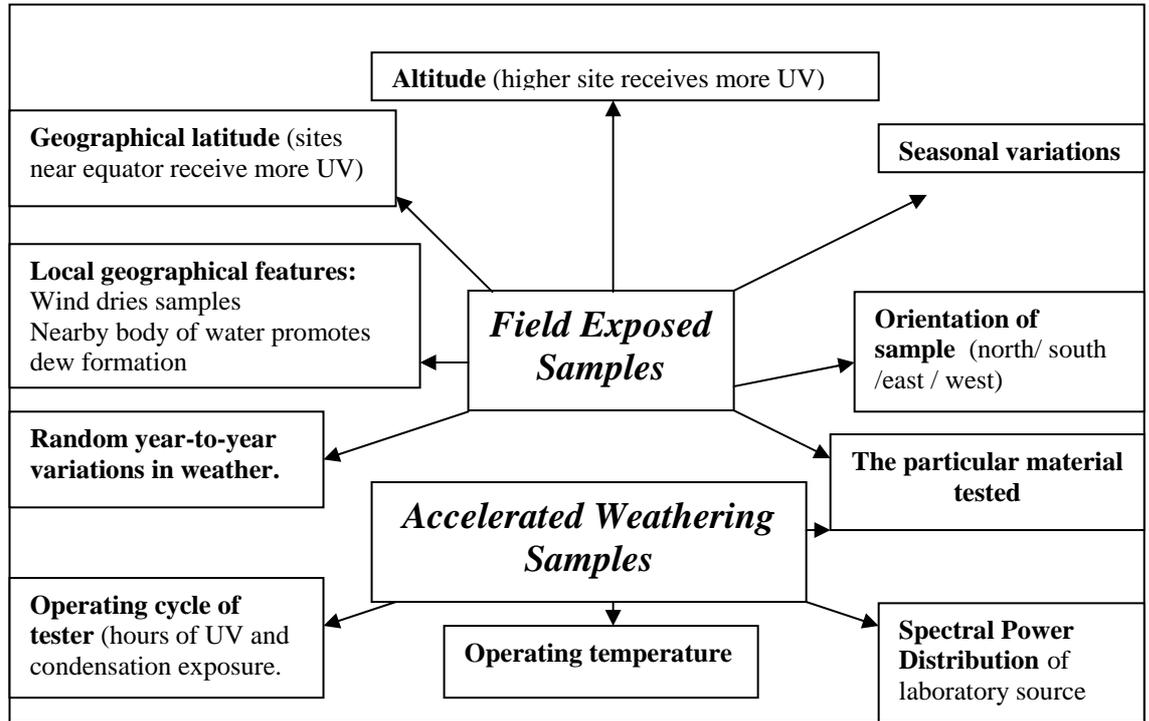
dark coloured polymers are more likely to contain fillers and carbon black, which is one of the most effective and cheapest UV stabilizer of polyolefins. Hence, the majority of studies tend to employ pure, light coloured polymer samples.

### **3.2 Irradiation (Accelerated)**

Accelerated weathering introduces the factor of continued irradiation, and as such during the course of such irradiation it has been observed that a larger number of radicals are formed than under natural ageing conditions.<sup>[21][82]</sup> In 1993, Tidjani et al studied the natural and accelerated ageing of LLDPE films; the former had an average ambient temperature of 25–32 °C whilst the latter had an average temperature of 60 °C, the recommended temperature for 'medium - accelerated' photo-ageing. The samples exposed to natural light suffered from lower molecular weights, as chain scission was apparent along with photo-oxidation products, together with a marked decrease in mechanical properties. The samples aged through an accelerated process however showed the presence of photo-oxidation products, but with no loss of mechanical strength and an increase in molecular weight through cross-linking reactions.<sup>[21]</sup> It has been noted previously that polyethylene samples usually undergo cross-linking reactions in preference to chain scission, however it should also be noted that the degree of branching in the polymer can also have an effect on the properties of the material after ageing.<sup>[21]</sup> To show this effect, Tidjani studied the photo oxidation of polypropylene under both natural and accelerated ageing conditions with samples containing different amounts of crystallinity. High crystallinity in samples was achieved by slow cooling of the polymer melt, low crystallinity by rapid cooling.<sup>[44]</sup> It was observed that the mechanical properties were different under natural ageing for the low and high crystallinity samples, the latter sample lost all mechanical strength and usefulness after a very short time, whilst the former retained its properties for approximately twice as long. This is attributed to chain scissions

being the predominant reactions in the sample of high crystallinity, whilst competing chain scissions and cross-linking occur in the sample with low crystallinity.<sup>[44]</sup> A similar observation was noted with the samples degraded in an artificially accelerated environment, samples of low crystallinity retained mechanical properties for longer periods, but both suffered from greater changes than anticipated. In conclusion it was stated by Tidjani that ‘the natural photo aging of polymers is necessary to minimize errors in the prediction of polymers life service, even if it is time consuming’. This was because the acceleration factor observed was lower than previously noted for LLDPE films, approximately 30 for the latter and 8 for the former, indicating that each type of polymer and formulation has a specific acceleration factor.<sup>[21][83]</sup>

The work by Shaner<sup>[74]</sup> estimated that 10 hours of real life weathering is equivalent to one hour of artificial weathering, but that only about 5% of the plastic in the real life sample will see any considerable exposure. However, it is theoretically impossible to use a single number that can be multiplied by the weathering tester exposure hours to compute years of outdoor exposure. The greatest obstacle is the inherent variability and complexity of outdoor exposure situations. The relationship between tester exposure and outdoor exposure depends on a number of variables as described in Figure 3.1



**Figure 3.1 Variables affecting comparison of accelerated weathering and field exposed data.**

Simms (1987)<sup>[84]</sup> used curve fitting to select the most apt acceleration factor for the weathering period. This ‘best fit’ acceleration factor was named the Acceleration Shift Factor (ASF), defined as ‘the single number that produces the best fit of one curve of weathering data to another.’ This study obtained accelerated weathering data on acrylic enamel and lacquer coatings using ‘appropriate’ time intervals (which was not a simple matter because of the implicit assumption of an ASF), then a curve fit with which to predict performance and then waited until the minimum amount of Florida testing was completed to indicate which ASF was most likely to be correct.

Further work in the correlation of real and accelerated weathering testing will certainly help to provide realistic relationships between the two for different materials.

In conclusion, it is imperative that comparisons are made, where possible, to actual naturally weathered products and direct correlations noted so that an "acceleration shift factor" can be determined for each specimen. This is not always possible and it is

therefore recommended that even samples of short outdoor exposure times be tested prior to accelerated ageing tests, in comparison to virgin materials, to gain an understanding of the actual acceleration factors for the formulation being studied.

### **3.3 Other factors affecting weathering**

Both the oxygen partial pressure and external contaminants (pollutants) can be controlled during artificial weathering tests; this is not possible in a natural ageing environment. It has been reported that an increase in oxygen partial pressure causes a shortening of the induction time for hydroperoxide formation, and an increase in the oxidation rate of the polymer.<sup>[80]</sup> It has been observed by Gijsman et al that this increase was enhanced only at elevated temperatures (40–50°C), although the actual amount of oxygenated degraded products was only slightly higher than those observed at 29°C. In outdoor tests at lower temperatures it was stated that since the rate of oxygen uptake has decreased, more oxygen was necessary than in accelerated tests at 40-50°C to obtain the same value for carbonyl absorbance or decline in elongation at break. This was attributed to two different degradation mechanisms of oxygen uptake by the polymers.<sup>[81]</sup> It was noted that the oxygen uptake by polymers undergoing natural outdoor weathering, the ‘normal’ oxidation mechanism, occurred at higher temperatures (30-35°C). Therefore oxygen pressure in accelerated testing should be kept to as near that at ambient temperature as possible.<sup>[81]</sup>

External contaminants can be readily excluded from artificial weathering tests, but are much harder to introduce. Atmospheric pollution is a global issue and varies according to the weathering site being used. These pollutants can affect the intensity of the radiation the sample is exposed to, and can also play very active roles in the photodegradation of polymers.<sup>[85] [86]</sup> One study on LDPE films screened samples from exposure to wind and rain, whilst allowing all other weathering influences, noted that these sheltered samples have lifetimes that are much longer than those that are measured in direct weathering.<sup>[46]</sup>

This highlights that the selection of weathering factors polymer samples undergo in accelerated conditions, often cited as being ‘probably relevant’, are in fact quite important and should be considered when comparing natural and accelerated polymer samples.<sup>[46]</sup>

### **3.3.1 Non–environmental factors**

The nature of the polymer sample itself has been shown to be important in the degradation path the polymer will follow. It has been stated that polyethylene and polypropylene samples undergo different degradation pathways, and that the degree of crystallinity of samples is also important.<sup>[21][44][46][83]</sup> The thickness of the polymer sample has also been shown to be of interest, this is because most research has focussed on the weathering behaviour of thin films.<sup>[87]</sup>

In the study by Furneaux et al, LDPE was degraded in two forms, injection moulded plaques of 3mm thickness, and films ‘sandwiched’ together under pressure (120 sheets of 25 $\mu$ m thickness, the same as 3mm).<sup>[87]</sup> Both types of sample were subjected to outdoor weathering tests. Artificially aged tests were only conducted on the sandwich samples, one exposed in air and the other in oxygen, and the sample aged in air agreed well with the outdoor sandwich specimen. The sample aged in pure oxygen showed a continuous level of degradation, throughout the entire thickness of the specimen, whereas the sample exposed in air showed a decrease in oxidised products after 0.8mm depth.<sup>[87]</sup> It was also shown that the difference in degradation at the surface of both specimens was very similar, which implies that the photodegradation of LDPE samples is independent of oxygen pressure and oxygen diffusion throughout the sample. However, in ambient conditions (air) and for samples greater than 2mm thick, the amount of photodegradation is determined by the oxygen supply.

This work was subsequently followed by a study by Lacoste et al, which examined the surface and bulk phase oxidation of polyolefins.<sup>[31]</sup> In both sets of studies it was observed

that the obverse surface (that which faces away from the source of irradiation) also undergoes a similar amount of oxidation. This is because oxygen diffuses through the 3mm thick sample and even though not under direct exposure to the radiation, approximately one-third of this radiation does reach the reverse surface. This is obvious from the results obtained by Furneaux et al, as a sample that had an aluminium back plate (on the obverse side) showed no sign of photo degraded products, because the plate prevented the entry of oxygen through the rear surface.<sup>[87]</sup>

The role of melt flow index (MFI) on polymer degradation has not been as well studied. However there are a few articles in the literature on the effect this property has on overall weatherability of the samples.<sup>[18][48][60][71][99]</sup> Most of the work relating melt flow properties to degradation has been discussed in the thermal ageing research as mentioned earlier.

It is also cited that the wavelength of light during irradiation also plays a role in the degradation of polypropylene,<sup>[88][89]</sup> although no such influence has been noted for polyethylene. The conclusions for this work indicated that wavelengths above 400 nm contribute little to the degradation. During short exposure times (less than 68 hours) wavelengths of between 300–350 nm accelerate the degradation, and for long periods of exposure (more than 68 hours) the most effective spectral region for enhancing degradation was between 335–360 nm.<sup>[88]</sup>

### 3.3.2 Degradation of Polymer Blends

Degradation studies of blended plastics are also not as prevalent as those of their homopolymers. This area is of interest, because the products studied in this project were blended recycled polymers supplied by Centriforce Ltd and BPI/ Plaswood. Most investigations have only studied molecular weight distributions or viscosity measurements. Blending of polymers is not a new concept; much developmental research in this area is widely available in the literature. Commercial polymer blends only really became available in the early 1980's, but research into the degradation properties of these materials only really begun in the late 1990's; much of this is due to the interest in polymer recycling of virgin and recycled resins.<sup>[90]</sup> The results of these studies vary in the depth of analysis of the polymer blends.<sup>[91][92][93][94][95] [96] [99][66][72][75]</sup> There is a lack of information about the mechanical properties for these blended materials.

The compatibility of blends is an important issue, and frequently the degradation products formed upon thermal processing can often act as a compatibilizer for the newly blended system. For example, the compatibility of a polymer blend is affected by the presence of carbonyl groups produced by thermo-oxidation. In several cases, these carbonyl groups act as a compatibilizer.<sup>[97]</sup> Also, it has been shown that low density polyethylene acts as a stabilizer for isotactic polypropylene by retarding the autocatalytic propagation of tertiary carbon radicals, probably by cross linking.<sup>[65][97]</sup> Another theory is that polypropylene can be stabilised by the addition of polyethylene, in small amounts due to the 'dilution' of the tertiary alkyl radicals in polyethylene 'domains'.<sup>[66][71]</sup> One assumption is that the chemical properties of a blend are a simple combination of the chemical properties of its components. In the case of polyolefin blends, the mechanisms of degradation are similar, both form free radical species upon thermal processing, although it is known that polypropylene prefers to undergo chain scission whilst polyethylene prefers chain branching; the synergistic or antagonistic effects of each much be considered.<sup>[66][91][98][66]</sup>

Blends of polypropylene and polyethylene, with small additions of PE (10%) to PP showed an improvement of the flow properties, i.e. a decrease in viscosity, but these materials were not examined for further mechanical characteristics.<sup>[99]</sup> As it is known that polyethylene cross-links and polypropylene undergoes chain scission, blends of the two were examined to observe if these opposing tendencies could be balanced out.<sup>[100]</sup> The question addressed in this research was whether the blend is actually a one-phase or two-phase system. In other words, do the polymers molecules mix together to create a single phase and subsequently interact with each other to form graft co-polymers, to counterbalance the opposing effects of chain scission and cross-linking? The conclusion from this study was that graft copolymers of PP and PE are formed in blend solutions, where the components are in intimate molecular contact, which counterbalances degradation effects of each polymer, but not in blend melts of the two polymers as they are phase separated or 'demixed'.<sup>[100]</sup>

The work by Camacho et al, used a variety of different techniques to assess the degradation of the homopolymers as well as the blends prepared.<sup>[91]</sup> A blend of mechanically mixed polypropylene and polyethylene appeared to be a two-phase system in the molten state. The polypropylene appeared to oxidise first and accelerated the oxidation polyethylene due to the presence of oxidation sites in the polyethylene-polypropylene interfaces.<sup>[91]</sup>

The oxidation process in PE/PP blends may not be a simple correlation of the individual components, but will depend upon composition, yet some work in the literature is contradictory.<sup>[68][101]</sup> For example, in known compositions the viscosity drop in the PP fraction of the blend (chain-scission) and the viscosity increase in the HDPE fraction of the blend (cross linking) may counter balance each other, resulting in no apparent change in viscosity.<sup>[62]</sup> This is even more evident when an excess of PP is present; the drop in viscosity is due to the major degradation mechanism being chain-scission. There has been quite an extensive range of work completed on multiple extruded homopolymers and their

blends,<sup>[72][99]</sup> but the actual effect of final lifetime and possible reprocessing has many unanswered questions.<sup>[98]</sup> Currently it has been stated that only through an upgrade of the blended resin by addition of a restabilising agent will the material serve a useful lifetime.<sup>[91]</sup>

### **3.3.3. The role of polymer manufacture and processing on photodegradation**

Industrially produced polymers contain various light-absorbing impurities created during the production process. These include internal impurities containing chromophoric groups such as catalyst residues attached to chain ends, anomalous structural units (branching), and charge transfer complexes with oxygen. External impurities, which may contain photoactive groups, include additives (pigments, dyes, thermal stabilizers and photostabilizers) and metal compounds.<sup>[9]</sup> In the case of stabilizers, the susceptibility of a polymer to weathering is dependent to a degree on the type and concentration of stabilizer compounds present.

Products from mixed waste plastics streams as well as from well-defined polyolefin streams are now becoming increasingly common. There is also a great deal of material becoming available as recycling schemes become more effective. There is therefore a need to define the physical characteristics of such materials and in particular the effects of both environmental degradation and reprocessing on the products.

Although work has been done to characterise the changes in molecular weight and its distribution and the consequent flow characteristics, little work has been done in classifying the effect on mechanical properties. Further study is required to determine how the addition of recycled polymer in blends with virgin material affects degradation, if at all, particularly for products other than film.

The future growth in the use of materials recovered from waste streams will depend very much on the confidence that manufacturers can have in the predictability of the behaviour of these materials.

The ageing of polyolefin materials has been studied by several researchers<sup>[23][102][103]</sup>. It has been shown that differences in the degradation of polyethylene and polypropylene are apparent. Polyethylene predominantly undergoes chain scission and cross-linking competitively, whilst polypropylene undergoes chain scission because of the higher reactivity of the tertiary carbon based radical. Both polymers experience some form of degradation during the first thermal processing (product manufacture) stage; the level of degradation in part depending on the synthesis of the polymer, i.e. catalyst residues.<sup>[59]</sup> The stereoregularity of the polymer is also important; the more regular (crystalline) the polymer structure, the less likely it is to experience large changes in properties during thermal oxidation.<sup>[21][44][104]</sup>

For most examples of polyethylene studied, cross-linking reactions predominated, giving the resultant recyclate increased stiffness. To some extent this improves the tensile impact strength of the polymer whilst other typical properties measured such as tensile strength and elongation at break, all decrease after the first reprocessing cycle. These properties can be improved by the use of restabilizers, although some work has shown that addition of virgin polymer to a recyclate can also improve the mechanical properties.<sup>[73][105]</sup>

As all polymers experience thermal processing during product manufacture,<sup>[46]</sup> weathering of polymers by artificial means have been compared to those from natural field use. It is apparent that there are several key factors that determine the level of degradation a polymer will undergo from natural sources (Figure 4). More recently, exposure models have been developed to account for the variations in photo-oxidation rate observed in different outdoor locations.<sup>[23][106][107][108][109]</sup> Variations in external factors, such as the temperature, play important roles in the level of degradation experienced. The nature and

formulation of the polymer is also important, together with its previous thermal history, and the development of these exposure models allow for reproducibility and reliability of accelerated tests.<sup>[97][98]</sup> They can also account for the variability that is observed in a given test with different materials and from one test to another.

## **4. Experimental methods**

### **4.1 Materials**

All the materials were acquired in product form as solid section and came from two different sources:

Centriforce Products Ltd supplied three sets of extruded samples. These were identified by their colour as blue, brown and black. Section dimensions were approximately 3 x 10 cm, and comprised a range of recycled HDPE from “jazz” (mixed colours) to natural (off-white) bottle scrap. According to the supplier, this recyclate could contain a nominal percentage of PP. The material also contained 4% polyethylene encapsulated pigments, 1% Hydrocerol BIN as a blowing agent and Northern European UV 10 stabilizer, a combination of hindered amine light stabilizers (HALS). Field-aged material had been exposed to natural weathering for approximately 1 year. This represented UV exposure of approximately 4500 hours assuming that exposure is limited to 12 hours per day.

Two sets of black extruded samples were supplied by British Polythene Industries plc (BPI). They were identified by product shape as square and rectangular sections with dimensions 8 x 8 cm and 9 x 5 cm across the section respectively. The material comprised black-pigmented polyethylene recyclate, known as ‘Plaswood’, which, according to the supplier, could include waste from agricultural applications. The recyclate is processed at BPI to produce ‘Plaswood’ sections using an extruder in line with a bank of steel moulds; a process more appropriately described as intrusion. The processing temperature range is 190-240 °C. The field-aged BPI samples had a weathering history of 3-4 years, representing 13000 to 17000 hours of real-time UV exposure. It was not possible to obtain the exact composition as the material provided was derived from different blends or batches. However, an approximation was given by BPI (Table 4.1.)

<b>Polymer</b>	<b>Typical Source</b>
60% LDPE	Industrial waste, bottle tops
20% HDPE	Plastic cores, crates, bottles
10% Carbon Black Masterbatch	Masterbatch Supplier
10% PP	Bins, cores, crates

**Table 4.1. Approximate composition of mixed polyolefin material from BPI**

#### **4.2. Test specimen injection moulding**

All the materials under investigation were supplied in the form of solid sections and required preparation before conversion into test specimens without further additions. All test specimens were produced and tested at atmospheric pressure in the presence of air and a temperature range of 18-24° C.

The sample material was cut into small sections initially to enable granulation. After granulation, the material was washed and oven dried at 60°C, and the granules were stored in desiccators ready for moulding. Test specimens were produced by injection moulding to type 1A tensile dumbbell configuration (BS 2782-9) using a Negri Bossi V 85. Shot size was 42 mm, injection pressure 75 bar with hold pressure of 25 bar for 5 seconds. Nozzle temperature was 180° C and barrel temperature 190° C.

##### **4.2.1 Accelerated Weathering: QUV cabinet parameter settings**

Tests were carried out using QUV accelerated weathering testers supplied by Q-Panel Lab Products, at an irradiance of 0.68 W/ m<sup>2</sup> @ 340 nm. This is considered a good match with noon summer sunlight in Northern Europe. Each twelve-hour cycle comprised eight hours of UV radiation at 60°C and four hours of condensation at 50°C. The UV exposure and condensation exposure occur separately to simulate natural weathering conditions. Test exposure times were 0,

100, 250, 500, 750, 1000, 3000 and 4000, with some continuing to 5000 hours. The UVA 340 lamps were calibrated every 400 hours.

### 4.3 Tensile Test

The tests were carried out at a speed of 6 mm/min and an ambient temperature of  $21^{\circ}\text{C} \pm 2^{\circ}\text{C}$  using a Shimadzu tensile tester, in general accordance with BS 2782, Method 320A to 320F.

Tensile strength or yield stress is defined as load at yield /original cross sectional area.

Failure stress is defined as load at failure/final cross sectional area.

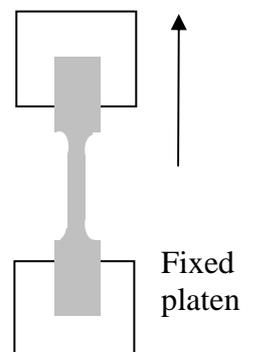
It was expected that as materials degrade, tensile properties such as yield stress or tensile strength would be affected. In addition the degradation should influence the fracture behaviour.

Unlike metals, solid polymers exhibit viscoelastic behaviour when subjected to a load. Deformation is dependent on the rate of loading (and therefore strain-rate), time of application of load, previous loading history and temperature.

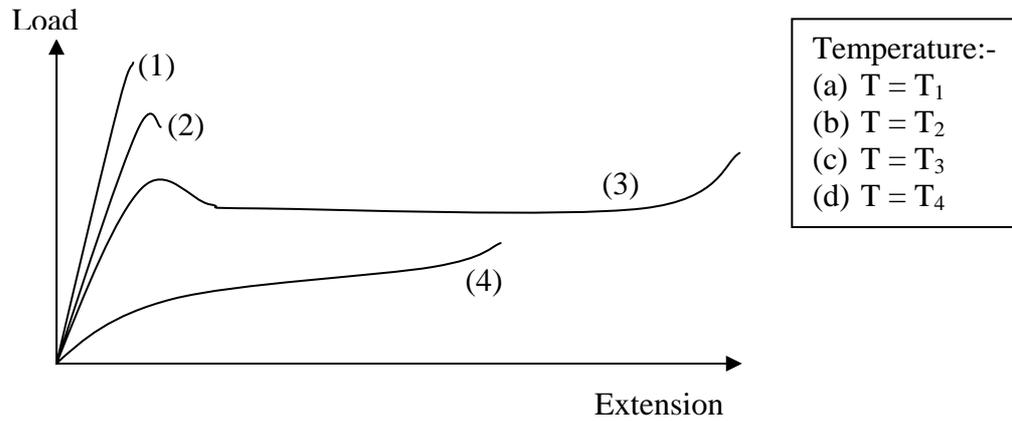
The tensile test is a constant cross-head speed test. The specimen is clamped between platens (Figure 4.1) and one platen is allowed to move at constant speed relative to the second. The temperature must also be kept constant.

Solid polymer behaviour can be classified using the mechanism of deformation exhibited as shown in Figure 4.2, where the principal factors determining the type of behaviour are the nature of

microstructure, whether amorphous or semicrystalline and the temperature of test relative to the glass transition temperature,  $T_G$ .



**Figure 4.1:**  
**Tensile Test**



**Figure 4.2: Typical Test results for solid polymers**

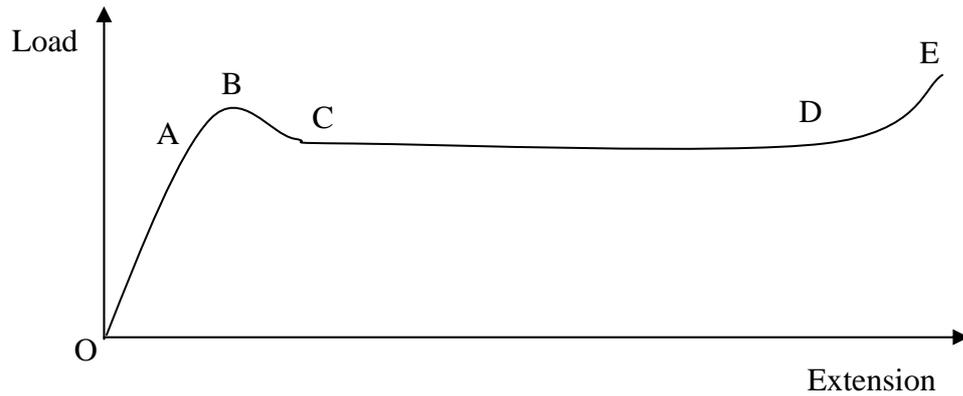
Curve (1) - At  $T_1 (\ll T_G)$ , there is almost linear extension with increasing load up to failure, which occurs in a brittle manner. Such behaviour is seen with amorphous and semicrystalline thermoplastics and thermosetting polymers.

Curve (2) - At  $T_2 (\sim T_G)$ , a yield point may be observed. Necking begins as the load reaches a peak and falls. The material begins to exhibit some ductility before failure and is seen with semicrystalline polymers.

Curve (3) - At  $T_3 (\gg T_G)$ , necking is followed by cold drawing. This is only possible with semicrystalline thermoplastics and indicates significant crystallinity. High-density polyethylene, which is more than 90 % crystalline, and syndiotactic and isotactic polypropylene, which are over 80 % crystalline show such behaviour, unlike low-density polyethylene, which is about 50 % crystalline.

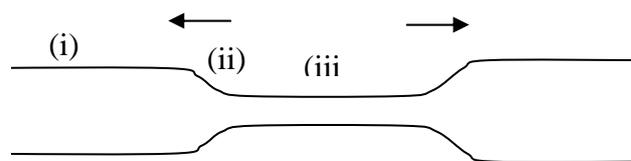
Curve (4) - As temperature is increased further ( $T_4 > T_3$ ), necking is no longer observed. This rubber-like behaviour is seen with both semicrystalline and amorphous thermoplastics, including low-density polyethylene.

The behaviour can be explained with reference to curve (3), which is reproduced as Figure 4.3.



**Figure 4.3: Tensile test behaviour incorporating cold drawing**

As the specimen is forced to extend at a constant velocity, the load increases and the material deforms in an elastic manner (area around Point A). The load eventually reaches a maximum at point B and deformation becomes localised. Until this point is reached, the specimen would have deformed uniformly and so changes in the shape of the specimen are hardly noticeable. The load drops quickly to point C as the cross-sectional area at a point along the specimen reduces, which is described as ‘necking’. Between points C and D, three regions are clearly defined. In Figure 4.4, the deformed region, (iii) remains stable while the remaining material undergoes necking. Necking is triggered and the shoulder region, (ii) moves into the part with little permanent deformation.



**Figure 4.4: Development of a neck at the onset of cold drawing**

The stress calculated from the load at C is regarded as the yield stress of the original material, also known as tensile strength or maximum stress. Although the load drops, the actual stress in the material remains approximately constant as the specimen extends between C and D while the deformation is concentrated in the necking region, (ii). This process by which the cross-section is reduced is called cold drawing.

Eventually, when all the material has undergone cold drawing, the load increases (from D to E) until failure occurs. An assessment of the degree of cold drawing and the subsequent strengthening of the material can be made by calculating a “fracture stress”. This is the load at failure divided by the estimated cross-sectional area at failure.<sup>[110]</sup> This quantity was chosen as a measure of the failure characteristics although it is not required in industry.

#### **4.4 Melt Flow Index (MFI)**

Melt Flow Index is commonly used as a measure of the viscosity of a polymer, given in units of g / 10 min. A reduction in viscosity results in higher MFI values, and can be indicative of chain scission, whereas an increase in viscosity gives lower MFI values and indicates that cross linking has occurred.

The tests were carried out on a RayRan Advanced Melt Flow system 5MBA, supplied by Ray-Ran Test Equipment Ltd, in accordance with BS 2782 Method 720A.

Test conditions used were as follows:

Melt temperature: 190°C

Applied load: 2.160 kg test load

Standard test die.

6 minute preheat cycle

Samples of extrudate were cut after 6 minutes of extrusion. The results were then converted to a flow rate over 10 minutes. For BPI samples, which have a higher MFI or lower viscosity than the Centriforce samples, extrudates were cut off after 3 minutes.

## 4.5 Gloss and Colour

UV degradation is concentrated at the surface of the material. Therefore the surface degrades more rapidly. As the surface structure is broken up, surface gloss is lost and colour perception is modified.

The gloss measurements were recorded by Rapra using a Minolta GM 60 gloss meter and the following test procedure because technically the samples were too small to perform a test in accordance with the gloss standard ASTM D2457: 1997.

A template was made and coated with matt black paint to hold the test sample in place whilst the gloss head was placed over the sample. A gloss range was recorded for each sample because of variability due to the size of the sample and surface marking.

The L\*a\*b\* colour space measurements were recorded using a calibrated hand-held Minolta Color Reader CR-10 in general accordance with BS3900: Parts D8 – D10: 1986. In the CIE L\*a\*b\* system includes an equation for the total colour difference between a trial and a standard sample. The total colour difference is the distance between the two points representing those colours in the colour space.

The distance, expressed as  $\Delta E^*$ , is determined using the equation

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

$\Delta E^*$  indicates colour difference, but not in what way the colours are different.

The colour space is organized in a cube form. The L axis runs from top to bottom. The maximum for L is 100, which would be a perfect reflecting diffuser. The minimum for L would be zero, or black. The a and b axes have no specific numerical limits. Positive a is red. Negative a is green. Positive b is yellow. Negative b is blue. The delta values ( $\Delta L$ ,  $\Delta a$ ,  $\Delta b$ ) associated with this colour scale indicate how much a standard and a sample differ from one another in L, a and b.

The scaling of the colour space was set up so that a distance of 1 between the points representing the colour of two samples should be just visually perceptible.

As a guide, if  $\Delta E^*$  is less than 0.8, the sample is an acceptable match to the standard.

Values between 0.8 and 1.2 are a possible match and values exceeding 1.2 are not a colour match. <sup>[111]</sup>

#### **4.6 Gel permeation chromatography (GPC)**

GPC is a chromatographic technique where the different molecular weight fractions of polymer are separated out to allow the molecular weight distribution to be measured. The polymerisation reactions used in the manufacture of polymers mean that the bulk material is made up of a range of different size (length) molecules. Careful process control and catalyst use can produce materials with high molecular weight and a relatively narrow distribution. The molecular weight distribution can indicate if the raw material is of poor quality and can also identify degradation.

The separation of molecules in GPC, more correctly termed as size exclusion chromatography occurs within a chromatographic column filled with beads of a rigid porous 'gel'. Highly cross linked porous polystyrene and porous glass are preferred column-packing materials. The pores in these gels are of the same size as the dimensions of polymer molecules.

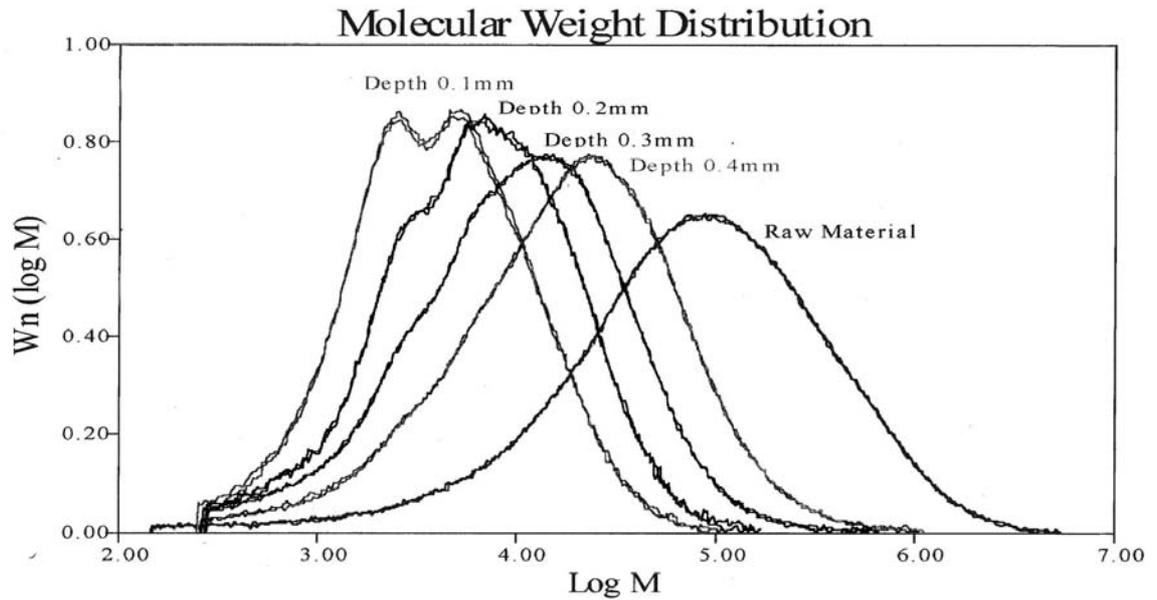
A sample of the dilute polymer solution is introduced into a solvent stream flowing through the column. As the dissolved polymer molecules flow past the porous beads, they can diffuse into the internal pore structure of the gel to an extent depending on their size and the pore-size distribution of the gel. Larger molecules can enter only a small fraction of the internal portion of the gel, or are completely excluded; smaller polymer molecules penetrate a larger fraction of the interior of the gel. Therefore, the larger the molecule, the less time it spends inside the gel and the sooner it flows through the column

GPC gives the molecular weight distribution of a polymer in the form of the following data. The number average molecular weight ( $M_n$ ) is the weight of all the polymer

molecules in a sample divided by the total number of molecules present. The weight average molecular weight ( $M_w$ ) takes into account that the larger molecules contain more of the total mass of a polymer sample than the smaller ones. The polydispersity is the ratio  $M_w/M_n$  and this gives an indication of the spread of molecular weight distribution. A ratio of around 1.0 indicates that the range of molecular weights in the mixture is narrow; a high ratio indicates that the polymer has a wide range of different molecular weight molecules present.

Chain scission during degradation results in the continual breaking of polymer chains and the shortening of the length of the molecules. The overall result is that there are more short chain (lower molecular weight) molecules present and the average molecular weight is reduced whilst the distribution of weights broadens. Therefore the distribution curve is seen to shift to the left with a lower and broader peak. As the degree of degradation continues there will be fewer long chain molecules remaining. Figure 4.5 shows the changes in molecular weight of a polypropylene exposed to UV radiation. The x axis shows molecular weight and the y axis the number of molecules. A highly degraded material will show a narrow distribution of low molecular weight material as a narrow peak, over to the left of the graph (Figure 4.5).

Cross-linking due to degradation leads to chain branching. Here the free radical polymer chains terminate by bonding to other free radical chains, resulting in larger branched molecules. In this case the average molecular weight increases; giving shift to the right for the curve. Again the peak broadens initially as a wide range of molecular weights is produced.



**Figure 4.5 Molecular weight of a Polypropylene exposed to UV radiation**  
*(Sample was not tested as part of this study. Courtesy of Rapra)*

Note:  $W_n(\log M)$  on the Y axis denotes the weight fraction per unit of log molecular weight. This can also be expressed as " $dw/d\log M$ ".

The raw material has a molecular weight of 100000. After experiencing UV degradation the surface molecular weight is reduced to as low as 1500. The molecular weight increases with depth into the sample. This is because more UV radiation is absorbed close to the surface. The molecular weight distribution can be seen to narrow with increased degradation.

#### **4.6.1 Sample Preparation**

A single solution of each sample was prepared at Rapra by adding 15 ml of solvent to 15 mg of sample and heating at 190°C for 20 minutes, with shaking to dissolve. The solution was then filtered through a metal sinter at 160°C and part of each filtered solution transferred to glass sample vials. The vials were then placed in a heated sample compartment and after an initial delay of thirty minutes to allow the samples to equilibrate thermally; injection of part of the contents of each vial was carried out automatically.

#### 4.6.2 Chromatographic Conditions

Instrument:	Polymer Laboratories GPC220,
Columns:	PL gel guard plus 2 x mixed bed-B, 30 cm, 10 microns,
Solvent:	1,2,4-trichlorobenzene with anti-oxidant,
Flow-rate:	1.0 ml/min (nominal),
Temperature:	60°C (nominal),
Detector:	refractive index (& Viscotek differential pressure).

Data capture and subsequent data handling was carried out using Viscotek 'Trisec' 3.0 software.

## **5. Material Characterization by Scanning Electron Microscopy (SEM) and Electron Probe Microanalysis (EDX)**

Scanning Electron Microscopy (SEM) provides images of the surface (topography) of virtually any solid material with magnifications from 20x to >50,000x. A thin layer of palladium is applied to the sample surface to dissipate any surface charge present and to facilitate image capture. The palladium layer can be seen as a peak on the EDX analyses.

The primary electron beam interacts with the sample in a number of key ways:-

- Primary electrons generate low energy secondary electrons, which tend to emphasise the topographic nature of the specimen
- Primary electrons can be backscattered which produces images with a high degree of atomic number (Z) contrast
- Ionized atoms can relax by electron shell-to-shell transitions, which lead to either X-ray emission or Auger electron ejection. The X-rays emitted are characteristic of the elements in the top few micrometres of the sample. A particular feature of the SEM is the large depth of focus of the images. The images for this thesis were obtained using a JEOL JSM 6310 Scanning Electron Microscope

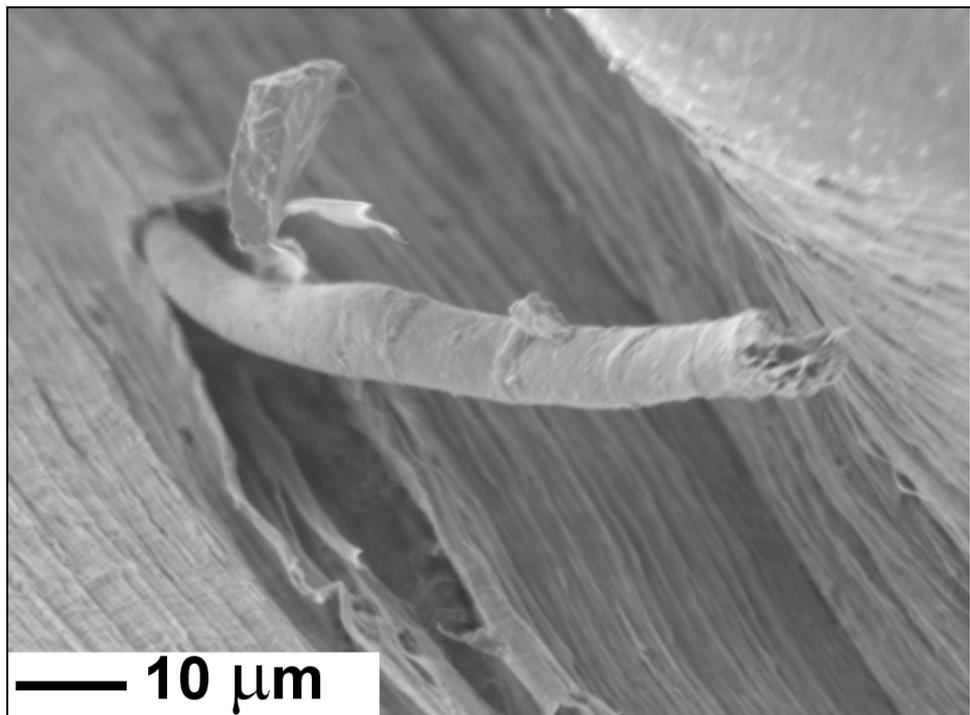
Electron Probe Microanalysis, also known as Energy Dispersive X-ray analysis (EDX), uses x-rays emitted from the sample (under investigation in the SEM) to determine the elemental composition (qualitative and quantitative) of areas or features, of the sample, with dimensions down to ~ 1 $\mu$ m. The instrument used was an Oxford ISIS.

The samples analysed using SEM and EDX were taken from the failed areas after tensile testing field aged and virgin unaged material, as well as material that had been conditioned in the Q-UV Weatherometer for 3000 hours in order to observe any changes resulting from either differences in composition or UV exposure.

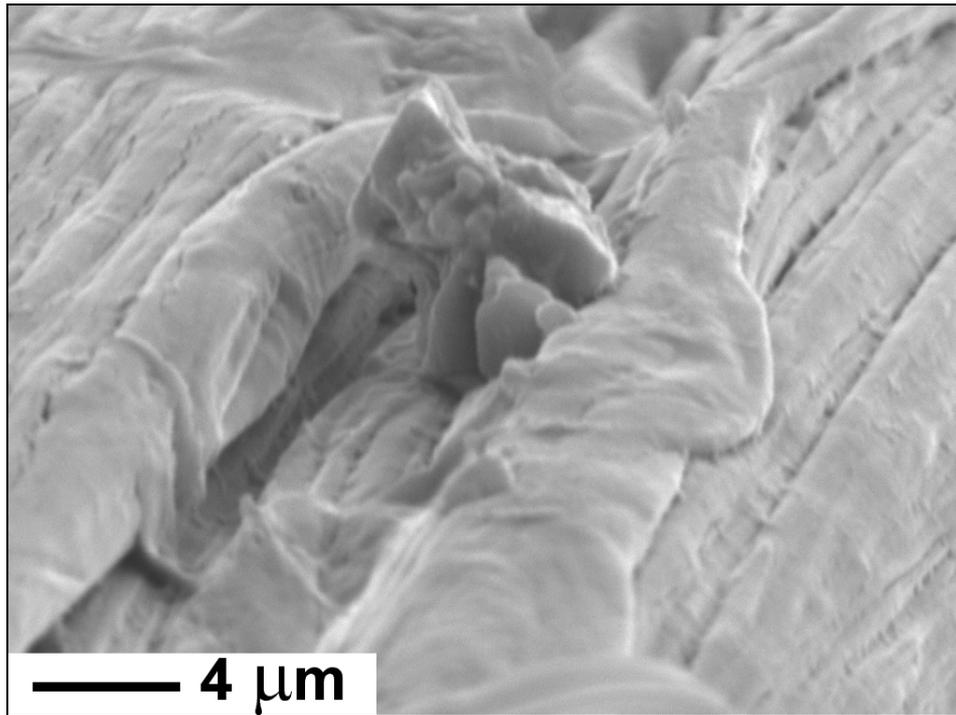
## 5.1 Characterization of Centriforce Materials

All the images are of failed tensile tests specimens, often showing the areas of failure.

Differences in material behaviour were observed visually using scanning electron microscopy (SEM). A clearly defined fibre can be seen breaking through the surrounding polymer material in a sample from the unaged blue Centriforce material (Image 6.1). This phenomenon was not observed in any other Centriforce or BPI samples.

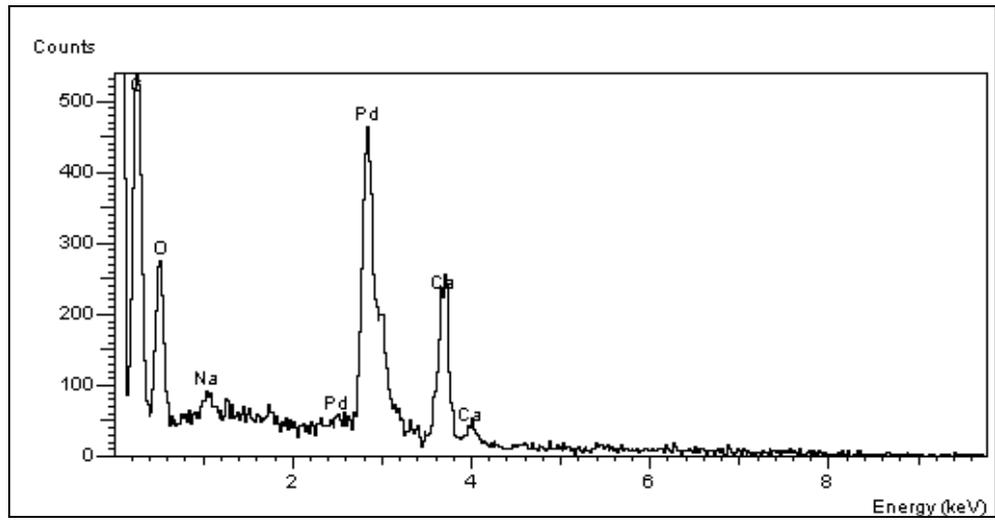


**Image 5.1: Fibre, Centriforce Blue (Unaged)**

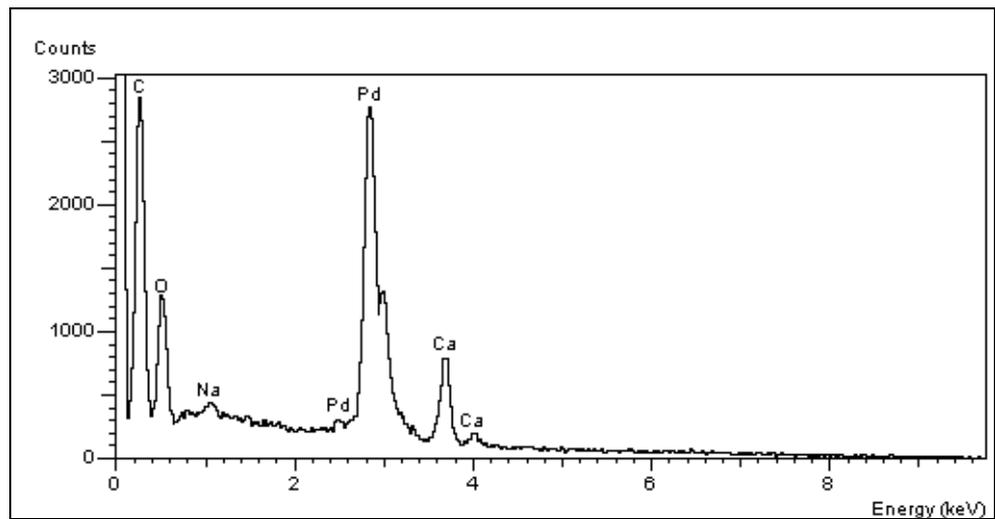


**Image 5.2 Centriforce Brown (Unaged)**

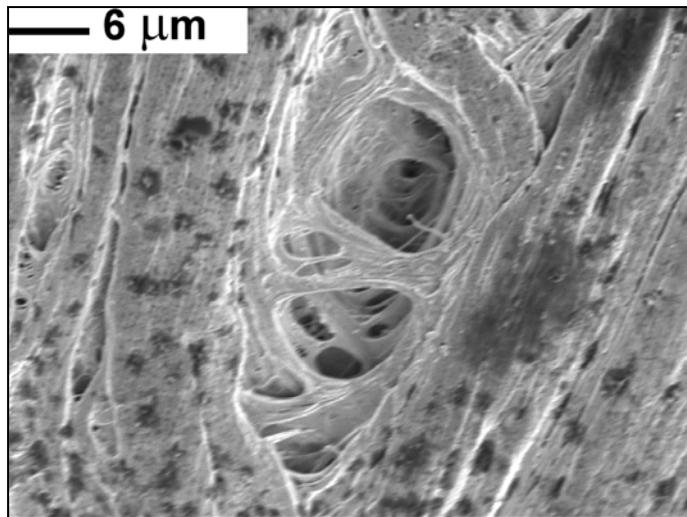
Some evidence of impurities or possibly heterogeneity of composition was found in the unaged Centriforce Brown material. In Image 5.2, a sharp angled, raised piece of material can be seen between two ‘folds’ of polymer material. Using EDX analysis it was found that the raised piece of material had a slightly different calcium composition to the surrounding polymer folds (Images 5.3 and 5.4). The host LDPE material should not have any calcium present. The angular material appears to be part of the polymer sample, possibly filler material and not contamination after test piece formation. The folds of material either side appear to have formed around the angular material during tensile testing.



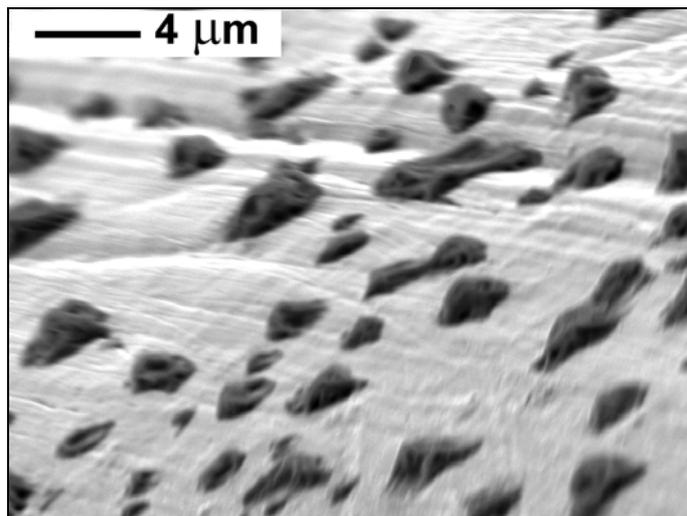
**Image 5.3 EDX Analysis of raised material in Image 5.2**



**Image 5.4: EDX Analysis of surrounding folds in Image 5.2**



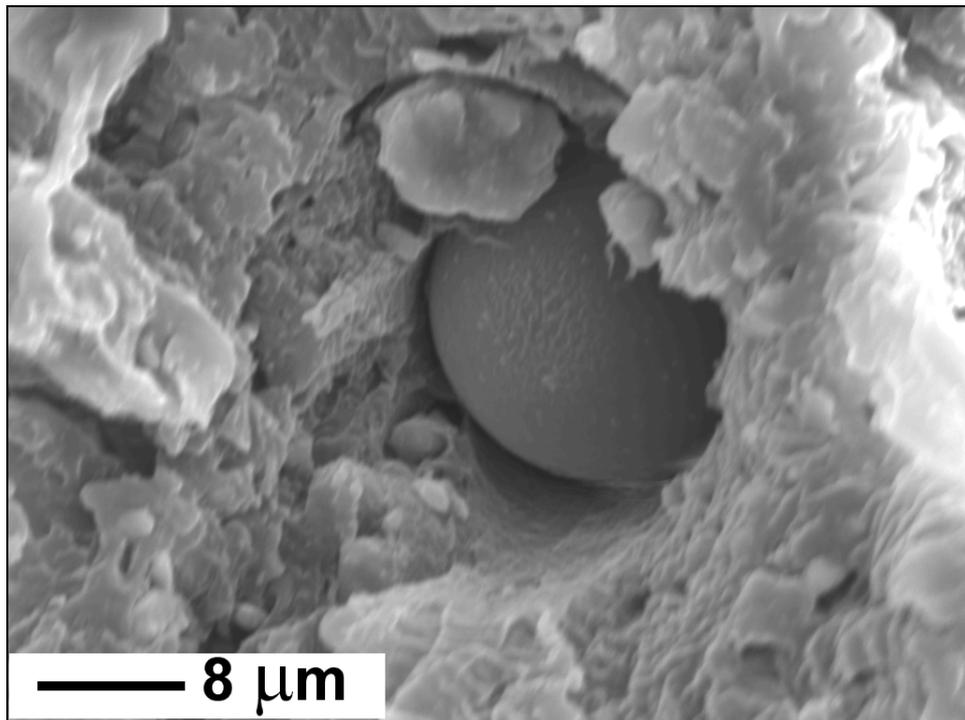
**Image 5.5: Centriforce Black Field Aged**



**Image 5.6: Centriforce Black Unaged**

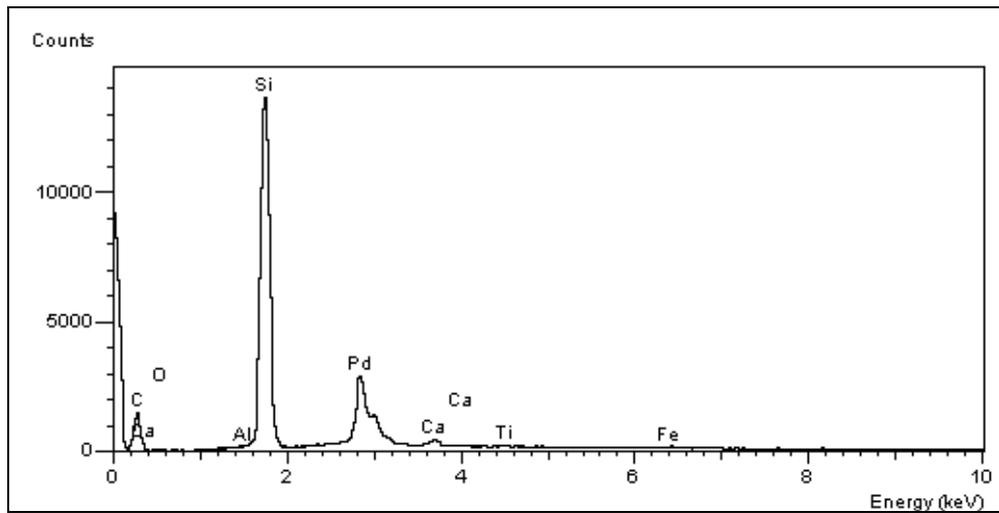
In Images 5.5 and 5.6, both from Centriforce Black material, darker spots are apparent in the polymer material. The darker areas appear to consist of different polymer material, possibly containing more agglomerated particles of carbon black, which has different MFI and tensile properties to the rest of the sample.

## 5.2 Characterization of BPI Materials

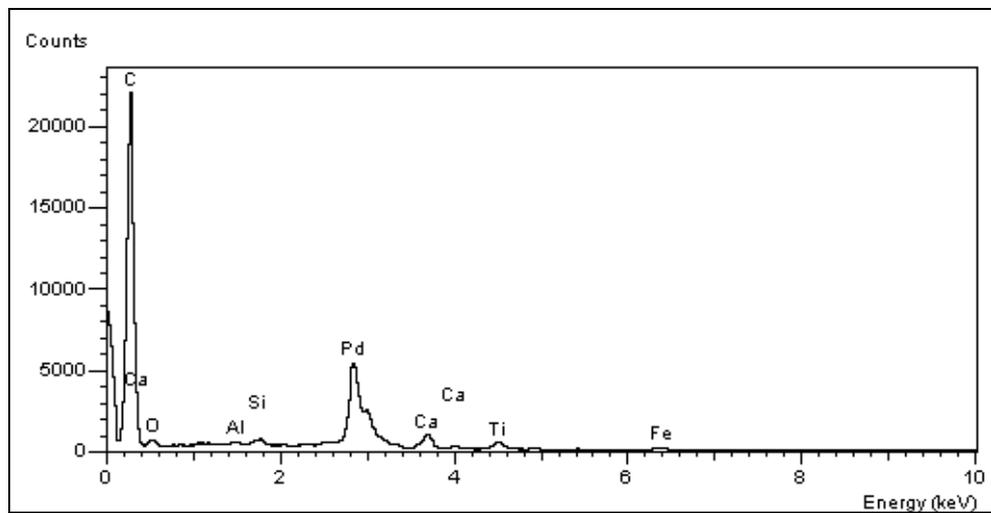


**Image 5.7: BPI Rectangular 3000 hours**

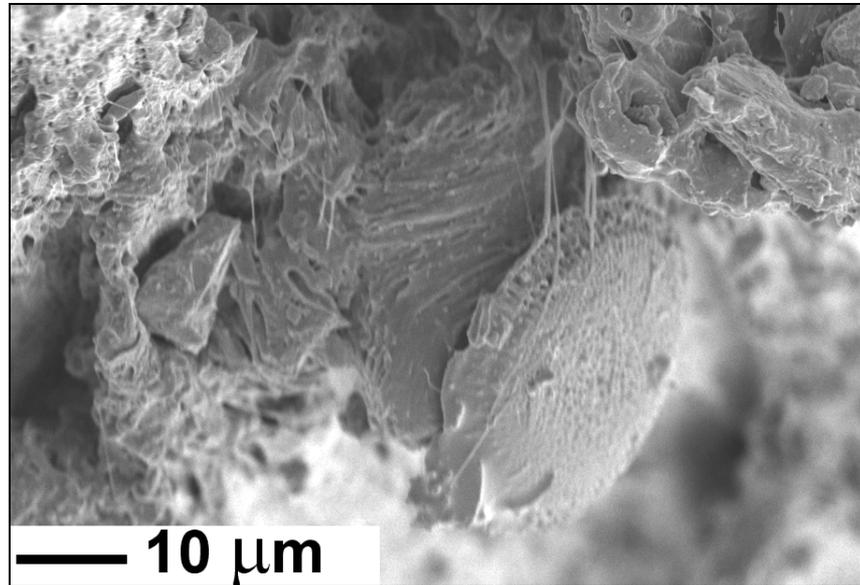
At 3000 hours exposure, impurities become more evident because of the breakdown in the host structure. Image 5.7 shows a spherical object embedded in the polymer matrix. EDX analysis of the sphere showed a high peak for silicon (Si), which was not seen in the surrounding polymer (Image 5.8 & 5.9). From this it was deduced that the sphere consisted of glass, which would be prevalent in recycling facilities. However, it is not possible to calculate the extent of the impact such contamination would have on tensile or melt flow properties.



**Image 5.8: EDX Analysis of Sphere in Image 5.7**

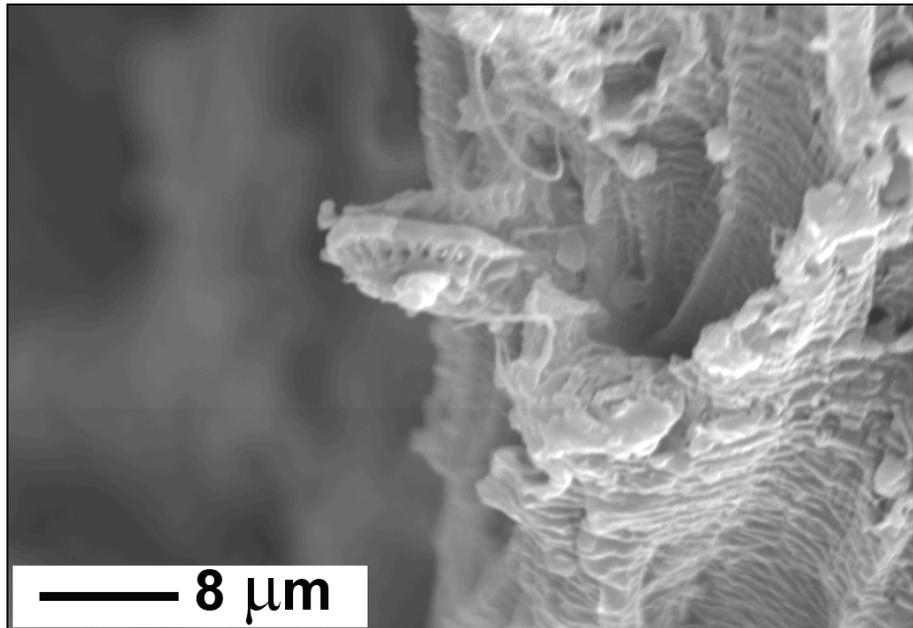


**Image 5.9: EDX Analysis of polymer matrix in Image 5.7**

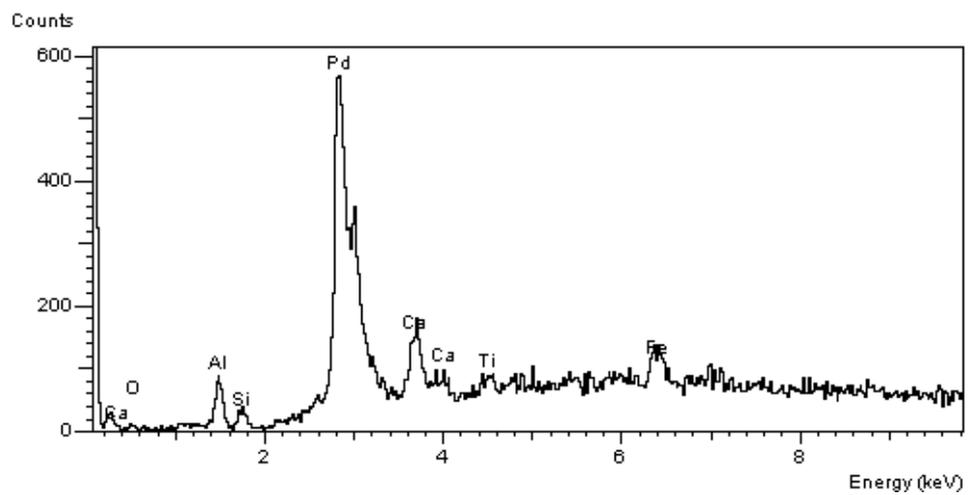


**Image 5.10: BPI Rectangular Unaged**

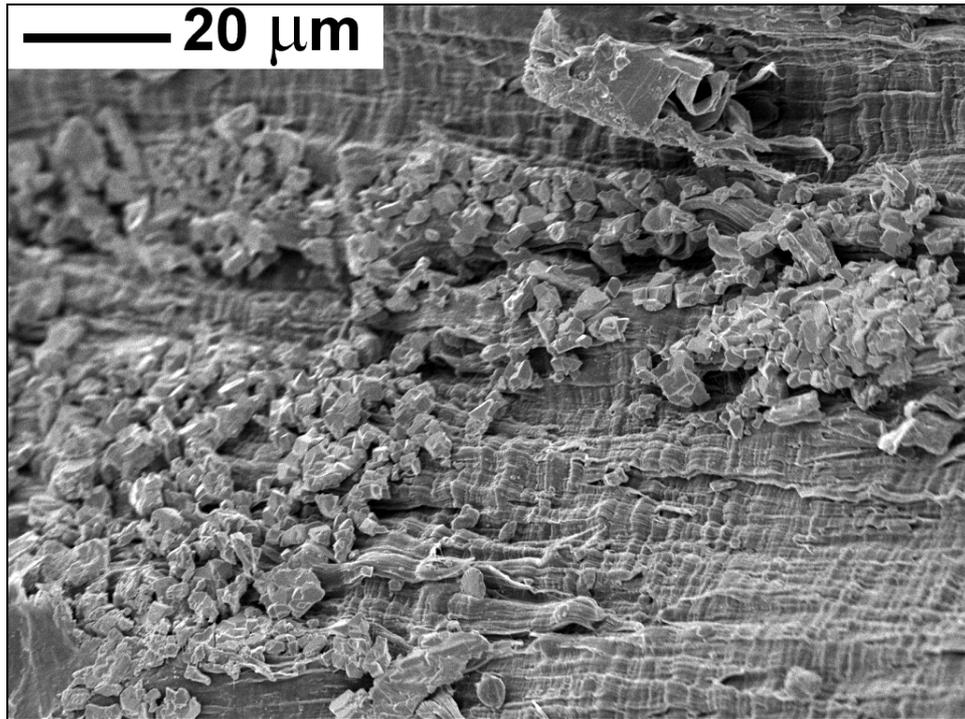
In Images 5.10 and 5.11 are examples of disc shaped objects that were found only in the BPI samples. These objects appear to be incorporated into the polymer matrix, and not dust or other contamination after test specimen formation. Strands of polymer can be seen joining the disc to the surrounding polymer. EDX analysis was inconclusive, except that it showed a different composition to the prevalent polymer material in BPI Rectangular specimens.



**Image 5.11: BPI Rectangular 3000 hours**



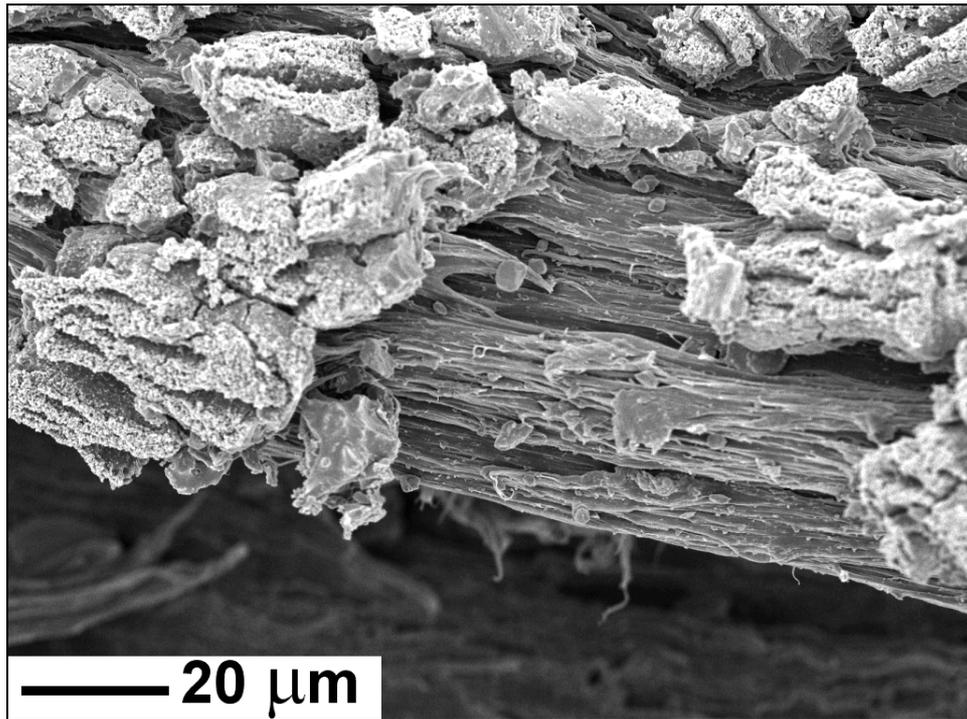
**Image 5.12: EDX Analysis of disc in Image 5.11**



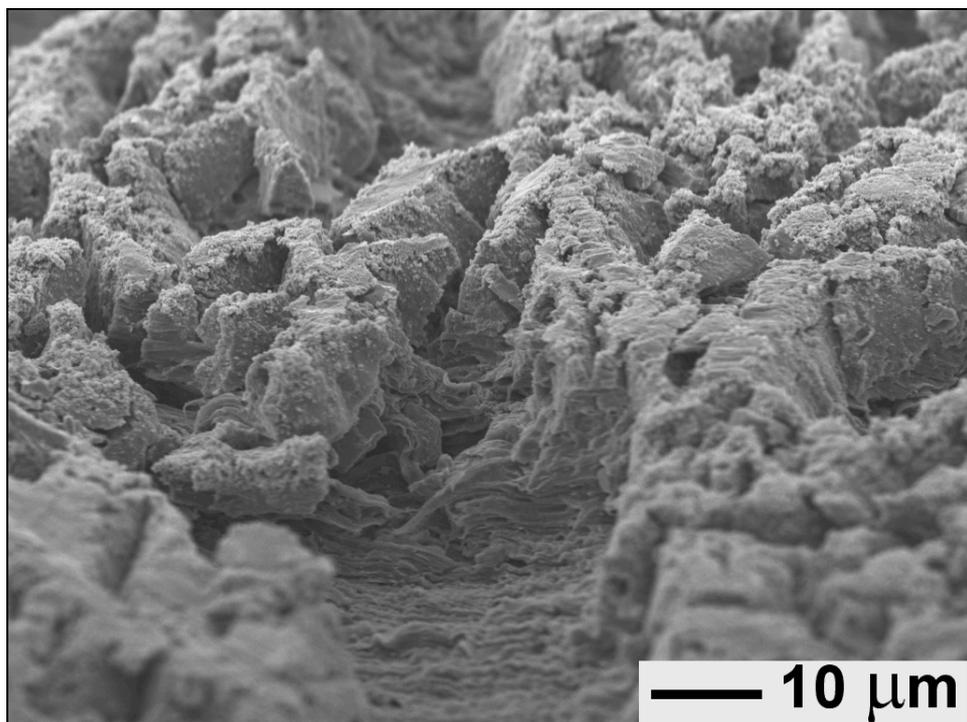
**Image 5.13: BPI Rectangular 3000 hours**

In Image 5.13 the sample surface appears to be fragmented, while polymer material stretched during tensile testing is clearly visible. This sample was exposed to UV radiation for 3000 hours. Similar surface topography was observed in field aged specimens also (Image 5.14 & 5.15), despite the samples being derived from different batches, indicating that the surface damage may have occurred as a result of UV exposure in the field aged and artificially weathered samples.

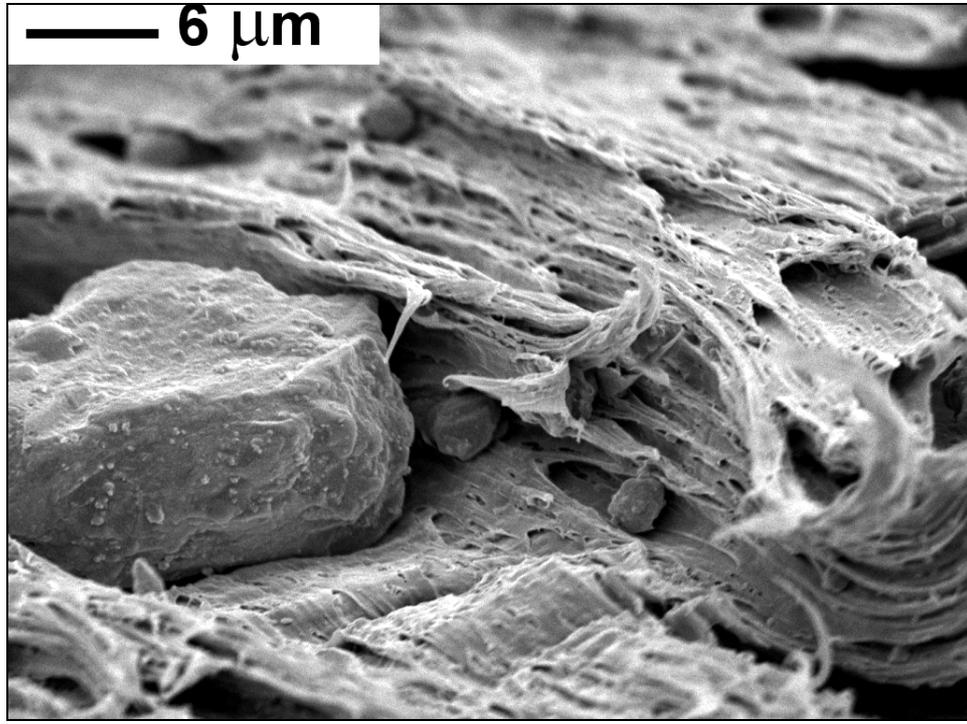
However, the surface layer may consist of polypropylene that has a lower viscosity than the phase segregated polyethylene in the material, has formed a 'skin' on the surface of the tests pieces during injection moulding. As mentioned previously, polypropylene is more susceptible to chain scission degradation than polyethylene due to the presence of the more reactive tertiary carbon. This could explain the changes in surface properties in the material, while the layer of polymer underneath remains largely unaffected.



**Image 5.14: BPI Rectangular Field Aged**

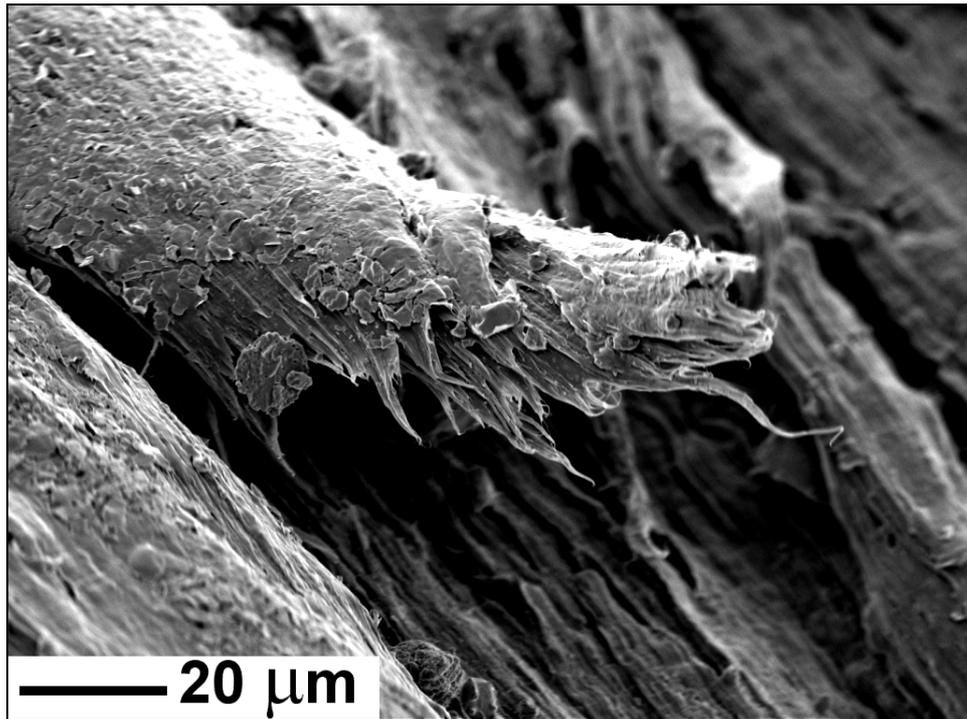


**Image 5.15: BPI Rectangular Field Aged**



**Image 5.16: BPI Rectangular Field Aged**

Further evidence of possible contamination can be seen in Image 5.16. The pebble shaped feature on the left of the image appears to be part of the polymer matrix and has affected the drawing of polymer fibres surrounding it.



**Image 5.17 BPI Square Unaged**

Evidence of surface fragmentation and flaking can also be seen on the failed fibre in Image 5.17. This cannot be attributed to UV exposure because the specimen is unaged, but may be the result of a polypropylene 'skin' formed during test piece formation as described previously.

## **6. Results and Discussion**

For convenience and clarity, the results for the unaged samples were plotted at an exposure of 2 hours to avoid being plotted on the y axis line. The results for field-aged samples were plotted as outline data points at an exposure time equivalent to the estimated length of outdoor UV exposure. It is important to note that whereas the artificially UV aged test pieces would have surface degradation due to this exposure, the field aged samples had been granulated and moulded into test pieces after ageing, thus removing any surface flaws.

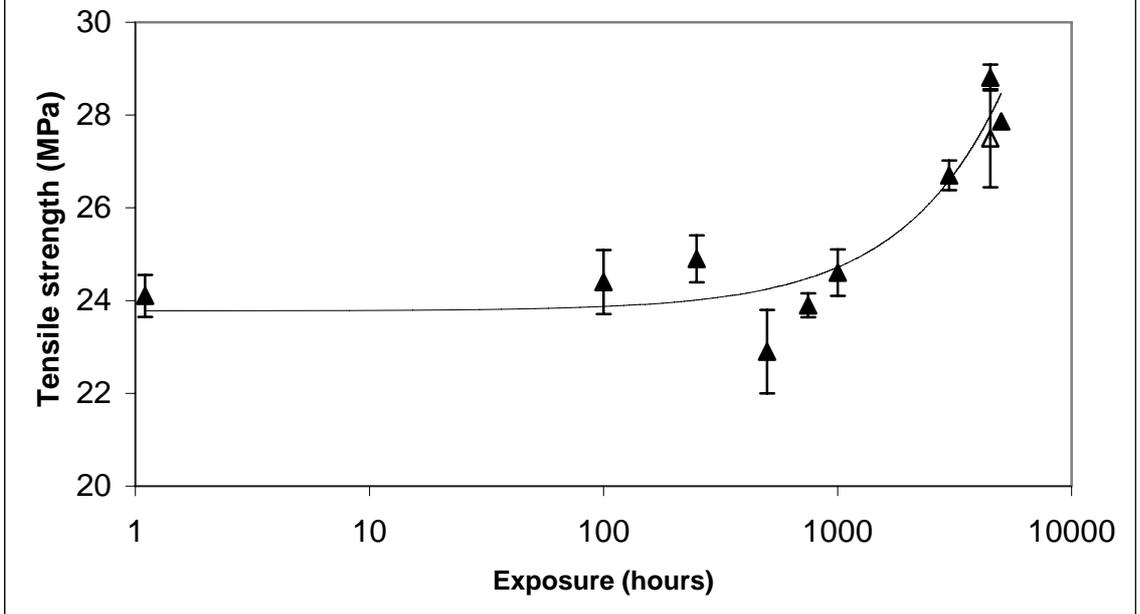
The lines on the graphs are to guide the eye and have no fundamental significance. Error bars show one standard deviation.

It was not possible to perform statistical tests such as the Student's t-test because of small sample numbers for some of the materials.

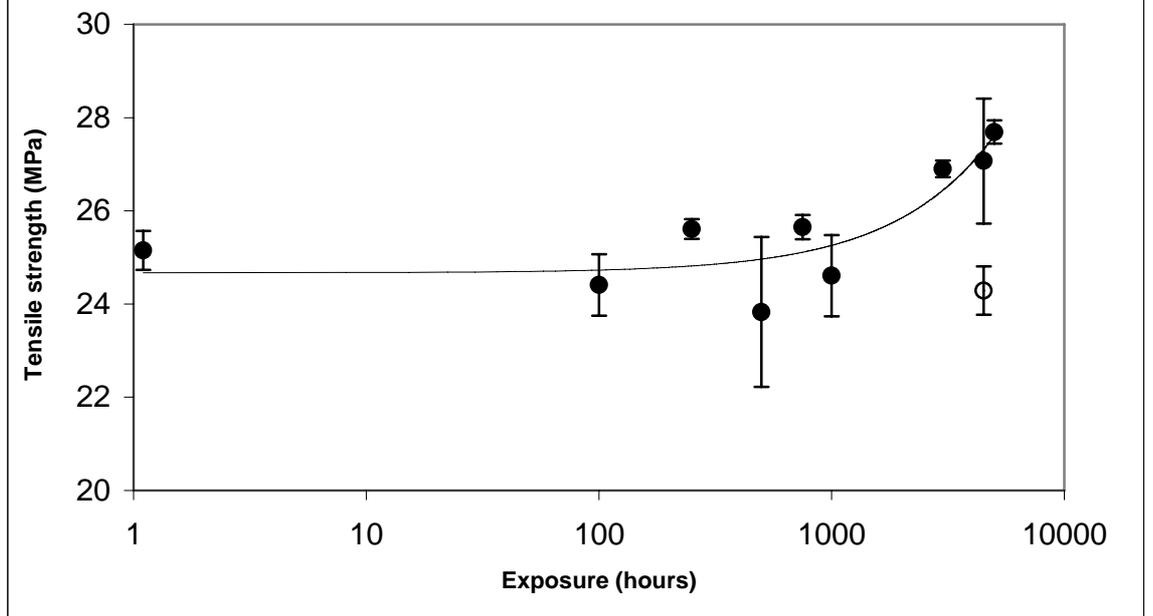
### **6.1 Material supplied by Centriforce**

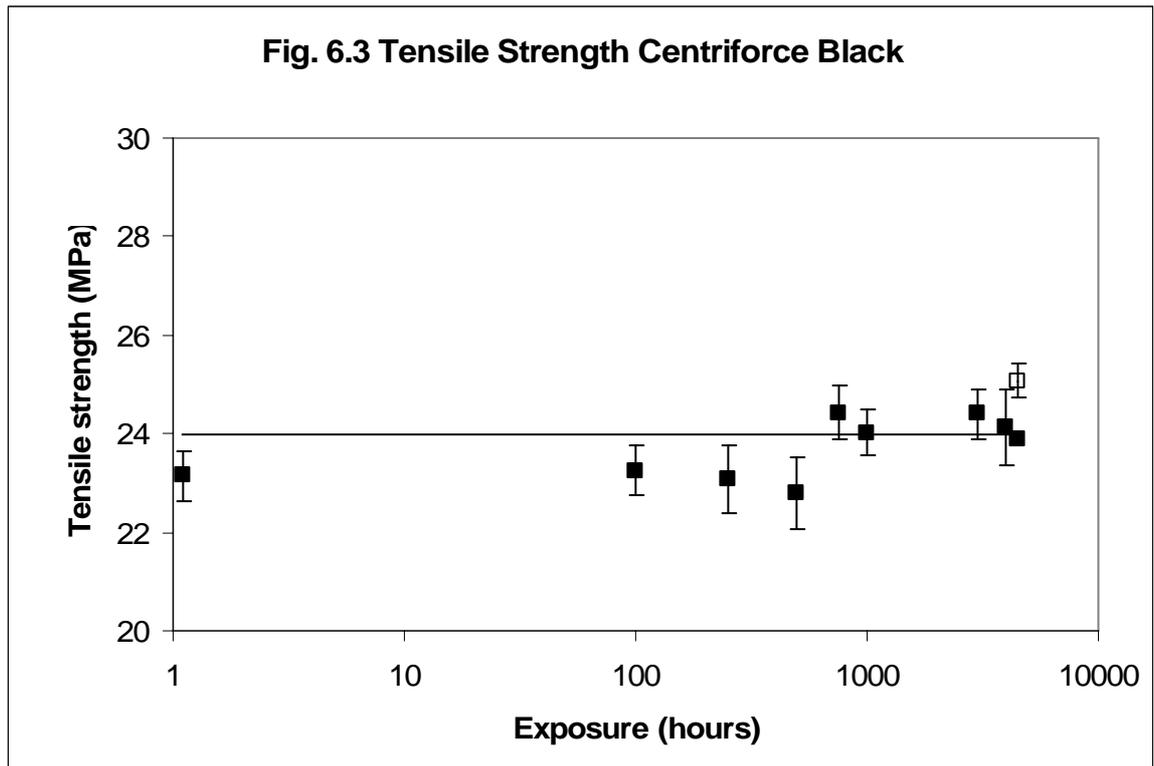
All three grades of material (blue, brown and black Figs 6.1-6.3) had very similar tensile strengths at around 25 MPa, which remained unaffected by UV exposure and in fact appeared to increase slightly for the blue and brown material. Both the field-aged blue and brown materials exhibited a tensile strength similar to samples exposed to ultra violet light for 1000 hours and more. The field aged black material gave a tensile measurement slightly higher than any of the black samples in the exposure regime.

**Fig. 6.1 Tensile Strength Centriforce Blue**



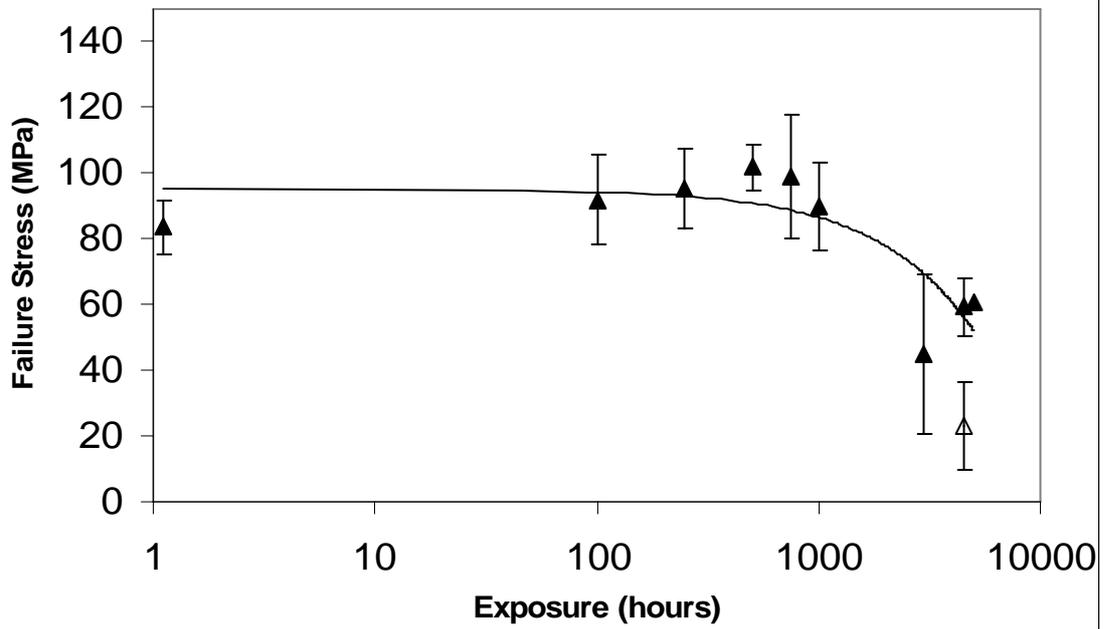
**Fig. 6.2 Tensile Strength Centriforce Brown**



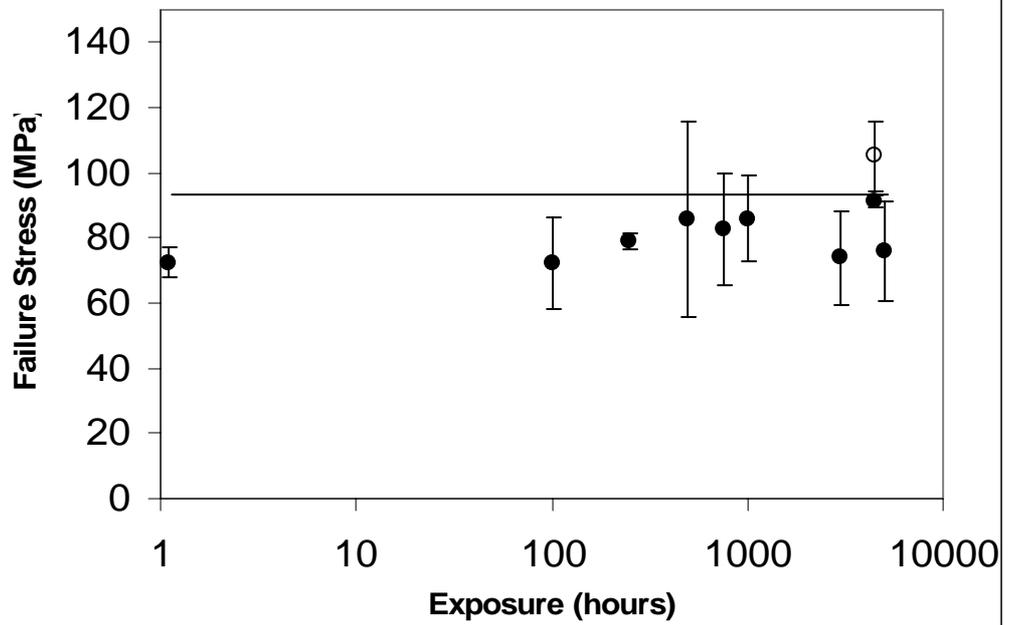


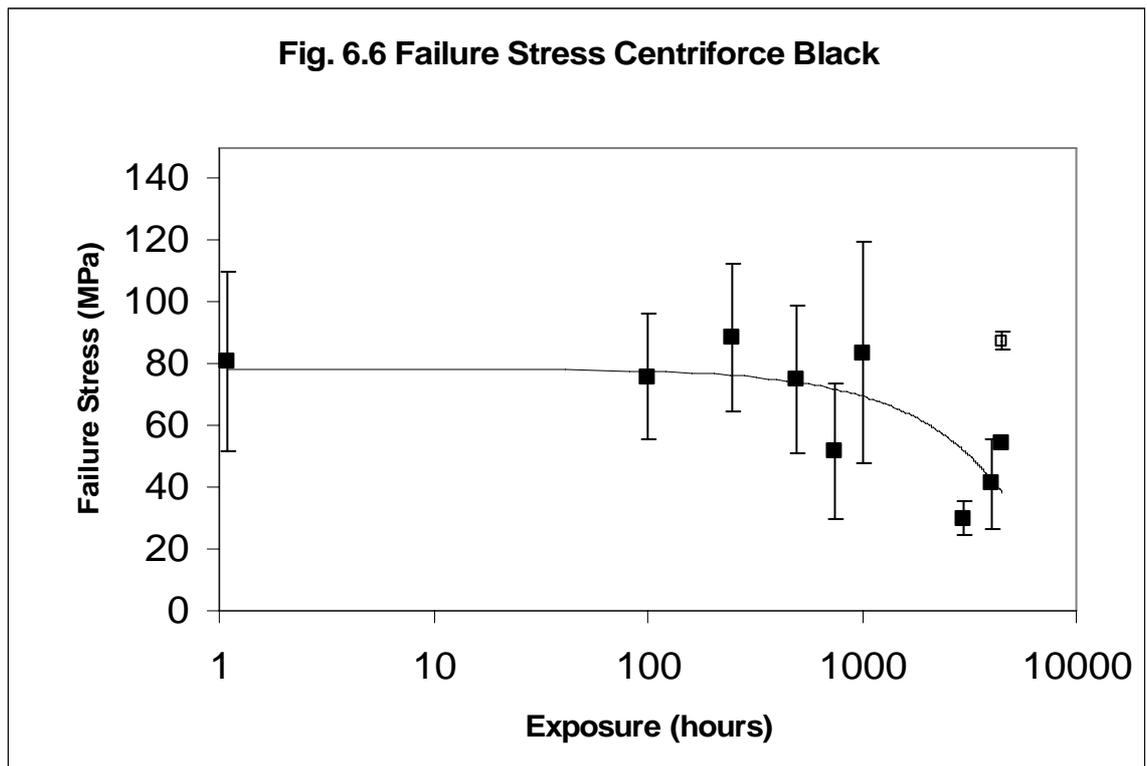
The failure stress remained constant between 70 and 100 MPa, although the value dropped considerably after 1000 hours of exposure for the blue and black materials (Figs.6.4-6.6). Since failure is initiated at flaws in the material, the amount of scatter in the failure stress data reflects the randomness of these flaws. For the blue grade, the field aged material showed a lower failure stress than any of the other blue samples. However, the field aged brown material showed a higher failure stress than any of the other brown samples, indicating that these materials had different compositions to the exposure regime samples.

**Fig. 6.4 Failure Stress Centriforce Blue**



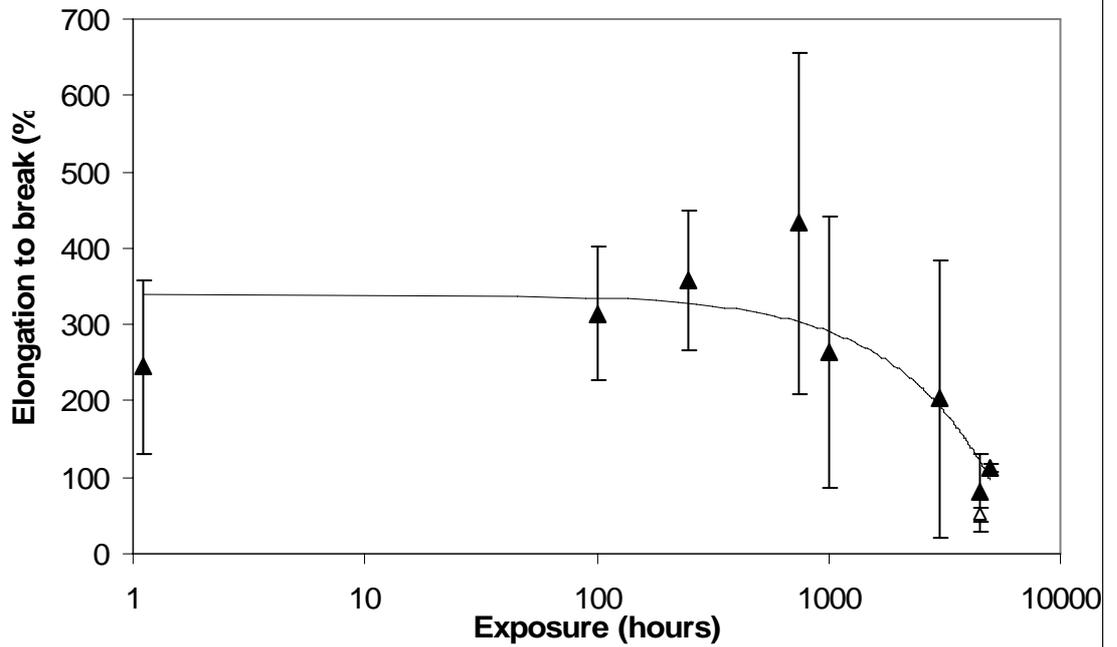
**Fig. 6.5 Failure Stress Centriforce Brown**



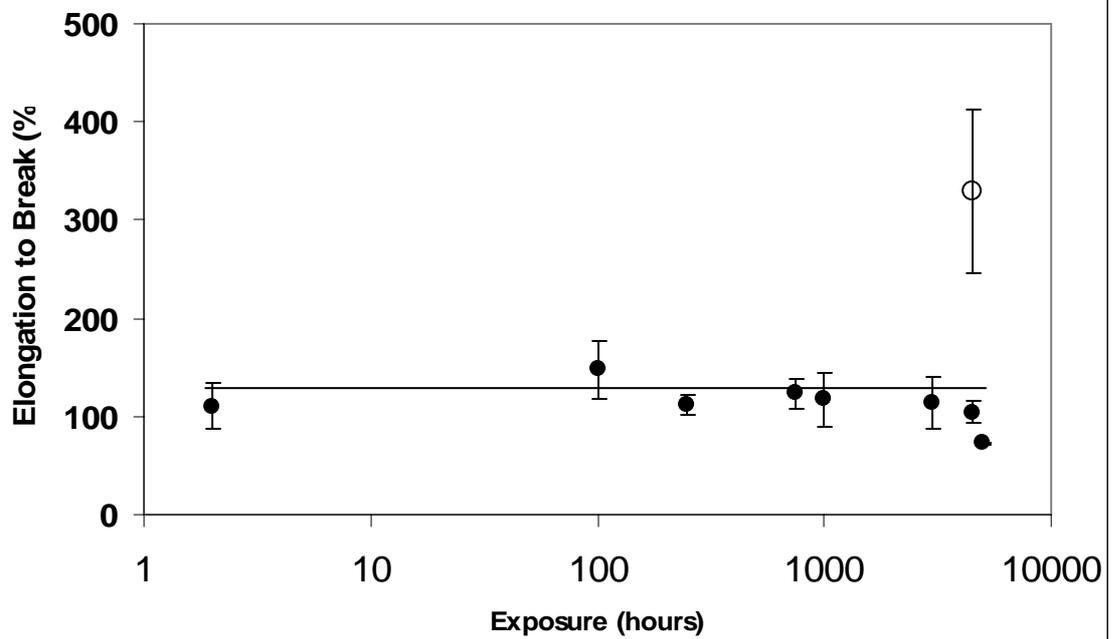


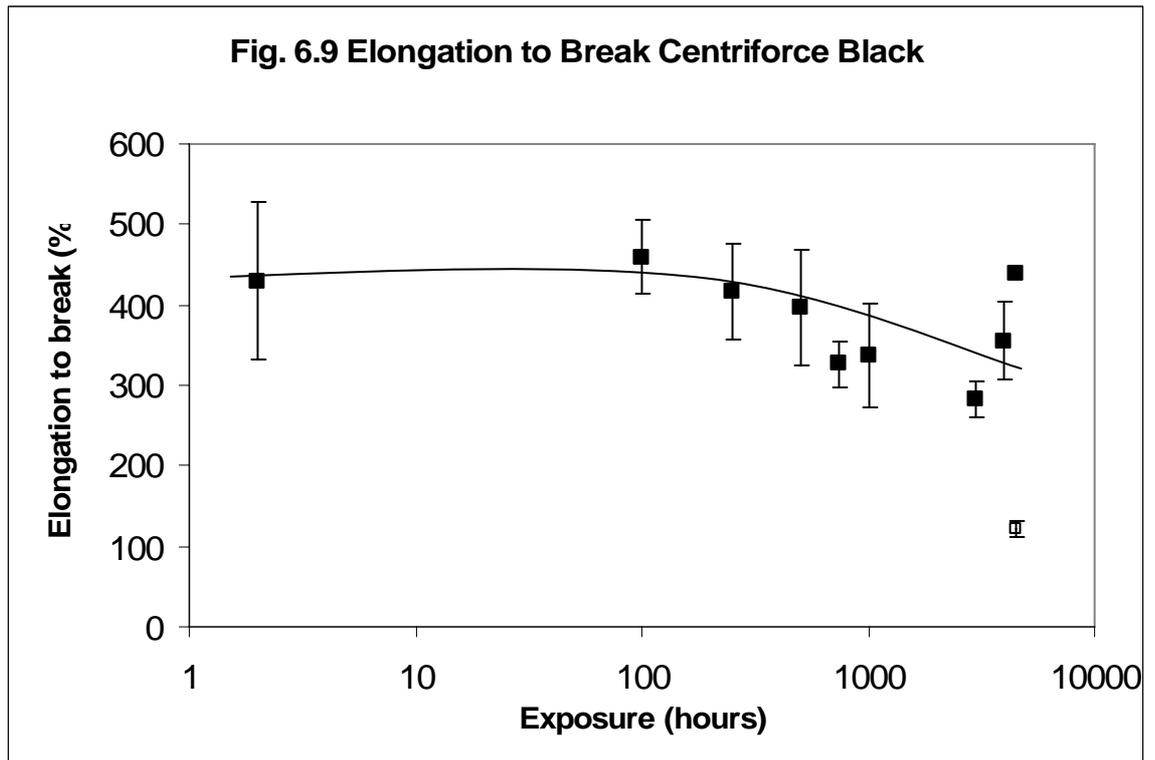
The blue material also showed a more pronounced decrease in the elongation at break beyond 1000 hours than the brown and black materials (Fig.6.7-6.9). The brown material exhibited lower values for elongation at break than the blue and black materials. The results suggest that pigmentation plays a significant role in the polymer structure. In addition, the large variability in these results indicates the presence of flaws in the materials. The field aged blue material gave the lowest elongation at break measurement (51.3%) for the blue samples. The field aged brown material exhibited an elongation at break measurement that was nearly three times that of any other brown samples (329% compared with a mean value of 125% for the exposure regime samples). Again, this indicated that the samples were made of different material composition.

**Fig. 6.7 Elongation to Break Centriforce Blue**



**Fig. 6.8 Elongation to Break Centriforce Brown**

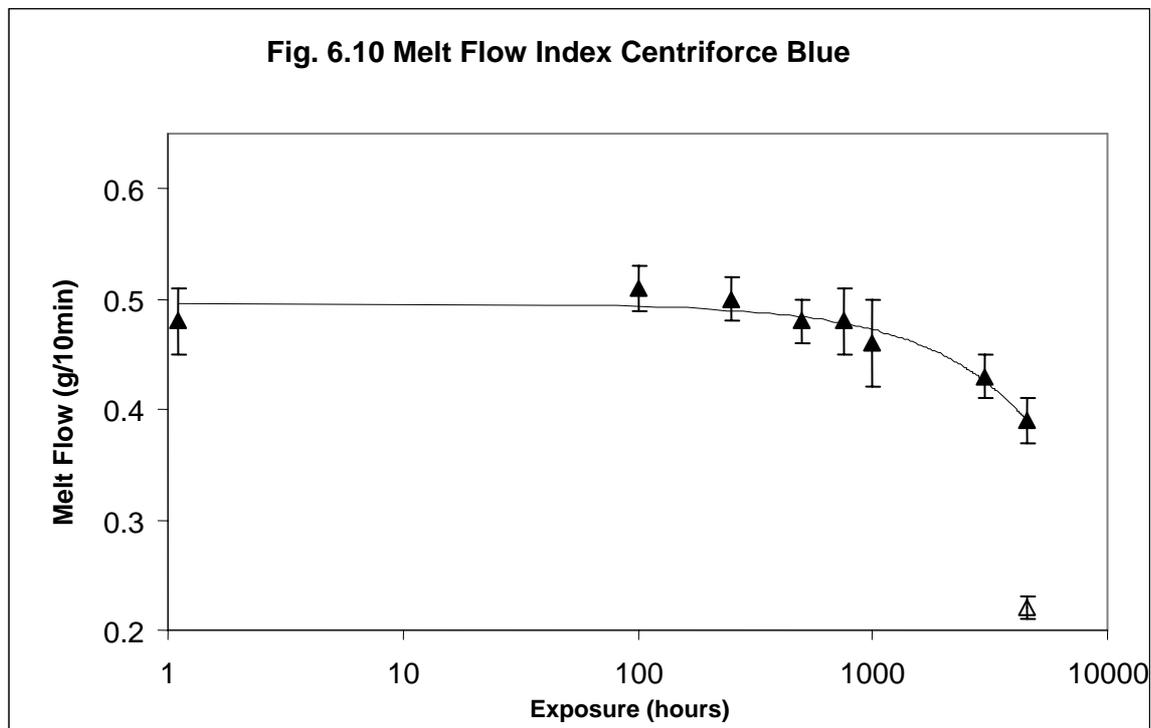




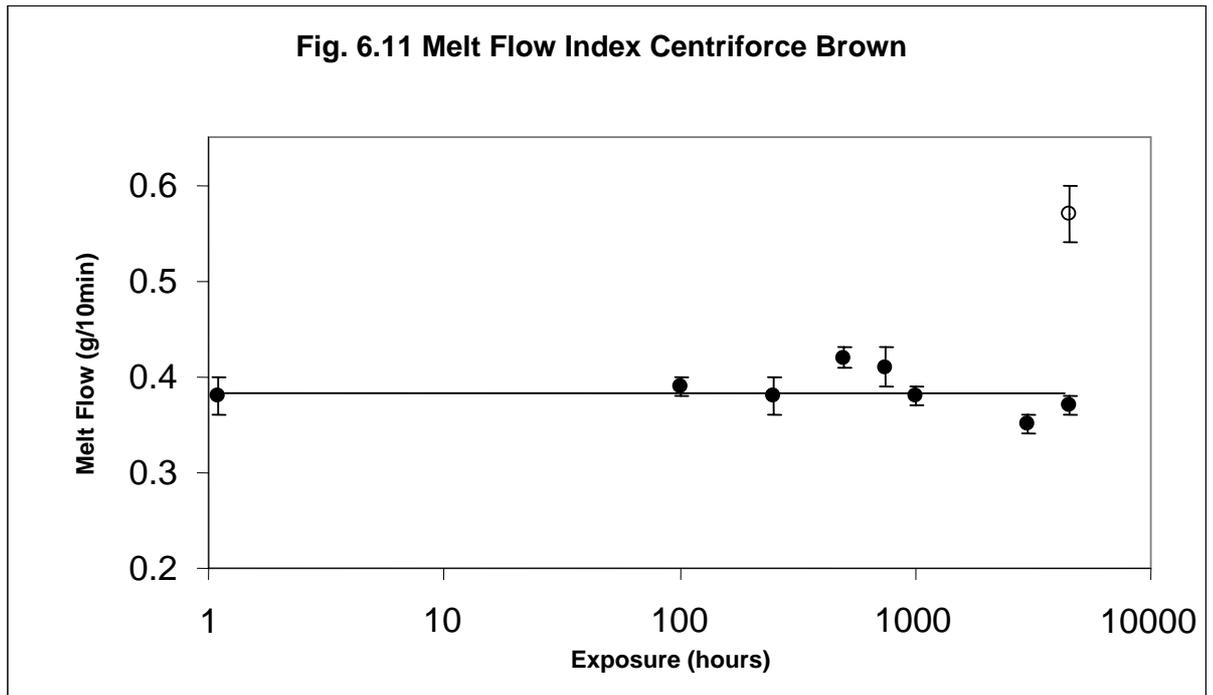
The tensile strengths of the field-aged material were similar to those of the unexposed samples for the brown and black materials. The amount of material exposed to UV at the sample surface was small as a proportion of total material in the samples. In the original solid sections, the proportion of material exposed to UV would be even smaller. So it appears that UV degradation, being a surface effect, does not damage the mechanical integrity of the material. The failure stress of the field-aged materials remained within the distribution of values for brown and black materials although the value was much lower for blue (Fig.6.4).

The elongation to break varied from 120 % for the brown to over 400 % for the blue and black grades. The blue and black grades showed a decrease in elongation to failure with UV exposure and significantly at around 1000 hours in the case of the blue (Fig 6.7). In this case, the elongation to break measurement showed that the material failed in a brittle manner. This indicates that the presence of pigments disrupts the crystallinity within the

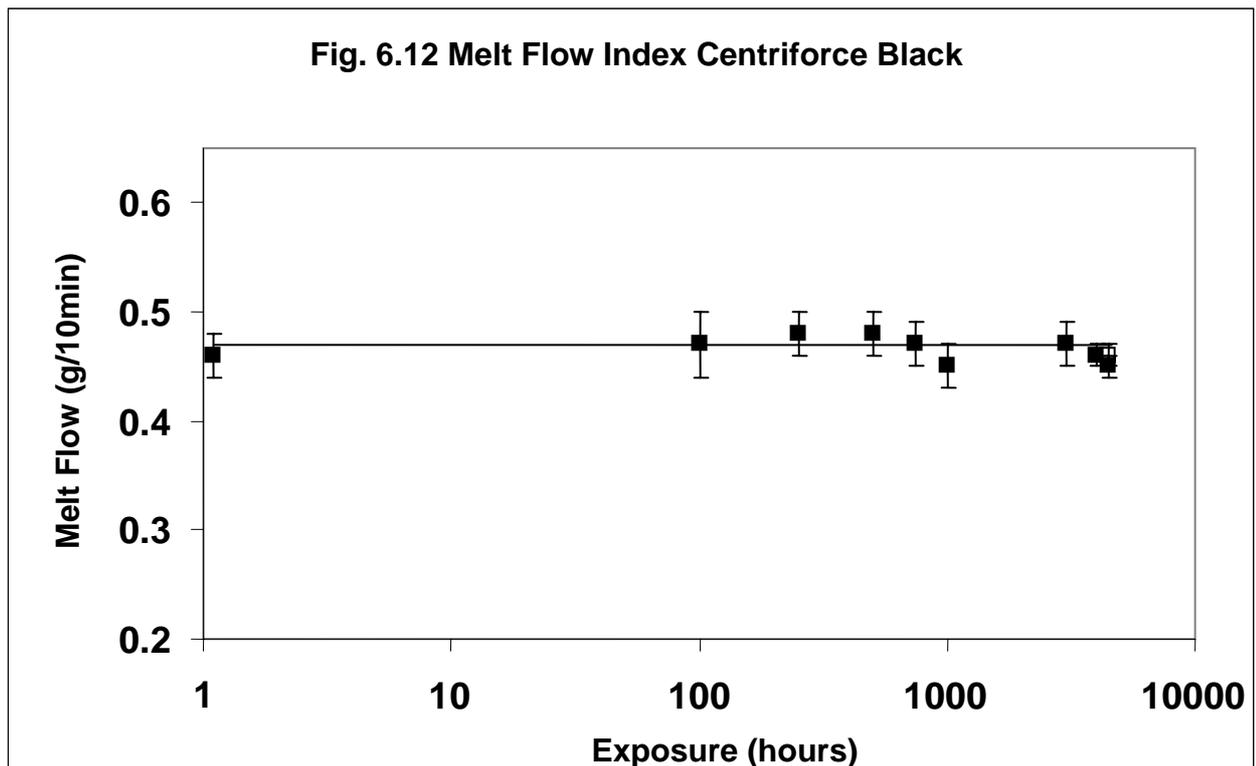
material and that UV exposure leads to the creation of significant surface damage after about 1000 hours.



The blue grade shows a decrease in MFI beyond 750 hours (Fig. 6.10), although the melt flow characteristics remained unaffected by the length of UV exposure for the brown and black materials (Fig.6.11 & 6.12).

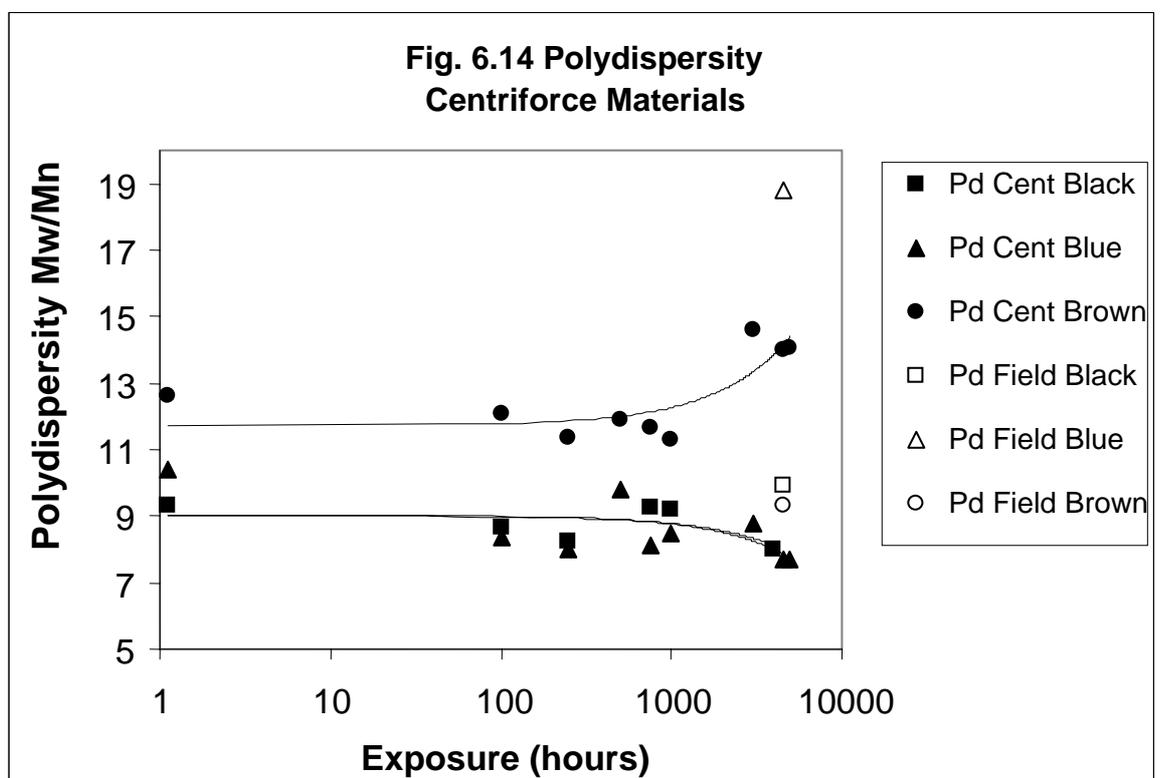
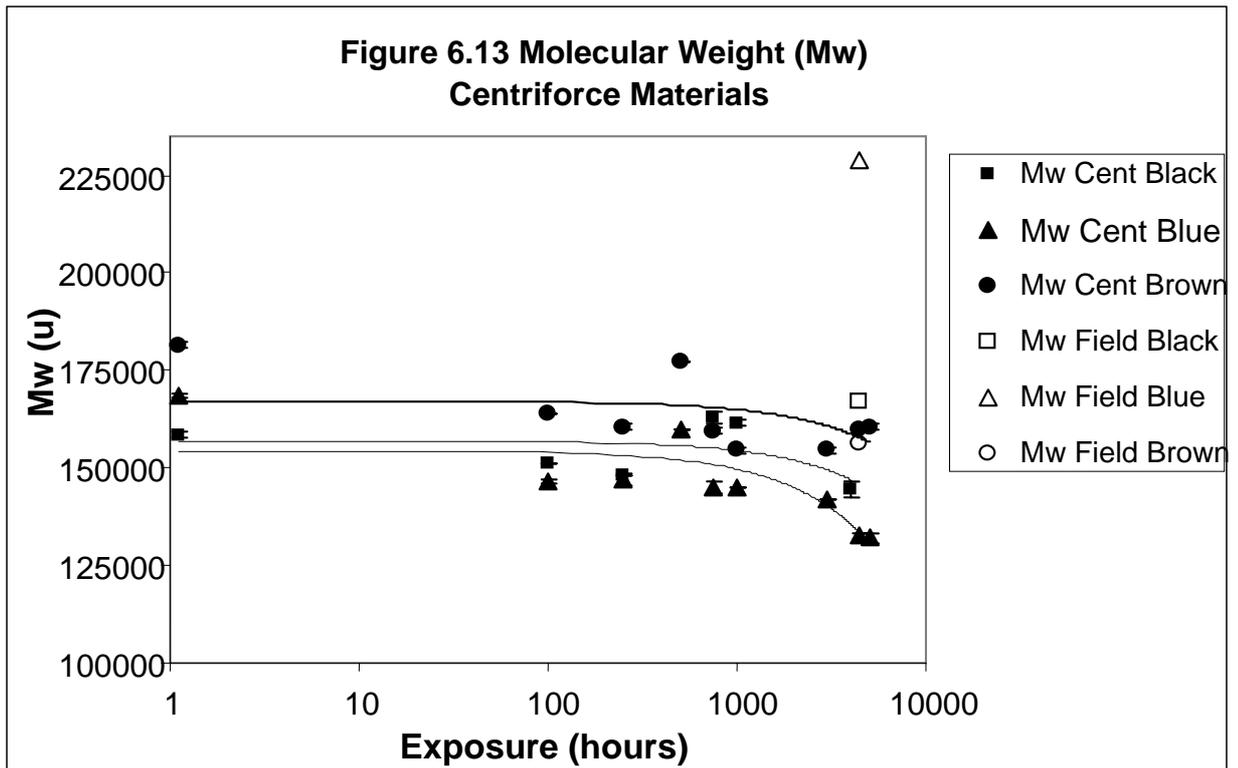


The Centriforce samples had the lowest MFI values of all the materials tested, which also confirmed that they were extrusion grades. The black grade gave a value of about 0.45 with little variation even for the field-aged sample (Fig.6.12). The field-aged MFI values for the blue and brown grades were significantly different from that for the materials used in the UV weathering tests, even before exposure. This indicates that the two samples were composed of different mixtures of recycled polymer material.



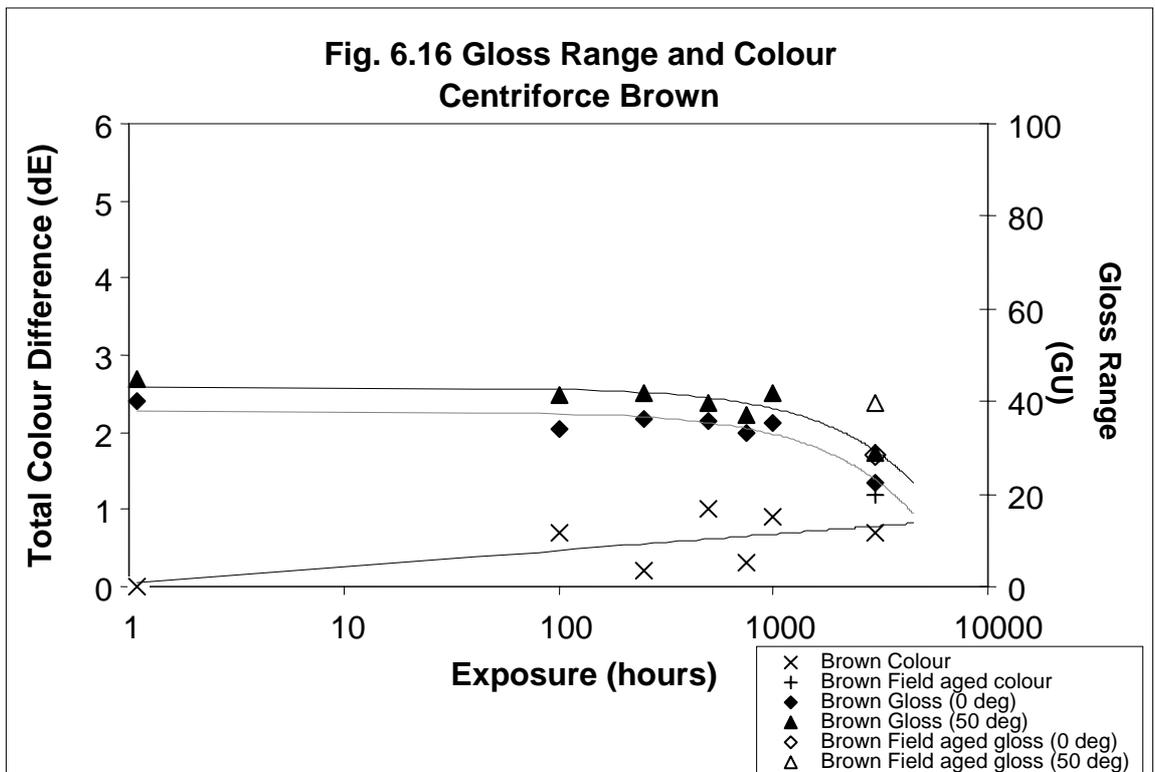
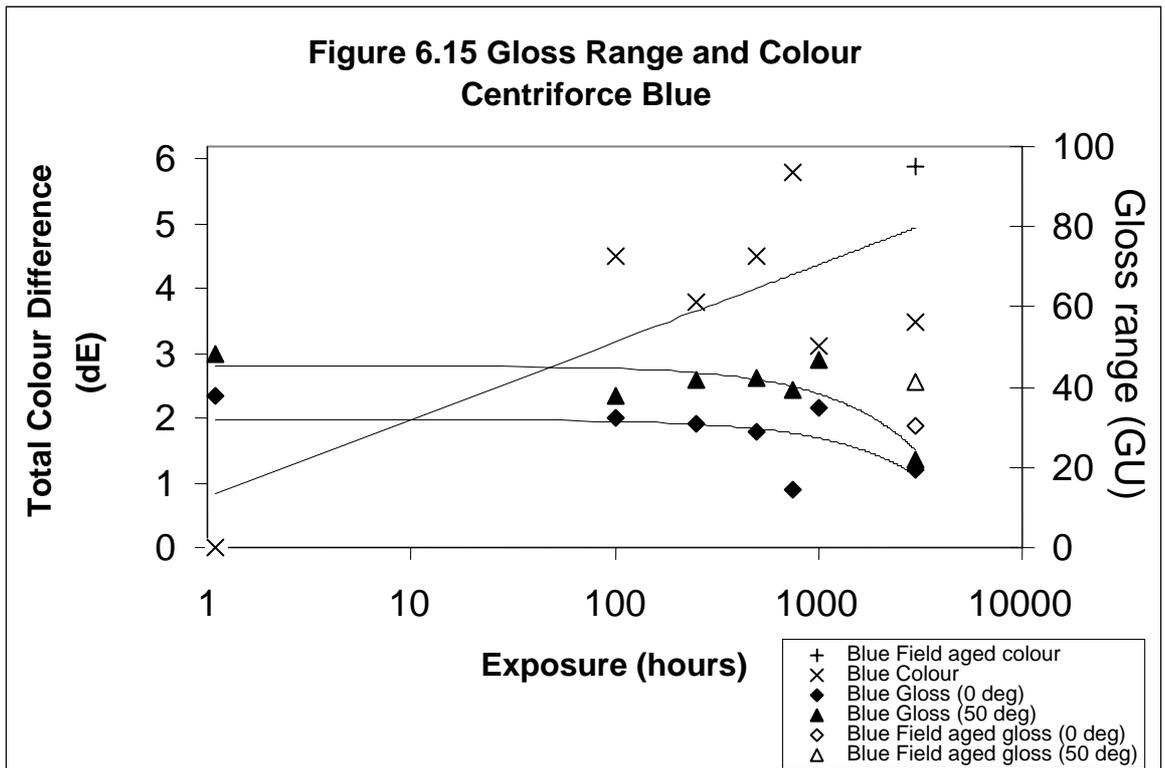
The GPC work carried out by Rapra showed that for all three material types  $M_w$  decreased initially then remained constant (Fig. 6.13). The initial drop in  $M_w$  at 100 hours was 13% for the blue grade, 9.6 % for the brown and 4.4 % for the black material, which suggested chain scission was the dominant event early on in the weathering profile. At 750 hours the drop in  $M_w$  was reduced to just 2.4% of the value for the unaged material for the brown grade and had even increased by 3% of the original values for the black grade, the latter indicating subsequent cross linking. For the blue material the fall in  $M_w$  was reduced to 4.8 % of the original value at 500 hours.

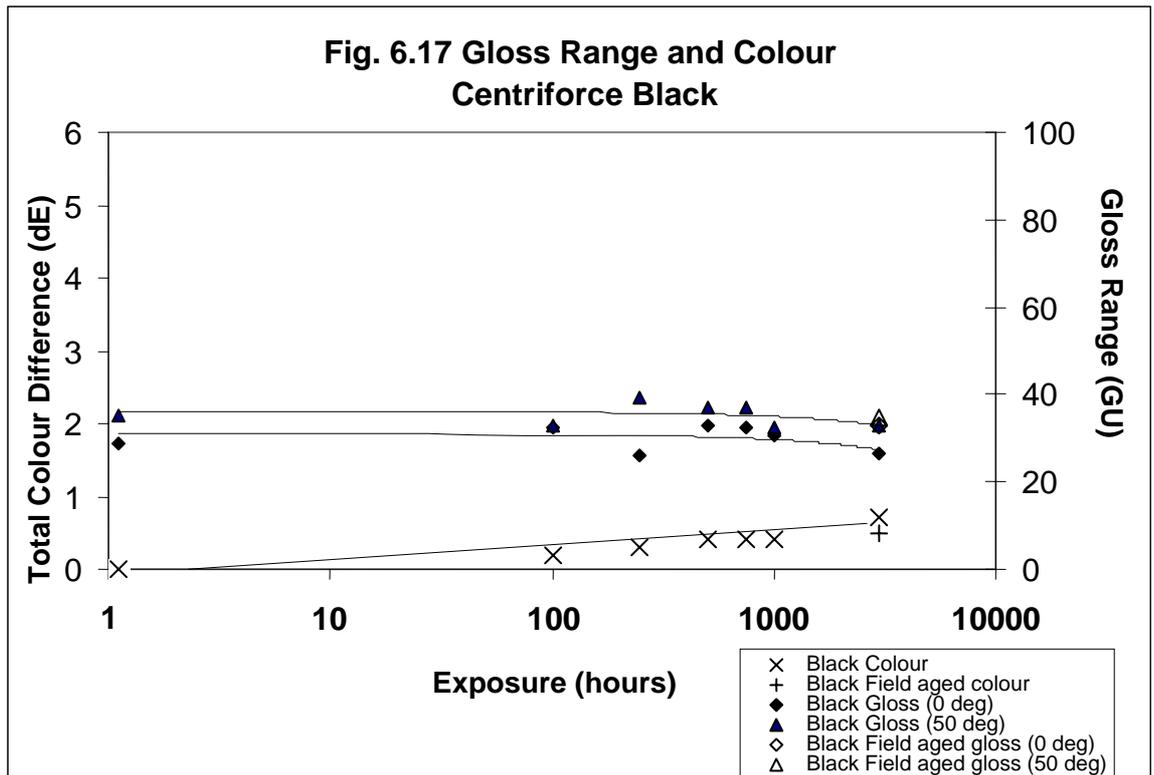
However, by 4500 hours of UV weathering,  $M_w$  values for all three grades dropped by 8.8%, 11.5% and 21.6% from the unaged material values for the black, brown and blue grades respectively (Fig 6.13). Thus, the blue grade showed the largest drop in  $M_w$ , indicating that this material was the most affected by UV exposure.



The increase in polydispersity index values for the brown grade at 3000 - 5000 hours by 13% of the value for the unexposed material indicates that the molecular weight distribution has increased, due to the reduction in Mn as chain scission reactions become dominant at longer exposure to UV radiation (Fig. 6.13 & 6.14). However, for the blue and black grades the polydispersity value dropped by 25% and 13% respectively. This does not necessarily mean that a narrowing of molecular weight distributions has occurred due to cross linkage,<sup>[112]</sup> but reflects the decrease in Mw values (Fig. 6.13).

The gloss and colour measurements by Rapra showed different levels of colour change for all three grades; the largest variations were observed in the blue grade by a factor of 10 compared with brown and black (Fig.6.15-6.17). There was a large degree of scatter, observed for both blue and brown grades. The gloss levels seemed to drop on initial exposure to UV in the case of the brown and the blue grades, then remained approximately constant up to about 1000 hours before falling by 40% and 50% respectively(Fig. 6.15-6.17), indicating some formation of surface flaws. For the black grade, there was little change in the gloss levels with exposure although there was a small but gradual increase in colour difference with increased exposure.

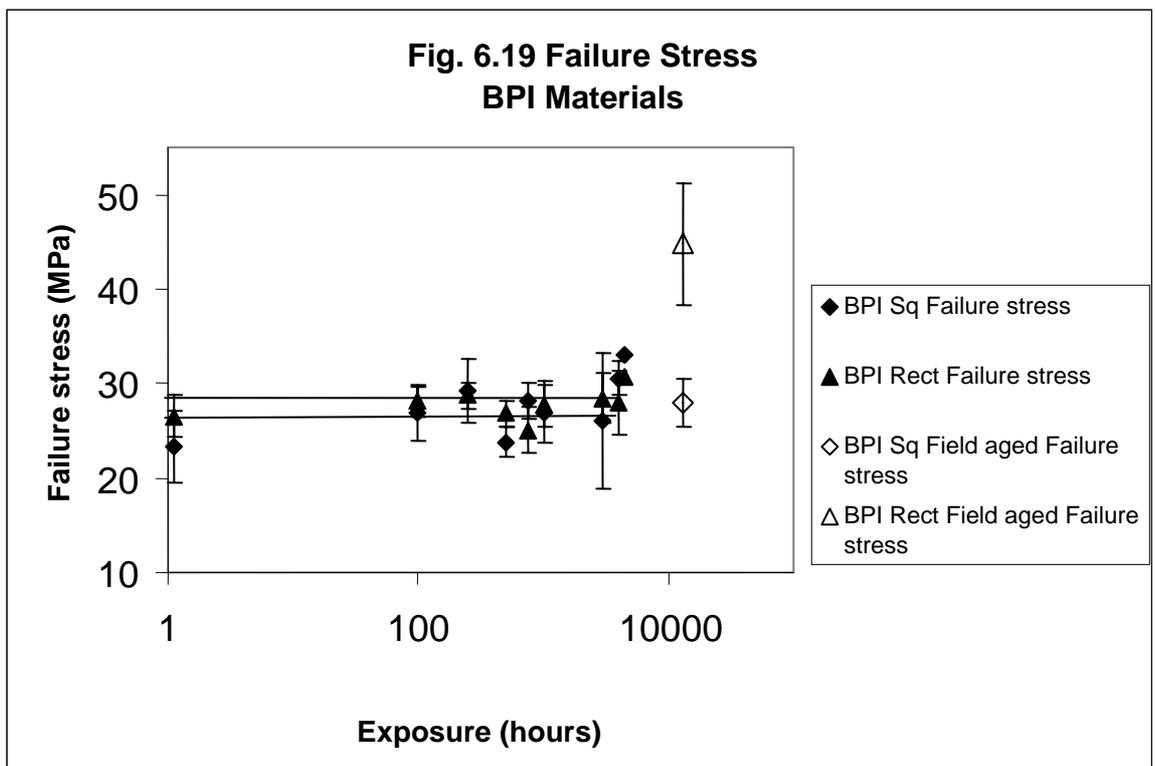
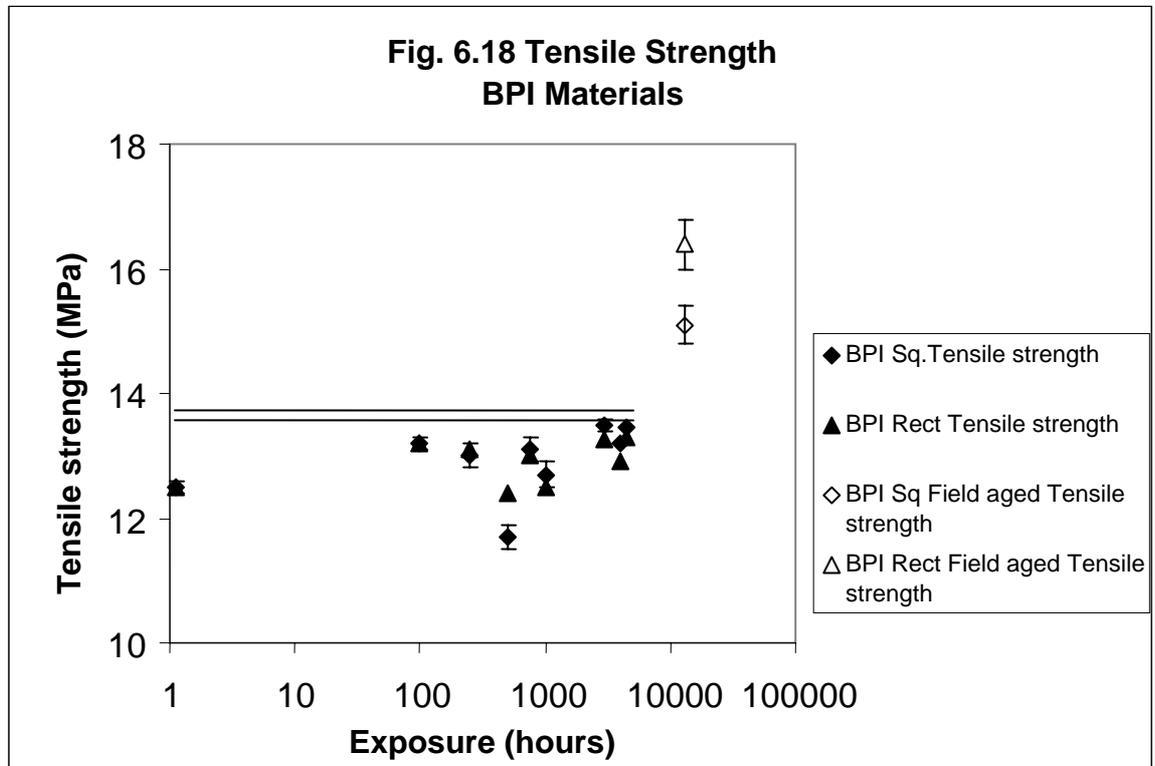


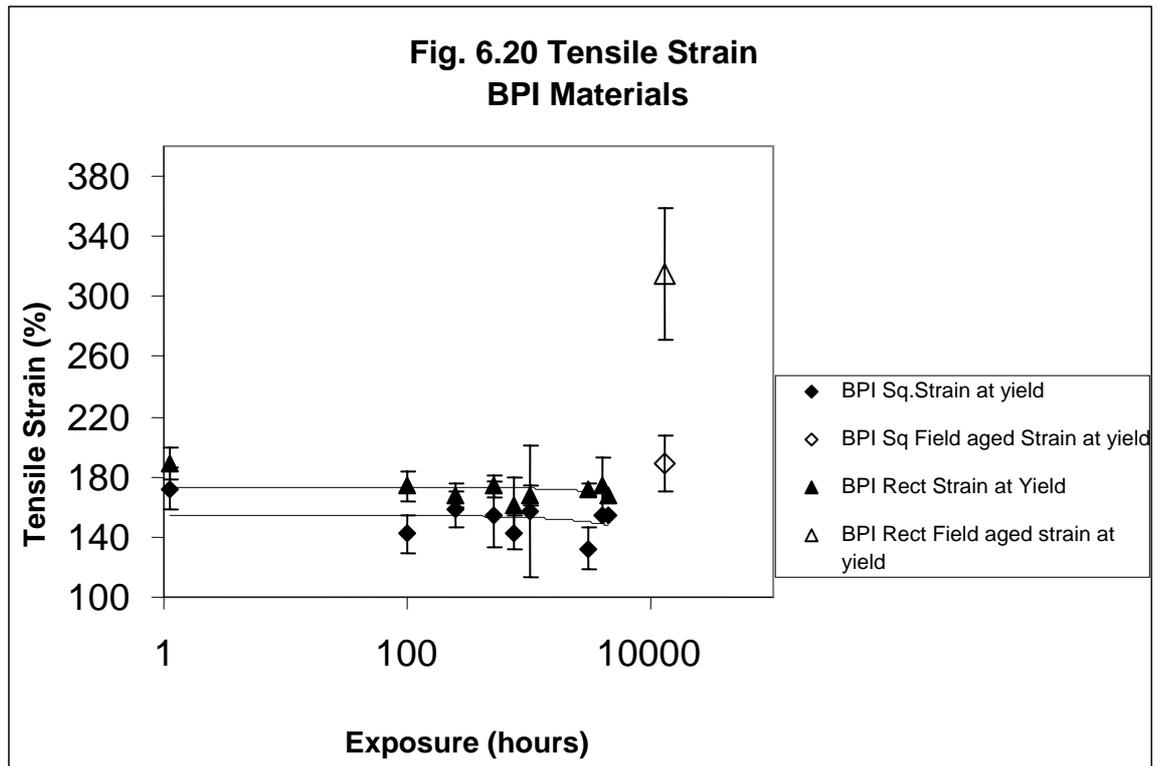


## 6.2 BPI samples

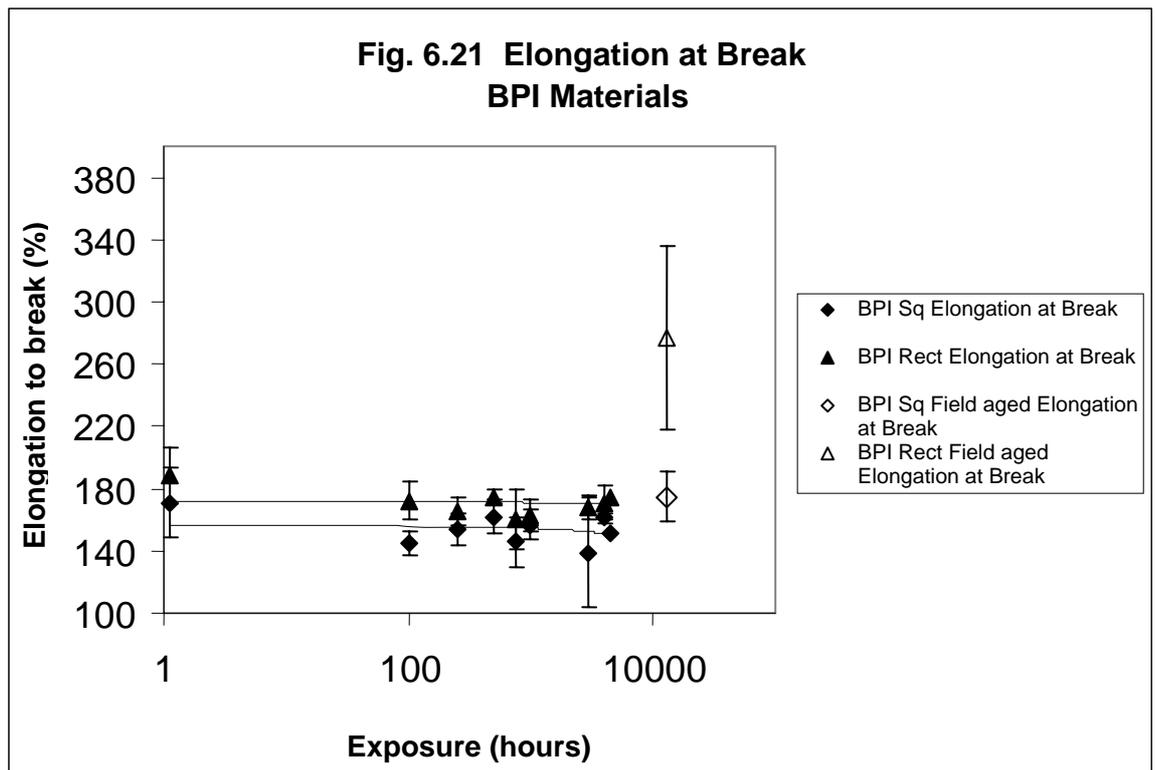
The BPI samples were virtually identical in mechanical terms and showed little change with prolonged UV exposure, which indicated the effectiveness of UV stabilizers in the

material. It was known that the material contained 10% Carbon Black Masterbatch (Table 6.1).

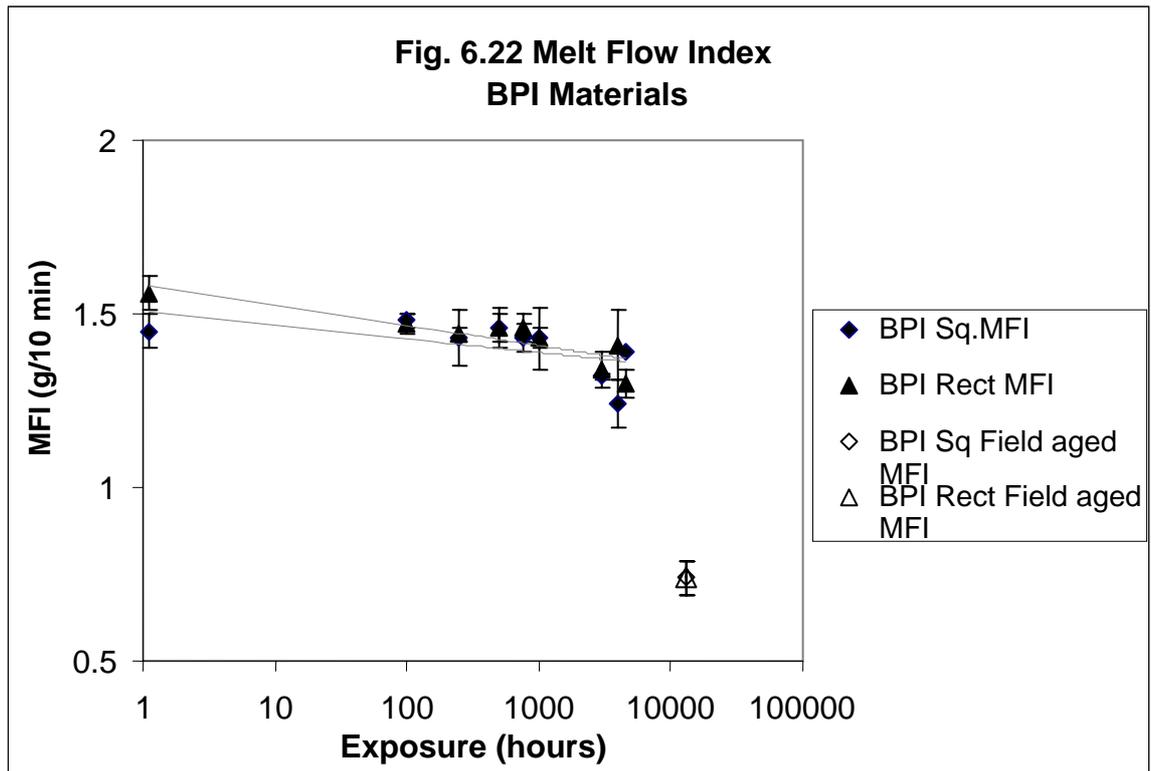




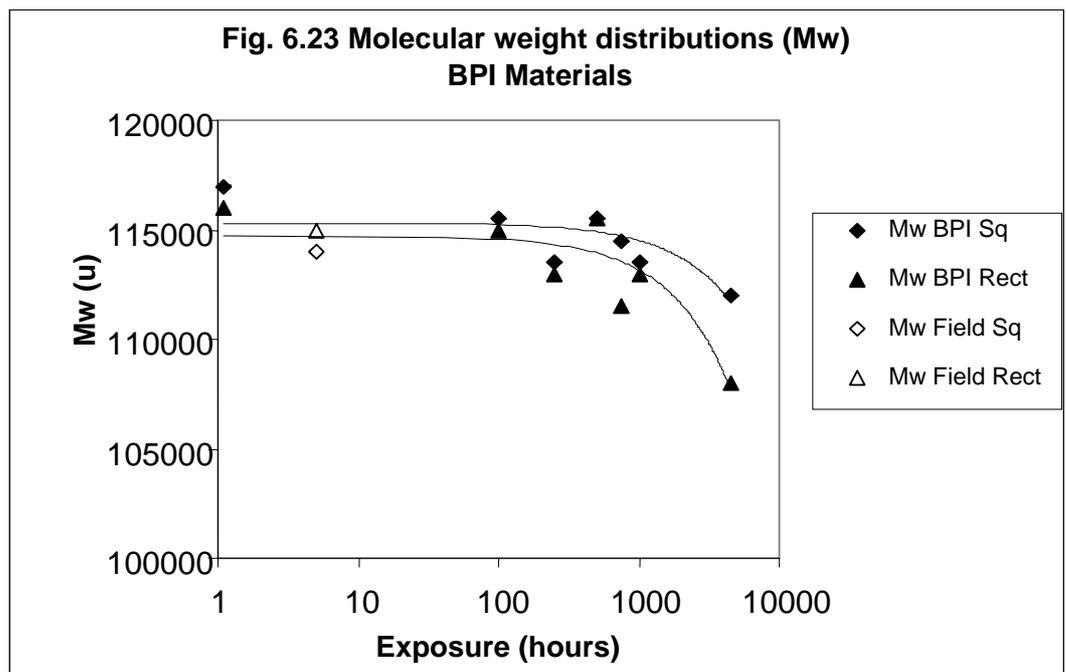
Their tensile strength of 12.5 MPa was expected for a grade of mixed polyolefins (Fig. 6.18). A slight increase in strength with exposure was observed for the square sections. The failure stress was twice as high and the Field-aged samples showed slightly higher corresponding limiting stresses (Fig 6.19). These materials possessed the highest strain to yield, which was virtually identical to the elongation at break (Fig.6.20-6.21). The results reflect the predominance of LDPE, which is significantly amorphous and also rubbery in character.



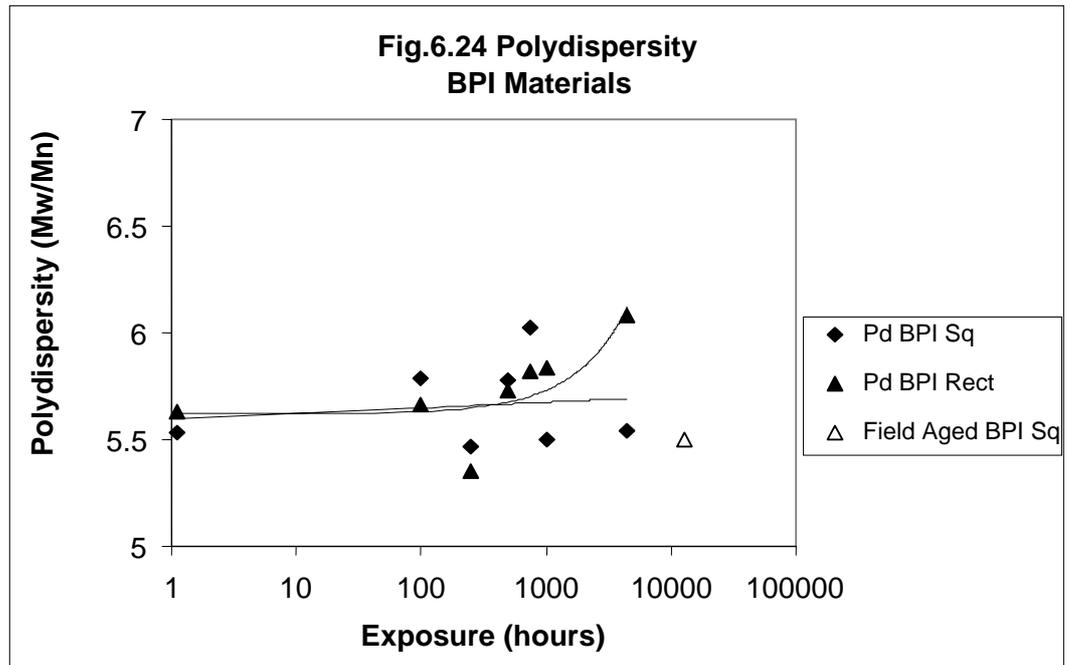
The MFI for both grades was approximately 1.5 g/10 min, decreasing slightly with exposure, indicating chain scission (Fig. 6.22). In both cases, the MFI of the field-aged samples was much less than that of the UV exposed samples. Again, this indicated that the field aged samples and exposure regime samples composed of different mixtures of recycled polymer material.

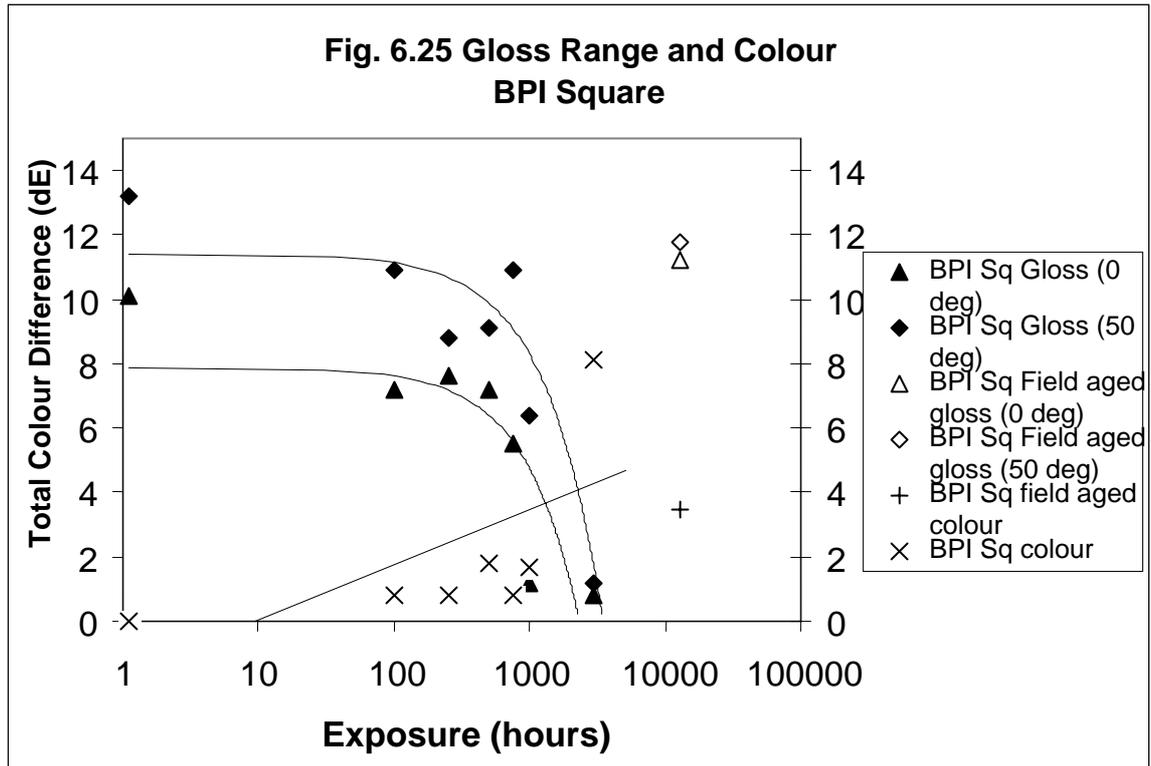


Overall, there was little change in mechanical properties with increase in exposure to UV radiation, indicating that any impurities within the polymer materials had little effect on behaviour.

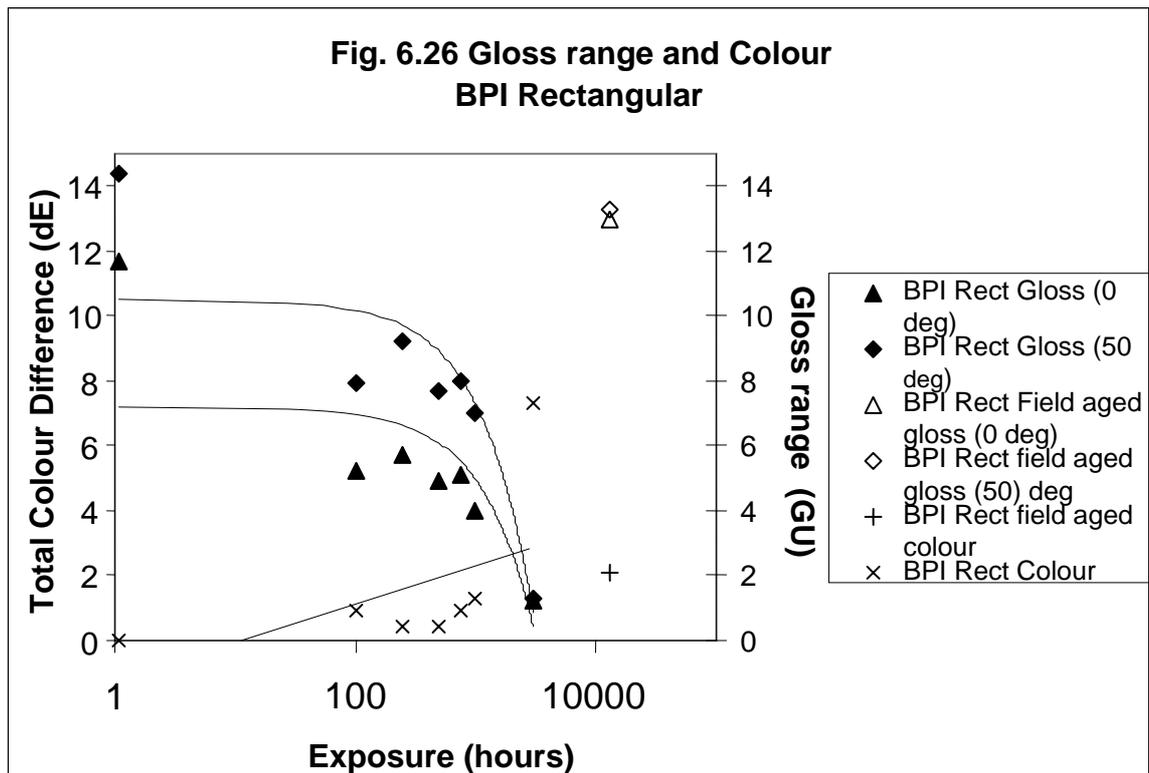


The BPI rectangular grade showed a slight decrease in Mw of 7% from the unexposed sample value, which indicated the occurrence of chain scission. This conclusion was supported by an increase in polydispersity, giving slightly widening distribution of molecular weights (Fig.6.23 & 6.24). The square grade showed a smaller drop of 4% in Mw values with exposure length.





For colour change, a stepwise increase on initial UV exposure was observed, followed by a sharp increase after 750 hours of exposure. This was mirrored by the gloss levels, which showed an initial decrease, then little variation up to 750 hours and subsequently a sharp drop to just 9% of the original values of the unexposed samples for both the square and rectangular material (Fig 6.25 & 6.26). The field aged material showed gloss readings comparable to the unexposed samples for both types of material.



The Centriforce and BPI material samples were provided both after use in the field and also before first use. However, most of the results for the field-aged material were very different to the artificially aged samples. The samples had all undergone the same processing into identical product shapes. However, given the time span between manufacture of the field-aged samples and those made available for laboratory studies, it was highly likely that the composition of the recycle used as raw material for these products had changed in the intervening period. The manufacturers keep records of materials, but these are dependent to a certain extent, on suppliers of materials and the changing sources of materials. It was not possible to check for any changes in recycle composition for this study.

The variation in field-aged materials and the artificially aged materials showed that it is likely that the difference in results for field aged and artificially aged material was due to variability in the source materials and showed that in practice, it is difficult to control the

composition of the mix coming from the waste suppliers. This was more significant for the properties of the materials than any UV exposure. The higher values for the field-aged materials could be due to degradative cross-linking. However, it was more likely to be caused by variability in the batches of raw material. Most recyclers manufacturing using mixed plastic streams create blends based on MFI results. High and low MFI materials are blended to give a suitable material for processing, resulting in a wide distribution of different molecular weight material. Mechanical properties can be effectively maintained by using suitable compatibilizers in polyolefin blends, subject to maintaining commercial competitiveness <sup>[24]</sup>.

The differences between field aged and artificially aged samples made it impossible to correlate the two sets of results. Outdoor weathering tests can give very different results to artificial tests on the same material.

All Centriforce materials had tensile strengths around 25 MPa, twice the value recorded for the BPI materials. However the failure stress values for BPI materials were similar to the tensile strength values recorded for Centriforce materials. Also, the BPI materials possessed the highest strain to yield, almost identical to the BPI elongation at break results. The results reflect the predominance of LDPE in the BPI material, which were more rubbery to touch than the stiffer Centriforce products.

The Centriforce samples had the lowest MFI values of all the materials tested. The field-aged MFI values for both Centriforce and BPI materials were significantly different from the exposure regime material, indicating a composition of different mixtures of recycled polymer material.

The  $M_w$  for all three Centriforce material types decreased initially then remained constant, which suggested chain scission was the dominant event early on in the weathering profile followed by cross linking and then further chain scission at longer exposures. The blue

grade showed the largest drop in Mw, indicating that this material was the most affected by UV exposure.

The increase in polydispersity index values for the brown grade at longer exposures hours indicated that the molecular weight distribution had increased, due to the reduction in Mn as chain scission reactions become dominant at longer exposure to UV radiation.

The BPI rectangular grade showed a slight decrease in Mw from the unexposed sample value, which indicated the occurrence of chain scission. This conclusion was supported by an increase in polydispersity, giving slightly widening distribution of molecular weights.

The largest variations in colour were observed in the Centriforce blue grade by a factor of 10 compared with brown and black. The gloss levels seemed to drop on initial exposure to UV in the case of the brown and the blue grades, then remained approximately constant up to about 1000 hours before falling, indicating some formation of surface flaws. For the black grade, there was little change in the gloss levels with exposure although there was a small but gradual increase in colour difference with increased exposure.

The BPI materials showed a stepwise increase in colour change on initial UV exposure, followed by a sharp increase after 750 hours of exposure. This was mirrored by the gloss levels, which showed an initial decrease, then a sharp drop after 750 hours, indicating some distortion of the material surface. The field aged material showed gloss readings comparable to the unexposed samples for both types of material.

Chain scission in polypropylene and cross-linking in polyethylene in mixed blends could have a compensating effect on each other and lead to non-degradative effects although evidence for this was inconclusive.

The thermal and shear damage during processing may be more significant than subsequent exposure to UV.

For the above reasons it was suggested that a simple quality test involving the measurement of the MFI both before processing and after processing would give a as good an indication of the potential integrity of the material as any more sophisticated tests.

SEM EDX Analysis was useful in identifying impurities in the recycle, but there was no conclusive evidence of degradation as a direct result of exposure to UV radiation.

Overall, the greatest changes in properties were observed for the blue material, which was expected as this was the lightest coloured material in the study. The amount and type of UV stabilizer present in the material was not known. The tensile results indicated that chain scission and surface degradative changes had occurred, although the decrease in MFI values was unexpected. Evidence of surface fragmentation was observed in the images obtained by SEM, which may have occurred because of the formation of an outer polypropylene layer formed during the injection moulding of the test pieces. There was little change in mechanical properties with increase in exposure to UV radiation for the BPI material, indicating that impurities within the polymer materials had little effect on behaviour.

The study has shown that all the materials tested have generally maintained their mechanical properties with little change under accelerated UV exposure. This has positive implications for the use of plastic recycle of this nature in manufacturing processes.

When the material is reprocessed during recycling, it is likely that stabilizer is redistributed uniformly in any new moulding, so that the material depleted from the surface during UV ageing is replaced. Therefore, although the overall stabilization is lowered, the surface characteristics are improved. Hence damaged or end-of-life products should not be discounted from recycling. In any case, the stabilizers being used currently in these materials were effective in negating any likely effects of UV radiation. The amount of restabilization required would depend on the levels of stabilizers remaining in the material.

This is important, as the net increase in stabilizer content with repeated recycling could significantly affect the material properties.

The 'nominal' percentage of Polypropylene (PP) present in the material may play a role in the surface changes. During injection moulding polymer molecules at the flow front undergo considerable shear. The material is deposited on the wall of the cooled mould where it solidifies instantly, forming a skin. In this flow field, the high friction forces can induce phase segregation at the mould surface. It has been proposed that during injection moulding of physical blends of PP and Ethylene-Propylene (EP) copolymer, when the viscosity of the PP is lower than that of the EP, a 'skin' of PP forms on the surface of the moulded item <sup>[21]</sup>. PP is more susceptible to chain scission degradation than PE due to the presence of the more reactive tertiary carbon. This could explain the changes in surface properties in the material, while the bulk properties remained largely unaffected.

Oxidation of semi-crystalline polymers such as polyolefins is generally considered to occur within the amorphous regions. Tie molecules, which connect crystallites through amorphous regions, are scissioned in the oxidation process, resulting in a decrease in elongation and changes in other physical properties <sup>[22]</sup>. This may lead to secondary crystallisation within the amorphous matrix, which is subsequently inhibited by the decreased mobility of the chains due to branching and cross-linking. This may explain the decrease in MFI for the blue material. However, polyolefins can be extremely tough, because at high stresses the chains slip through the crystalline regions giving large-scale deformations <sup>[23]</sup>.

If the composition of the materials is effectively the same then crystallinity effects may explain the difference in behaviour. Pigments and additives can have quite a dramatic effect on the rate of crystallisation during processing. Some pigments act as nucleating agents and so although the overall degree of crystallinity is higher than expected; the crystal structure is very fine. Hence a brittle material may result.

## **7. Conclusions**

The study showed that the effect of UV exposure, whether in the field or in the artificial environments, was not significant up to 1000 hours as far as the mechanical properties of the materials are concerned. Some changes occurred when the materials were taken all the way to failure. In particular, the scatter in the results increased. This was consistent with the fact that surface damage did occur, especially beyond about 1000 hours of exposure.

For most recycled material processors this will not cause much concern since products tend to be of large wall thickness and so any surface effects would not compromise the mechanical integrity of the product. However, surface appearance may be an issue. In the example of a decking board, the surface degradation by UV may lead to accelerated wear with pedestrian use and subsequent safety issues if the surface became slippery.

The flow characteristics as measured by the melt flow index (MFI), showed little change in most cases. This was not unexpected for these thick section applications as any UV degradation was limited to the surface.

Changes in molecular weight distribution and polydispersity index indicated that after an initial change the values remained constant for shorter exposures, indicating that some cross linking reactions were taking place. However, chain scission was the predominant reaction type with longer exposure to UV radiation, especially for the lighter coloured materials. The colour and gloss measurements also showed gradual change with increased exposure to UV radiation, which indicated that degradation was occurring on the surface of the materials.

However, on reprocessing of the materials during recycling, it is likely that stabilizer is redistributed uniformly in any new moulding, so that the material depleted from the surface during UV ageing is replaced. Therefore, although the overall stabilization is lowered, the surface characteristics are improved. Hence damaged or end-of-life products should not be discounted from recycling. In any case, the stabilizers being used currently in these

materials were effective in negating any likely effects of UV radiation. The amount of restabilization required would depend on the levels of stabilizers remaining in the material. This is important, as the net increase in stabilizer content with repeated recycling could significantly affect the material properties.

The variation in field-aged materials and the artificially aged materials showed that it is likely that the difference in results for field aged and artificially aged material was due to variability in the source materials and showed that in practice, it is difficult to control the composition of the mix coming from the waste suppliers.

In mixed blends, chain scission in polypropylene and cross-linking in polyethylene could have a compensating effect on each other and lead to non-degradative effects although evidence for this was inconclusive.

SEM EDX Analysis was useful in identifying impurities in the recyclate, but there was no conclusive evidence of degradation as a direct result of exposure to UV radiation.

Overall, the study has shown that all the materials tested have generally maintained their mechanical properties with little change under accelerated UV exposure. This has positive implications for the use of plastic recyclate of this nature in manufacturing processes.

## **8. Further Work**

The effect of processing during recycling should be examined with particular emphasis being paid to changes in surface characteristics and molecular weight and its distribution.

The amount of restabilization required needs to be examined with regard to the levels of stabilizers remaining in the material. This is important, as the net increase in stabilizer content with repeated recycling would significantly affect the material properties.

There are very few studies available on materials without any stabilizers. Hence a long-term study should be undertaken with materials without stabilizers in order to understand the mechanism of UV degradation fully.

The use of colour should be considered carefully as the study has suggested that different pigments can influence the crystallisation process to a greater or lesser degree and thus influence properties.

The fracture characteristics of the materials should be studied further so that the effects of the mixing of materials and contaminants can be understood.

Criteria for Standards for materials should be developed in collaboration with suppliers and users of the materials to meet the needs of particular industries. These should include the composition of the original products form the recyclate mix. Ideally, this would include stabilizer content, but information on stabilizer type and content is often viewed as commercially sensitive information by product manufacturers.

More work is required to establish and quantify any potential adverse affects of incorporating photochemically degraded recyclate such as polypropylene into virgin polypropylene material.

The removal of any polypropylene material from the recyclate mix may help to reduce surface defects in the final products.

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## 9. References

- [1] *European parliament and Council Directive 94/62/EC, 20 /12/94 on Packaging and Packaging waste*, Official Journal of the European Community L 365, 31/12/1994 P. 0010 – 0023
- [2] *The Producer Responsibility Obligations (Packaging waste) Regulations 1997, Statutory Instrument 1997, No. 648*, Crown Copyright 1997
- [3] *Survey of Applications, Markets & Growth Opportunities for Recycled Plastics in the UK*. WRAP (Waste Resource Action Programme) Publication, Aug 2003
- [4] Papineschi J. *Standards and Specifications Affecting Plastics Recycling in the UK*, Waste Resource Action Programme, Jan 2003
- [5] Wilson S. *Plastic Bottle Recycling in the UK*, Waste Resource Action Programme, Aug 2003
- [6] *Protocol for Verification of Plastic Packaging Recycling in the United Kingdom* WRAP (Waste Resource Action Programme) Dec 2005
- [7] *Recycled Plastic Packaging – the Consumer’s view* WRAP (Waste Resource Action Programme) April 2005
- [8] Billingham N.C & Calvert P.D. in Allen N.S (Ed.) *Degradation and Stabilization of Polyolefins* Applied Science Publishers 1983 Chp.1
- [9] Rabek J.F *Polymer Photodegradation: Mechanisms and Experimental Methods* Chapman & Hall 1995
- [10] Wojtala A. *The Effects of Properties of Polyolefins and Outdoor Factors on the Course of Their Degradation* Int. Polym. Sci. Tech. **28** (2001), , No.7,
- [11] Duwez A.S & Nysten B. *Mapping Ageing Effects on Polymer Surfaces* Langmuir **17** (2001), 8287-8292

- 
- [12] Vasile C., in *Handbook of Polyolefins: Synthesis and Properties* (Ed.: Seymour R.B), Marcel Dekker, New York, 1993
- [13] Scott G., *Polymers and the Environment* (1<sup>st</sup> Edition), Royal Society of Chemistry, Cambridge, 1999
- [14] Stevens M.P., *Polymer Chemistry: An Introduction* (3<sup>rd</sup> Edition), Oxford University Press, Oxford, 1999
- [15] Vulic, Stretanski & Sanders *UV Stabilization of Polyolefin Systems* *Polymers & Polymer Composites* **8** (2000) 8
- [16] Pospisil J., Sitek.A & Pfaendner R *Upgrading of Recycled Plastics by Stabilization – an Overview*, *Polym. Degrad. Stab.* **48** (1995) 351-358
- [17] Incarnato I., Scarfato P. & Acierno D., *Rheological and Mechanical Properties of Recycled Polypropylene* *Polym. Eng. Sci.*, **39** (April 1999), No.4 749-755
- [18] Kartalis C.N., Papaspyrides C.D., Pfaendner R., Hoffmann K & Herbst H *Mechanical Recycling of Post- Used HDPE Crates Using the Restabilization Technique II: Influence of Artificial Weathering* *J. Appl. Polym. Sci.*, **77** (2000), 1118-1127
- [19] Andradý A.L., Hamid S.H., Hu X. & Torikai A. *Effects of Increased Solar Ultraviolet Radiation on Materials* *J. Photochem. & Photobiol. B: Biology* **46** (1998) 96-103
- [20] Herbst H., Hoffmann K., Pfaendner R. & Sitek F *Improving the quality of recyclates with additives* Hanser, Munich 1995
- [21] Tidjani A., Arnaud R., & Dasilva A. *Natural and Accelerated Photoaging of Linear Low-Density Polyethylene: Changes of the Elongation at Break* *J. Appl. Polym. Sci.*, **47** (1993) 211-216
- [22] Tomasetti E., Nysten B., Rouxhet P.G., Poleunis C., Bertrand P., & Legras R. *Surface characterization of Polypropylene/ (Ethylene-Propylene) Copolymer Blends*

---

(PP/EP): *Applications to Injection-moulded Systems*. Surf.Interface.Anal. **27** (1999) 735-742.

[23] Hamid S.H & Amin M.B *Lifetime Prediction of Polymers* J.Appl.Polym.Sci. **55** (1995) 1385-1394

[24] Attwood J., Philip M., Hulme A., Williams G., Shipton P., *The effects of ageing by ultraviolet radiation of recycled polyolefin blends* Polymer Degradation and Stability **91** (2006) 3407-3415

[25] Cicchetti O., *Mechanisms of oxidative photodegradation and of UV stabilization of polyolefins* Advances in Polymer Science **1970**, 7, 70.

[26] Hinsken H., Moss S., Pauquet J. & Zweifel Z. *Degradation of Polyolefins during Melt Processing*, Polym. Degrad. Stab. **34** (1991) 279-293

[27] Maia D.R.J., Balbinot L., Poppi R.J. & De Paoli M-A *Effect of conducting carbon black on the photostabilization of injection molded poly(propylene-co-ethylene) containing TiO<sub>2</sub>* Polym. Degrad. Stab. **82**, (2003), 1, 89-98

[28] Pospíšil J., Nešpurek S., Pfaendner R., Zweifel H., *Material Recycling of Plastics Waste for Demanding Applications: Upgrading by Restabilization and Compatibilization* Trends in Polymer Science **1997**, 5, 294.

[29] Broska R., Rychlý J., *Double stage oxidation of polyethylene as measured by chemiluminescence*, Polymer Degradation and Stability **2001**, 72, 271.

[30] Barkhudaryan V.G *Alteration of molecular characteristics of polyethylene under the influence of UV radiation* Polymer **41** (2000) 5787-5791

[31] Lacoste J., Deslandes Y., Black P., Carlsson D. J., *Surface and Bulk Analyses of the Oxidation of Polyolefins* Polymer Degradation and Stability **1995**, 49, 21.

[32] Baum B. *The Weathering Degradation of Plastics*, Predicting Plastics Performance, Downington, PA, **1973**, pp. 180.

- 
- [33] Lynch J. K., Nosker T. J., Renfree R. W., Krishnaswamy P., Francini R., *Weathering Effects on Mechanical Properties of Recycled HDPE based Plastic Lumber* in ANTEC, Dallas Texas, **2001**, Paper 392.
- [34] J. M. Hutchinson, *Physical Aging of Polymers* Progress in Polymer Science **1995**, *20*, 703.
- [35] Bhuiyan A. L., in *Advances in Polymer Science: Synthesis and Degradation, Rheology and Extrusion* **1982**, *47*, 43.
- [36] McCallum J. R. & , Wright W.W., *Macromolecular Chemistry: Polymer Degradation* Chp 16 & 17 **1982**, 296 - 378.
- [37] Mathur A. B. & Mathur G. N., *Weathering of polyolefins (polyethylene and polypropylene)* Popular Plastics **1977**, 17.
- [38] Severini F., Gallo R., Ipsale S., *Environmental Degradation of Polypropylene* Polymer Degradation and Stability **1988**, *22*, 185.
- [39] Yoshii F., Meligi G., Sasaki T, Makuuchi K., Rabie A. M., Nishimoto S.-i. *Effect of Irradiation on the degradability of Polypropylene in the Natural Environment*, Polymer Degradation and Stability **1995**, *49*, 315.
- [40] Pagès P, Carrasco F, Saurina J, Colom X, *FTIR and DSC Study of HDPE Structural Changes and Mechanical Properties Variation When Exposed to Weathering Aging During Canadian Winter* Journal of Applied Polymer Science **1996**, *60*, 153.
- [41] Yanai G, Ram A., Miltz J., *Accelerated Weathering Induced Degradation of unprotected multilayer Polyethylene Slabs*, Journal of Applied Polymer Science **1995**, *57*, 303.

- 
- [42] G. Yanai, A. Ram, J. Miltz, *Accelerated Weathering Induced Degradation of unprotected multilayer Polyethylene Slabs II* Journal of Applied Polymer Science **1996**, 59, 1145.
- [43] N. M. Livanova, G. E. Zaikov *The Initiation of Polypropylene Oxidation*, Polymer Degradation and Stability **1997**, 57, 1.
- [44] A. Tidjani, *Photooxidation of Polypropylene under Natural and Accelerated weathering Conditions*, Journal of Applied Polymer Science **1997**, 64, 2497.
- [45] F. Carrasco, P. Pagès, S. Pascual, X. Colom, Artificial Aging of high-density polyethylene by ultra-violet irradiation *European Polymer Journal* **2001**, 37, 1457.
- [46] J. Sampers, *Importance of Weathering Factors other than UV Radiation and Temperature in Outdoor Exposure* Polymer Degradation and Stability **2002**, 76, 455.
- [47] Rabello M. S., White J. R., *The Role of Physical Structure and Morphology in the photodegradation behaviour of Polypropylene*, Polymer Degradation and Stability **1997**, 56, 55.
- [48] Kartalis C. N., Papaspyrides C. D., Pfaendner R., Hoffmann K., Herbst H., *Mechanical Recycling of postused High Density Polyethylene Crates using the Restabilization Technique. 1. Influence of Reprocessing*, Journal of Applied Polymer Science **1999**, 73, 1775.
- [49] Zahavich A. T. P., Latto B., Takacs E., Vlachopoulos J., *The Effect of Multiple Extrusion Passes During Recycling of High Density Polyethylene* Advances in Polymer Technology **1997**, 16, 11.
- [50] Gijsman P., Meijers G., Vitarelli G., *Comparison of the UV Degradation chemistry of Polypropylene, Polyethylene, Polyamide 6 and Polybutylene Terephthalate*, Polymer Degradation and Stability **1999**, 65, 433

- 
- [51] Gijsman P., Dozeman A., *Comparison of the UV-degradation chemistry of unstabilized and HALS-stabilized Polyethylene and Polypropylene*, Polymer Degradation and Stability, **1996** 53 45
- [52] Kostadinova Loultcheva M., Proietto M., Jilov N., La Mantia F. P., *Recycling of High Density Polyethylene Containers*, Polymer Degradation and Stability **1997**, 57, 77.
- [53] Clauss M., Herbst H., Botkin J. H., *Automotive Plastics Recycling: Successful Projects* in GPEC 2002: Plastics Impact on the Environment, Detroit MI, **2002**, pp. 341.
- [54] Dunn J. R., *Unsolved Problems in Polymer Degradation*, Rubber Chemistry and Technology **1978**, 51, 686.
- [55] Schaaf R., *Effect of Thermal and Oxidative Degradation on the Overall Properties of HDPE and PP* in Recycling of Thermoplastic Wastes (Ed.: V. D. Ingenieure), Dusseldorf, **1979**, pp. 153.
- [56] Drake W. G., Pauquet J. R., Todesco R. V., Zweifel H., *Processing Stabilization of Polyolefins* Die Angewandte Makromolekulare Chemie **1990**, 176/177, 215.
- [57] Pospíšil J., Sitek F., Pfaendner R., *Upgrading of recycled Plastics by Restabilization. An Overview*, Polymer Degradation and Stability **1995**, 48, 351.
- [58] Papaspyrides C.D., Kartalis C.N., Pfaendner R., Hoffmann K., Herbst H., *HDPE Bottle Crates – Closed Loop Recycling Example from Greece*, Paper at Recovery, Recycling, Re-integration Conference **1999**
- [59] Moss S., Zweifel H., *Degradation and Stabilization of High Density Polyethylene during Multiple Extrusions*, Polymer Degradation and Stability **1989**, 25, 217.
- [60] Hinsken H., Moss S., Pauquet., Zweifel H., *Degradation of Polyolefins during Melt Processing*, Polymer degradation and Stability **1991**, 34, 279
- [61] Kumar R., Madras G., *Thermal Degradation Kinetics of Isotactic and Atactic Polypropylene* Journal of Applied Polymer Science **2003**, 90 , 2206

- 
- [62] La Mantia F. P., Valenza A., Acierno D., *Thermomechanical Degradation of Blends of Isotactic Polypropylene and High Density Polyethylene* Polymer Degradation and Stability **1985**, 13, 1.
- [63] Doyon J.-F., Lafleur P. G., Carreau P. J., Vergnes B., *Recycling of Polyolefins: Processibility and Degradation* in ANTEC, **1994**, pp. 2876.
- [64] Boldizar A., Gevert T., Markinger M., *Quality assessment of Polymeric Recyclates. Part 1: Repeated Processing and Thermo-oxidative Ageing of LDPE*, Polymer Recycling **1995**, 1, 249.
- [65] Bonelli C. M. C., Martins A. F., Mano E. B., Beatty C. L., *The Influence of Degraded Recycled Polypropylene on Incompatible Blends*, ANTEC, Vol. III, Atlanta GA, **1998**, pp. 2901.
- [66] Waldman W. R., De Paoli M. A., *Thermo-mechanical Degradation of Polypropylene, Low Density Polyethylene and their 1:1 Blend*, Polymer Degradation and Stability **1998**, 60, 301.
- [67] Epacher E., Fekete E., Gahleitner M., Pukanszky B., *Chemical Reactions during the Processing of Stabilized Polyethylene. 2. Structure/Property Correlations*, Polymer Degradation and Stability **1999**, 63, 499.
- [68] Epacher E., Tolveth J., Stoll K., Pukanszky B., *Two-Step Degradation of High-Density polyethylene During Multiple Extrusion*, Journal of Applied Polymer Science **1999**, 74, 1596.
- [69] Teteris G., *Degradation of Polyolefins during Various Recovery Processes*, Macromolecular Symposia **1999**, 144, 471.
- [70] Edidin A. A., Jewett C. W., Kalinowski A., Kwarteng K., Kurtz S. M., *Degradation of Mechanical Behaviour in UHMWPE after Natural and Accelerated Weathering*, Biomaterials **2000**, 21, 1451.

- 
- [71] Kartalis C. N., Papaspyrides C. D., Pfaendner R., Hoffmann K., Herbst H., *Recycled and Restabilized HDPE Bottle Crates: retention of Critical Properties after Heat Aging*, Polymer Engineering and Science 2001, 41, 771.
- [72] Santos A. S. F., Santana R. C., Agnelli J. A. M., Manrich S., *Degradation of HDPE and PP Blends Deriving from Municipal Plastic Waste (MPW)*, Polymer Recycling **2001**, 6, 57.
- [73] Incarnato L., Scarfato P., Acierno D., *Rheological and Mechanical Properties of Recycled Polypropylene*, Polymer Engineering and Science **1999**, 39, 749
- [74] Shaner B.E., *The Effects of UV Stabilizers in Post-Consumer Recycled High Density Polyethylene* ANTEC Vol III, Boston MA, **1995** , 4218
- [75] Bernado C.A., Cunha A.M., Oliveira M.J., *The Recycling of Thermoplastics: Prediction of the Properties of Mixtures of Virgin and Reprocessed Polyolefins*, Polymer Engineering and Science **1999**, 39, 1661
- [76] Satoto R., Subowo W. S., Yusiasih R., Takane Y., Watanabe Y., Hatakeyama T., *Weathering of High-density Polyethylene in Different Latitudes*, Polymer Degradation and Stability **1997**, 56, 275.
- [77] Barkhudaryan V.G., *Alterations of Molecular Characteristics of Polyethylene under the influence of UV-radiation*, Polymer, **2000**, 41, 5787
- [78] Al-Madfa H., Mohamed Z., Kassem M. E, *Weather Ageing Characterization of the Mechanical Properties of the Low Density Polyethylene*, Polymer Degradation and Stability **1998**, 62, 105.
- [79] Kato Y., Carlsson D. J., Wiles D. M., *The Photo-oxidation of Polypropylene: Some effects of molecular order*, Journal of Applied Polymer Science **1969**, 13, 1447.
- [80] Gijnsman P., Sampers J., *Influence of Oxygen Pressure and Temperature on the UV-Degradation Chemistry of Polyethylene*, Polymer Degradation and Stability **1997**, 58, 55.

- 
- [81] Gijsman P., Sampers J., *Oxygen Uptake Measurements to Identify the Cause of Unexpected Differences between Accelerated and Outdoor weathering*, Die Angewandte Makromolekulare Chemie **1998**, 261/262, 77.
- [82] Patel J. N., Westwood J. R. B., *European Artificial Weathering Standards*, Journal of the Oil and Colour Chemists' Association **1990**, 73, 484.
- [83] Hoekstra H. D., Spoomaker J. L., Breen J., Audouin L., Verdu J., *UV-Exposure of Stabilized and Non-stabilized HDPE Films: Physico-chemical Characterization*, Polymer Degradation and Stability **1995**, 49, 251.
- [84] Simms J.A., *Acceleration Shift Factor and its Use in Evaluating weathering Data*, Journal of Coatings Technology, **1987**, 59, 45
- [85] Jellinek H.H.G., Flajsman F., Kryman F.J., *Reaction of SO<sub>2</sub> and NO<sub>2</sub> with Polymers*, Journal of Applied Polymer Science, *13*, 107
- [86] Kaczmarek H, *The Environmental Aspects of Polymers* Polimery **1997**, 42, 521.
- [87] Furneaux G. C., Ledbury K. J., Davis A., *Photo-Oxidation of Thick Polymer Samples- Part 1: The Variation of Photo-Oxidation with Depth in Naturally and Artificially Weathered Low Density Polyethylene* Polymer Degradation and Stability **1981**, 3, 431.
- [88] Zhenfeng Z., Xingzhou H., Zubo L., *Wavelength Sensitivity of the Photooxidation of Polypropylene*, Polymer Degradation and Stability **1996**, 51, 93.
- [89] Philippart J.-L., Sinturel C., Gardette J.-L., *Influence of Light Intensity on the Photooxidation of Polypropylene*, Polymer Degradation and Stability **1997**, 58, 261.
- [90] La Mantia F. P., Curto D., *Recycling of Degraded Polyethylene: Blends with Nylon 6*, Polymer Degradation and Stability **1992**, 36, 131.

- 
- [91] Camacho W., Karlsson S., *Assessment of Thermal and Thermo-oxidative Stability of Multi-extruded Recycled PP, HDPE and a Blend Thereof*, *Polymer Degradation and Stability* **2002**, 78, 385.
- [92] Waldman W. R., De Paoli M. A., *Thermo-mechanical Degradation of Polypropylene, Low Density Polyethylene and their 1:1 Blend*, *Polymer Degradation and Stability* **1998**, 60, 301.
- [93] Santos A. S. F., Santana R. C., Agnelli J. A. M., Manrich S., *Degradation of HDPE and PP Blends Deriving from Municipal Plastic Waste (MPW)*, *Polymer Recycling* **2001**, 6, 57.
- [94] Bernado C.A., Cunha A.M., Oliveira M.J., *The Recycling of Thermoplastics: Prediction of the Properties of Mixtures of Virgin and Reprocessed Polyolefins*, *Polymer Engineering and Science* **1999**, 39, 1661
- [95] Braun D., Ritcher S., Hellmann G. P., Ratzsch M., *Peroxy-Initiated Chain Degradation, Crosslinking and Grafting in PP-PE Blends*, *Journal of Applied Polymer Science* **1998**, 68, 2019.
- [96] Albano C., de Freitas E., *Thermogravimetric Evaluation of the Kinetics of Decomposition of Polyolefin Blends*, *Polymer Degradation and Stability* **1998**, 61, 289.
- [97] La Mantia F. P., Mongiovi C., *Thermomechanical Degradation of Compatibilized and uncompatibilized nylon 6/Polypropylene Blends*, *Polymer Degradation and Stability* **1999**, 66, 337.
- [98] Pospíšil J., Horák Z., Kruliš Z., Nešpurek S., Kuroda S., *Degradation and Aging of Polymer Blends I. Thermomechanical and Thermal Degradation* *Polymer Degradation and Stability* **1999**, 65, 405.
- [99] Liang J. Z., Ness J. N., *Investigation on the Melt Flow Properties of Polyethylene and Polypropylene Blends*, *Polymer Testing* **1997**, 16, 379.

- 
- [100] Braun D., Ritcher S., Hellmann G. P., Ratzsch M., *Peroxy-Initiated Chain Degradation, Crosslinking and Grafting in PP-PE Blends*, Journal of Applied Polymer Science **1998**, 68, 2019.
- [101] Epacher E., Fekete E, Gahleitner M., Pukanszky B., *Chemical Reactions during the Processing of Stabilized PE. I. Discolouration and Stabilizer Consumption*, Polymer Degradation and Stability **1999**, 63, 489.
- [102] Busfield W. K., Taba P., *Photo-oxidative Degradation of Mechanically Stressed Polyolefins*, Polymer Degradation and Stability **1996**, 51, 185.
- [103] Boldizar A., Jansson A., Gevert T., Möller K., Polymer Degradation and Stability **2000**, 68, 317.
- [104] Tidjani A., Dasilva A. O., Fanton E., Arnaud R., *Natural and Accelerated Weathering of Stabilized Copolymer Ethylene-Propylene (Low Ethylene Content)*, JMS - Pure Applied Chemistry **1999**, A36, 633.
- [105] Incarnato L., Scarfato P., Gorrasi G., Vittoria V., Acierno D., *Structural Modifications induced by Recycling of Polypropylene*, Polymer Engineering and Science, **1999**, 39, 1661
- [106] Jacques L. F. E., *Accelerated and Outdoor/Natural Exposure Testing of Coatings*, Progress in Polymer Science **2000**, 25, 1337.
- [107] D. R. Bauer, *Global Exposure Models for Automotive Coating Photo-oxidation*, Polymer Degradation and Stability **2000**, 69, 297.
- [108] D. R. Bauer, *Interpreting weathering Acceleration Factors for Automotive Coatings using Exposure Models*, Polymer Degradation and Stability **2000**, 69, 307.
- [109] J.-L. Philippart, C. Sinturel, R. Arnaud, J.-L Gardette, *Influence of Exposure Parameters on the Mechanism of Photooxidation of Polypropylene*, Polymer Degradation and Stability **1999** 64, 213.

---

[110] I.M Ward *An Introduction to the Mechanical Properties of Solid Polymers* (2nd Ed)  
Wiley 1983

[111] Wandell B., *Foundations of Vision* , Sinauer Assoc. 1995

[112] Rogosic M., Mencer H.J., & Gomzi Z., *Polydispersity Index and Molecular Weight Distributions of Polymers* Eur. Polym. J. Vol.32, No.11 pp. 1337-1344, 1996

## 10. Appendices

Table 1. Results for Centriforce Blue											
Exposure	Tensile strength		Failure stress		Elongation at break		MFI		Colour	Gloss range	
hrs	MPa	sd	MPa	sd	%	sd	g/10min	sd	dE	min	max
0	24.1	0.45	83.6	8.2	244.3	114.2	0.48	0.03	0	37.6	48.3
100	24.4	0.69	92	13.4	314.2	86.8	0.51	0.02	4.5	32.3	37.7
250	24.9	0.51	95.1	12.2	358.5	91.3	0.5	0.02	3.8	30.8	41.8
500	22.9	0.9	101.9	7	514.2	222.9	0.48	0.02	4.5	28.7	42.4
750	23.9	0.26	99	18.9	432.7	177.7	0.48	0.03	5.8	14.2	39.3
1000	24.6	0.5	90	13.2	262.8	181.9	0.46	0.04	3.1	34.6	46.7
3000	26.7	0.32	44.9	24.4	203.1	51.2	0.43	0.02	3.5	19.3	22
4500	28.81	0.28	59.44	8.85	80	4.35	0.39	0.02			
5000	27.86		60.5		112						
Aged in field	27.5	1.06	22.9	13.3	51.3	10	0.22	0.01	5.9	30.1	41.3

Table 2. Results for Centriforce Black											
Exposure	Tensile Strength		Failure stress		Elongation to break	sd	MFI		Colour	Gloss range	
	hrs	MPa	sd	MPa	sd		%	g/10min		sd	dE
0	23.15	0.5	80.8	29.2	430	98	0.46	0.02	0	28.8	35.1
100	23.25	0.5	75.9	20.4	459.7	46	0.47	0.03	0.2	32.5	32.8
250	23.08	0.69	88.7	23.9	417.2	60	0.48	0.02	0.3	25.9	39.1
500	22.8	0.74	75.1	24.1	396.6	71	0.48	0.02	0.4	33	36.9
750	24.43	0.56	51.8	21.8	326.2	29	0.47	0.02	0.4	32.3	37
1000	24.02	0.46	83.6	35.8	337.2	65	0.45	0.02	0.4	30.8	32.6
3000	24.4	0.5	30	5.5	283.1	23	0.47	0.02	0.7	26.3	32.9
4000	24.13	0.77	41.1	14.7	355.4	48	0.46	0.01			
4500	23.89		54		438.5		0.45	0.01			
Aged in Field	25.08	0.34	87.5	2.9	120.9	10.1	0.46	0.01	0.5	33.1	34.5

Table 3. Results for Centriforce Brown											
Exposure	Tensile strength		Failure stress		Elongation to break		MFI		Colour	Gloss range	
hrs	MPa	sd	MPa	sd	%	sd	g/10min	sd	dE	min	max
0	25.15	0.42	72.5	4.6	110.3	22.9	0.38	0.02	0	40	44.8
100	24.41	0.66	72.4	14.2	148.3	29.5	0.39	0.01	0.7	34.1	41.4
250	25.61	0.21	79.2	2.5	111.7	9.7	0.38	0.02	0.2	36.4	41.8
500	23.83	1.61	86	30	224	170.6	0.42	0.01	1	35.8	39.7
750	25.65	0.26	82.6	17	123.3	15.5	0.41	0.02	0.3	33	37.1
1000	24.61	0.87	85.9	13.2	117.1	26.7	0.38	0.01	0.9	35.5	42
3000	26.9	0.18	73.9	14.4	114.7	26.4	0.35	0.01	0.7	22.6	29
4500	27.07	1.34	91.38	1.89	104.62	10.88	0.37	0.01			
5000	27.69	0.25	75.98	15.44	73.08	1.09					
Aged in Field	24.29	0.52	105.1	10.7	328.8	82.8	0.57	0.03	1.2	28.3	39.5

Table 4 Results for BPI Rectangular													
Exposure	Tensile strength		Strain at yield		Failure stress		Elongation at break		MFI		Colour	Gloss range	
	hrs	MPa	sd	%	sd	MPa	sd	%	sd	g/10min	sd	dE	0 Deg
0	12.5	0.3	189	11	26.5	2.2	189	18	1.56	0.05	0	11.7	14.4
100	13.2	0.2	174	10	28.2	1.7	172	12	1.47	0.03	0.9	5.2	7.9
250	13.1	0.1	168	8	28.7	1.3	166	9	1.44	0.02	0.4	5.7	9.2
500	12.4	0.3	174	7	26.8	1.3	175	5	1.46	0.04	0.4	4.9	7.7
750	13	0.1	161	18	25.1	2.5	160	19	1.46	0.04	0.9	5.1	8
1000	12.5	0.2	168	7	27.8	2.4	163	10	1.43	0.09	1.3	4	7
3000	13.27	0.26	172.15	3.89	28.46	2.71	168.21	7.74	1.34	0.05	7.3	1.2	1.3
4000	12.9	0.17	173.7	19.2	28	3.34	170.8	10.9	1.41	0.1			
4500	13.3		167.3	4	30.8		173.8		1.3	0.04			
Aged in Field	16.4	0.4	315	44	44.8	6.5	277	59	0.74	0.05	2.1	13	13.3

Table 5 Results for BPI Square													
	Tensile strength		Strain at yield		Failure stress		Elongation at break		MFI		Colour	Gloss range	
hrs	MPa	sd	%	sd	MPa	sd	%	sd	g/10min	sd	dE	0 Deg	50 Deg
0	12.5	0.2	172	23	23.4	3.8	171	22	1.45	0.05		10.1	13.2
100	13.2	0.1	142	14	26.8	2.9	145	8	1.48	0.05	0.8	7.2	10.9
250	13	0.1	158	13	29.3	3.4	154	10	1.43	0.02	0.8	7.6	8.8
500	11.7	0.2	155	12	23.8	1.6	162	11	1.46	0.08	1.8	7.2	9.1
750	13.1	0.2	143	22	28.2	1.9	146	16	1.43	0.06	0.8	5.5	10.9
1000	12.7	0.2	157	11	26.8	3	157	10	1.43	0.04	1.7	1.2	6.4
3000	13.5	0.2	132	44	26.1	7.2	139	35	1.32	0.03	8.1	0.8	1.2
4000	13.2	0.1	155	14	30.5	1.8	161	3	1.24	0.01			
4500	13.45		155		33		151		1.39	0.07			
Aged in Field	15.1	0.3	189	18	27.9	2.5	175	16	0.77	0.07	3.5	11.2	11.8

Table 6. Results for Gel Permeation Chromatography									
Centriforce Materials									
	Black	Blue	Brown	Black	Blue	Brown	Black	Blue	Brown
UV Exposure	Mw	Mw	Mw	Mn	Mn	Mn	Pd	Pd	Pd
Unexposed	158500	168500	181500	17050	16200	14350	9.3	10.4	12.65
100	151000	146500	164000	17400	17550	13550	8.68	8.347	12.1
250	148000	147000	160500	18000	18400	14150	8.22	7.989	11.34
500		160000	177000		16300	14850		9.815	11.92
750	163000	145000	159500	17550	17850	13650	9.29	8.123	11.68
1000	161500	145000	154500	17600	17100	13650	9.18	8.479	11.32
3000		142000	154500		16200	10600		8.765	14.58
4000	144500			18100			7.98		
4500		132500	160000		17200	11450		7.703	13.97
5000		132000	160500		17100	11400		7.719	14.08
Field Aged	167000	229000	156000	16900	12200	16800	9.92	18.82	9.312

Table 7. Results for Gel Permeation Chromatography						
Mw BPI Materials			Mn BPI Materials		Polydispersity BPI Materials	
	BPI Rect	BPI Square	BPI Rect	BPI Square	BPI Rect	BPI Square
UV Exposure	Mw	Mw	Mn	Mn	Pd	Pd
Unexposed	116000	117000	20600	21150	5.631	5.532
100	115000	115500	20300	19950	5.665	5.789
250	113000	113500	21100	20750	5.355	5.469
500	115500	115500	20150	20000	5.732	5.775
750	111500	114500	19150	19000	5.822	6.026
1000	113000	113500	19350	20650	5.839	5.496
4500	108000	112000	17750	20200	6.084	5.544
Field Aged		114000		21400		5.327